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ALVIN J. COX, M. A., PH. D.
GENERAL EDITOR

SECTION A

CHEMICAL AND GEOLOGICAL SCIENCES AND THE INDUSTRIES

EDITED WITH THE COÖPERATION OF
W. E. PRATT, A. M.; H. C. BRILL, PH. D.; J. R. WRIGHT, PH. D.;
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THE PHILIPPINE

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A. CHEMICAL AND GEOLOGICAL SCIENCES
AND THE INDUSTRIES

VOL. XI JANUARY, 1916 NO. 1

NOTES ON THE WATER SUPPLY OF THE CITY OF MANILA[1]

By GEORGE W. HEISE

(*From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila, P. I.*)

The object of this paper is to present some of the factors influencing the quality of the water used in supplying the city of Manila, with special reference to the disinfection of the water by means of choride of lime.

THE MANILA WATER-SUPPLY SYSTEM

The construction of a water-supply system for the city of Manila was undertaken in 1878 by the municipality under the Spanish Government; the installation was first used by the public in 1882. The system derived its water from Mariquina River at Santolan, where a pumping station having a daily capacity of about 28,400 cubic meters (7,500,00 gallons) was installed. From the river the water was pumped to a "deposito," or reservoir, consisting of a series of underground chambers having a capacity of about 60,000 cubic meters (16,000,000 gallons); thence it was piped by gravity to the city distributing system. The total daily capacity of the installation was from 113 to 114 liters (30 gallons) per capita, on the basis of the estimated population of Manila.

As Mariquina River passes through a thickly populated area including a number of large towns before it reaches the Santolan pumping station, it was a difficult matter to keep the water uncontaminated; therefore, it was not long before it became necessary to look for a new source of supply of better quality, large enough to furnish the city of Manila and to provide for the natural increase in population.

Plans were accordingly drawn up in 1902 for a new supply system (completed in 1908) deriving its water from Mariquina River at a point above which it entered inhabited districts. A dam was constructed at Montalban Gorge about 25 kilometers

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[1] Received for publication November 11, 1915.

(15.7 miles) from Manila, and the watershed above that point, about 1,550 square kilometers (60 square miles), was reserved from settlement. The minimum daily flow in the river during the dry season is estimated at 41,700 cubic meters (11,000,000 gallons). The storage capacity of the dam was estimated at something over 4,700,000 cubic meters (1,250,000,000 gallons), although this figure is not effective owing to leakage at the dam, a loss which fissures and cracks in the limestone composing the walls and floor of the gorge make more or less unavoidable. A new reservoir having a capacity of about 206,000 cubic meters (54,500,000 gallons) was constructed on high ground near the city.

With this arrangement Manila now has a complete gravity system, the water flowing from Montalban to the new reservoir, thence to the city distribution system. The consumption of water (October, 1915) is about 57,000 cubic meters (15,000,000 gallons) a day, corresponding to a per capita consumption of approximately 220 liters (58 gallons). At this rate the storage capacity of the new reservoir is about three and one-half days.

There are generally enough rains in the dry season to maintain a supply of water adequate for the city's needs, and if it were not for leakage at the dam, the supply would probably be sufficient; in periods of extended drought, however, it frequently happens that there is not sufficient water from Montalban to supply Manila. At such times it becomes necessary to augment the supply by using the old Santolan pumping station and the old deposito, whose capacity is now about 72,000 cubic meters (19,000,000 gallons). While the Santolan system is in operation, guards are placed along the banks of Mariquina River to prevent contamination of the water so far as possible.

The new supply system is a tremendous improvement over the old installation. The Bureau of Health [2] has pointed out that there were 300 per cent more deaths from intestinal diseases in the years just preceding the installation of the new supply system than in the years immediately following, and has shown [3] further that when the inadequacy of the Montalban supply made it necessary to resort to the old Santolan system to supplement the city supply a marked increase in the death rate occurred. At the time these observations were made, the water was used just as it came from Montalban, no attempt being made to purify it.

At the present time there is no provision made for filtration

[2] *Ann. Rep. P. I. Bur. Health* (1912), 5.

[3] Ibid., 47.

or for any sedimentation except that naturally occurring at Montalban and at the reservoir. The only method of purification employed consists of the addition of chloride of lime to the water, just as it leaves the reservoir.

QUALITY OF THE WATER FROM MONTALBAN

Chemically the quality of the water from Montalban leaves little to be desired so far as its use for city supply is concerned. The water is moderately hard, usually slightly turbid, and has a low mineral content. Its turbidity is not great enough to be objectionable, but as it is due mainly to extremely fine particles of clay and silt, sedimentation is comparatively slow. As already pointed out by Bliss, [4] seasonal variations in the water are surprisingly slight, in spite of the heavy rains of the wet season, which greatly change the amount and appearance of the water coming from the watershed.

Typical analyses of the Manila water, coupled, for comparison, with older analyses of the Mariquina supply, are shown in Table I.

TABLE I.—*Analyses of Manila water supply.*

[Results expressed as parts per million.]

	1903 [a]		1906 [b]	9109 [c]	1913 [c]
	Minimum.	Maximum.			
Total solids	153	220	215	157	154
Fixed solids	127	190	---------	125	---------
Loss on ignition	16	46	---------	32	---------
Silica (SiO_2)	---------	---------	44.7	---------	23.7
Oxides of iron and aluminium	---------	---------	---------	---------	1.7
Calcium (Ca)	---------	---------	16.4	---------	31.2
Magnesium (Mg)	---------	---------	5.4	---------	6.5
Sodium (Na)	---------	---------	8	---------	12.7
Potassium (K)	---------	---------	2.3	---------	1.9
Normal carbonates (as CO_3)	---------	---------	---------	---------	0
Bicarbonates (as CO_3)	---------	---------	---------	---------	139
Sulphates (SO_4)	---------	---------	18.7	---------	13.8
Nitrates (N)	trace	0.36	---------	0.02	0.046
Nitrites (N)	0	trace	---------	trace	trace
Free ammonia (N)	0	0.036	---------	0.12	0.03
Albuminoid ammonia	0.031	0.100	---------	0.1	0.116
Oxygen consumed	0.65	2.20	---------	1.65	---------
Total hardness (as $CaCO_3$)	58.8	109	99	90	---------
Chlorine (Cl)	2.1	4.4	3.9	3.1	4.1

[a] Analysis by C. H. Bliss, chemist, Bureau of Science.
[b] Analysis by L. A. Salinger, chemist, Bureau of Science.
[c] Analysis by V. Q. Gana, chemist, Bureau of Science.

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[4] *Pub. P. I. Bur. Govt. Lab.* (1905), No. 20, 10.

The constancy in quality is further indicated by the chlorine content and oxygen-consuming capacity of the water in the reservoir, as shown by determinations made during the rainy season, at a time when the greatest variation in quality might reasonably have been expected.

Chlorine was determined by Mohr's method. The oxygen-consuming capacity was measured by the method designated as standard by the American Public Health Association,[5] except that the sample was acidulated and heated to boiling before the addition of the permanganate, and that the digestion was made on a steam bath instead of in a bath of boiling water.

TABLE II.—*Daily variation in chlorine content and oxygen-consuming capacity of the water at the reservoir.*

[Results expressed as parts per million.]

Date.	Chlorine.	Oxygen consumed.	Date.	Chlorine.	Oxygen consumed.
1915.			October 5	3.7	1.33
September 20	3.5	0.67	October 6	3.5	1.43
September 21	3.5	0.8	October 7	3.4	1.27
September 22	3.5	0.8	October 8	4.1	1.29
September 23	3.5	0.77	October 11-16[a]	3.9	----------
September 24	3.5	0.85	October 18	3.5	----------
September 25	3.5	0.96	October 19	3.0	----------
September 27	3.5	0.71	October 26	3.6	----------
September 28	3.9	0.78	October 27	3.4	----------
September 29	3.8	1.01	October 28	3.5	----------
September 30	4.1	1.23	October 29	3.6	----------
October 1	3.9	1.30	October 30	3.1	----------
October 2	3.6	1.26	November 1	3.3	----------
October 4	3.8	1.01	November 2	3.3	----------

[a] Composite sample.

The constancy of the results in this table show the improvement in the present water supply over that of the old Mariquina system. Thus the chlorine content varied only from 3.5 to 4.1, while that of the old supply (Table I) varied from 2.1 to 4.4; the oxygen-consuming compacity of the former fluctuated between 0.67 and 1.4, that of the latter between 0.65 and 2.2.

Bacteriologically the water shows the fluctuations naturally to be expected from a surface water. After a heavy rain the colony count of the Montalban supply sometimes reaches an enormous figure, although the water as it leaves the reservoir generally has a count below 1,000. Pathogenic organisms in all probability are generally absent, although *B. coli* is occasion-

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[5] Standard methods of water analysis (1912), 29.

ally reported. Ciliates, flagellates, and amœbæ are frequently present, but it is doubtful whether these are objectionable, especially as Walker [6] has shown that the amœbæ normally present in water do not cause dysentery, and that the dysenteric amœbæ rapidly die in water.

However, in view of the great fluctuation in bacteria count and the occasional presence of organisms of the *B. coli* group, it is evident that the water should be subjected to some sort of purifying treatment before it is used for domestic supply. The combination of turbidity and high bacterial content would point to filtration as the most logical method of treatment. At the present time large numbers of small fishes, shrimps, and quantities of other foreign substances find their way into the distribution system and give rise to troubles, most of which would be eradicated by filtration.

SELF-PURIFICATION AT THE RESERVOIR

Although the Manila city reservoir has only a little over three days' capacity, a surprisingly great degree of bacterial purification seems to be effected during the brief storage period. As the water is often decidedly turbid when it arrives at the reservoir, it is probable that the improvement is due in a great measure to sedimentation. None but preliminary observations on bacterial self-purification have been made, and these only at one season of the year, so that the results are hardly conclusive; however, they show good agreement and probably give a good indication of the magnitude of the purifying action. Samples were taken daily both at the inlet and at the outlet of the reservoir. The average temperature of the water was 26° C. at the inlet and 27° C. at the outlet. The experimental data are given in Table III.

TABLE III.—*Self-purification of water in reservoir.*[a]

Date.	Inlet.		Outlet.		Reduction.
	Colony count.	Test for *B. coli.* [b]	Colony count.	Test for *B. coli.* [b]	
1914.					*Per cent.*
July 16	2,900	Positive	48	Positive	98
July 21	2,800	do	400	do	86
July 22	425	do	24	do	94
July 23	625	do	48	do	92
July 30	750	do	90	do	88
Average reduction					92

[a] Examination by O. Schöbl, bacteriologist, Bureau of Science.
[b] In 2 cubic centimeter samples.

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[6] *This Journal, Sec. B* (1911), 6, 259; (1913), 8, 253.

CHLORINATION

In spite of the purification effected by storage, the city water as it leaves the reservoir has a rather high bacteria count, and as it is a surface water, there is always a chance of contamination. Therefore chlorination has been resorted to further to purify the water. The method of application is simple. Chloride of lime is mixed with water to form an emulsion, strained to exclude large particles, and poured into the water just as it leaves the reservoir and enters the main service pipe. The addition of disinfectant is regulated according to the flow of water, the latter being determined by means of a Venturi meter. The water has a fairly high velocity and is sufficiently agitated by its own motion to insure thorough mixing within a few minutes.

There are a number of factors militating against the efficiency of the chlorination. The turbidity and high content of organic matter greatly reduce the sterilizing action of the chlorine. Only limited amounts of chloride of lime can be used on account of the disagreeable odor imparted to the water by relatively small additions, probably because of the high temperature (27-29°) of the water and because of the lack of a period of storage between the time the water is chlorinated and the time it enters the service pipes. There is no provision made for destroying any excess chlorine.

Owing to sedimentation in the distribution pipes and to other factors, comparison of the unchlorinated water in the reservoir and the water from the city taps has given confusing results. In the series of observations here enumerated, therefore, it has been found advisable to study the water at two places, the first at the reservoir, the second at a point in the supply pipe where the main distribution system has not been reached and where the velocity of the water has not appreciably diminished. At this second place, located at San Juan bridge, there is a much-used public hydrant in almost direct connection with the main supply pipe at which the water, it is calculated, arrives about forty-five minutes after it leaves the reservoir. As nearly as could be ascertained, by bacteriological tests of the water in different parts of the distribution system, the chloride of lime reached its maximum effect at about this point.

As might be expected, the chemical change in the water caused by chlorination is slight. There is an insignificant increase in turbidity, while alkalinity, hardness, and total solids show no appreciable change. The variation in chlorine and oxygen-consuming capacity are shown in Table IV, in which the analyses of water, taken from the Bureau of Science tap, are added for comparison.

At the time these observations were made, chlorination at the rate of approximately 0.5 part of available chlorine per million parts of water was being employed.

TABLE IV.—*Daily variation in chlorine content and oxygen-consuming capacity.*

[Results expressed as parts per million.]

Date.	San Juan.		Tap.	
	Chlorine.	Oxygen consumed.	Chlorine.	Oxygen consumed.
1915.				
September 20	4.0	----------	4.0	0.65
September 21	4.0	>0.8	4.2	0.7
September 22	4.0	0.65	4.0	0.8
September 23	4.0	0.77	3.5	0.86
September 24	4.0	0.74	4.4	0.88
September 25	4.5	0.73	5.0	0.92
September 26	----------	----------	4.8	----------
September 27	3.7	0.84	3.4	1.09
September 28	3.7	0.85	4.0	0.94
September 29	4.0	1.12	4.1	1.47
September 30	4.9	1.33	3.7	1.44
October 1	4.4	1.23	4.1	2.33
October 2	3.8	1.20	3.9	1.40
October 4	3.8	0.96	4.1	2.23
October 5	6.8	1.17	4.0	1.59
October 6	3.9	1.41	3.7	1.62
October 7	9.4	0.92	5.5	1.09
October 8	4.7	1.20	4.1	1.23
October 9	4.4	1.18	3.8	1.49

The results show that the oxygen-consuming capacity[7] increased greatly between the time the water entered the city mains and the time it reached the Bureau of Science, indicating that a large amount of organic matter was taken up by the water in its course through the city distribution system.

In order to study the chloride of lime treatment, daily bacterial examinations were made both at the reservoir and at San Juan bridge. The amounts of disinfectant added were varied, from an addition representing 0.5 part of "available chlorine" in a million parts of water to one representing 0.75 part per million.

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[7] Owing to the disturbing influence of small amounts of hypochlorite on the determination of oxygen consumption, the results obtained are not strictly comparable with the data in Table II.

At this latter concentration the odor of the city water was marked, and complaints were so numerous that it was deemed inadvisable further to increase the addition rate.

The effects of different quantities of chlorine are shown in Tables V to IX, inclusive.

TABLE V.—*Effect of 0.5 part available chlorine per million parts of water.*[a]

Date.	Reservoir.		San Juan.		Reduction.
	Colony count.	Test for *B. coli* group.[b]	Colony count.	Test for *B. coli* group.[b]	
1914.					*Per cent.*
June 1	110	Positive	80	Positive	27
June 2	350	Negative	80	Negative	77
June 3	180	Positive	120	Positive	33
June 4	38	do	26	Negative	32
June 5	60	do	36	do	40
June 6	210	do	190	do	10
June 7	120	do	360	Positive	
June 8	48	do	36	do	25
June 9	34	do	26	Negative	24
June 10	14	do	18	Positive	
June 27	10	do	8	Negative	20
June 28	128	do	36	do	72
Average reduction less than					50

[a] Examination by O. Schöbl, bacteriologist, Bureau of Science.

[b] In 2 cubic centimeter samples. *Bacillus coli* removed six out of eleven times=55 per cent.

The next series, representing the addition of 0.56 part of chlorine per million, is probably not conclusive because of the uniformly low bacterial content of the water during the time of examination and because of the small number of observations; it is included, however, for the purpose of comparison.

TABLE VI.—*Effect of 0.56 part available chlorine per million of water.*[a]

Date.	Reservoir.		San Juan.		Reduction.
	Colony count.	Test for *B. coli* group.[b]	Colony count.	Test for *B. coli* group.[b]	
1914.					*Per cent.*
June 11	70	Positive	18	Negative	74
June 12	4	do	12	do	
June 13	48	do	18	do	63
June 14	46	do	16	do	65

[a] Examination by O. Schöbl, bacteriologist, Bureau of Science.

[b] In 2 cubic centimeter samples. *Bacillus coli* removed three out of three times.

Another set of observations was made while 0.625 part of chlorine per million parts of water was being added, and as this rate of addition was employed at two different periods, the two series of tests are recorded independently.

TABLE VII.—*Effect of 0.625 part available chlorine per million of water.*[a]

Date.	Reservoir.		San Juan.		Reduction.
	Colony count.	Test for *B. coli* group.[b]	Colony count.	Test for *B. coli* group.[b]	
1914.					*Per cent.*
June 15	18	Positive	4	Negative	78
June 16	55	do	12	do	78
June 17	95	do	42	do	56
June 18	240	do	110	do	54
June 19	90	do	14	do	84
June 20[c]	450	do	170	Positive	62
June 21	450	do	325	Negative	28
Average reduction in bacteria count					63

[a] Examination by O. Schöbl, bacteriologist, Bureau of Science.
[b] In 2 cubic centimeter samples. *Bacillus coli* removed six out of seven times=86 per cent.
[c] Typhoon; muddy water.

TABLE VIII.—*Effect of 0.625 part available chlorine per million of water.*[a]

Date.	Reservoir.		San Juan.		Reduction.
	Colony count.	Test for *B. coli* group.[b]	Colony count.	Test for *B. coli* group.[b]	
1914.					*Per cent.*
June 29	180	Positive	55	Negative	69
June 30	90	do	55	do	39
July 1	12	do	4	do	67
July 2	12	do	contaminated.		
July 3	150	do	18	Negative	88
July 4	210	do	10	do	94
July 5	750	Negative	46	do	94
July 6	600	Positive	85	do	86
July 7	1,900	do	1,000	do	47
July 8	120	do	95	do	21
July 9	130	do	120	Positive	8
Average reduction in bacteria count					61

[a] Examination by O. Schöbl, bacteriologist, Bureau of Science.
[b] In 2 cubic centimeter samples. *Bacillus coli* removed eight out of nine times=89 per cent.

The greatest addition of chloride of lime, representing 0.75 part of free chlorine per million of water, was employed for only a short time, because of the complaints against the disagreeable odor of the water.[8]

[8] Recent experiments would indicate that the disagreeable odor was in reality due to irregularities in dosing the water at certain times of the day. There is good reason to believe, however, that during the hours the samples for the series of experiments here enumerated were taken chlorination proceeded with regularity and at the rates recorded.

TABLE IX.—*Effect of 0.75 part of free chlorine per million of water.*[a]

Date.	Reservoir.		San Juan.		Reduction.
	Colony count.	Test for *B. coli* group.[b]	Colony count.	Test for *B. coli* group.[b]	
1914.					*Per cent.*
June 22	275	Positive	180	Negative	35
June 23	450	do	70	do	84
June 24	120	do	48	Positive	60
June 25	190	do	38	Negative	80
June 26	150	Negative	44	do	71
Average reduction in bacteria count					55

[a] Examination by O. Schöbl., bacteriologist, Bureau of Science.
[b] In 2 cubic centimeter samples. *Bacillus coli* remained in one instance.

It will be noted that in no case has the sterilization efficiency reached a figure comparable with those generally reported. According to a committee report to the American Public Health Association[9] the bacterial reduction which may be reasonably expected of typical installations in American cities is about 98 per cent, with which the 50 to 70 per cent reductions here obtained compare rather poorly. However, since the Manila water comes from a watershed well guarded against trespass, pathogenic organisms are probably absent or at any rate very few in number; and since the pathogenes succumb more readily than other forms to the attack of chloride of lime, it is reasonable to suppose that the water is safer, so far as potability is concerned, than would appear from the actual reduction in bacteria count. It is interesting to note the greatly increased efficiency of 0.625 part of available chlorine per million as compared with 0.5 part and the relatively slight increase in efficiency of 0.75 part over 0.625.

The results of these tests show that hypochlorite treatment is not adapted to a turbid water high in organic matter. The high temperature of the Manila water is an added complicating factor which probably accounts in a large measure for the disagreeable odor chlorination imparts to the water.

The low efficiency of the chlorination treatment finds a ready explanation in the high chlorine-consuming power of the Montalban water. The results of the chlorination tests indicate both that a large amount is taken up immediately, which accounts for the low efficiency of small additions of chloride of lime, and that the reaction proceeds more slowly with time, though a definite end point is not reached for many hours, so

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[9] *Am. Journ. Pub. Health* (1915), 5, 918.

that even the higher concentrations of chlorine failed to operate successfully. It is known that waters have the power of chemically combining with free chlorine, and as pointed out by Haïri,[10] this power varies widely for different waters. This chlorine-consuming capacity is not equal or necessarily proportional to the oxygen-consuming capacity, although a high organic content is generally associated with a high chlorine-consuming capacity. A few rough experiments on the unchlorinated water from the city reservoir showed that the chlorine consumption in one hour varied from 0.5 to 1.0 part per million of chlorine consumption in samples taken on different days.

The chlorine consumption was determined by digesting reservoir water in the dark with a measured amount of clear, filtered chloride of lime solution of known strength, and determining the available chlorine from time to time by adding potassium iodide and phosphoric acid,[11] and titrating the liberated iodine with 0.02 N sodium thiosulphate solution, using starch indicator.

Adding a quantity of chloride of lime corresponding to 1 milligram of available chlorine per liter of water, approximately 60 per cent was generally used up in one hour. A typical series of determinations follows:

TABLE X.—*Decomposition of chloride of lime in water.*[a]

Digestion.		Chloride of lime.	
		Left.	Consumed.
Hrs.	*min.*		
0	3	0.8	0.2
0	35	0.45	0.55
1	45	0.35	0.65
3	45	0.20	0.80
20	0	0.14	0.86

[a] One milligram available chlorine added per liter of water.

The results obtained show how rapidly the chlorine loses its effect. It is possible that the chlorine has such highly selective action that dangerous organisms are generally eliminated; however, the bacteriological data (Tables V to IX) indicate that the chlorine loses its effect before the bacteria count is sufficiently reduced to render the water absolutely safe.

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[10] *Zeitschr. f. Hyg.* (1913), 75, 46.

[11] Winkler, *Zeitschr. f. angew. Chem.* (1915), 28, 1.

RELATION BETWEEN CHEMICAL AND BACTERIOLOGICAL DATA

I have tried without much success to correlate the chemical analyses with the bacteriological data at hand. It is noteworthy that the water was almost constant in composition during the period of observation, in spite of the enormous fluctuations (from 120 to 10,000) in the daily colony counts during that time.

The chlorine content was almost constant, its slight variation showing no traceable connection with the fluctuation in bacterial content. There was no apparent relation between chlorine content and oxygen consumed. It is, therefore, evident that except for sudden and great contamination the chlorine content of the city water supply is of little significance.

Barnard[12] and others have repeatedly pointed out that a high nitrogen content is not always an indication of contamination and have shown the futility of isolated nitrogen determinations. This is confirmed by the results obtained in this laboratory and by a critical study of the work on the city water supply previously quoted,[13] in which there is no traceable connection between the bacteria counts and nitrogen determinations, though both showed great variations.

The best indication of the purity of the water was probably furnished by the oxygen-consuming capacity, which showed a number of maxima and minima corresponding fairly well with bacteriological data, but here, too, the agreement was not very good.

In short, little more than the rather trite statement that in a series of determinations made at short intervals a high bacteria count generally appears to be associated with a high organic content seems to be justified. The truth of this is further indicated by the following analysis of the results of the studies on Manila water:

TABLE XI.—*Relation between bacterial content and oxygen-consuming capacity.*

Series No.	Year.	Source.	Oxygen consumed.	Average colony count per cubic centimeter.	Determinations.
1	1903-4	Tap	>1.5	360	5
	1903-4	do	<1.5	195	18
2	1915	Reservoir	>1.0	4,300	10
	1915	do	<1.0	3,400	7

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[12] *Eng. Rec.* (1913), 68, 297.

[13] Bliss, *Pub. P. I. Bur. Govt. Lab.* (1905), No. 20, 10.

SUMMARY AND CONCLUSIONS

The present water supply of Manila, although insufficient in amount during dry seasons of long duration, is a vast improvement over the old supply.

Chemically the water is satisfactory for domestic use, but its bacterial content makes artificial purification necessary. Preliminary experiments indicate that the self-purification of the water in the reservoir was about 90 per cent, although the average storage period was only a little over three days.

Chlorination effected a bacterial reduction of less than 70 per cent. Turbidity, temperature, and especially chlorine-consuming capacity are the factors probably accounting for the low efficiency of the treatment.

The oxygen consumption seems to be the chemical factor which gives the best indication of fluctuations in quality of the water and which shows the greatest similarity with bacteriological data.

Of the procedures discussed, it appears obvious that a daily determination of the oxygen-consuming capacity, supplemented by a bacteriological colony count and a test for the presence or absence of *B. coli,* furnishes the most reliable data concerning the quality of the water. In addition, the frequent determination of chlorine-consuming capacity is of great help in fixing the amount of chloride of lime that will be most effective.

PHILIPPINE BEESWAX[1]

By HARVEY C. BRILL and FRANCISCO AGCAOILI

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

The determination of the purity of beeswax is a somewhat difficult matter, especially so when the adulteration is slight or ingenuity has been practiced in the preparation of the adulterated product.

Seiichi Neno[2] has given figures for the beeswax of Korea and states that these are not different from the constants of the beeswax of Japan and India, but are different from the constants for the European and American products.

The beeswax of Korea is produced by *Apis indica;* that of India by *A. indica, A. florea,* and *A. dorsata;* that of Europe and America by *A. mellifica;* that of the Philippine Islands by *A. zonata, A. dorsata,* and *A. indica.* According to the figures given by the Bureau of Customs of the Philippine Islands[3] 42,602 kilograms of beeswax were exported in 1913 and 44,148 kilograms in 1914.

In view of the difference in the properties of the Japanese and Korean waxes from the European and American and the likelihood of the local waxes being different and in order that standards might be established for the determination of the purity of any samples submitted for examination and thus honesty in the preparation of the commercial product be encouraged, the Bureau of Science has determined the constants of a number of samples of local beeswax.

Samples were purified by boiling in water, then separating from the impurities and drying at 100° C.

For the purpose of comparison some results found by Shibasaki[4] for Japanese beeswax and by Neno[5] for Korean beeswax are included.

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[1] Received for publication January 11, 1916.

[2] *Analyst* (1915), 40, 343.

[3] Bur. Customs, Foreign Commerce of the Philippine Islands, Manila (1915).

[4] *Analyst* (1915), 40, 343.

[5] Ibid.

TABLE I.—*Constants of Philippine beeswaxes.*

Sample No.	Origin.	Color or quality.	Specific gravity at 15.5°C.	Melting point.	Saponification value.	Acid value.	Ester value.	Ratio number.	Iodine value (Hanus).	Unsaponifiable.	Clouding point.
					°C.					*Per cent.*	°C.
1	Catanduanes	Yellow	0.9739	62.0	100.5	7.5	93.0	12.4	10.8	56.8	59.5
2	Caluyugan barrio, Santa Maria, Laguna	White[a]	0.9654	64.5	107.0	6.9	100.1	14.5	10.4	58.6	59.5
3	Napsan, municipality of Princesa, Palawan Province	Refined[ab]	0.9226	63.5	106.8	7.7	99.1	12.9	9.2	60.4	60.0
4	Babuyan	Crude[c]	0.9554	63.0	104.8	7.9	96.9	12.3	8.4	54.7	59.0
5	Marcosatubig, Zamboanga, Mindanao	Refined[a]	0.9309	62.0	101.4	6.8	93.6	13.8	9.2	55.4	60.0
6	Basao, Gattaran, Cagayan	Crude[d]	0.9641	64.0	103.9	6.3	97.6	15.5	8.8	55.6	59.0
7	Davao, Mindanao	do	0.9654	63.5	103.4	7.6	95.8	12.6	9.6	55.6	59.5
8	Do	Refined[a]	0.9589	63.0	98.2	6.9	91.3	13.2	8.5	51.6	60.0
9	Caligayan, Isabella	Crude	0.9891	63.0	96.3	6.3	90.0	14.3	8.2	57.0	60.0
10	Panakan, Davao, Mindanao	do	0.9481	63.5	99.8	6.3	93.5	14.8	7.4	57.8	59.5
11	Bongon, Davao, Mindanao	do	0.9918	64.0	99.4	6.2	93.2	15.0	9.6	53.0	59.0
12	Pili barrio, Surigao, (Mindanao)	do	0.9565	63.0	100.5	6.4	94.1	14.7	8.5	52.7	60.0
13	Ilog barrio, Mindoro	do	0.9601	62.5	99.8	6.0	93.8	15.6	8.6	55.3	60.0
	Maximum		0.9918	64.5	107.0	7.9	100.1	15.6	10.8	58.6	60.0
	Minimum		0.9309	62.0	96.3	6.0	90.0	12.4	7.4	51.6	59.0
	Average		0.9601	63.2	101.7	6.8	94.8	13.9	9.0	55.7	59.6

[a] Refined by boiling in water.
[b] First class.
[c] Not refined.
[d] Third class.

TABLE II.—*Constants for Japanese and Korean beeswaxes.*

	Japanese.			Korean.		
	Maximum.	Minimum.	Average.	Maximum.	Minimum.	Average.
Specific gravity at 100 °C.	0.8207	0.8135	0.8160	0.8358	0.8090	0.8229
Melting point °C	66.5	64.9	65.9	65.0	65.0	65.6
Saponification value	103.34	86.35	89.85	87.72	79.24	84.56
Acid value	8.19	5.61	6.40	7.70	4.46	5.85
Ester value	95.14	80.45	83.44	87.98	74.23	78.71
Ratio munber	----------	----------	----------	17.63	10.23	13.45
Iodine value (Wijs)	14.14	10.18	12.27	12.93	10.04	11.41

A study of the average values of the constants of Tables I and II brings out the fact that they differ somewhat, namely, the specific gravities are not comparable since they have been determined at different temperatures; the melting points run 63.2, 65.9, and 65.6, respectively, for the Philippine, Japanese, and Korean products; the saponification values are 101.7, 89.85, and 84.56 in the above order; the acid values 6.8, 6.4, and 5.85 in the same order; the ester values 94.8, 83.44, and 78.71 in the same order; and the ratio numbers 13.9 and 13.45, respectively, for the Philippine and Japanese waxes. The unsaponifiable portion for the Philippine product averages 55.7 per cent, which is somewhat higher than 52.38 per cent, the value given by Allen and Thomson[6] for beeswax. The clouding point has been included. This value was determined according to the directions of Salamon and Seaber.[7] The authors saponify 1 gram of wax for one hour with 20 cubic centimeters of N/4 alcoholic potash. The flame is then removed, a thermometer inserted, and the liquid stirred continuously until the solution becomes cloudy. The end point is sharp and constant. In the case of pure waxes the cloudiness is followed by the immediate appearance of a flocculent precipitate; with adulterated samples the clouding is gradual and flocculation does not occur until a lower temperature is reached. Under the above conditions they assert that genuine beeswax of the European type (acid value 17 to 20, ester value 68 to 78, a definition including many African samples) clouds at 60 ± 0.5° C., and that East Indian (including Chinese) beeswaxes cloud at 56.5 ± 0.5° C. As little as 5 per cent of paraffin wax (melting point 50° to 60° C.) raises the clouding point of European waxes to 64° and East Indian

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[6] *Chem. News* (1881), 43, 267.

[7] *Journ. Soc. Chem. Ind.* (1915), 34, 461.

to 62° C.; 10 per cent raises it to 74° and 70° C., respectively. By ingenious compounding, beeswax can be adulterated with paraffin and with tallow, resin, or Japanese wax without a deviation in the saponification value and with very slight change in the melting point. In such cases the clouding point would be useful in the detection of the adulteration.

SUMMARY

The constants for Philippine beeswax are given in Table I. Comparison of these with the constants of the Japanese and Korean is made.

The clouding point of the local beeswax compared with that for European and East Indian waxes is added.

THE POZZUOLANIC PROPERTIES OF MEYCAUAYAN VOLCANIC TUFF[1]

By Albert E. W. King
(From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila, P. I.)

ONE TEXT FIGURE

During June, 1914, the Bureau of Science received for compression test twelve 6-inch tuff (adobe stone) cubes taken from the Tayawanak quarry, Cavite Province, Luzon. Similar material was to be used in the construction of bridge abutments. The specimens were exposed in air and tested for compressive strength. Table I shows the results obtained.

Table I.—*Compressive strength of 6-inch Tayawanak tuff cubes.*

Age.	Total strength.				Strength per square centimeter.		Strength per square inch.	
	First crack.	Ultimate.	First crack.	Ultimate.	First crack.	Ultimate.	First crack.	Ultimate.
Days.	*Kilos.*	*Kilos.*	*Lbs.*	*Lbs.*	*Kilos.*	*Kilos.*	*Lbs.*	*Lbs.*
35	1,315	1,394	29,000	30,750	56.66	60.04	806	854
35	545	1,042	12,000	22,950	23.41	44.85	333	638
35	516	1,262	11,350	27,800	22.14	54.34	315	773
35	523	1,098	11,500	24,200	22.42	47.31	319	673
35	882	1,098	19,400	24,200	37.82	47.31	538	673
35	302	925	6,650	20,350	13.00	39.79	185	566
63	999	1,476	23,000	32,500	44.85	63.48	638	903
63	1,184	1,248	26,100	27,500	50.97	53.71	725	764
63	908	1,161	20,000	25,550	39.09	49.77	556	708
63	1,348	1,348	29,700	29,700	28.00	58.00	825	825
63	1,549	1,549	34,100	34,100	66.65	66.65	948	948
63	550	1,057	12,100	23,300	23.60	45.48	336	647

The material is very soft, porous, and fine-grained and as the results show is not suitable for construction subjected to high unit stresses. Cox[2] describes the occurrence and properties of tuffs in general:

> . . . . volcanic sediments and pyroclastic tuffs occur quite widely distributed in the Philippines. They are especially abundant in west central Luzon, extending almost unbrokenly from near Lingayen Gulf to the seacoast of Batangas, practically blanketing or covering nearly all of the massive rocks of this region. Mr. Ickis found volcanic tuff in the Agusan Pulangi region, interior from Cagayan Misamis.
>
> In the absence of a better stone, in certain places this has been used extensively for building purposes. In Bulacan and along the Pasig River,

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[1] Received for publication December 21, 1915.

[2] *This Journal, Sec. A* (1908), 3, 393.

especially near Guadalupe, this stone is unusually abundant. Large quantities of it have been quarried and used in the construction of many churches and other buildings and in the walls and fortresses of Manila. It is very workable. Before it is distributed it is so soft that it can be quarried with an axe, but it hardens rapidly on exposure.

Philippine tuffs vary considerably in texture, color, density, and chemical composition. Some are fine-grained and soft like those quarried at Santa Mesa, Rizal, and at Tayawanak, Cavite; others are coarse-grained and hard like those taken out in the vicinity of Meycauayan, Bulacan. The harder varieties are preferred for construction, though much of the softer material is used locally because it is cheaper. Cox[3] reports a microscopic examination of the tuff found in the vicinity of Manila and shows it to be composed of (1) feldspar, (2) magnetite, (3) hornblende, (4) quartz, (5) and a cementing material, largely composed of oxide of iron.

It was thought that the spalls and débris remaining after the compression test on the Tayawanak tuff might possess pozzuolanic properties if finely ground and mixed with hydrated lime. The problem is not a new one, but there seem to be no published results on the properties of Philippine tuffs when mixed with slaked lime. Such an investigation should be of considerable local industrial value. Trass or pozzuolan cements were used by the ancients and are still used to a considerable extent in Europe. Vitruvius and Pliny both make mention of their utility. Of late, considerable activity has been shown in various circles regarding the efficacy of tuffs mixed with Portland cement when the latter is to be used in sea water.[4] Although the tuff mixtures studied in this laboratory do not harden to the same degree as does Portland cement, nevertheless they could be used very advantageously under certain conditions as a cheap and efficient building material.

[3] Loc. cit.

[4] Duryee, Puzzolan-Portland cement; a suggestion for an improved hydraulic cement. *Eng. News* (1910), 64, 596.

Gebrauch von Trass bei Eisenbeton. *Tonind.-Zeitg.* (1913), 37, 1857.

Poulsen, A., Diatomeerde als Puzzolane. *Tonind.-Zeitg.* (1913), 37, 1132. (Mixing of Portland cement with ground diatomaceous earth.)

Duryee, E., Further investigations of Puzzolan-Portland cements. *Eng. News* (1912), 68, 297.

Martin, Hr., Über den Wert von Trass Zuschlägen zum Zement und Kalkmörtel (1914), 13, 286–8, 298–306.

Lippincott, J. B., Tufa cement as manufactured and used on the Los Angeles aqueduct. *Chem. Ab.* (1911), 5, 1672; (1913), 7, 236.

Jacobs, E., Use of trass in reinforced concrete. *Ingenieur*, 27, 134–8. See *Chem. Ab.* (1913), 7, 237.

PRELIMINARY WORK

For the purpose of ascertaining whether or not the Tayawanak tuff possessed any hydraulic properties, the fragments remaining after the compression test were dried in the sun, reduced in a crusher, and ground in a ball mill until 100 per cent passed through a sieve having an average of 22,500 meshes per square inch. Dry slaked lime, containing 96.98 per cent calcium hydroxide, and the pulverized tuff were mixed in equal parts by weight. The lime had the same fineness as the tuff. The resulting mixture, after being tempered with water in the usual way and allowed to harden, was tested for compressive and tensile strengths and setting time. In the test pieces 27 per cent of water was used. After two days in moist air the specimens were stored in water until broken.

The approximate setting time was determined by the Gilmore needle.

In Table II are tabulated the results obtained.

TABLE II.—*Tensile strengths of briquettes and compressive strengths of 2-inch cubes made from tuff fragments.*[a]

TENSILE STRENGTH OF BRIQUETTES.

	Kilograms per square centimeters.	Pounds per square inch.
7 days neat (2 days in moist air, 5 days in water)	11.60	165
90 days neat (2 days in moist air, 88 days in water)	17.58	250
180 days neat (2 days in moist air, 178 days in water)	18.71	266
7 days mortar (2 days in moist air)[b]	9.98	142
90 days mortar (2 days in moist air)[b]	21.45	305
180 days mortar (2 days in moist air)[b]	26.72	380

COMPRESSIVE STRENGTH OF 2-INCH CUBES.

	Kilograms per square centimeter.	Pounds per square inch.
7 days neat (2 days in moist air)	71.52	1017
28 days neat (2 days in moist air)	78.69	1119
90 days neat (2 days in moist)	218.28	3104
180 days neat (2 days in moist air)	268.42	3817

[a] Initial setting time, 23 hours.

[b] Briquettes were made from one part by weight of the tuff-lime mixture and three parts by weight of standard Ottawa sand.

When mixed with lime, the tuff exhibits very marked hydraulic properties, developing considerably higher compressive strength per unit area than the original tuff blocks as taken out of the quarry. The tensile strength of the mortar at the 90- and 180-day periods is greater than that of the corresponding neat briquettes and equals the strength of the average Portland cement-mortar briquettes tested in the Bureau of Science. The results show that the tuff possesses well-defined pozzuolanic properties. The quarry where this tuff was obtained unfortunately has little economic importance at present because it is situated in the interior of Cavite Province at a considerable distance from both rail and water transportation. It was, therefore, decided to use a different tuff in making the more extensive tests. The tuff obtained near Meycauayan, Bulacan Province, was finally chosen because of the favorable location of the quarry and the superior quality of the material.

On April 6, 1915, I made a trip to the quarry at the barrio of Ligtong on Ligtong River, about twenty minutes' walk from the Meycauayan railroad station. The quarry, known as "Tibagan," is owned by Francisco Carreon. The Tibagan is one of the oldest tuff quarries near Manila, having been worked during the early Spanish period. It furnishes the hardest and most durable tuff found on the Manila market. It is of interest to note that the quality of the tuff in this one quarry is variable; some pits produce a much softer stone than adjacent ones and are for that reason preferred by the workmen, since quarrying is easier. Large quantities of débris resulting from the dressing and quarrying of the tuff are strewn about; these served as the source of the sample secured for this investigation.

EXAMINATION OF THE MEYCAUAYAN TUFF

A megascopic examination of the Meycauayan tuff shows it to be constituted of comparatively large, irregular fragments of igneous material embedded in a fine-grained matrix. It may be designated as a water-laid agglomerate. Most of the coarser components are volcanic ejecta. These cemented ejecta consist of sharp fragments of basalt, coarse pieces of pumice, volcanic glass, and scoria. The tuff is gray, with a bluish green cast. It is fairly resistant, but is easily scratched with the sharp point of a pocket knife.

An analysis of the tuff is given in Table III.

TABLE III.—*Analysis of Meycauayan tuff.*[a]

Constituent.	Per cent.
Insoluble silica (SiO_2)	42.81
Soluble silica (SiO_2)	12.22
Aluminium oxide (Al_2O_3)	7.12
Ferric oxide (Fe_2O_3)	16.56
Calcium oxide (CaO)	5.53
Magnesia (MgO)	2.24
Sodium and potassium oxides ($K_2O + Na_2O$)	5.34
Water at 110°C.	3.09
Loss on ignition[b]	4.34

[a] Analysis by Rafael H. Aguilar, chemist, Bureau of Science.
[b] Mostly water above 110° C.

The percentage of soluble silica is low. No published results of soluble-silica determinations on Philippine tuffs are at hand for comparison, and it is impossible to state whether the quantity found here is characteristic of Philippine tuffs in general or is a peculiarity of the Meycauayan tuff. Kiushi volcanic ash, produced at Karatsu, Sagaken, Japan, and analyzed at the Industrial Experimental Station at Osaka, contains 19.99 per cent of soluble silica. When compared with the results obtained by E. Schwarz in his investigation of some European tuffs possessing well-defined hydraulic properties, the result is also low.[5]

About 84 per cent of the tuff used for this determination passed through the 200-mesh sieve. The error introduced in the analysis with this fineness due to the solvent action of the alkali upon the quartz is very slight and ordinarily can be neglected. Lunge and Millberg[6] state that it reaches from 0.1 to 0.2 per cent of the total amount of silica. As a result the percentage of amorphous silica obtained will be in excess of that actually present. If anything, therefore, the results shown are probably too high.

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[5] The method of determining the soluble silica in Table III is based upon the procedure recommended by W. Hillebrand in The analysis of silicate and carbonate rocks [*Bull. U. S. Geol. Surv.* (1906), 305, 165]. According to G. Lunge and Milberg [*Zeitschr. f. angew. Chem.* (1897), 393, 425], quartz is not nearly so insoluble in solutions of the caustic alkalies as has been supposed; if given a sufficient degree of subdivision, it can be brought wholly into solution. It is impossible to secure correct separation of quartz and opaline silica by the use of either caustic or carbonated alkalies. Digestion on the water bath for fifteen minutes with 5 per cent solution of sodium carbonate is the only way to secure exact separation of unignited precipitated silica from quartz, and then only when the finest flour has been removed by levigation.

[6] Loc. cit.

One gram of the finely ground tuff was digested in a Jena beaker with dilute hydrochloric acid for eight hours. The insoluble residue was separated from the liquid by filtration. The residue with the filter paper was transferred to a platinum dish and digested for fifteen minutes with a 5 per cent solution of sodium carbonate on the water bath. The soluble silica was determined in the filtrate.

The method employed by Schwarz,[7] is practically the same, except that he digests for a longer time with sodium carbonate. Some of the results obtained by him are shown in Table IV.

TABLE IV.—*Soluble silica in various materials, as recorded by Schwarz.*

	Per cent.
Tuff from Rottenheim	17.75
Nettetaler tuff	35.75
Brohltaler tuff	28.95
Vulkan trass	24.74
Mountain trass	27.89
Tuff from the Imperial Construction Bureau of Celle	35.80
Tuff from Hungary	34.80

THEORIES OF HYDRAULICITY

Soluble silica is considered by several authorities as being the cause of the hydraulic properties of tuffs and other pozzuolanic materials. Kasai[8] shows that the strength of Portland cement-pozzuolan mortars is directly proportional to the percentage of soluble silicic acid contained in the added pozzuolan. Johnson[9] says:

> While the exact chemical reactions have not yet been determined for slag cements, it seems certain that the hardening of slag cements consists of a gradual action of an active form of silica on the free lime, as in the case of puzzuolanas or trass.

Dammer[10] states:

> The natural puzzuolanas have the property in common of containing appreciable amounts of silicic acid which react with the added lime and by substitution form the necessary compounds for the induration of the mortar.

On the other hand, there are investigators who maintain that the hydraulic properties of pozzuolanas, tuffs, and trasses are

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[7] *Tonind.-Zeitg.* (1912), 36, 1122.

[8] Portlandzement with Puzzolanzusatz. Tonind.-Zeitg., G. m. b. H., Berlin (1911). Abstracted in *Tonind.-Zeitg.* (1911), 35, 1644.

[9] The Materials of Construction. John Wiley & Sons, New York (1912), 191.

[10] Chemische Technologie der Neuzeit. Stuttgart, Verlag von Ferdinand Enke (1910), 741.

due to the presence of water of hydration, which, as it were, predisposes the material to chemical activity when mixed with hydrated lime and tempered with water. The Meycauayan tuff contains only 4.34 per cent of water of hydration, which is considered low for this class of material. The German Society for the Testing of Technical Material, in October, 1909, adopted new norms for the testing of tuffs and specified a minimum content of 7 per cent of water of hydration. Water undoubtedly has had a great deal to do in determining the chemical and physical properties of tuffs, but just to what extent is a question which has as yet not been completely solved. Tetmajer[11] has shown that blast-furnace slags, analogous in every way to natural slag such as is investigated in this paper, when allowed to cool in the ordinary way into a solid mass and then crushed to powder, with the addition of lime, exhibit no hydraulic properties to speak of, whereas by suddenly cooling the melted vitreous slag in water a product is obtained that possesses very pronounced hydraulic properties when mixed with lime. In fact, some tuffs that have been deprived of their water of hydration by heating to 700° C. no longer show hydraulic properties. This led Tetmajer to make the statement that the efficacy of tuffs and trasses as cementing material could be judged according to the loss on ignition.

F. Tannhaeuser[12] is of altogether a different mind concerning the cause of the hydraulicity of trasses. He maintains that the pozzuolanic properties of trass from the Brohl and Nette Valleys depend upon the content of sodalite minerals which are found in the groundmass. Tannhaeuser has shown that the alkalies of the sodalite minerals are replaced by the calcium of the hydrated lime with the formation of difficultly soluble silicates and that a precipitation of chemically active silicic acid does not occur at this time. Furthermore he concludes from his investigation that the water content has nothing to do with the hydraulic activity of the tuff.

Pozzuolanas or tuffs possessing marked hydraulic properties vary widely in their chemical and mineralogical compositions. They are not fixed chemical compounds having a constant com-

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[11] Vol. 7, 95, cited by Johnston in the Materials of Construction. John Wiley & Sons, New York (1912), 95.

[12] Ein Beitrag zur Petrographie des Trasses und zur Erklärung seines hydraulischen Wirkungsweise. Bautechnische Gesteinuntersuchung, *Mitt. a. d. Min.-Geol. Inst. d. k. Tech. Hochschule* (1911), 2, 34–44. Abstracted in *Tonind.-Zeitg.* (1912), 36, 739.

position, but rather mechanical mixtures of several compounds. Hydraulicity does not depend entirely upon the ultimate chemical composition, upon the presence of opaline silica, nor upon the presence of water of hydration. In the light of present knowledge it seems as though hydraulicity depends upon a number of factors, which apparently vary with the material. The mineralogical composition of the tuff is an important factor in this connection and has been overlooked by several investigators. To be able conclusively to prove the cause of the induration under water of pozzuolanas or tuffs when mixed with lime involves a study of the minerals present in the original material before mixing with lime and a study of the compounds and minerals formed after mixing and the addition of water. With the aid of the mineralogical microscope it would be possible to identify such compounds as are formed.

PREPARATION OF THE RAW MATERIALS

TUFF

The entire sample of tuff, amounting to about 272 kilograms, was first reduced in a jaw crusher to the size of a hazelnut and then fed into a gyratory grinder. The product from the gyratory grinder was comminuted to a fineness of approximately 80 per cent through the 200-mesh sieve. No difficulty was encountered during the reduction process. Although considered locally as a hard tuff, the material, judged from a technological standpoint, is very soft. During the preliminary reduction in the jaw crusher, what especially attracted my attention was the apparent ease with which the tuff was disintegrated; there was an entire absence of flying fragments, sharp snapping, and straining of machine parts, such as are characteristic when crushing even a soft limestone. The softness of the material would be of considerable advantage in case the tuff were used commercially in the manufacture of a pozzuolan cement; grinding costs could be maintained at a minimum. The tuff was not dried, but was ground just as taken out of the quarry. Analysis showed 3.09 per cent moisture. The sample was collected during the dry season, which accounts for the comparative absence of water.

LIME

The lime used was made from Montalban limestone in the Bureau of Science experimental kiln. This stone is hard, fine grained, and has grayish to bluish and yellowish tinges. An analysis made by F. B. Beyer, formerly chemist of the Bureau of Science, gave the following composition:

TABLE V.—*Composition of limestone from Montalban.*

	Per cent.
Moisture	0.25
Silica (SiO_2)	0.94
Ferric and aluminium oxides (Fe_2O_3 plus Al_2O_3)	1.14
Calcium oxide (CaO)	54.61
Magnesia (MgO)	0.22
Loss on ignition	42.79

The calcined product is white, with a slight yellowish tinge. It slakes very rapidly and violently, evolving considerable heat. When sufficient water is added to form a paste, the resulting mass is very plastic and shows the characteristic properties of a fat lime. For this investigation the quick lime was dry slaked by sprinkling with just sufficient water to produce a fluffy, dry, impalpable powder. The slaked powder was separated from lumps of quicklime and the underburned material by sieving through a 100-mesh sieve.[13] The fine lime powder was very white and showed the following composition:

TABLE VI.—*Composition of fine lime powder from lime made from Montalban limestone.*[a]

	Per cent.
Silica (SiO_2)	0.58
Aluminium oxide (Al_2O_3)	0.11
Ferric oxide (Fe_2O_3)	0.41
Calcium oxide (CaO)	74.04
Moisture	23.56
Carbon dioxide (CO_2)	0.30
Magnesia (MgO)	0.93
Sodium and potassium oxides (K_2O plus Na_2O)	0.30

[a] Analysis by R. H. Aguilar, chemist, Bureau of Science.

MIXTURES OF TUFF AND HYDRATED LIME

Tests were carried out on three different mixtures containing 90, 75, and 50 per cent of tuff mixed with 10, 25, and 50 per cent of hydrated lime, respectively. The tuff and lime were weighed separately and mixed, for fifteen minutes, in a ball mill. The mixes were designated as A, B, and C, respectively. They had the appearance of ordinary Portland cement, except the color was somewhat lighter; this difference in color was more noticeable when the tuff mixtures were made up into

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[13] The resulting powder when placed in a metal drum preparatory to incorporation with the tuff exhibited a property that very closely approached the flow of a liquid when the container was moved. This phenomenon is due to the film of air that surrounds the minute particles and keeps them in suspension, thus reducing friction to a minimum.

specimens. Mix C having the largest amount of lime had the lightest color; it resembled in appearance white Portland cement. The following tests were made: (1) Percentage of water necessary for normal consistency; (2) fineness; (3) specific gravity; (4) setting time; (5) tensile strength, neat, in air; (6) tensile strength, neat, in water; (7) tensile strength, mortar, in air; (8) tensile strength, mortar, in water; (9) compressive strength, neat, in air; (10) compressive strength, neat, in water; (11) compressive strength, mortar, in air; (12) compressive strength, mortar, in water. All mortars were made with one part by weight of the tuff-lime mixture and three parts by weight of standard Ottawa sand.

RESULTS OF TESTS

The results obtained are shown in Table VII.

Fig. 1 shows curves obtained by plotting the tensile and compressive strengths in pounds per square inch against time in days. There is a very marked difference in curve slope between air specimens and those kept in water. The strength of those specimens stored in air is practically negligible, whereas the strength developed by some of the test pieces kept in water is considerable. The compressive neat strengths in water of mix C are remarkable in that the curve is practically a straight line and at ninety days still does not show any tendency to parallelism to the X-axis as do the rest. The increment in strength per unit of time during ninety days is constant—about 300 pounds. All other specimens show a falling off in the increment of strength after the 60-day period. When the neat specimens of mixture C stored in water were tested at the 90-day period, failure was accompanied by a sharp report; the spalls had a stonelike ring. The ultimate strength per square inch is 2,202 pounds.

Mix A gave good results, also, although the unit strength did not reach the high figure shown by mix B.

All test specimens, with the exception of those made out of mix C, were allowed to remain in moist air for two days just as made without removing the molds. Mix C was kept in moist air with molds for five days on account of the softness of the specimens. I tried removing some of the test pieces at the end of the second day, as in the case of mixes A and B, but found them so frail that removal without injury was impossible. Two series of tests were conducted upon the various mixtures. One half was stored in air, and the other half was immersed in water. It is common practice in making tests of these kinds to keep the specimens in moist air for a short period,

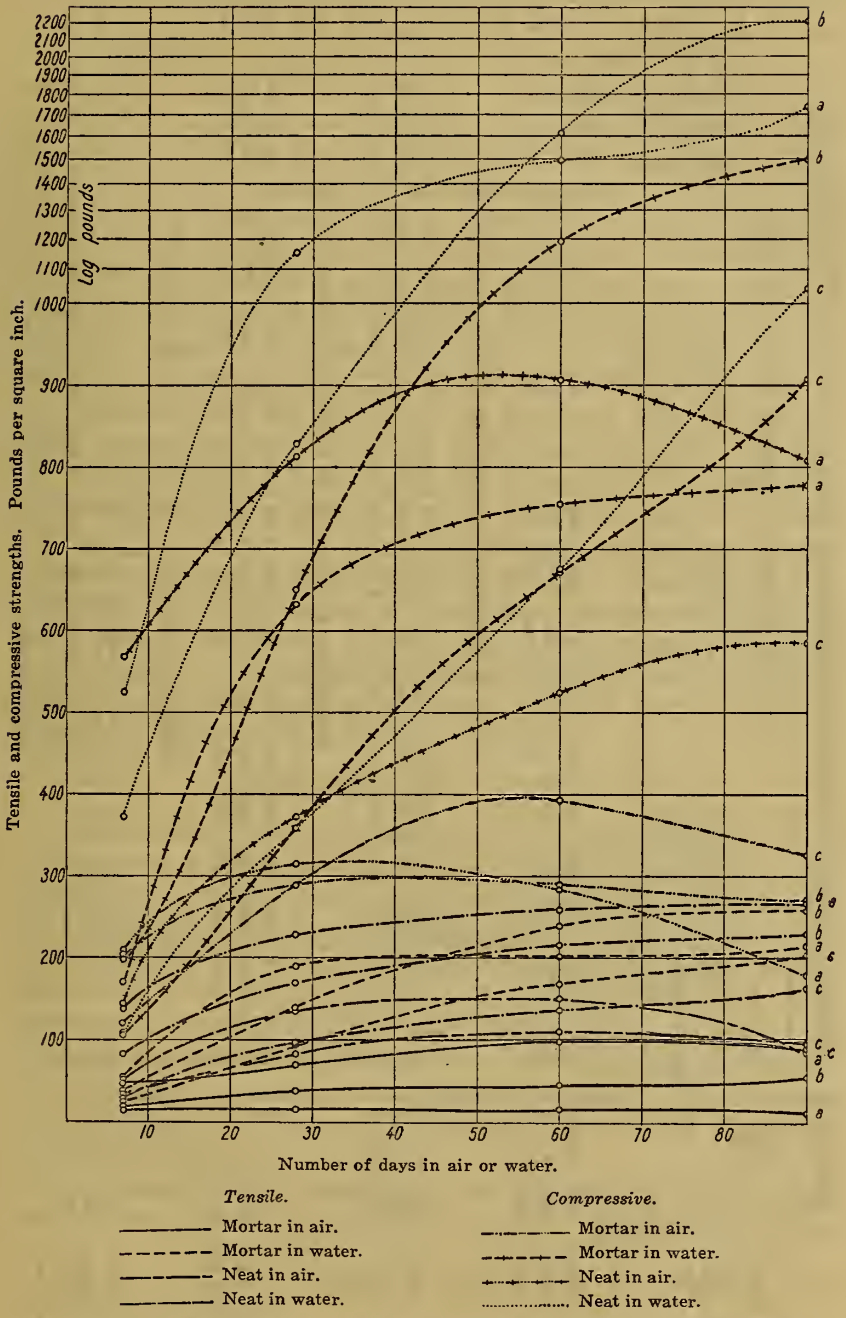

FIG. 1. Curves showing tensile and compressive strengths of volcanic tuff cement.

TABLE VII.—*Showing pozzuolanic properties of Meycauayan tuff when mixed with hydrated lime.*

Mixture No.	Specific gravity.	Time of setting.	Parts by weight.		Fineness.		TENSILE STRENGTH IN POUNDS PER SQUARE INCH.															
			Tuff.	Hydrated lime.	Through 200 mesh.	Through 100 mesh.	Neat in air.				Neat in water.				1 : 3 mortar in air.				1 : 3 mortar in water.			
							7 days.	28 days.	60 days.	90 days.	7 days.	28 days.	60 days.	90 days.	7 days.	28 days.	60 days.	90 days.	7 days.	28 days.	60 days.	90 days.
		Hours.			*Per cent.*	*Per cent.*																
A	2.52	25	90	10	81.2	95.6	49	133	154	84	138	227	251	267	13	15	15	11	54	189	205	215
B	2.51	165	75	25	83	96	72	(a)	99	(a)	82	168	214	229	18	37	45	56	38	138	240	257
C	2.43	237	50	50	79	94.6	33	82	110	95	29	96	137	163	47	69	97	90	22	92	168	204
							TENSILE STRENGTH IN KILOS PER SQUARE CENTIMETER.															
A	2.52	25	90	10	81.2	95.6	3.44	9.36	10.83	5.90	9.70	15.96	17.65	18.77	0.914	1.05	1.05	0.774	3.79	13.29	14.41	15.2
B	2.51	165	75	25	83	96	5.06	(a)	6.96	(a)	5.76	11.81	15.05	16.10	1.27	2.60	3.16	3.94	2.67	9.70	16.88	18.07
C	2.43	237	50	50	79	94.6	2.32	5.76	7.73	6.68	2.04	6.75	9.63	11.46	3.31	4.85	6.82	6.33	1.54	6.47	11.82	14.34
							COMPRESSIVE STRENGTH IN POUNDS PER SQUARE INCH.															
A	2.52	25	90	10	81.2	95.6	568	812	906	808	524	1,152	1,497	1,734	209	313	283	179	170	631	753	778
B	2.61	166	75	25	83	96	354	682	635	678	371	828	1,612	2,202	203	288	289	269	198	649	1,187	1,498
C	2.43	237	50	50	79	94.6	144	372	523	586	105	356	675	1,043	120	314	393	326	108	358	672	906
							COMPRESSIVE STRENGTH IN KILOS PER SQUARE CENTIMETER.															
A	2.52	25	90	10	81.2	95.6	39.94	57.10	63.71	56.82	36.84	81.01	105.28	121.91	14.69	22.01	19.90	12.69	11.95	44.37	52.95	54.71
B	2.51	165	75	25	83	96	24.89	47.96	44.65	47.67	26.09	68.22	113.36	154.82	14.27	20.25	20.32	18.91	13.92	45.64	83.47	105.34
C	2.43	237	50	60	79	94.6	10.12	26.16	36.77	41.21	7.38	25.03	47.46	73.39	8.43	22.08	27.63	22.92	7.59	25.17	47.25	63.71

[a] All cracked.

until they possess sufficient cohesion to stand handling, and then store them for the remaining time in water. The results thus obtained are supposed to indicate the behavior of the material when used in construction. In practice, however, the concrete is sometimes kept moist for a time by covering with damp cloths and afterward sprinkling occasionally with water. At other times, and this is the usual practice, the work is not kept covered with wet cloth or earth, but is simply allowed to dry under the influence of the sun and air currents. It is rarely totally immersed in water. Laboratory tests should be made as nearly as possible in conformity with construction practice. In order to note the effect of air storage equivalent to ordinary construction practice on the tuff mixtures, one half of the test specimens was stored in air, the other half was kept in fresh water, up to the time of testing. The results obtained on the specimens stored in air are altogether different from those obtained on specimens kept in water, as shown in Table VII and fig. 1. It would be interesting to conduct similar experiments upon Portland cement mortars. Tensile and compressive tests were made at the end of seven, twenty-eight, sixty, and ninety days. The briquettes, both mortar and neat, were broken in a standard Fairbanks testing machine. Compression tests were made on a four-screw Olsen testing machine, having a capacity of thirty thousand pounds.

CONCERNING TEST SPECIMENS

For the purpose of carrying out this investigation, a set of 30 cast-iron cylindrical compression molds having a diameter of 3.568 inches (9.063 centimeters) and a height of 7.136 inches (18.125 centimeters) were specially made. The diameter was made 3.568 inches so that the area of the bearing faces would be exactly 10 square inches (64.514 square centimeters); this greatly facilitates the calculation of the strength per square inch and is a very desirable feature when a considerable number of determinations are made. The height was made twice the least lateral diameter in order to secure the correct shearing angle during rupture.

Bauschinger[14] has shown that the following equation holds true for sandstone and similar substances.[15] The equation show-

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[14] Johnson, J. B., The Materials of Construction. John Wiley & Sons, New York (1912), 31.

[15] In my opinion this equation is applicable to the tuff mixtures under study; at least, a few comparative tests, using cubical and cylindrical speci-

ing the relation between the strength of a prism to the strength of a cube, using Bauschinger's data, is

$$\frac{\text{strength of prism}}{\text{strength of cube}} = 0.778 \text{ plus } 0.222 \frac{d}{h}$$

in which *d* equals the least lateral diameter and *h* equals the height of the prism. The equation shows that the strength of a prism having a height twice as great as its least lateral diameter is only 88.9 per cent of that shown by a cube. Cubes are very generally used in making compressive tests, but their use is not to be recommended. Not only do they give results that are too high in calculating the factor of safety, but since the theoretical angle of rupture approaches 60° and not 45°, as was formerly thought to be the case, it is apparent that the ratio between the height and the least lateral dimension $\left(\frac{h}{d}\right)$ should have a minimum of not less than 1.5, so that failure may proceed along the normal angle. Bauschinger has made a very careful and detailed study of this problem,[16] and the conclusions cited are inferred from data obtained during the investigation of a uniformly fine-textured sandstone.

A cylindrical specimen possesses a very desirable feature over a cubical one in that there is an absence of the numerous edges and sharp corners characteristic of the cube. With cylindrical specimens, molding operations are simplified, there is less danger of getting a defective test piece, and, finally, there is less possibility of injury during manipulation.

CHARACTERISTICS OF MATERIAL

In this investigation three or four compression specimens were made for each test; the results shown in the table were obtained by taking the average of at least three breaks. In the tensile tests a minimum of eleven briquettes were broken at each test; in some instances, seventeen. As was to be expected, the compression results were much more uniform than the

mens with the height twice the least lateral diameter, gave results that fitted the equation. The cylindrical shape with $\frac{d}{h}=\frac{1}{2}$ gave strengths varying from 60 per cent to 80 per cent of the strengths shown by the cubical specimens. Not enough tests were made to calculate an accurate constant for this tuff, but the results obtained were sufficiently significant to indicate that Bauschinger's equation is applicable.

[16] Bauschinger, J., *Mitt. a. d. Mech. Tech. Lab. d. k. Tech. Hochschule,* Muenchen (1876), 6.

tensile strength. Great variation was noticed between the strengths of briquettes in the same lot; this was especially true of the briquettes stored in air. I attribute this variation to shrinkage cracks set up by unequal rates of drying and to fine grinding; in part it is characteristic of this kind of cementing material.

Before tempering the various mixtures, the normal consistency of each was determined by the ball method. Mix A required 35 per cent of water; mix B, 36 per cent; and mix C, 36 per cent.

The quantity of material mixed at one time was of such bulk as to prohibit working directly with the hands. For the neat batches about 65 kilograms of the cement were weighed out and formed into the shape of a cone with a crater in the center. The mixing was done upon a concrete surface. Water was poured into the crater and the mass thoroughly mixed for twenty minutes by three assistants using shovels. The work of mixing was laborious on account of the sticky nature of the paste. It adhered tenaciously to the shovels, somewhat like stiff clay, and had a tendency to ball up into separate lumps. During the molding process considerable tamping was necessary to make the cement coalesce. Especial care had to be taken to tamp the paste into the molds in order to reduce the air bubbles and voids to a minimum; even with the care taken, some of the specimens contained excessive voids, which in part account for the variation in some of the results obtained. The mortar mixtures worked much more easily and produced better specimens. More water would make the operation of mixing less laborious, but the additional amount added would cause undue shrinkage of the air specimens and thus lead to serious cracks which would make the specimens worthless. In fact all specimens showed more or less shrinkage. No measurements were made, but shrinkage was easily noticeable twenty-four hours after the specimens had been made and allowed to stand in the air. Some of the briquettes of mix B stored in air were cracked into several pieces by shrinkage, and therefore no results were obtained for these periods. Some of the neat compressive specimens stored in air were also slightly cracked on the surface through the same cause. All neat specimens stored in air showed a tendency to develop hair cracks; the troweled surface of these specimens flaked or peeled off, exposing a rough undersurface. This tendency was not noticed in the mortar specimens. The addition of sand reduced the shrinkage considerably.

SUMMARY

Three mixtures of Meycauayan tuff with hydrated lime were made and subjected to a number of physical tests. Mix A contained 90 per cent tuff; B, 75 per cent; and C, 50 per cent. The following conclusions are based on the results obtained:

1. A mixture of Meycauayan tuff and hydrated lime possesses hydraulic properties. It is not suitable for construction permanently exposed to the air, but develops considerable strength in water.
2. Increasing percentage of lime is accompanied by a retardation of set and a decrease in the specific gravity.
3. The tensile strength is influenced by the fineness of the material. A coarser grind shows lower tensile strength, but the specimens are less liable to crack when stored in air.
4. In general, mix B gave the most satisfactory results.

ILLUSTRATION

TEXT FIGURE

THE OXYGEN-CONSUMING POWER OF NATURAL WATERS *

By GEORGE W. HEISE and R. H. AGUILAR
(From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila, P. I.)

Although the determination of the oxygen-consuming capacity of a water as measured by its ability to reduce potassium permanganate is known to have marked limitations, there can be little question that a series of determinations at regular intervals is of great value in determining the quality of a water supply, especially when studied in conjunction with bacteriological data.[1] The oxygen-consuming capacity is a sensitive index of the fluctuation in the quality in a water supply, and it is especially valuable because it shows relatively small differences rapidly and with some degree of accuracy.

Many methods for measuring the oxygen-consuming power have been proposed and discussed, among them are the determination in acid solution after digestion with potassium permanganate at boiling temperature (Kubel method), the digestion with permanganate in alkaline solution (Schulze method),[2] the digestion with acid permanganate at room temperature or at even lower temperatures,[3] and the digestion with alkaline permanganate solution at reduced temperatures.[4] No less than six different procedures for digestion and titration of samples are recorded by the American Public Health Association.[5] As very slight modifications in method lead to great discrepancies in results, it becomes of interest to study the various procedures, with a view to comparing the results obtained by different methods, as well as for the purpose of studying the factors influencing the determination.

That the oxygen consumption is not a reliable measure of the organic matter in water has repeatedly been pointed out.[6] Tiemann and Preusse,[7] in experiments with various substances such as tartaric acid, cane sugar, asparagin, aniline hydrochloride, and the like, found that the oxidation by means of permanganate was usually less than the value corresponding to the

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* Received for publication December 8, 1915.

[1] Barnard, *Eng. Rec.* (1913), 68, 297.

[2] *Dingler's polytech. Journ.* (1868), 188, 197.

[3] Dupré, *Analyst* (1886), 10, 188.

[4] Winkler, *Zeitschr. f. analyt. Chem.* (1914), 53, 561.

[5] Standard Methods of Water Analysis, 2d ed. New York (1912), 28.

[6] Flugge, Hygienische Untersuchungsmethoden. Veit & Co., Leipzig (1881), 244.

[7] *Ber. d. deutsch. Chem. Ges.* (1879) (II), 12, 1906.

known content of organic matter, in some cases (benzoic acid) there was little or (for urea) no action whatever. Cavel,[8] working with known concentrations of various organic substances, including alcohols, aldehydes, acids, ketones, amides, phenols, sugars, indole, urea, skatole, etc., came to the conclusion that the determination as applied to water gave no indication of the nature or quantity of organic matter present.

The determination of oxygen consumed not only fails to measure accurately the amount or kind of organic matter present, but it is also greatly affected by the presence of different foreign substances. Unoxidized mineral substances, such as ferrous salts, sulphides, and nitrites,[9] introduce errors which it is generally sought to overcome by digesting the sample for three minutes in the cold with sulphuric acid and direct titration with permanganate. M. Dittrich[10] recommends that any sulphur in water should be precipitated before the regular procedure for oxygen consumption is begun.

As early as 1886, Dupré[11] called attention to the fact that a high content of soluble chlorides greatly affected the oxygen-consuming capacity when the digestion was made at boiling temperature, owing to the decomposition of the permanganate in the presence of sulphuric acid and chlorides, chlorine being set free. He found that as little as 15 parts per million of chlorine (1.05 grains per gallon) would appreciably affect the results. It is probaly due to his work that, in the English standard methods,[12] digestion is carried on at 27° C. (80° F.), a correspondingly longer digestion period being used than when digestion is carried on at boiling temperature.

In short, the determination of the oxygen-consuming capacity gives comparable results only when a fixed method is strictly adhered to, and even in this case certain errors may creep in which go far toward destroying the value of the analysis.

We have attempted to study quantitatively some of the factors which influence the determinations. All the data recorded are the average of two or more concordant determinations. Duplicate titrations which did not check each other within 0.5 cubic centimeter were rejected.

[8] *Rev. gen. Chem.* (1912), 15, 73.

[9] Standard Methods of Water Analysis, 2d ed. Am. Pub. Health Assoc., New York (1912) 28.

[10] *Zeitschr. f. analyt. Chem.* (1912), 50, 697.

[11] *Analyst* (1886), 10, 188.

[12] Cf. Sutton, Volumetric Analysis, 10th ed. P. Blakiston's Son & Co., Philadelphia (1911), 485.

EFFECT OF TIME OF DIGESTION

A sample of river water (from the reservoir of the city of Manila) containing less than 5 parts per million of chlorides was used for these determinations. The oxygen-consuming capacity was determined practically as outlined by the American Public Health Association [13] by adding 10 cubic centimeters of dilute (1: 3) sulphuric acid and 10 cubic centimeters of potassium permanganate (1 cubic centimeter=0.1 milligram oxygen) to 200 cubic centimeter samples of water in the cold and digesting for varying periods in a boiling-water bath. After digestion, 10 cubic centimeters of oxalic acid were added, and the sample was titrated at boiling temperature with permanganate.

The analytical results are recorded in Table I.

TABLE I.—*Effect of time of digestion on the determination of the oxygen-consuming capacity.*

[Temperature of digestion, 100° C.]

Time.	Permanganate required.	Oxygen consumption (parts per million).
Min.	*cc.*	
0	0.82	0.35
15	1.10	0.49
30	1.27	0.57
45	1.29	0.58
60	1.34	0.61
120	1.75	0.81
240	2.46	1.16

The decomposition showed no signs of reaching an end point, and proceeded regularly, although at the end of a four-hour digestion the volume of the sample was greatly reduced. The time of digestion is, therefore, a very important factor, and strict adherence to a fixed digestion period is necessary to ensure concordant results.

With digestion at room temperature, the effect, although less marked, is still appreciable, as shown by Table II.

TABLE II.—*Effect of time of digestion on oxygen consumption.*

[Temperature of digestion, 28° C.]

Hours.	Oxygen consumption. (Parts per million.)
2	0.60
4	0.64
6	0.68
8	0.69
24	0.74

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[13] Op. cit., 27.

Even at 10° C. the effect is still marked, although in this case the difference between four- and eight-hour digestion is negligible for practical purposes. An end point is apparently reached after about seven hours, as is shown by the data in Table III.

TABLE III.—*Effect of time of digestion on oxygen consumption.*

[Temperature of digestion, 10° C.]

Hours.	Oxygen consumption. (Parts per million.)
2	0.63
4	0.66
6	0.67
8	0.71
24	0.71

In digestion at or below room temperature with the method described above, the oxygen consumed is the summation of that used up during the digestion period and that required during the time the sample is being heated to boiling temperature. The latter amount is far from negligible; hence better results are obtained by titrating the excess of potassium permanganate in the cold with sodium thiosulphate, using potassium iodide and starch indicator, than are obtained by adding an excess of oxalic acid and titrating back with permanganate at boiling temperature. The difference in results is shown in Table IV.

The fact that no definite end point is attained, except perhaps at low temperature, seems to show that great concordance need not be expected when the digestion is carried on at different temperatures. The discrepancy in results is indicated by the data in Table IV.

TABLE IV.—*Effect of temperature and method of titration on oxygen-consuming capacity.*

Temperature of digestion.	Time.	Oxygen consumed (parts per million).	
		Cold titration with thiosulphate.	Hot titration with oxalic acid and permanganate.
°*C.*	*Hours.*		
10	24	0.34	0.62
28	4	0.55	0.64
100	0.5	--------------	0.79
100	([a])	--------------	0.5

[a] Just heated to boiling.

EFFECT OF CHLORIDES

As chlorides have a marked effect on permanganate digestion at boiling temperature, and as the typical Philippine waters submitted to this laboratory for analysis are generally high in chlorine, it seemed worth while to us to make accurate measurements on waters of varying chloride content.

The determinations were made with the ordinary distilled water of the laboratory, a water which still contained a small amount of organic matter. The same water was used in making up a standard solution of fused sodium chloride, portions of which were then diluted with varying amounts of water to give samples of the desired concentrations. The determinations of oxygen consumption were made in the usual manner, using 100 cubic centimeter samples and digesting at 100° C. for thirty minutes.

The analytical results are recorded in Table V.

TABLE V.—*Effect of dissolved chlorides on determinations of oxygen-consuming capacity.*

[Sample, 100 cubic centimeters; digested for thirty minutes at 100° C.]

SERIES 1.

Chlorine content (parts per million).	Permanganate required.	Difference in permanganate required.	Error introduced in terms of oxygen consumed (parts per million).
	cc.	*cc.*	
0	1.14		
5	1.20	0.06	0.01
10	1.22	0.08	0.03
20	1.33	0.19	0.14
50	1.36	0.22	0.17
100	1.40	0.26	0.21

SERIES 2.

0.0	0.56		
43.3	0.73	0.17	0.16
65.0	0.85	0.29	0.27
77.0	0.85	0.29	0.27
93.4	0.94	0.38	0.37
118.3	1.02	0.46	0.44
161.0	1.10	0.54	0.52
197.0	0.90	0.34	0.32
253.0	1.13	0.57	0.55
355.0	1.32	0.76	0.73
442.5	1.97	1.41	1.37
522.0	1.78	1.22	1.20
710.0	2.07	1.51	1.49
887.5	3.62	3.06	2.99
1,183.0	4.80	4.24	4.14
1,775.0	4.70	4.14	4.05
3,550.0	7.11	6.55	6.41

When the concentration of salt increased beyond 250±, it became difficult to obtain concordant results, as the reaction then appeared to be far from equilibrium at the end of the half-hour digestion period.

It is clear from the data presented that the analysis will give concordant, comparable results only when the chlorine content is extremely low. As little as 5 parts per million introduce an appreciable error, while 50 parts per million, according to our results, will cause a decomposition of permanganate corresponding, in a 100 cubic centimeter sample, to an increase of 0.2 part per million in oxygen-consuming capacity.

It is interesting to note that the method of digesting at room temperature does not overcome the errors noted. Indeed Dupré[14] had already pointed this out and recommended that the digestion be carried on at a temperature as near 0° C. as possible. We conducted a series of digestions at room temperature (30° C.) over four hours and obtained the results shown in Table VI.

TABLE VI.—*Effect of dissolved chlorides on the determinations of the oxygen-consuming capacity.*

[Sample, 100 cubic centimeters; digested for four hours at 30° C.]

SERIES 1.

Chlorine content (parts per million).	Permanganate required.	Difference in permanganate required.	Error introduced in terms of oxygen consumed (parts per million).
	cc.	*cc.*	
0	1.31	-------------	-------------
5	1.38	0.07	0.07
10	1.46	0.15	0.15
20	1.48	0.17	0.17

SERIES 2.

[Twenty-four hours digestion period.]

0	0.73	-------------	-------------
253	0.80	0.07	0.06
355	0.88	0.15	0.14
442.5	1.00	0.27	0.26
591	1.18	0.45	0.44
887.5	1.31	0.58	0.56
1,183	1.62	0.89	0.87
1,775	2.50	1.77	1.73
3,550	3.93	3.20	3.13

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[14] *Analyst* (1886), 10, 188.

In these series the odor of chlorine could be plainly detected during digestion with permanganate and sulphuric acid in the samples containing over 10 parts per million of chlorides. The results, although lacking somewhat in uniformity, showed that an appreciable error is introduced even at 30° if the final titration is made at boiling temperature.

At 10° C. the error, although slighter, is still appreciable, as is shown by the data in Table VII.

TABLE VII.—*Effect of chlorides on the oxygen-consuming capacity.*

[Temperature of digestion, 10° C.]

Chlorine content (parts per million).	Permanganate required.	Error introduced in terms of oxygen consumed (parts per million).
	cc.	
0	11.43	0.0
10	11.50	0.03
100	11.50	0.03
250	11.61	0.09
1,000	12.98	0.8

Only part of the error can be ascribed to interaction of the permanganate and chlorides during digestion, as this reaction goes on at greatly accelerated speed while the sample is being heated to boiling; in fact, the amount of permanganate reduced during digestion at low temperature, although not negligible, is small as compared with that reduced during the short heating period. It is, therefore, possible to eliminate to some extent the error due to chlorides by performing the digestion at a moderate temperature (preferably below 15° C.) and titrating the excess of permanganate with sodium thiosulphate in the presence of potassium iodide and starch indicator. This is shown by the data in Table VIII.

TABLE VIII.—*Effect of chlorides on titration methods.*

Temperature of digestion.	Time of digestion.	Chlorine content (parts per million).	Oxygen consumed (parts per millon).	
			Cold titration with thiosulphate.	Hot titration with permanganate.
°C.	*Hrs.*			
10	24	0	0.34	0.62
10	24	1,000	0.78	1.53
28	4	0	0.55	0.64
28	4	1,000	0.72	1.03

It is evident that the error due to the presence of chlorides persists even when digestion is carried on at moderate temperatures. In order to eliminate this error, digestion should be carried on in alkaline solution according to the method of Shulze or Winkler.[15]

Even in alkaline solution the presence of chlorides may introduce discrepancies. After digestion, when the solution is acidified before the addition of potassium iodide and titration with thiosulphate, sufficient chlorine may be liberated seriously to affect the results. With a chlorine content as high as 250 parts per million no serious error could be detected; with a chlorine content of 1,000 parts per million the discrepancy was appreciable.

A further error is caused by the actual reduction of potassium permanganate to potassium manganate in the presence of chlorides in alkaline solution, even when digestion is carried on at room temperature (30°C.). This was clearly indicated in a series of 24-hour digestions carried on at room temperature in alkaline solution by the change in color from red to green in the samples containing much salt.

A large number of experiments have been performed on digestions with alkaline solutions, but their results were not sufficiently conclusive to warrant their being included in this paper. As might be expected, the results obtained in alkaline solution are highly dependent on the concentration of alkali and on the temperature and time of digestion, so that comparable results can be obtained only by adhering to fixed procedure.

EFFECT OF HYPOCHLORITES

In studying the daily variation in oxygen consumption of a municipal supply, certain discrepancies were noted which induced us further to study the effect of hypochlorites or "free chlorine" on the amount of oxygen consumed. Glaser[16] states that through the addition of chloride of lime the oxygen consumption is first increased, because more organic matter is brought into solution—that is, into a more rapidly oxidizable form. After that a reduction in the required quantity of permanganate occurs, owing to the oxidation of organic material by the chloride of lime itself. He believes that the initial increase in oxygen consumption could not be ascribed to inter-

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[15] *Dingler's polytech. Journ.* (1868), 188, 197; *Zeitschr. f. analyt. Chem.* (1914), 53, 561.

[16] *Arch. f. Hyg.* (1913), 77, 268.

action between hypochlorite and potassium permanganate in acid solution.

The presence of hypochlorites introduces an error in addition to, and opposite in sign from, the one caused by an increased chloride content. In hot digestion the hypochlorite changes to chlorate,[17] probably in accordance with the equation

$$3CaCl_2 \cdot Ca(OCl)_2 = 5CaCl_2 + Ca(ClO_3)_2$$

and reacts with the organic matter present or with the oxalic acid generally used for titration purposes. The amount of permanganate required is, therefore, reduced, and a low oxygen consumption is recorded.

When chloride of lime is added to a water of known organic content, the oxygen consumption as determined by the standard method is invariably low, even when digestion is performed at room temperature (the sample being brought to boiling at the end of the digestion period and titrated in the regular way). This is clearly shown by the results of the following experiments:

TABLE IX.—*Effect of hypochlorites on oxygen consumption.*

SERIES 1.

[Distilled water, 200 cubic centimeter samples, digested thirty minutes at 100° C. with a standard permanganate solution, decolorized with standard oxalic acid solution, and titrated with permanganate at boiling temperature.]

	Available chlorine (parts per million).	Permanganate required.	Error involved in terms of oxygen consumed (parts per million).
		cc.	
Sample A	0	10.45	0
	1·75	10.15	0.15
	4.3	9.45	0.5
	17.5	8.8	0.8
Sample B	0	10.8	0
	5	10.1	0.3
	10	9.7	0.5

SERIES 2.

[River water treated as in series 1.]

Available chlorine added (parts per million).	Permanganate required.	Errors involved in terms of oxygen consumed (parts per million).
	cc.	
0	12.0	0
0.5	11.6	0.2
1.0	11.6	0.2

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[17] Bhaduri, *Zeitschr. f. anorg. Chem.* (1897), 13, 385.

The following data were secured when samples were digested in the cold:

TABLE X.—*Effect of digestion at room temperature.*

[Distilled water, 200 cubic centimeter samples, digested four hours at 30° C., titrated hot.]

Available chlorine added (parts per million).	Permanganate required.	Errors involved in terms of the oxygen-consuming power (parts per million).
	cc.	
0	10.55	0
5	9.25	0.65
10	8.6	1.0

The errors recorded in this last series are of the same order of magnitude as those previously mentioned (Table IX); hence the action of hypochlorite on organic matter proceeds at moderate temperature as well as at high temperature.

That the hypochlorite reacts with the organic matter and that its effect can be only partially eliminated by boiling with sulphuric acid according to the equations

$CaCl_2 \cdot Ca(OCl)_2 + 2H_2SO_4 = 2CaSO_4 + 4HCl + 2O$ and $4HCl + 2O \rightleftarrows 2H_2O + 4Cl$

are indicated by the following data, which resulted on boiling chlorinated samples with sulphuric acid for fifteen minutes before digesting with permanganate:

TABLE XI.—*Effect of boiling with sulphuric acid in presence of hypochlorites.*

Available chlorine added (parts per million).	Permanganate required.	Errors involved in terms of the oxygen-consuming power (parts per millon).
	cc.	
0.0	11.9	0.0
2.0	11.1	0.4
8.0	10.9	0.5
0.0	10.4	0.0
8.0	8.0	2.4
0.0	12.0	0.0
1.0	11.6	0.2

The hypochlorite changes partially to chlorate even in acid solution at boiling temperature. Thus a hypochlorite solution equivalent to 5 milligrams of available chlorine, boiled with sulphuric acid for five minutes, still had the power to oxidize 0.9 milligram of oxalic acid.

Obviously, then, the presence of hypochlorites in appreciable quantities introduces errors into the determination of oxygen consumption, although this determination is at best so notoriously inaccurate that the error introduced by free chlorine is generally of minor importance unless great accuracy is desired. The effect of hypochlorites can readily be eliminated by the addition of a few milligrams of sodium sulphite. After a few hours the excess sodium sulphite is decomposed and it has no appreciable effect on the determination. Before proceeding to the final digestion, however, it is best to digest the sample, which has been standing in contact with sodium sulphite, for three minutes with sulphuric acid, in the cold, and to add a drop of permanganate to make sure that the sulphite has all been destroyed.

SUMMARY AND CONCLUSIONS

Some of the factors influencing the determination of the oxygen-consuming capacity by means of potassium permanganate in acid solution have been studied quantitatively. Time and temperature have so great an effect that concordant results cannot be obtained unless great care is exercised to have all determinations made under identical conditions.

The influence of dissolved substances, especially of chlorides, is very large. The effect of the latter is reduced, although not eliminated, if digestion is carried on at or below room temperature. The final titration of excess potassium permanganate should be made with sodium thiosulphate (in the presence of potassium iodide and starch indicator). The error due to chlorides is reduced by digesting the water samples with potassium permanganate in alkaline (Schulze method), instead of in acid solution, the final titration being made with sodium thiosulphate.

Hypochlorites oxidize organic matter in cold or hot solution and should be eliminated before a determination of the oxygen-consuming power is made.

The determination of oxygen consumption at best is not an accurate measure of the organic content of a water, and it gives such uncertain results that isolated determinations are of very little value. It is only when a water supply is to be examined repeatedly that the determination becomes very useful.

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VOL. XI MARCH, 1916 No. 2

THE CHEMISTRY OF THE VITAMINES[1]

By ROBERT R. WILLIAMS
(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

Since the appearance of the last article in which I collaborated with Doctor Vedder,[2] I have made more than forty attempts to obtain pure vitamine from large quantities of rice polishings. While other methods were tried, the prime endeavor was to perfect the method described by Funk,[3] as it appeared to be preferable to that of Edie et al.[4] or Suzuki[5] and his coworkers, with whose methods I have experimented. The modification of Wellman, Eustin, and Scott[6] was also tested. It failed to facilitate the final purification of the vitamine and apparently resulted in greater loss of curative power in the vitamine fraction. On the other hand, it possesses the great advantage of effecting an enormous saving in the quantities of phosphotungstic acid and barium hydroxide used.

In addition to these methods, many other precipitants have been tried, such as mercuric acetate and zinc and cuprous salts, but of these none produced promising results and may be dismissed. Other attempts were directed to finding a better method of decomposing the phosphotungstates produced by Funk's method. For this purpose amyl alcohol was used as

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[1] Received for publication April 26, 1915.

[2] *This Journal, Sec. B* (1913), 8, 175.

[3] *Journ. Physiol.* (1911), 43, 395; (1912), 45, 75; *Ergeb. d. Physiol.* (1913), 13, 125.

[4] *Bio-chem. Journ.* (1912), 6, 234.

[5] *Bio-chem. Zeitschr.* (1912), 43, 89.

[6] *Am. Journ. Prev. Med.* (1914), 1, 295.

suggested by Jacobs.[7] This, however, afforded no particular advantage, as the vitamine apparently distributed itself more or less equally between the amyl alcohol and water layers. It was also discovered that the phosphotungstate of the vitamine dissolved fairly readily in an excess of phosphotungstic acid, thus enabling it to be separated from the bulk of the precipitated phosphotungstates. But since barium hydroxide was the only reagent found which could be used effectively for decomposing the separated phosphotungstates, this method was also abandoned.

When it was desired to isolate considerable quantities of vitamine in a fairly pure or at least highly concentrated condition, it was necessary to fall back on the method of Funk in practically its original form as nearly as I now understand it. This was the method used for the treatment of the human cases recently reported by Doctor Saleeby and me.[8]

Every resource has been exhausted to avoid mixed deposits from the final liquor and to increase the yield of needles melting at 233°, but without avail. Every step in the process has been modified in turn, but without materially improving the final result. Among such modifications may be mentioned the following:

1. Varying degrees of expression of the original polishings.
2. The use of neutral alcohol for extraction and subsequent hydrolysis of the aqueous extract with dilute sulphuric acid.
3. The use of a glass still and high vacuum for concentrating the extract.
4. More or less prolonged maceration of the phosphotungstates with barium hydroxide.
5. Removal of ammonia from the resulting solution with a stream of air.
6. Varying the strength of reagents and solvents at many points in the process.

I was, therefore, at a loss for an adequate explanation of the discrepancies between my results and those of Funk. Recent work[9] now shows that Funk was in error in reporting the isolation of the curative substance as a pure chemical individual and that the substance melting at 233° consisted almost entirely of nicotinic acid. A number of other differences exist between Funk's results and my own, which are not as yet wholly accounted for. I have noted that the quality of the rice

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[7] *Journ. Biol. Chem.* (1912), 12, 429.

[8] *This Journal, Sec. B* (1915), 10, 99.

[9] Drummond and Funk, *Biochem. Journ.* (1914), 8, 598.

polishings appears to affect the yield of curative substances considerably and have selected the raw material accordingly. Perhaps more suggestive is the idea which has but recently occurred to me that rice polishings, like yeast,[10] may undergo an autolysis which splits the mother substances of the vitamines in a different way than does acid hydrolysis. Funk obtained his entire supply of rice polishings from the Orient,[11] and the bran was well aged before being submitted to chemical manipulation. Here comparatively fresh material has been used uniformly on account of the difficulty of protecting it during storage from the attacks of insects which multiply in it with tremendous rapidity. The presence of large quantities of enzymes in rice polishings is readily demonstrable, as there is rapid production of carbon dioxide from its suspensions in water in the presence of sufficient formaldehyde or phenol to prevent bacterial growth.

In as much as Funk's descriptions of his chemical methods have been so brief and incomplete as to puzzle me greatly, the method as used by myself is recorded in detail, with notes on the apparent discrepancies in results.

Hope of isolating large quantities of an individual vitamine from rice polishings having been abandoned, it was decided to attempt the synthesis of curative substances, which might throw light on the nature of the vitamines. As a discontinuance of the work for the present is now necessary, the very incomplete results are reported in the experimental part.

In choosing the direction for a beginning in this work, the facts adduced by Funk and others pointed to the pyridine ring as the most promising nucleus. The most important facts in favor of this choice are the occurrence of nicotinic acid with the vitamine in several natural substances and the resistance of the vitamine to the Kjeldahl method of digestion for the determination of nitrogen. That this property of the vitamine is shared to the greatest degree by bodies containing the pyridine ring has been shown by the as yet incompleted work of Doctor Brill and Mr. Agcaoili of the Bureau of Science who have kindly communicated their results to me. This resistance is well exemplified by the method of Weidel and Murmann [12] for preparing pyridine sulphonic acids.

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[10] Cooper, *Biochem. Journ.* (1914), 8, 250; Abstract in *Zentralbl. Biochem. u. Biophysik.* (1914), 17, 481.

[11] *Journ. Physiol.* (1911-1912), 43, 400.

[12] *Monatsh. f. Chem.* (1895), 16, 749.

The earlier surmise of Funk that the vitamines are purine or pyrimidine derivatives, on the other hand, does not appear to agree with the known facts above cited. It is supported by the semicurative properties of allantoin and other purine and pyrimidine bodies, which is, however, largely offset by the similar though less-marked property of nicotinic acid. No doubt the conception of the vitamines as necessary foodstuffs for the elaboration of certain tissue constituents had weight with Funk in this surmise. Experience with human beriberi, however, throws much doubt on the truth of this conception, the evidence against which is presented elsewhere.[13]

EXPERIMENTAL PART

METHOD OF SEPARATION OF THE VITAMINE OF RICE POLISHINGS

Twenty-five kilograms of selected, finely ground, light-colored rice polishings are allowed to macerate with occasional stirring for from twelve to twenty-four hours in a mixture of 75 liters of 95 per cent alcohol and 5 liters of concentrated hydrochloric acid. The mass is then pressed out at a pressure of about 1,000 pounds to the square inch. The collected liquid amounts to from 60 to 65 liters. It is evaporated in a copper still at a pressure of from 10 to 12 centimeters of mercury to a volume of about 3 liters. The concentration requires about seven hours. The temperature should not rise above 50°. The concentrated extract separates into layers of fat and aqueous liquid. The aqueous extract is separated from the fat while still warm and is filtered from a copious black sediment, which after being washed is discarded with the fat. The filtered extract and washings are further concentrated in glass under a good vacuum to 2 liters.

Phosphotungstic acid is added gradually till permanent precipitation is complete. An excess must be avoided. Some samples of phosphotungstic acid were encountered which produced temporary precipitates which later redissolved when concentrated solutions were added to an extract already completely precipitated. Therefore care should be taken that the further precipitation is permanent. After standing overnight, the precipitated phosphotungstates are collected and thoroughly washed with 5 per cent sulphuric acid till the washings show only traces of chlorides. When thoroughly air-dried the phosphotungstates so produced weigh from 2,200 to 2,500 grams, com-

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[13] Williams and Johnston, *This Journal, Sec. B* (1915), 10, 337.

pared with about 450 grams obtained by Funk[14] from the same quantity of polishings. This large yield is somewhat, but not greatly, reduced if the original extract is made with neutral alcohol and the concentrated extract hydrolyzed by boiling with 10 per cent sulphuric acid under a reflux condenser for five hours. However, the maceration in acid alcohol produces an extract which cures neuritic fowls in doses corresponding to 50 grams, whereas extracts made by the latter method must be given in doses corresponding to 100 grams to produce the same result.

The mass of dry phosphotungstates is ground intimately with two and a half times its weight of barium hydroxide. During this process the mixture becomes pasty and develops an evanescent green. The odor evolved is somewhat distinctive and resembles that of methyl amine. The pasty mass is collected in a large bottle and is shaken with 3 liters of water for five hours and filtered. The residue is again shaken twice with water for an hour each time. The combined filtrates, from which in the meantime the excess of barium hydroxide has been completely removed with sulphuric acid without the least unnecessary delay, are now carefully tested for excess of sulphuric acid or barium. Any excess of either having been carefully removed, the solution is neutralized with nitric acid, using litmus paper as indicator, and is concentrated in vacuo to a volume of about 1 liter. At this point the toxic properties of the liquid are so great that it is impossible to demonstrate its curative power.

To the concentrated liquid a 10 per cent solution of silver nitrate is added till no further precipitation occurs. The bulky yellow precipitates of purine bases are separated by filtration, and the filtrate is reserved for further fractionation. The purine bases are discarded. I am yet uncertain whether or not Funk carried out this separation of the purine bases in the case of rice polishings, although he reports having done so with yeast. At all events the purine bases so separated, although considerable in amount, do not when freed from silver possess curative properties to a high degree. Moreover it would be quite hopeless under my conditions of work to try to insolate any substance in a pure state from the vitamine fraction if the purines were included with it.

A small aliquot part of the filtrate from the purine bases is titrated with a 5 per cent silver nitrate solution till a drop of

[14] *Journ. Physiol.* (1912), 43, 396.

the clear titration liquid placed on a test plate gives with a saturated solution of barium hydroxide a distinctly brown rather than white or pale yellow precipitate. To the main portion of the filtrate from the purine bases is added an amount of silver nitrate slightly less than that calculated from the above titration.

A small aliquot part of the resulting liquid is now titrated with a saturated solution of barium hydroxide. A white precipitate forms, which at first redissolves on stirring. Later the precipitate becomes permanent and gradually darkens. As long as insufficient barium hydroxide is present the precipitate will settle on standing a few minutes, leaving the supernatant liquid bright and clear. Upon the addition of an excess of barium hydroxide the supernatant liquid becomes cloudy or muddy in proportion to the excess of barium hydroxide. Having thus determined the quantity of barium hydroxide necessary, the aliquot part is combined with the main portion and the calculated quantity of barium hydroxide solution is added. A slight deficiency is preferable to an excess.

The method suggested by Funk of testing with ammoniacal silver nitrate to determine the necessary quantity of barium hydroxide was of very little use to me, as this reagent at no stage produces more than a faint precipitate with the filtrate from the vitamine fraction.

When the precipitation with barium hydroxide is completed, the precipitate is allowed to settle and after decantation of the clear liquid is collected on a Büchner funnel and is thoroughly washed with water. The precipitate, which has by this time assumed a dark green, is suspended in 100 cubic centimeters of water, into which is led a stream of hydrogen sulphide. The suspension is shaken continuously during the passage of the hydrogen sulphide, which continues for from thirty to forty minutes. The solution is filtered, and the precipitate is repeatedly macerated and washed with small quantities of water containing hydrogen sulphide. The combined washings and filtrate from the silver sulphide are carefully treated with very dilute sulphuric acid until all traces of barium are just removed. After filtering from barium sulphate, the solution is evaporated at room temperature to a volume of 50 cubic centimeters. One hundred cubic centimeters of 70 per cent alcohol are added. A rather copious, brown, flocculent precipitate results, which is separated by filtration and washed with 70 per cent alcohol. This precipitate has rather slight curative powers, a dose equivalent to 15 or 20 kilograms of the original polishings being necessary to cure a fowl. It gives the uric acid reaction.[15] It is fairly freely soluble in water, but is very slightly soluble in alcohol. From it considerable nicotinic acid can be crystallized from hot water.

The alcoholic filtrate and washings, which are now curative for fowls in doses equivalent to 3 kilograms of the original polishings as compared with 100 grams in the case of the original extract,[16] are collected and evaporated in a dessicator over sulphuric acid at ordinary pressure. A vacuum dessicator produces too rapid an evaporation for the best results. This solution is now distinctly acid to litmus, but not to methyl orange. As evaporation proceeds, the acidity diminishes. Occasionally a faint alkalinity is developed, resulting in considerable loss of curative power on further standing. In the course of a week's standing in the dessicator, a few needle crystals, 2 to 3 millimeters in length, appear. These show a marked tendency to float on the surface of the mother liquor. At the same time a deposit collects in the bottom of the vessel, consisting of mixed forms of crystals and much amorphous matter. The floating crystals when removed and dried melt at 233° and produce cures in fowls in doses of from 10 to 20 milligrams. The yield, however, amounts to only from 30 to 40 milligrams. If the crystals are allowed to remain in the mother liquor, there is no further accumulation. The amorphous material, however, gradually increases in amount. If separated when the volume has diminished to 10 or 12 cubic centimeters, it shows curative power in fowls in doses of from 20 to 30 milligrams. The yield from 25 kilograms of polishings amounts to 0.2 to 0.25 gram. It is difficultly soluble in water and alcohol and when recrystallized from dilute alcohol is very little altered in appearance or character. This is the product which was used in treating the human cases recently reported.[17]

On further evaporation of the mother liquor from this product either with or without the addition of alcohol, a syrup results which eventually dries to a hard clear film, weighing from 0.2 to 0.3 gram. It possesses curative properties in mod-

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[15] Folin and Macallum, jr., *Journ. Biol. Chem.* (1912), 11, 265; (1912–13), 13, 363.

[16] Funk's statement that the vitamine fraction retains nearly the whole of the curative substance does not appear to be borne out by his own experimental results.

[17] *This Journal, Sec. B* (1915), 10, 99.

erate doses and gives a blue color with phosphotungstic acid and alkali.[18]

SYNTHETIC PRODUCTS

The following derivatives of nicotinic acid were prepared and their curative properties tested by feeding to neuritic fowls per os:

TABLE I.—*Derivatives of nicotinic acid fed to neuritic fowls.*

Substance.	Dose.	No. of fowl.	Effect.
	Grams.		
Nicotinic acid	0.05 to 0.2	6	Little improvement, but some prolongation of life.
Trigonellin	0.05 to 0.2	3	Do.
Hydrochloride of methyl ester of nicotinic acid.	0.1 to 0.2	2	Marked, but temporary improvement.
P-oxynicotinic acid.	0.1 to 0.3	4	Approximately the same as nicotinic acid.

The nicotinic acid was prepared by oxidizing nicotine with nitric acid;[19] trigonellin, by the method of Hantzsch;[20] the methyl ester, by allowing nicotinic acid chloride to react at ordinary temperature with methyl alcohol; and the *p*-oxynicotinic acid, from methyl coumalat.[21] Oxynicotinic acid gives an intense blue reaction with phosphotungstic acid and alkali.[22] This color reaction given by the vitamine fraction of rice polishings may well be due to oxypyridine derivatives.

The methods used by Fischer were tried for the purpose of condensing nicotinic with *p*-oxynicotinic acid and the latter with itself. *P*-oxynicotinic acid was dissolved in aqueous acetone and the theoretical amount of dimethylaniline. To this solution was added finely ground hydrochloride of nicotinic acid chloride, for which no suitable solvent could be found. It decomposed to nicotinic and hydrochloric acids, while the oxynicotinic acid was largely recovered unchanged. As the residue from the reaction mixture did not possess marked curative properties, it was not further investigated.

An attempt to make the carbomethoxy derivative of *p*-oxyni-

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[18] Folin and Macallum, jr., *Journ. Biol. Chem.* (1912), 11, 265; (1912–13), 13, 363.

[19] *Chem. Centralbl.* (1898), 1, 677.

[20] *Ber. d. deutsch. chem. Ges.* (1886), 19, 31.

[21] Pechmann, *Welsh Ber.*, 17, 2390.

[22] Folin and Macallum, jr., *Journ. Biol. Chem.* (1912), 11, 265; (1912–13), 13, 363.

cotinic acid likewise failed to produce satisfactory yields. A small percentage of a substance which from its solubilities appeared to be carbomethoxy derivative was obtained. The body, however, was so unstable as to make its isolation in a pure state difficult. As the yield was very unpromising, this method was abandoned. If, however, carbomethoxy derivatives could be obtained the acid chlorides of which are soluble in some neutral solvent, they would possess a great advantage. The greatest difficulty encountered in working with the pyridine carboxy acids and their derivatives is their slight solubility in all ordinary solvents.

An attempt to condense *p*-oxynicotinic acid with itself by the use of fuming sulphuric acid resulted in a mixture of what appeared to be sulphonated bodies which possessed no marked curative properties. Phosphorus pentoxide gave better results.

Oxynicotinic acid was intimately ground with an excess of phosphorus pentoxide. The mass was quickly transferred to a dry flask fitted with a calcium chloride tube and heated in an oil bath to 150° for twelve hours. The mass gradually softened and was converted into a brown gum, which was taken up in a small quantity of warm water. On cooling, some crystals of oxynicotinic acid separated out together with a quantity of an amorphous, rather flocculent precipitate. This was separated and tested on three neuritic fowls, using a dose of 0.1 gram per os. Great improvement resulted in two cases and an apparently complete cure in the third.

In another experiment acetic anhydride was used as a condensing agent. Oxynicotinic acid was boiled with acetic anhydride under a reflux condenser for thirty minutes. On cooling, a mass separated very similar to that obtained in the previous experiment. Three neuritic fowls were each given by mouth 0.1 gram of this substance. Considerable improvement followed in all cases, but the effect seemed less promising than that of the previous preparation.

DIETHYLSUCCINOSUCCINATE: II

A STUDY OF THE ABSORPTION SPECTRA OF SOME DERIVATIVES[1]

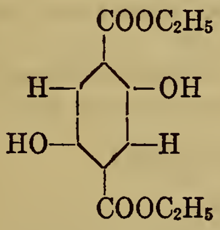
By Harvey C. Brill
(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

FOUR TEXT FIGURES

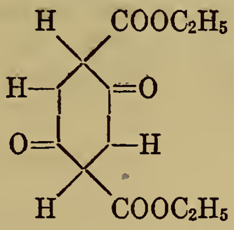
In a recent article by Gibbs and Brill[2] a study of the absorption spectra of diethylsuccinosuccinate and some derivatives was presented. It was shown that ethylsuccinosuccinate exists in the enol and keto forms with slightly different solubilities, thus allowing the separation of the one modification in partial freedom from the other; that the selective absorption of these compounds was due to the joint influence of the carbonyl and carboxyl groups; that the substitution of an acetyl group for the enol hydrogen destroys selective absorption in the case of succinosuccinate, but not in the case of salicylic acid; and the prediction was made that diketohexamethylene would show selective absorption.

In order to add evidence to these conclusions, some additional compounds have been prepared and examined under the iron-nickel arc.

p-DIOXYTEREPHTHALIC ESTER



or



This compound, which was mentioned by Geuther,[3] and proved to be the compound represented by the above formula by the investigation of Ebert,[4] was prepared by treating ethylsuccinosuccinate dissolved in carbon disulphide with bromine according

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[1] Received for publication April 6, 1915.

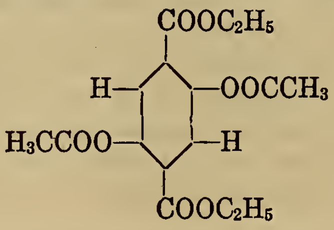
[2] *This Journal, Sec. A* (1915), 10, 51.

[3] *Ann. d. Chem.* (1883), 219, 125.

[4] Ibid. (1885), 229, 45.

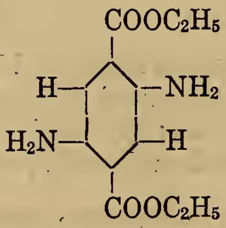
to the method of Herrman.[5] The compound melted at 133°, the melting point given by the latter. It was titrated with alcoholic bromine solution [6] to determine the percentage content of enol and keto modifications. This titration showed that 90 per cent of *p*-dioxyterephthalic ester exists in alcoholic solution in the keto form and only 10 per cent in the enol form. The alcoholic solution was greenish yellow with a deep blue fluorescence under the arc. It showed two bands, one heading near the visible region at $1/\lambda=2,660$ and a much more refrangible one in the ultra-violet region at $1/\lambda=4,010$. This compound was also photographed in the presence of two equivalents of sodium ethylate. The same bands appear, and the position of the first lay largely in the visible region, heading at $1/\lambda=2,375$, while the second had not shifted.

p-DIACETATE OF TEREPHTHALIC ESTER



The acetate was prepared in the manner described by Nef [7] for the preparation of the diacetyl derivative of succinosuccinate by treating the sodium salt of dioxyterephthalate with acetylchloride. After crystallizing from glacial acetic acid and later from alcohol, it was obtained in colorless white plates melting at 154°. The alcoholic solution gave only a very faint blue fluorescence in the light of the arc. An incipient band appears at $1/\lambda=2,900$, while a more decided band appears at $1/\lambda=3,390$.

p-DIAMIDOTEREPHTHALIC ESTER



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[5] Ibid. (1882), 211, 327.
[6] Ibid. (1911), 380, 212.
[7] *Am. Chem. Journ.* (1890), 12, 416.

P-diamidoterephthalic ester was prepared by the method of Baeyer.[8] The compound dissolved in alcohol gave a reddish yellow solution which fluoresced bluish green in the light of the arc. The band appears in the visible region at $1/\lambda=2{,}310$, with a great increase in the general absorption in the ultra-violet region from $1/\lambda=3{,}500$ to $1/\lambda=4{,}200$. By adding an excess of hydrochloric acid, the solution became almost colorless, fluorescence was still visible in the light of the arc although less pronounced, and the band was shifted outside the visible region,

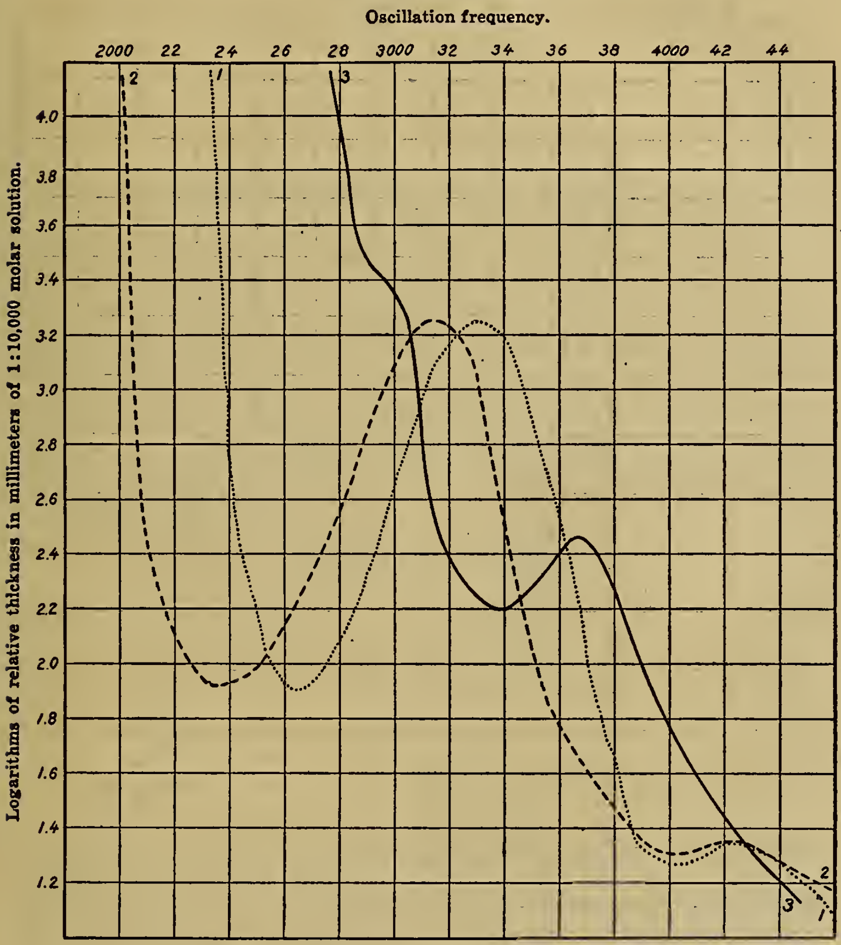

FIG. 1. *Curve 1.* Dioxydiethylterephthalate in alcohol. *Curve 2.* Dioxydiethylterephthalate in alcohol, plus 2 equivalents of sodium alcoholate. *Curve 3.* Diacetyl of dioxydiethylterephthalate in alcohol.

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[8] *Ber. d. deutsch. chem. Ges.* (1886), 19, 430.

appearing at the same concentration as in the case of the free base.

Attempts were made to prepare the diimidodihydroterephthalate by treating p-dioxyterephthalate with ammonium acetate in the manner described for the preparation of the diimide of ethylsuccinosuccinate,[9] but without success.

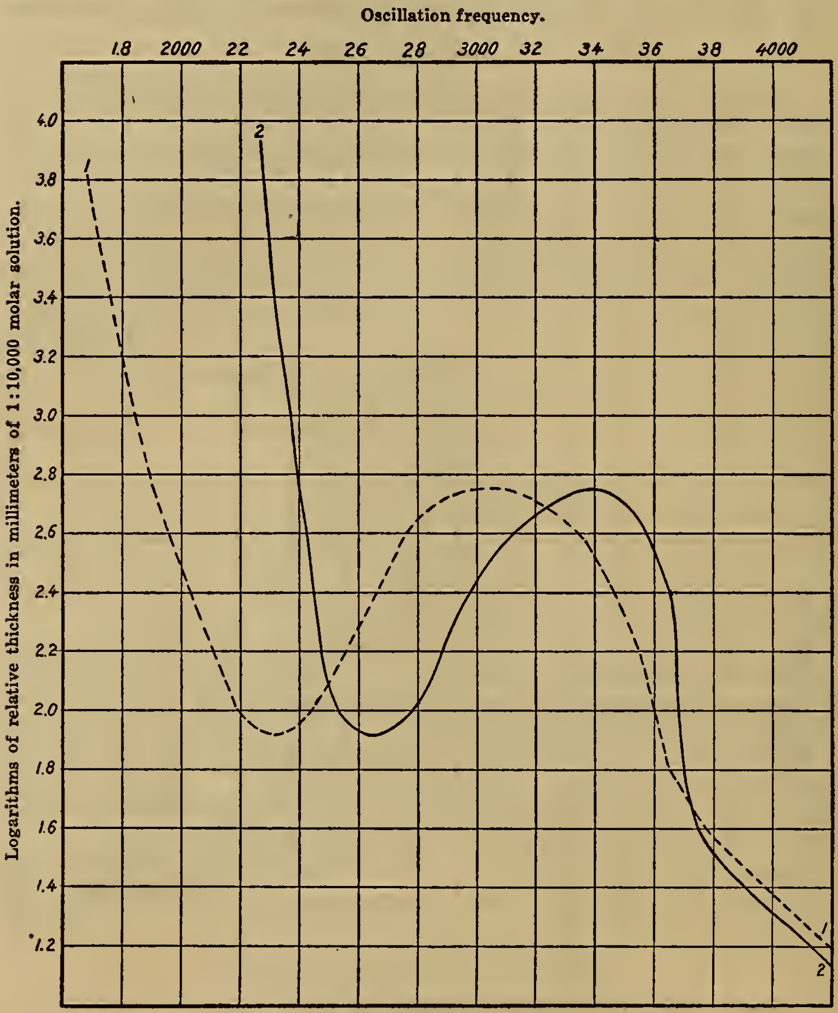

FIG. 2. *Curve 1.* Diamidodiethylterephthalate in alcohol. *Curve 2.* Diamidodiethylterephthalate in alcohol plus 2 equivalents of hydrochloric acid.

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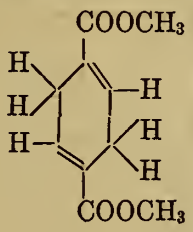
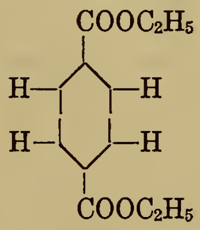
[9] Baeyer, ibid. (1886), 19, 430.

$\Delta_{1,4}$-DIHYDROTEREPHTHALIC ESTER



The $\Delta_{1,4}$-dihydroterephthalic methyl ester was prepared by treating a solution of the sodium salt of terephthalic acid with sodium amalgam[10] for some time, warming at intervals, and afterward forming the methyl ester by adding methyl alcohol to the intimate mixture of phosphorus pentachloride[11] and $\Delta_{1,4}$ dihydroterephthalic acid. This ester melts at 133° when purified by repeated crystallization from methyl alcohol, in which it is readily soluble. When photographed, a very shallow band is seen at $1/\lambda = 3,480$ with a decidedly refrangible band at $1/\lambda = 4,140$. The alcoholic solution shows slight blue fluorescence in the light of the arc.

TEREPHTHALIC ESTER



The ethyl ester of terephthalic acid prepared from terephthalic acid by the method used for the preparation of the methyl ester of dihydroterephthalic acid is a colorless crystalline body, melting at 43° C. when purified by crystallization from alcohol. It gives two rather well-defined bands in the ultra-violet region, one at $1/\lambda = 3,480$ and the other at $1/\lambda = 4,175$, at lower concentration than the bands for the dihydroterephthalate.

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[10] Baeyer, *Ann. d. Chem.* (1889), 251, 290.

[11] Baeyer, ibid. (1888), 245, 140.

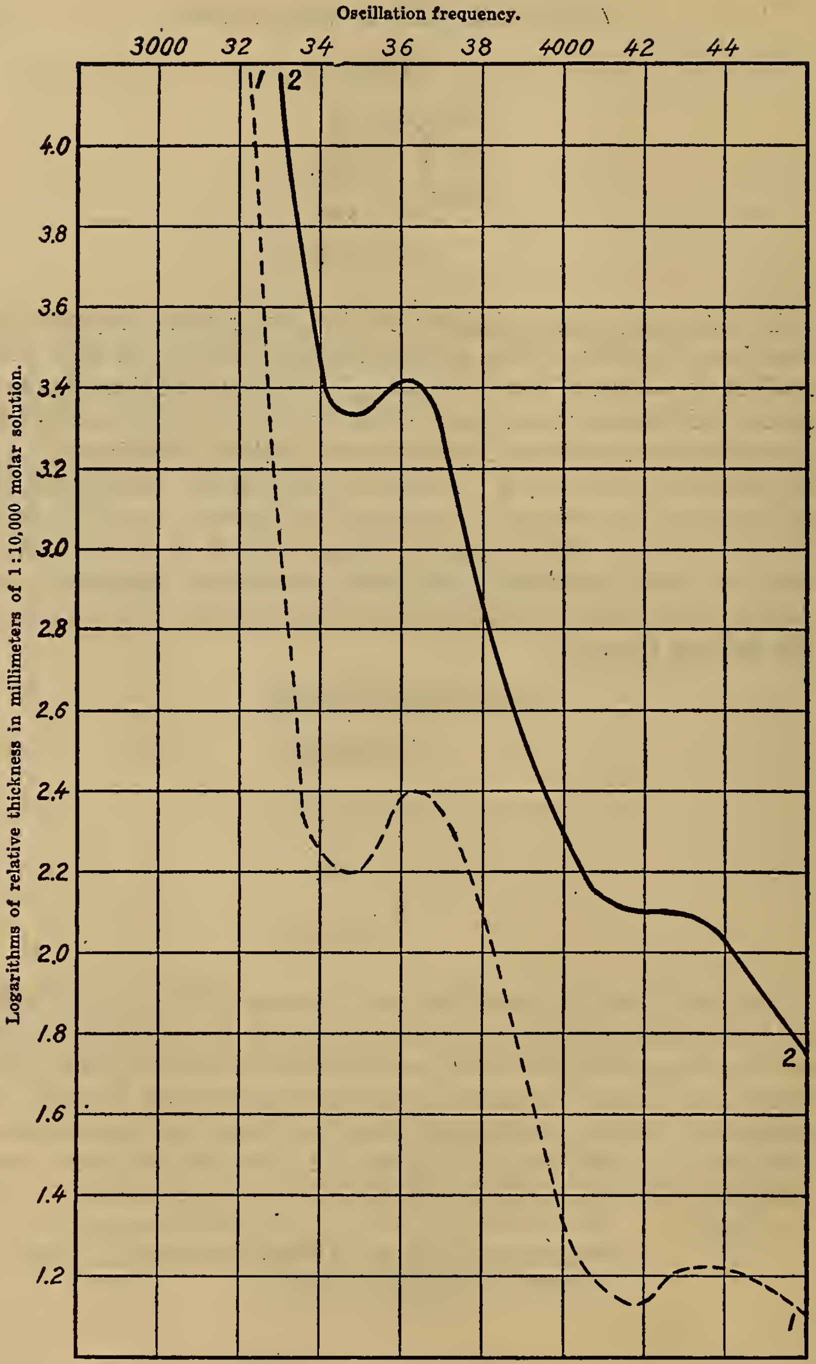
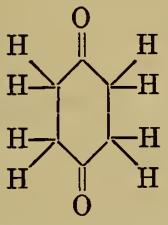


FIG. 3. *Curve 1.* Diethylterephthalate in alcohol. *Curve 2.* Diethyldihydroterephthalate in alcohol.

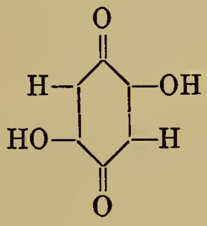
DIKETOHEXAMETHYLENE



Diketohexamethylene was made by the method described by Baeyer.[12] After repeated crystallizations it melted at 78°. It was examined immediately after having been crystallized, as it was noticed that on standing in a dessicator the compound slowly changed from pure white to a yellow tint. Titrated with bromine solution in accordance with the directions of Kurt H. Meyer,[13] it reacted for practically the pure keto form in alcohol solution.

In alcohol solution a very refrangible band appeared in approximately molar solution at $1/\lambda=3{,}500$.

p-HYDROXYQUINONE



Kehrman [14] describes a method for the preparation of hydroxyquinone by treating dianilinoquinone with a mixture of 3 parts of concentrated sulphuric acid and 2 parts of alcohol. However, as the yields obtained by me by the use of this method were exceedingly small, a modified method was adopted. Much better yields were obtained by warming dianilinoquinone in a tenth normal alcoholic potash solution on the steam bath under a reflux condenser until it had gone into solution and the solution had become a certain shade of red easily detected by experience. This usually required from three to five hours' warming. Alcohol of approximately 85 per cent strength was more influential to good yields than stronger alcohol. A large part of the alcohol

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[12] Ibid. (1894), 278, 91.
[13] Loc. cit.
[14] *Ber. d. deutsch. chem. Ges.* (1890), 23, 903.

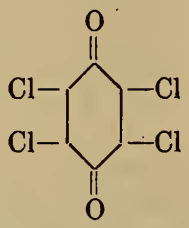
was then distilled off in an open vessel on the steam bath, and the last portions allowed to evaporate in a vacuum dessicator or in the air at room temperature. Usually the heavy, dark red needles of the potassium salt crystallized out on standing. This crystallization could often be hastened by the addition of a few crystals of the salt. The free hydroxyquinone was then obtained from the salt by very carefully adding dilute sulphuric acid to the aqueous solution of the salt and extracting with ether.

The quinone was obtained as a deep straw-yellow compound, decomposing without melting, very easily soluble in alcohol and alkalies, and readily turning brown on exposure to light.

The color of the alcoholic solution is due to general absorption in the red-color region, there being no color band, but a very rapid increase in general absorption from $1/\lambda=2,100$ to $1/\lambda=3,200$, with faint evidence of an incipient band heading at approximately $1/\lambda=2,400$. Selective absorption is shown by the compound in the ultra-violet region with a band at $1/\lambda=3,580$.

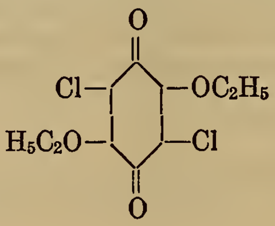
The potassium salt has caused a broadening of the incipient band of the quinone at $1/\lambda=2,400$ into a color band heading at $1/\lambda=2,030$. The second band is still present, although slightly shifted toward the red, heading now at $1/\lambda=3,450$.

CHLORANIL



Kahlbaum's chemically pure chloranil was recrystallized from glacial acetic acid and afterward photographed in this solvent. The olive-colored solution showed general absorption in the visible region, with a band appearing near, namely at $1/\lambda=2,725$, and a much deeper band in the ultra-violet region heading at $1/\lambda=3,520$.

p-DICHLORDIETHOXYQUINONE



Kehrman[15] prepared dichlordiethoxyquinone melting at 95–96° by treating an alcoholic suspension of chloranil at a temperature of 50° C. with a 1 per cent solution of alcoholic potash. Later[16] he claims to have prepared two modifications which he calls "allo-isomers," by treatment of chloranil with alcoholic potash at different temperatures.

His so-called α-compound melted at 107–108° C. Kehrman prepared this isomer by treating an alcoholic suspension of chloranil with alcoholic potash at a temperature near the boiling point of alcohol. It was obtained in the form of crystalline needles. The β-compound melting at 98° was formed by treating an ice-cooled alcoholic suspension of chloranil with a 1 per cent alcoholic potash solution. By this method he claims to have prepared the β-compound entirely free from the α-modification. In his preparation of the α-modification he freed it from the β-modification by making use of their difference in solubility in alcohol, the α-compound being more soluble in cold alcohol, but less soluble in hot than the β-compound. These compounds could not be transformed, the one into the other, by heating alone, with alkalies or with acids.

I have undertaken to make these two modifications in the manner described above, but without success in the case of the α-compound. Even with the most minute attention to the details of his method, no α-compound could be obtained, the β-compound resulting in every trial, and by repeated crystallization from alcohol no separation of this modification from the β-modification was attained.

The compound used here was prepared by treating an alcoholic suspension of chloranil with alcoholic potash at a temperature of 50° and later warming to boiling.[17] By repeated crystallization from alcohol, glacial acetic acid, and ether a platelike crystalline body was obtained melting at 96° C.

The alcoholic solution is chrome yellow, with a refrangible band in the color region heading at $1/\lambda=2,420$ and a second deeper band in the ultra-violet region heading at $1/\lambda=3,350$.

Attempts were made to prepare the oxime by treating a solution of the quinone with free hydroxylamine, but without success. Kehrmann[18] records unsuccessful experiments to prepare the oximes of tetra-substituted quinones by various methods

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[15] *Journ. f. prakt. Chem.* (1889), 39, 318.

[16] Ibid. (1889), 40, 365.

[17] Kehrman, loc. cit.

[18] *Ber. d. deutsch. chem. Ges.* (1888), 21, 3315.

and states that the oximes of such quinones cannot be obtained by direct treatment of the substituted quinone.

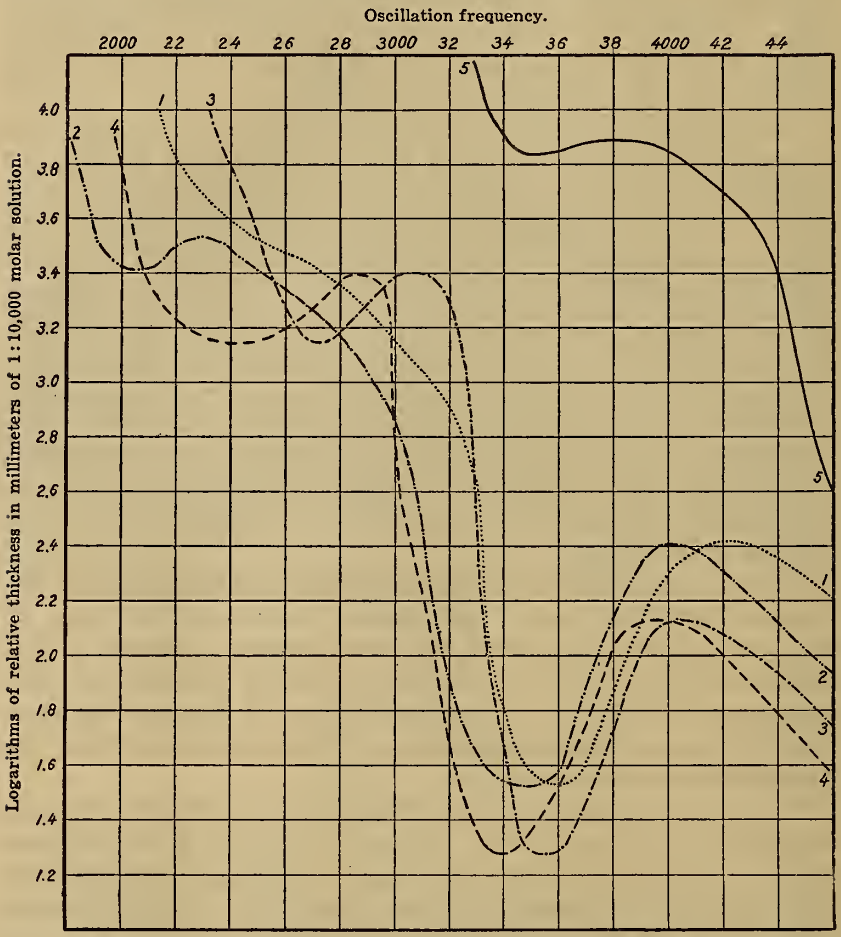

FIG. 4. *Curve 1.* *P*-hydroxyquinone in alcohol. *Curve 2.* Potassium salt of *p*-hydroxyquinone in 80 per cent alcohol. *Curve 3.* Chloranil in glacial acetic acid. *Curve 4.* *P*-dichlordiethoxyquinone in alcohol. *Curve 5.* Diketohexamethylene in alcohol.

DISCUSSION OF RESULTS

Hydroxyterephthalic ester in the light of the arc shows an absorption curve differing somewhat in the intensity of its selective absorption from that of diethylsuccinosuccinate,[19] but heading at about the same point—namely, $1/\lambda=2{,}660$. In the former respect it more closely resembles salicylic acid,[20] the band of

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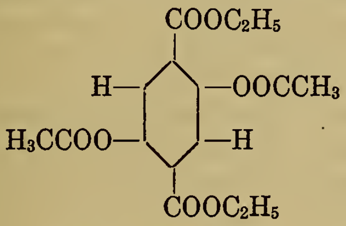
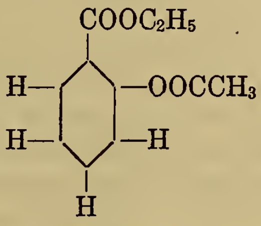
[19] Gibbs and Brill, loc. cit.

[20] Gibbs and Pratt, *This Journal, Sec. A* (1913), 8, 45.

which heads at $1/\lambda=3{,}300$. The similarity of the bands of diethylsuccinosuccinate and of diethyldioxyterephthalate argues for a like cause of the absorption, and it was found that they were both made up of about 90 per cent enol form and 10 per cent keto form. The acetyl derivative of the latter still shows selective absorption, but the bands are shifted, heading at different points and appearing at different concentrations. The absorption curve is very similar to that found for acetyl methyl salicylate by Gibbs and Brill.[21] The constitution of these compounds is analogous; consequently one would expect to find the same type of absorption spectra and not have the selective absorption almost destroyed as is the case for the acetyl derivative of diethylsuccinosuccinate.


Terephthalate.


Salicylate.

Diamidoterephthalic ester gives an absorption curve bearing a slight resemblance to that of the diimide of diethylsuccinosuccinate in that both head at $1/\lambda=2{,}300$, but the former appears at a lower concentration. When a slight excess of two molecules of hydrochloric acid is added, the band does not disappear, but is somewhat shifted toward the ultra-violet region, indicating that the free valencies of the nitrogen have not been saturated by the acid, but that the acid has been added to form a salt of the same character as that formed by thiophthaloxime[22] with sulphuric acid.

Baeyer[23] points out that dihydroterephthalic ester no longer possesses the properties of an aromatic compound, but must be classified as an aliphatic compound. However, it shows selective absorption, although to a less extent than terephthalic ester itself. If one accepts the partial valency theory as announced by Collie and adapted by Pratt[24] to be the explanation of selec-

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[21] Loc. cit.

[22] Pratt and Brill, *This Journal, Sec. A* (1914), 9, 115.

[23] *Ber. d. deutsch. chem. Ges.* (1886), 19, 1797; *Ann. d. Chem.* (1888), 245, 103.

[24] *This Journal, Sec. A* (1913), 8, 420.

tive absorption of light by organic compounds, a ready explanation of the occurrence of selective absorption of light in dihydroterephthalate is at hand. The double bonds of the ring are fixed by the addition of a molecule of hydrogen to the terephthalate; consequently no selective absorption of light waves can arise from the vibration of the bonds in the benzene ring, but must arise from oscillation of the double bonds of the carbonyl groups.

Baly and Collie [25] state in regard to nitrobenzene—

> It seems probable that this very great absorption is due to some form of strained condition having been set up in the benzene molecule until the making and breaking of linking between the carbon atoms has ceased in nitrobenzene, and it seems not unlikely therefore that the presence of the active residual affinity as possessed by ketonic oxygen in the position tends to lock up or restrain the internal motions of the benzene ring.

The theory of partial valency as formulated by Pratt has the advantage of being simple enough to be understood readily, of portraying an easily grasped picture of the condition in the molecule, and of being broad enough to explain all the recorded instances of compounds possessing selective absorption, while the explanation of Baly and Collie, quoted above, presents a much more complex picture, which would be grasped only with exceeding difficulty and would not readily explain the occurrence of selective absorption in such compounds as dihydroterephthalic ester and diketohexamethylene. However, even they are agreed that the carbonyl oxygen has an important influence on the selective absorption of the compound.

To determine if the carbonyl groups alone possess the quality of selective absorption of light, diketohexamethylene, in which the bonds of the ring are all fixed, thus precluding their influence on the selective absorption, was photographed in the light of the iron-nickel arc. As predicted by Gibbs and Brill [26] in accordance with the theory of partial valency, this compound shows selective absorption giving a refrangible band heading at $1/\lambda=3{,}500$ and does not show only general absorption as noted by Hartley.[27]

Baeyer and Noyes [28] report that diketohexamethylene reacts with acetylchloride in ether solution, forming a white precipitate in the presence of sodium alcoholate and that, therefore, it may exist in two forms, the enol and keto. This acetyl com-

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[25] *Journ. Chem. Soc.* (1905), 87, 1340.

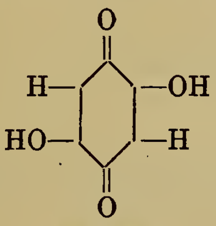
[26] Loc. cit.

[27] *Journ. Chem. Soc.* (1898), 73, 598.

[28] *Ber. d. deutsch. chem. Ges.* (1889), 22, 2168.

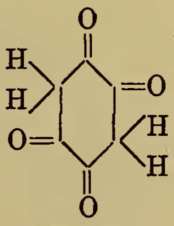
pound was not stable and decomposed at once in the air. An attempt was made to photograph diketohexamethylene in the presence of two equivalents of sodium ethylate, but decomposition took place with darkening of the solution, and the absorption curve obtained was not different from the curve obtained from the solution of the compound alone. This result taken with that obtained by the titration of the alcoholic solution with alcoholic bromine solution is considered conclusive evidence that diketohexamethylene exists in alcoholic solution only in the keto form.

Two forms are possible for *p*-hydroxyquinone.



Keto-enol.

and



Keto-keto.

As the potassium salt can exist in only the keto-enol form, chloranil in only the keto form, and dichlordiethoxyquinone in only the keto-enol form and as the absorption curves of these compounds are very similar, the evidence is fairly conclusive for the existence of *p*-hydroxyquinone in the keto-enol form.

SUMMARY

1. The absorption curves have been studied of dihydroxyterephthalate in alcohol, and in the presence of two molecules of sodium alcoholate; of *p*-diamidoterephthalate in alcohol, and in the presence of two molecules of hydrochloric acid; of diketohexamethylene in alcohol; of chloranil in glacial acetic acid; of *p*-hydroxyquinone in alcohol; of the potassium salt of the latter in dilute alcohol; and of dichlordiethoxyquinone in alcohol.

2. The spectra of both diketohexamethylene and dihydroterephthalate shows selective absorption, thus affording new evidence of the correctness of the theory that the selective absorption of organic compounds is intimately associated with the partial valency equilibrium of the compound.

ILLUSTRATIONS

TEXT FIGURES

FIG. 1. *Curve 1.* Dioxydiethylterephthalate in alcohol.
Curve 2. Dioxydiethylterephtalate in alcohol, plus 2 equivalents of sodium alcoholate.
Curve 3. Diacetyl of dioxydiethylterephthalate in alcohol.
2. *Curve 1.* Diamidodiethylterephthalate in alcohol.
Curve 2. Diamidodiethylterephthalate in alcohol plus 2 equivalents of hydrochloric acid.
3. *Curve 1.* Diethylterephthalate in alcohol.
Curve 2. Diethyldihydroterephthalate in alcohol.
4. *Curve 1.* *P*-hydroxyquinone in alcohol.
Curve 2. Potassium salt of *p*-hydroxyquinone in 80 per cent alcohol.
Curve 3. Chloranil in glacial acetic acid.
Curve 4. *P*-dichlordiethoxyquinone in alcohol.
Curve 5. Diketohexamethylene in alcohol.

HYDNOCARPUS VENENATA GAERTNER: FALSE CHAULMOOGRA[1]

By Harvey C. Brill

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

Owing to the inaccessibility of the habitat considerable obscurity envelopes the source of the chaulmoogra oil of commerce which is used in the treatment of leprosy. For a long time it was supposed that this oil came from the seeds of *Gynocardia odorata* R. Br.,[2] and this belief has given rise to the name "oleum Gynocardiae," the name by which chaulmoogra oil is still often designated. However, true chaulmoogra oil is obtained from the seeds of *Taraktogenos kurzii* King,[3] although the oil from the seeds of *Hydnocarpus wightiana* Blume, *H. anthelminticus* Pierre, and *H. venenata* Gaertner, belonging to the same family, is probably often substituted for chaulmoogra oil. Oil from these last-named trees is known as "kavetel" in Malabar, also as false chaulmoogra oil in many places, and is so similar in all its properties that a distinction by chemical means is hardly possible.

Dr. E. E. Francis, chief medical officer, Asam-Bengal Railway, and technical adviser to the Indian Forests Economics Products Co. Ltd., in an open letter of February 21, 1914, to the editors of the pharmaceutical and medical journals in England, France, Germany, and America, quotes Mr. E. J. Parry as making the following statements in answer to questions put to him by certain vendors of these hydnocarpus oils:

> I would draw your attention, however, to the fact that persistent attempts have been made to restrict the description of chaulmoogra oil to the products of the seeds of Taraktogenos. Your oil is, in my opinion, the product of the seeds of Hydnocarpus which certain authorities consider the only genuine chaulmoogra oil.
>
> As a matter of fact the products from both seeds are so similar as to be nearly identical in properties, and I am of the opinion that your sample is properly described as chaulmoogra oil.
>
> I have examined the above described sample and am of the opinion that it is a genuine chaulmoogra oil free from any adulteration.

Doctor Francis attacks this opinion and challenges the good

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[1] Received for publication November 6, 1915.

[2] Watt, Economic Products of India. W. H. Allen & Co., London (1890), 4, 192.

[3] Brandis, Indian Trees. A. Constable & Co. Ltd., London (1907), 721.

faith of Mr. Parry in making this statement and the vendors for selling hydnocarpus oils as a substitute for chaulmoogra oil.

The controversy aroused by the expressed opinion of Mr. Parry in regard to the oils included under the nomenclature chaulmoogra is illustrative of the uncertainty surrounding the sources and properties of these oils. Similar uncertainty is found in the literature elsewhere. The United States Dispensatory,[4] under *Gynocardia odorata,* gives the name of the oil as chaulmoogra oil and states that it owes its physiological activity to the presence of free gynocardic acid. This uncertainty should be cleared up as promptly as possible, since the well-being of a very unfortunate, large class of people is dependent on our accurate knowledge of the properties of chaulmoogra oil. Chaulmoogra oil is recognized as the most promising remedy for the treatment of leprosy. If the hydnocarpus oils have properties giving them similar physiological effects, to have this definitely proved will bring about a lowering in the cost of the chaulmoogra treatment, since larger quantities of oil will be available for use, and will allay the fear of fraudulent substitution of chaulmoogra by hydnocarpus.

Attention is called to the investigations directed by Mr. Power on the oils from the seeds of *Taraktogenos kurzii,*[5] *Hydnocarpus wightiana,*[6] *Hydnocarpus anthelminticus,*[7] and *Gynocardia odorata.*[8] It is the purpose of this article to present some data obtained by me in an investigation of the seeds of *Hydnocarpus venenata.*

A summary of the results obtained by investigators will be found in the latter part of this article.

HYDNOCARPUS VENENATA [9]

Hydnocarpus venenata belongs to the same family as *Taraktogenos kurzii, Hydnocarpus wightiana, Hydnocarpus anthelminticus, Hydnocarpus alcalae,* and *Pangium edule.* The last two species are indigenous to the Philippine Islands, and I hope to secure material for an investigation of their properties. There are other indigenous species of the Bixineæ which possibly may become sources of chaulmoogra oil.

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[4] U. S. Dispensatory, 18th ed. (1899), 1678.

[5] Power and Gornall, *Journ. Chem. Soc. London* (1904), 85, 838.

[6] Power and Barrowcliff, ibid. (1905), 87, 884.

[7] Ibid. (1905), 87, 884.

[8] Ibid. (1905), 87, 896.

[9] These nuts were obtained through the kindness of Mr. H. G. Carter, economic botanist, Calcutta, India.

EXAMINATION OF THE SEEDS

Approximately 4 kilograms of the kernels, which had been heated at 100°C. for some time in order to destroy the activity of any enzymes present and afterward dried at a temperature between 80° and 90°C., were ground, and the oil was expressed. This oil is greenish yellow, possesses an odor resembling that of crude chaulmoogra oil, and is mobile at room temperature (30°C.).

The nuts yielded 45.57 per cent of dry kernels, which gave by expression a yield of 51.18 per cent of oil with the following properties:

The oil is optically active, being dextrorotatory.
Average rotation 30°/D for a 5-centimeter tube is +24.65°, making the specific rotation +52.03°.
Melting point, 19° to 20° C.
Specific gravity at 30°, 0.9475.
Index of refraction at 30° C., 1.4770.
Saponification value, 200.3.
Iodine value, 99.1.
Acid value cc. N/10 NaOH, 4.4.

EXAMINATION OF THE PRESS CAKE

The ground nuts and the press cake gave qualitative tests for hydrocyanic acid when crushed, suspended, and incubated at 38° C. for forty-eight hours in a solution of emulsin, indicating the presence of a cyanogenetic glucoside. Attempts were made to isolate this glucoside in the following manner: The press cake was extracted with strong alcohol, a large amount of glucose was removed from the alcoholic solution, the alcohol was recovered by distillation under a partial vacuum, and the resulting black, gummy residue was washed with ether to remove the fatty oil. The remainder was dissolved in water and extracted with chloroform. This resulted in a separation into two nearly equal portions. Both were concentrated to dryness, the chloroform portion in the air and the aqueous fraction in a vacuum dessicator over sulphuric acid. The dessicated aqueous extract was then extracted with hot absolute alcohol. This alcoholic solution was allowed to evaporate slowly in the hope that the glucoside would crystallize out, but without any success. In every trial, even after treatment with animal charcoal, infusorial earth, gypsum, etc., the resulting mass came out with a gummy consistency. This gum had the bitter taste of a cyanogenetic glucoside and gave qualitative tests for hydrocyanic acid and glucose. The product obtained by the treatment with alcohol was very small—about 1 gram from 4 kilograms of dry shelled nuts. On account of the small quantity of the material isolated, further attempts to obtain the glucoside in a pure state were discontinued. Nothing definite regarding the amount of the glucoside originally present can be adjudged from the small quantity of material isolated, since nothing is known concerning the previous history of the nuts received. They had the appearance of having been exposed to the weather; consequently hydrolysis of the glucoside due to the activity of the enzyme probably occurred. Fresh seeds have been requested in order that a quantitative determination of the amount of glucoside present can be made.

The water and chloroform portions were combined, acidified with hydrochloric acid, and subjected to steam distillation. The distillate gave tests for acetic and formic acids.

COMPOSITION OF THE OIL

One hundred grams of the oil were saponified with alcoholic potash, the alcohol was distilled off, and the dried mass was extracted with petroleum ether. An oil was extracted which on recrystallization from alcohol possessed a melting point of 132° C. and gave all the reactions of phytosterol.

For a complete examination of the fatty acids 500 grams of the oil were saponified with alcoholic potash and the acids were freed in the aqueous solution by the addition of acid. The free acids were then extracted with ether. A white solid mass was obtained with the following values: A melting point of 43° C., an iodine value of 102.9, a saponification value of 203.3, and specific rotation of +60.96°. The mixture of free acids was dissolved in alcohol with warming, and on cooling the part separating out was removed. After recrystallization from alcohol and ethylacetate it had a melting point of 68° C., identical with the melting point of the chaulmoogric acid found by Power and Barrowcliff[10] in the oil from *Taraktogenos kurzii*, *H. anthelminticus*, and *H. wightiana*. A solution of 2.071 grams in 50 cubic centimeters of chloroform produced in a 2-decimeter tube a rotation of +4.95°, whence $[\alpha]\frac{30}{D} = +59.75^\circ$.

2.1409 grams required 76.16 cubic centimeters N/10 NaOH for neutralization. Theoretical, volume N/10 alkali for neutralization of 2.1408 grams $C_{17}H_{31}COOH$ requires 76.38 cubic centimeters.

0.7990 gram of the sodium salt gave 0.1862 gram Na_2SO_4, whence Na = 7.55 per cent. Theoretical for $C_{17}H_{31}COONa$ = 0.1878 gram Na_2SO_4, or Na = 7.62 per cent.

0.2029 gram absorbed 0.1833 gram iodine, whence I = 90.32 per cent. $C_{18}H_{32}O_2$ with one ethylenic linking requires I = 90.60 per cent.

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[10] Loc. cit.

The alcoholic mother liquor from the chaulmoogric acid separation was then fractionally treated with a concentrated aqueous solution of barium acetate according to the method described by Power and others in the references cited. Five fractions of barium salts were obtained. The acid was freed by adding dilute sulphuric acid and extracting the resulting suspension with ether. The melting points of the fractions ranged: I, 48°; II, 53°; III, 43°; IV, 56°; V, 55°. Fractions IV and V on recrystallization from alcohol and ethylacetate melted at 59° to 60° C. This is the same melting point found by Power and Barrowcliff for hydnocarpic acid. Other values found for this acid are:

A solution of 1.7172 grams in 50 cubic centimeters of chloroform produced in a 2-decimeter tube a rotation of +4.62°, whence $[\infty]$ 30/D = +67.26°.

2.6095 grams required 102.2 cubic centimeters N/10 NaOH for neutralization. Theoretical for neutralization of 2.6095 grams of $C_{15}H_{27}COOH$ requires 103.4 cubic centimeters N/10 alkali.

1.0920 grams of the sodium salt gave 0.2808 gram Na_2SO_4, whence Na = 8.33 per cent. Theoretical for $C_{15}H_{27}COONa$ would give 0.2829 gram Na_2SO_4, or Na = 8.38 per cent.

0.1533 gram absorbed 0.1548 gram of iodine, whence I = 101 per cent. Theoretical for $C_{15}H_{27}COOH$ with one ethylenic linking requires I = 100.6 per cent.

DISCUSSION

The chemical constitution of the oils from *Taraktogenos kurzii*, *Hydnocarpus wightiana*, *Hydnocarpus anthelminticus*, and *Hydnocarpus venenata* is similar, but the oil from *Gynocardia odorata* is different. Table I gives the chemical properties of these oils.

TABLE I.—*Chemical constants of the oils from the seeds of Taraktogenos kurzii (chaulmoogric), Hydnocarpus wightiana, Hydnocarpus anthelminticus, Hydnocarpus venenata, and Gynocardia odorata.*

	Chaulmoogra.[a]	*H. wightiana.*[a]	*H. anthelminticus.*[a]	*H. venenata.*	*Gynocardia odorata.*[a]
Melting point	22°	22°	23°	20°	Liquid at 20°.
Specific gravity	0.951 at 25°	0.958 at 25°	0.953 at 25°	0.948 at 30°	0.925 at 25°.
Specific rotation	+52.0°	+57.7°	+25.5°	+52.03°	Inactive.
Iodine value	103.2	101.3	86.4	99.1	152.8.
Acid value	23.9	3.8	7.5	4.4	4.9.
Saponification value	213	207	212	200.3	197.
Index of refraction	1.476		1.473	1.477	
Cyanogenetic glucoside	Present	Present	Present	Present	Present.
Chaulmoogric acid	do	do	do	do	Absent.
Hydnocarpic acid	do	do	do	do	Do.

[a] Taken from the data published by Power et al. in the references already cited.

The oil from *Gynocardia odorata* can very easily be distinguished from the others because of its optical inactivity and the absence of chaulmoogric and hydnocarpic acids. A study of Table I will convince one that chemical tests will not give conclusive evidence in a differentiation of the other oils, since their constants are so similar. Reasoning from these properties one would expect the physiological action of the oils from the seeds of *Taraktogenos kurzii, Hydnocarpus wightiana, Hydnocarpus anthelminticus*, and *Hydnocarpus venenata* to be analogous, although perhaps varying in degree. If the physiological effects of these oils depend on the distinctive unsaturated acids present, the oil from *Gynocardia odorata* should act differently from the other four; on the other hand, if the activity is dependent on the presence of a cyanogenetic glucoside, the gynocardia oil should be as physiologically active as the others.

In a later paper I expect to be able to present some information as to the physiologically active portion of several of these oils.

SUMMARY

The results of an investigation of the chemical properties and constitution of the oil from the seeds of *Hydnocarpus venenata* are given.

These results would indicate that the physiological properties of the chaulmoogra and hydnocarpus oils should be identical, since the chemical constituents are identical, and that the properties of the gynocardia oil may be different, depending on whether the physiological activity is caused by the unsaturated acids present in the chaulmoogra and hydnocarpus oils or by the glucoside present in all the seeds.

THE SALICYLIC ACID REACTION OF BEANS[1]

By Harvey C. Brill

(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

One of the most important economic plants with which man has to deal is the bean. It belongs to a group of plants called the pulse family, which contains members varying in size from the low annual plant to the tall broad-spreading tree. The bean is especially important since it not only furnishes food for man and beast, but enriches the soil in which it grows by taking nitrogen from the air and converting it into compounds available for plant growth. The Chinese and Japanese have recognized this fact from time immemorial, and their culture of the soy bean (*Glycine hispida*) has assumed large proportions. The shipments of dry beans from Manchuria are given in Table I.

Table I.—*Shipments of dry beans from Manchuria.*

	Tons.
1909	1,470,870
1910	1,200,000
1911	1,500,000

[a] Address, Soya bean oil as paint materials, by Maximillan Toch.

During the fiscal year 1914 there were imported into the Philippine Islands the quantities of beans recorded in Table II.

Table II.—*Dry beans imported into the Philippine Islands during 1914.*[a]

Country.	Quantity.		Value.	
	Kilos.	Per cent.	Pesos.[b]	Per cent.
China	1,763,015	63.00	131,272	41.70
Japan	501,022	17.90	64,146	20.40
Spain	113,409	4.05	30,560	9.70
United States	415,805	14.85	86,904	27.65
All others	4,964	0.20	1,462	0.50
Total	2,798,215		314,344	

[a] Report, Philippine Bureau of Customs for 1914.

[b] One peso Philippine currency equals 100 centavos, equals 50 cents United States currency.

China leads in the sales of beans in the Islands, followed by the United States and by Japan. Practically 60 per cent of

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[1] Received for publication November 1, 1915.

the beans shipped into the Philippines—the combined shipments of China and Japan—are soy beans.

The consumption of beans by the inhabitants of the Archipelago is a good sign, indicating as it does the consumption of a more nearly balanced diet than can be obtained by the use of the common local cereals and vegetables, since the soy bean is a cheap source of protein matter and fat. It is superior to any other cultivated bean in this respect, as is proved by the data given in Tables III and IV.

TABLE III.—*Analyses of soy beans.*[a]

Variety.	Country.	Protein.	Fat.	Nitrogen free extract.	Protein and fat.
		Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Soy black	Germany and France.	32.18	14.03	31.97	46.21
Soy yellow	China, Germany, and Austria.	33.41	17.68	29.31	51.09
Soy brown	do	32.90	18.03	30.17	50.93
Soy black, round	do	33.97	17.11	28.41	51.08
Unknown	France	35.00	13.60	29.92	48.60
Do	Japan	37.80	20.90	24.00	58.70
Do	India	36.00	18.00	25.00	54.00
Soy yellow	America	34.63	17.98	30.50	52.61
Soy white	do	27.56	19.09	28.24	46.64
Soy black	do	26.25	16.38	26.57	42.63

[a] Langworthy, *Farmers' Bull., U. S. Dept. Agr.* (1899), 58, 20.

TABLE IV.—*Analyses of kidney, frijole, and Lima beans, and of lentils, peas, and cowpeas.*[a]

Variety.	Protein.	Fat.	Carbohydrates.	Protein and fat.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*
Kidney beans	22.50	2.00	59.50	24.50
Frijoles	22.00	1.20	65.20	23.20
Lima beans	18.00	1.60	66.00	19.60
Lentils	26.00	1.00	59.00	27.00
Peas	24.63	1.00	61.86	25.63
Cowpeas	21.40	1.40	60.80	22.80

[a] Abel, *Farmers' Bull., U. S. Dept. Agr.* (1900), 121, 30.

The maximum protein content, 37.80 per cent, for the soy bean is shown by a variety grown in Japan, while the maximum fat content, 20.90 per cent, is shown by the same variety; the minimum protein content, 26.25 per cent, is shown by a black variety grown in America, while the minimum fat content, 13.60

per cent, is shown by a black variety grown in Germany and France. Contrast these yields with the maximum protein content, 26.00 and 22.50 per cent, for lentils and kidney beans, respectively, and the maximum fat content, 1.40 and 2.00 per cent, for cowpeas and kidney beans, respectively, and the superiority of soy beans as an adjunct food for carbohydrates is very clearly brought out.

These beans are used in the preparation of so many and so varied kinds of foods, such as milk, cheese, casein, oil, jellies, flour, bread, biscuits, cakes, and sauces, that any information regarding their properties is particularly interesting and important; when these data are concerned with a property, such as the giving of a test for salicylic acid in the generally used ferric chloride color test, the recording of such data becomes doubly important. One very prominent duty of a government food laboratory is the testing of foods to determine if they are in accord with the laws regulating their preparation for consumption. The use of salicylic acid and the salicylates in foods has been prohibited.[2] In the light of this prohibition it seems very essential that the knowledge that a food under certain conditions gives this test should be generally known, in order that no injustice may be done to it.

In the test for salicylic acid, a substance volatile in steam, soluble in ether, capable of sublimation and crystallization, and giving a violet color with ferric chloride is usually considered to be salicylic acid.[3]

However, such a test is not conclusive evidence that salicylic acid is present.

Brand[4] found that an extract of caramel malt gave a reaction with ferric chloride like that given by salicylic acid. One year later he succeeded in isolating a crystalline substance obtained by condensing the vapors given off during the roasting of so-called malt coffee.[5] This compound is soluble in ether or water (much less soluble in cold water than in hot water), volatile in steam, and gives a violet color with ferric chloride, but does not give the red color with Millon's reagent which is given by salicylic acid. This compound, called maltol by Brand, he found to be phenolic in character and to agree with

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[2] *Food Inspection Decision, U. S. Dept. Agr.* (1907), 76.

[3] *Bull. U. S. Dept. Agr.* (1908), 107, 197; Leach, Food Inspection and Analysis. John Wiley & Sons, New York (1907), 671.

[4] *Zeitschr. f. d. ges. Brau.* (1893), 15, 303.

[5] *Ber. d. deutsch. chem. Ges.* (1894), 27, 806.

the formula $C_6H_6O_3$. The results obtained by Brand were corroborated by Erich[6] and Munsche.[7]

Kiliani and Bazlen[8] studied the chemical behavior of maltol. Will[9] studied its behavior toward yeast. Abraham[10] pointed out that dark-colored beers may readily contain maltol and that any test made for salicylic acid with ferric chloride which results positively could not be considered an absolute evidence of the presence of salicylic acid. He recommends the use of the Jorissen reaction.[11]

Jorissen's reaction.—To the solution to be tested add 4 to 5 drops of a 10 per cent solution of potassium nitrite, 4 or 5 drops of acetic acid, and 1 drop of a 10 per cent solution of copper sulphate and heat to boiling. In the presence of salicylic acid the solution turns reddish and in the presence of more than a trace it becomes blood red.

Jorissen points out that phenol reacts in the same manner with this reagent. However, phenol has no use as a preservative in foods, so offers few possibilities of confusion in this regard. Abraham recommends the reaction as the most reliable test for salicylic acid. He found that maltol gave no color with the Jorissen reagent.

Sherman[12] found a body similar to maltol in bread. He believes this body is formed during the process of baking. A. Backe[13] states that certain baked farinaceous foods, such as bread and biscuits, contain small quantities of a compound which show many of the reactions of salicylic acid. He believes the compound is produced when starchy foods and sugars are heated after being acted on by an unknown enzyme occurring together with ordinary amylase in flour and malt.

EXPERIMENTAL

The sentitiveness of ferric chloride solution, Millon's reagent, and Jorissen's reagent toward solutions of salicylic acid was investigated. Ferric chloride gave a distinct violet color with a solution of 0.0008 gram salicylic acid in 100 cubic centimeters of water. This same solution gave a noticeable red in Jorissen's

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[6] *Der Bierbrauer* (1893), 24, 465.

[7] *Wochenbl. f. Brauerei* (1893), 10, 739.

[8] *Ber. d. deutsch. chem. Ges.* (1894), 27, 3115.

[9] *Zeitschr. f. d. ges. Brau.* (1898), 21, 304.

[10] *Journ. Pharm. Liége* (1898), 5, 173.

[11] *Bull. Acad. Roy. Sci., Lettres, et Beaux Arts Belgique* (1882), III, 3, 259.

[12] *Journ. Ind. Eng. Chem.* (1910), 2, 24.

[13] *Compt. rend. Acad. Sci.* (1910), 150, 540.

reaction. Millon's reagent reacted, giving a faint pink with a solution of 0.002 gram of salicylic acid in 100 cubic centimeters of water. I found it somewhat less sensitive than either the ferric chloride solution or the Jorissen reagent; consequently only the last two were used in the following tests.

Various methods of treatment were used in the preparation of the extract from the bean samples. The method described below gave the most satisfactory results: Fifty grams of the ground bean sample were allowed to stand for twenty-four hours, covered with 70 per cent alcohol. The use of 70 per cent alcohol prevented the extraction of large quantities of the fat. Extraction in a soxhlet with strong alcohol was tried, but it was found difficult to free the resulting extract from the fat, and the fat always interfered with the sensitiveness of the tests. They were then filtered with suction, the alcohol was carefully evaporated from the filtrate on the steam bath, the residue made slightly acid with dilute sulphuric acid and extracted with ether, the ether evaporated, and this residue dissolved in very dilute alcohol, made acid, and then tested with the testing reagents. The solution to be tested did not give a decidedly positive reaction except when acidified. Brand points out this difference in the properties of maltol and salicylic acid. This difference would serve as a means of differentiation, but is liable to error in the hands of a careless manipulator, since, if any of the acidified liquor is included in the ether extract, the conditions are present for a positive test for salicylic with ferric chloride solution.

Fifty grams of the ground beans which had given a positive test with iron chloride were suspended in water which was acidified with phosphoric acid and were then subjected to steam distillation.[14] The fractions passing over gave a positive test with iron chloride, but a negative test with Jorissen's reaction. Tests on several cereals and cereal products are included in Table V.

TABLE V.—*Results of tests on beans and several cereals.*[a]

Origin and name.	Description.	Ferric chloride test.	Jorissen's reaction.
Philippine beans.			
1. Similar to Mexican	Brown beans	Positive	Negative.
2. Mongo	Yellow beans	Negative	Do.
3. Similar to navy	White beans	do	Do.

[a] Most of these examinations were made by F. W. Hauch, chemist, Bureau of Science.

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[14] Sherman, *Journ. Ind. Eng. Chem.* (1910), 2, 24.

TABLE V.—*Results of tests on beans and several cereals*—Continued.

Origin and name.	Description.	Ferric chloride test.	Jorissen's reaction.
Japanese beans.			
1. Tokachi-mame	White with black spot; small.	Positive (about 0.02 per cent).	Negative.
2. Nakate-Ohsaya-Eda-mame.	White with black spot; large.	Positive (about 0.05 per cent).	Do.
3. Sodefuri-mame	Slightly green; large	do	Do.
4. Munada-Shiro-daidzu	do	do	Do.
5. Tanokuro-mame	Deep green with black spot; large.	Positive (about 0.025 per cent).	Do.
6. Shiro-mame	Yellow; large	Positive (about 0.075 to 0.1 per cent).	Do.
7. Tenruko-mame	do	Positive (about 0.05 to 0.1 per cent).	Do.
8. Snagoro-eda-mame	Yellow; small	do	Do.
9. Wase-Ohsaya-Eda-mame.	White; large	Positive (about 0.02 per cent).	Do.
10. Ao-daidzu	Deep green; large	Traces	Do.
11. Ao-Shiro-daidzu	Light green; large	Positive (about 0.008 to 0.01 per cent).	Do.
12. Gan-Wase-Eda-mame	Yellow with black spot; large.	Positive (about 0.03 to 0.05 per cent).	Do.
13. Kirro-mame	Black; large	Positive (about 0.05 to 0.075 per cent).	Do.
Chinese beans.			
1. American consul, Amoy, China.	Green; small	Positive (about 0.005 per cent).	Do.
2. American consul, Harbin district, down Sungari River.	Yellow with black spot; small.	Negative	Do.
3. District up Sungari River.	do	do	Do.
4. District along western line of Chinese Eastern Railroad.	do	Traces	Do.
5. District along eastern line of Chinese Eastern Railroad.	do	do	Do.
6. American consul, Amoy, China.	Black; small	Positive (about 0.05 to 0.075 per cent).	Do.
Chinese beans from American Consul, Mukden, Manchuria.			
1	White; small	Negative	Do.
2	Yellow; small	Slight	Do.
3	White; small	Negative	Do.
4	Red; small	Slight	Do.
5	Black; small	do	Do.
6	Green; small	Negative	Do.
American beans.			
1. Lima beans		do	Do.
2. Michigan navy		Traces	Do.
3. California navy		Negative	Do.
4. American peas		do	Do.

TABLE V.—*Results of tests on beans and several cereals*—Continued.

Origin and name.	Description.	Ferric chloride test.	Jorissen's reaction.
American beans—Cont.			
5. Cracked peas		Traces	Negative.
6. Kidney beans		Positive (about 0.025 to 0.05 per cent).	Do.
7. Mexican red beans		Negative	Do.
Breakfast foods.			
1. Grape nuts		Strongly positive	Do.
2. Quaker white oats		Negative	Do.
3. Quaker corn meal		do	Do.
4. Graham flour		do	Do.
5. Quaker wheat, puffed		do	Do.
6. Shredded wheat biscuit		do	Do.
7. Toasted corn flakes		do	Do.
8. Pop corn		do	Do.
Coffee substitutes.			
1. Lab. No. 120375	Roasted coffee and soy bean.	Strongly positive	Strongly positive.
2. Lab. No. 120384	do	do	Do.
3. Lab. No. 120388	do	Negative	Negative.
4. Lab. No. 120373	do	Strongly positive	Strongly positive.
5. Lab. No. 120381	do	do	Do.
6. Lab. No. 120378	do	Negative	Negative.
Flour.			
1. Lab. No. 120176		do	Do.
2. Lab. No. 120691		do	Do.
3. Lab. No. 120187-I		do	Do.
4. Lab. No. 120187-II		do	Do.
Tiqui-tiqui extract.			
1. Bureau of Science	Dilute alcoholic extract of rice polishings.	Slightest	Do.
2. Manuel Zamora	do	Negative	Do.
3. Botica de Santa Cruz	do	Slightest	Do.
Cacao.			
1	Fermented	Negative	Do.
2	Unfermented	do	Do.

Numbers 6 and 7 of the Japanese beans were cooked and then tested for salicylic acid with the same result as with the uncooked beans. Numbers 1, 2, 3, and 4 of the Japanese beans were ground, suspended in water, and allowed to stand for forty-eight hours until fermentation had actively begun and continued for some time. The same result was obtained as with the fresh beans—the amount of the reacting substance was not increased. Fermentation itself did not cause the formation of any of the reacting compound.

DISCUSSION

In the tests on the Japanese soy beans the ferric chloride test was positive in every case, usually strongly positive; the American, Chinese, and native beans tested gave either negative or somewhat faintly positive tests with ferric chloride. It would appear that the beans from Japan are slightly different from those of the other places cited. Climate, soil, or methods of handling could account for these differences in the tests given by the Japanese and Chinese beans, since the latter are soy. Fermentation alone did not bring about a synthesis of the reacting substance, as we have shown by experiment on Japanese soy beans, numbers 1, 2, 3, and 4. Brand has proved that malt which undergoes a peculiar kind of fermentation forms a compound giving the test. Sherman states that moisture and baking or roasting cause the formation of a similar compound in cereal products. He ignores in his statement the influence that the fermentation process which takes place before the baking of the bread on the addition of the yeast may have on the formation of this reacting substance. Among the breakfast cereals tested, grape nuts, which contains roasted wheat bread and malt, alone gave a positive test. Puffed wheat and shredded wheat biscuit which had been baked and had had moisture present when this baking process occurred gave negative results. This would indicate that moisture and baking are not sufficient to cause the synthesis of a reacting substance similar to maltol and would throw doubt on the surmise of Sherman that moisture and baking effects its formation. Backe, in his statements that the formation of the color substance is due to the action of an enzyme on farinaceous substances, seems much nearer the truth. As soy beans contain no starch, his statement would need to be broadened to include substances such as soy beans.

A very interesting test is the positive reaction given by four of the coffee-soy-bean mixtures with Jorissen's reagent. As these are commercial products, we have no way of accounting for the negative results in the other two cases except the surmise that the compound was probably volatilized by too long roasting.

The reacting compound in the beans is volatile in steam, can be sublimed, is soluble in dilute alcohol and in ether, and gives a violet color with ferric chloride. In this respect it answers the requirements for the very generally used ferric chloride color test for salicylic acid, and it appears to be a compound similar in nature and composition to the maltol of Brand and the color compound found by Sherman to exist in baked farinaceous foods. By reason of the presence of a compound with the above enumerated properties, we believe Jorissen's reagent should be used in the test for the presence of salicylic acid in beans.

SUMMARY

The importance of the soy bean as an article of diet for the Philippine Islands has been shown.

These beans have been found to give the ferric chloride color test for salicylic acid and a negative test for salicylic acid with the Jorissen reagent and with the Millon reagent in the cases tried.

This compound is undoubtedly similar to the maltol of Brand, and I believe that it is formed by enzymic action in the beans.

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SOME VEGETABLES GROWN IN THE PHILIPPINE ISLANDS [1]

By FRANCISCO AGCAOILI

(*From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.*)

The question of food and food supply is a matter that early concerns the minds of a people no matter how primitive they may be, and the degree to which they have solved this problem is a fair measure of the stage of civilization at which they have arrived. When a majority of the inhabitants of a country is necessarily employed in the cultivation of nurture crops, no high state of civilization has been attained nor is it possible to attain such a state until a radical change has been made in the food supply of that country.

This is not meant to imply that food alone controls the civilization of a country, for one can readily conceive of a state enjoying the greatest supply of food with the least necessary effort in the obtaining of this supply and yet falling far short of being a highly civilized community. But the converse is more nearly always true, that a nation must have leisure from the harrowing toil in the field for mere existence, in order that other fields of labor may be developed and that individuals may have time to cultivate the graces of the mind and body. Consequently the preparation of some fairly concentrated food is needed to bring about this condition—the condition where man need not devote a large proportion of his time to the merely routine task of preparing and taking nourishment.

However, this is but one phase of the result of eating an ill-

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[1] Received for publication December 15, 1915.

nourishing food. Other important results are the undersized body and low vitality. These conditions react one on the other, making it more difficult for the weakling to obtain his food and complicating the effect still further.

Therefore I contend that to raise a nation in the scale of civilization her food supply and the preparation of her food supply should receive early consideration.

Experts in nutrition claim that man instinctively attempts to obtain a complete diet and point out that such combinations as mush and milk; maize porridge (*polenta*) and cheese; corn and beans; rice, fish, and fat; potatoes and meat; and analogous combinations are well-known examples of this instinctive desire to consume a well-balanced diet. But the gratification of such a desire necessitates the cultivation of these foods.

Recently I have had occasion to determine the nutritive value of a number of the vegetables indigenous to the Philippine Islands and imported here, which are used for food by the people. A brief description of the methods of preparation and a table of nutritive values follow:

Eggplant.—Solanum melongena L., *berengena* (Sp.),[2] *tarong* (Il.), *talong* (T., V.), *balasenas* (Pam.). The eggplant is very plentiful in the markets at all times owing to the ease with which it can be grown. It is prepared for food by boiling and seasoning.

Squash.—Cucurbita maxima Duchesne, *calabaza* (Sp., V.), *carabasa* (Il.), *calabasang bilog* (T.), *culubasa* (Pam.). The squash grows best during the dry season under irrigation. The fruit is eaten green or ripe, and the leaves and flowers are stewed.

Cowpea.—Vigna sesquipedalis L., *sitao* (Il., T.), *hamtac* (V.), *camangian* (Pam.). The unripe pods and the ripe seeds and leaves are used for food. They should eventually find a place as a forage crop and as an excellent crop to use for the improvement of the soil, since they grow well here. A peculiar dish is made from the sprouted seeds of the cowpea. It is known as *tógue* in the Manila market.

Bottle gourd.—Lagenaria leucantha (Lam.) Rusby, *calabasa blanca* (Sp.), *tabuñgao* (Il.), *upo* (T., Pam.), *sicay calubay* (V.). The green fruit is used like the squash. Another variety, the sponge gourd (*Luffa cylindrica* Roem.), *patola* (Sp., T., V., Pam.), *cabatiti* (Il.), is used in soups and in stews when unripe.

Wax gourd.—Benincasa cerifera Savi, *condol* (T., Pam.), *tan-*

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[2] Letters in parentheses indicate the source of the local names: Il., Ilocano; Pam., Pampanga; Sp., Spanish; T., Tagalog; V., Visayan.

cuy (Il.). The wax gourd is a beautiful fruit, being similar in outward appearance to a watermelon. The meat is made into preserve or cooked like the squash.

Horse-radish tree.—Moringa oleifera Lam., *marungay* (Il.), V.), *malungay* (T.). The fruit and young leaves are boiled and eaten.

Chick-pea.—Cicer arietinum L., *garbanzos* (Sp., Il., T., V., Pam.). Extensively imported from Spain and used for food in most parts of the Philippines.

Common bean, habichuelas.—Many varieties of beans are grown in the Philippine Islands and their value as an article of diet is becoming more and more appreciated. Most of them are consumed when green.

Tomato.—Tomate (Sp.), *camatis* (Il., T., V., Pam.). Tomatoes can usually be obtained in the market. During the rainy season, however, they are somewhat scarce, so that the relative cost is high. A favorite dish is a mixture of rice, fish, and tomatoes.

Breadfruit.—Artocarpus communis Linn., *rima* (Sp.), *pacac* (Il.), *camansi* (T., V., Pam.). The seedless breadfruit may be roasted or used to make preserves. The seeded fruit is often boiled with squash and meat. However, breadfruit is not plentiful, and it is not a very common article of diet.

Batao.—Dolichos lablab L., *batao* (Sp., T.), *parda* (Il.). Batao is very similar to the bean in appearance. Only the young pods are eaten.

Papaya.—Carica papaya L., *papaya* (Sp., Il., T., V., Pam.). Papayas grow in the cultivated and wild state in the Philippine Islands and can be obtained in quantities, except during a part of the rainy season. Those introduced from the Hawaiian Islands are the finest. The ripe ones are eaten raw with salt or lemon, or both, or as a salad, while the green ones are cooked for sauce and with meat. They have the property of making meat more tender, due to the presence of the proteolytic ferment, papain.

Cucumber.—Cucumis sativus L., *pepino* (Sp., Il., T., V., Pam.). The cucumber grows very readily in the vicinity of Manila, although it cannot always be purchased in the market. This is probably due to the need for cultivation and care in its growth. Gardening has not reached a high degree of development; consequently vegetables requiring attention are not plentiful.

Amargoso.—Momordica charantia L., *amargoso* (Sp.), *paria* (Il.), *ampalaya* (T.), *sampalla* (V.), *apalia* (Pam.). *Amargoso* is a Spanish word for "bitter," a property of this fruit. It grows both wild and in the cultivated state. The green fruits are sliced and cooked in salted water to reduce the bitterness and are then eaten with meat as a relish. The fruits are also pickled. The leaves and flowers are also cooked and eaten.

Cangcong.—Ipomoea reptans Poir, *balangeg* (Il.), *cangcong* (T.), *tangcong* (V.), *cancong* (Pam.). This plant resembles the sweet potato vine and belongs in the same genus. It is commonly used as a pot herb. It is very plentiful.

Pepper.—Capsicum annum L., *pimento* (Sp.), *silit sairo* (Il.), *sili* (T.), *lara* (Pam.). Not only the fruit of the pepper, but also the leaves are used in the various foods for seasoning and condimental purposes.

Sweet potato.—Ipomoea batatas (L.) Poir, *camote* (Sp., T., Pam.), *camutig* (Il.), *tigsi* (V.). The sweet potato is becoming much more common, and as it grows luxuriantly, is of fine quality, and is much more palatable than the yam, it will eventually largely displace the latter as it has done in the United States. The Irish potato can be grown only at higher altitudes, and consequently it would appear that the sweet potato should become a staple crop for consumption. Because of the simple culinary devices of the people, most of the potatoes are baked. This is fortunate, as dietitians agree that the most economical and digestible method of preparing potatoes is by roasting.

Yam.—Dioscorea spp., *ube* (Sp., T., V., Pam.), (*D. alata* L.). The yam can always be bought in the markets at a very low price. It is prepared for eating in the same way as the sweet potato.

Yam bean.—Pachyrrhizus erosus (L.) Urb, *sincamas* (T., Pam.), *lincamas* (V.), *lancamas.* The tender, unripe pods are eaten in the same manner as beans. The roots, which are similar to the turnip in appearance, are eaten raw as a salad or cooked like the turnip. They are not well known.

Coriander.—Coriandrum sativum L., *unsuy* (T.). The young, tender leaves are added to *pansit,* a dish made from *bihon, misua,* or *mique,* and meat, such as pork or lobster, or are cooked with meat. The fruits are used for flavoring purposes, for flavoring candy, alcoholic drinks, and various preserves.

Celery.—Apium graveoleus L., *kinchay* (T.), *quiamse* (Pam.). Celery is used in salads and soups and is eaten with salt. It is an excellent relish and as it grows readily should be much more common as an article of diet.

Endive.—Chichorium endivia, escarola (T.). Endive grows well in the Philippine Islands during the cool season. It is eaten as a salad the same as lettuce.

Garlic.—Allium sativum L., *bauang* (T., Il., V., Pam.). Garlic is very generally used in oriental countries for flavoring meats and stews.

Sugar pea.—Pisum sativum L., *chicharro* (T., Pam.), *guisantes* (Il., V.). The sugar pea grows readily in the Philippine Islands, and if the pods are kept picked before they ripen, it is very productive. The young tender pods are boiled in preparing them for food.

Lima bean.—Phaseolus lunatus L., *patani* (T., Il., V.), *bule* (Pam.). The Lima bean is the best edible bean that is grown in the Philippine Islands. It is easy to raise, bears well, and if properly cared for will produce pods for a year or longer.

Parsley.—Petroselinum sativum, peregil (T.). Parsley is used to flavor soups or stews or to garnish meats and salads.

Leek.—Allium porrum L., *cuchay* (T. Il.), *suche* (Pam.). Leek is used to flavor soup and stews in the same way as garlic.

Pigweed.—Amaranthus oleraceus, culitis (T., V.). Pigweed is sold in the local market (Manila) and is prepared for food in the same manner as spinach.

Carrot.—Daucus carota L., *carot* (Sp.), *zanahoria* (T.). The carrot thrives best in the highlands, but it can be grown successfully in the lowlands also. Carrots are very appetizing when cooked in the same way as sweet peas and improve the quality of soups and stews when added to these.

Kale.—Brassica sp., *colis maluco* (T.). Kale is a variety of cabbage with curly, fleshy leaves that do not form a head. The leaves and stems are eaten as a salad or are stewed in the same manner as cabbage.

Onion.—Allium ceha, sebuyas (T., Pam.), *lasona* (Il.), *cebuyas* (V.). Much difficulty is experienced in raising large onions in the tropics, but small onions can be produced very readily. These are useful for flavoring soups or salads or may be eaten raw.

Cassava.—Manihot utilissima Pohl, *camoting cahoy* (T., V., Pam.). Cassava grows readily in the Philippine Islands, but at present is utilized for feeding hogs and only to a minor degree as an article of food for man. Considerable prejudice prevails regarding its use as a food owing to the presence in it of a cyanogenetic glucoside which gives off free prussic acid when allowed to stand or to ferment. As cooking destroys the activity of the accompanying enzyme that liberates the prussic acid, no evil effects should be experienced in its use as an article of food when cooked.

It is the source of one of the finest starches, consequently feeding it to hogs is an extravagance that should not be practiced, but it should be used for the preparation of commercial starch. The glucoside can be eliminated in the preparation of commercial starch by very careful washing.

Japanese mongo.—These beans are of various colors—green, yellow, or black. They are an excellent food to accompany rice because of their high protein content. They are cooked and eaten or may be mixed with shrimp and batter and made into a fritter. As this plant belongs to the legumes, its cultivation would be excellent for the improvement of the soil.

Pechay.—*Brassica chinensis* L., *pechay* (Sp., Il., T., V., Pam.). Pechay is one of the best vegetables for greens. It can be raised any time during the year and should thus be available at all times for the table. Unfortunately it is not cultivated extensively.

Chinese mustard.—*Brassica juncea* L. var., *mostaza* (Sp., Il., T., V., Pam.). Chinese mustard is used in the same way as pechay and is no more plentiful.

Cabbage.—*Brassica oleracea* L., *repollo* (Sp., Il., T., V., Pam.). Cabbage is scare in the lowlands, but is raised to some extent in the higher altitudes. The price of cabbage is too high for the poorer inhabitants.

Pasao.—*Corchorus olitorius* L., *saluyot* (Il.), *pasao* (T.), *lamhay* (V.). Pasao is another plant used in the same way as spinach. It is a common and widely distributed species in all settled areas of the Philippines.

Fern shoots.—*Athyrium esculentum* Copel., *pacó* (T.). This plant grows wild and is prepared for food, the young fronds being used in the same manner as spinach. It is also commonly eaten uncooked as a salad.

Taro.—*Colocasia antiquorum* Schott, *gabi* (Sp., T., V.), *aba* (Il.), *gandus* (Pam.). Taro has one parent root from which grow many smaller tubers. These tubers will keep for several months if they are sound when stored. They are prepared for food in the same way as sweet potatoes and are comparatively plentiful.

Chinese white radish.—*Raphanus sativus* L., *rabano* (Sp., Il., T., V., Pam.). Radishes are eaten raw, but very often they are cooked with yams.

Pungapong.—*Amorphophallus campanulatus* Blume, *tigui*

(Il.), *pungapong* (T.). This plant is locally very abundant, but is not cultivated. The young stems are cooked and eaten, but cannot be used raw on account of the presence of myriads of minute stinging crystals of oxalate of lime. The tubers are also sometimes used for food and for feeding hogs.

Bamboo shoots.—Caña (Sp.), *rabong* (Il.), *labong* (T., Pam.), *tambo* (V.).

Banana-flower buds.—Musa sapientum L., *corazon* (Sp.), *susup* (Il.), *puso nang saguing* (T., Pam.), *puso* (V.). Bamboo shoots and banana-flower buds are used only in making salads. Bamboo shoots are abundant and cheap because of the plentifulness of bamboo and the quick growth of the sprouts. Only the young shoot is used in this preparation.

The bud of the banana is plentiful, but as cutting the bud from the plant means the loss of a bunch of bananas, one understands why its use for salads is not more general. Both of the above make delicious salads.

A study of the cost of the vegetables examined shows that the price is relatively high. This condition will continue until each inhabitant has learned to have his own vegetable garden. In a climate such as this, where vegetation flourishes the year around, garden produce should be plentiful and the prices reasonable. Certain kinds of greens are cheap in a sense, but when one considers their food value they are found to be good for use only as a relish. Parts of the year some of the people are dependent on such greens for sustenance, because they have not yet learned the food value of the various vegetables.

The highest percentage of protein and highest food value are given by the various beans. In a country where large quantities of rice, composed chiefly of carbohydrates, are consumed, a food containing a high percentage of protein and some fat should supplement the diet. Native meat other than fish and chicken is scarce, and when one considers the high price of this commodity throughout the world, it would appear to be necessary to obtain a substitute for it in the diet. If the protein and fat food requirement is to be dependent on meat for fulfillment, the poorer people can hardly look forward to enjoying a more nearly perfect diet. An ideal food of this type is the soy bean. However, officials of the Philippine Bureau of Agriculture inform me that they have not succeeded in profitably growing the soy bean in the Islands. But they have not given up hope of ultimately succeeding and doubtless have good chances of eventually accomplishing their aim, since there are so many varieties of this bean that one or several of them are almost sure to grow here.

TABLE I.—*Analyses of the commonest Philippine vegetables used as food as purchased in the Manila market and their approximate cost and food values.*

Vegetable.[b]	Water.	Ether extract.	Protein N X 6.25.	Ash.	Crude fiber.	Carbohydrate (by difference).	Approximate cost of 1 kilo of food.	Cost of 1 kilo of protein.	Food needed to obtain 1 kilo of protein.	Calories per kilo of food.
FRUITS.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*	*Pesos.*[b]	*Pesos.*	*Kilos.*	
Eggplant (talong)	90.98	0.45	1.07	0.54	0.82	6.14	0.14	13.09	93.5	437.5
Squash (calabaza)	87.20	0.43	1.33	1.01	0.70	9.33	0.16	12.03	75.2	477.1
Cowpea (sitao)	86.75	0.18	2.65	0.90	2.03	7.49	0.20	7.55	37.7	452.5
Sponge gourd (patola)	94.58	0.13	0.63	0.28	0.13	4.25	0.11	17.46	158.7	212.2
Bottle gourd (upo)	95.44	0.09	0.50	0.37	0.26	3.34	0.11	22.00	200.0	165.8
Horse-radish tree (malungay)	88.24	0.16	7.29	0.94	0.76	2.61	0.18	2.47	13.7	320.8
Chick-pea (garbanzos)	13.63	5.38	19.94	2.86	2.26	55.93	0.44	2.20	5.0	3,611.1
Tomato (camatis)	94.32	0.23	0.99	0.62	0.64	3.20	0.16	16.16	101.0	191.2
Cowpea seed (mongo)	9.21	0.88	18.30	4.23	4.89	62.49	0.22	1.21	5.5	3,394.2
Breadfruit (camansi)	89.16	0.55	2.24	0.88	1.09	6.08	0.22	9.83	44.7	392.3
Tomato (camatis na ligao)	90.59	0.19	1.76	1.03	2.38	4.05	0.12	6.78	56.5	255.9
Batao (batao)	87.56	0.25	3.32	0.95	1.73	6.19	0.16	4.83	30.2	413.2
Papaya (papaya)	93.98	0.17	1.09	0.41	0.65	3.70	0.07	6.42	91.7	212.2
Cucumber (pepino)	94.14	0.19	0.52	0.46	0.30	2.39	0.22	42.31	192.3	137.0
Common bean (habichuelas)	15.07	1.70	18.09	3.80	4.28	57.06	0.35	1.93	5.5	3,239.3
Mongo seed (Japanese mongo)	14.70	0.93	20.44	3.01	4.36	56.56	0.35	1.72	4.9	3,243.5
Amargoso (ampalaya)	92.73	0.03	1.26	0.68	0.12	5.18	0.22	17.60	80.0	266.8
Winged bean (ciguidillas)	91.70	0.53	1.83	0.62	----------	----------	0.25	13.66	54.7	----------
Sugar pea (guisantes)	85.08	0.26	3.88	0.72	1.35	8.71	0.60	15.46	25.8	540.4
Lima bean (patani) fresh seed	65.50	1.26	7.30	1.84	0.77	23.37	0.40	5.48	13.7	1,374.7
Wax gourd (condol)	95.90	0.46	0.17	0.37	0.54	2.56	0.06	29.41	588.2	154.7
Sprouted cowpea (tógue)	92.85	0.45	2.38	0.41	0.69	3.91	0.05	2.10	42.0	299.8
LEAVES.										
Cangcong (cangcong)	89.70	0.04	4.25	1.67	0.70	3.64	0.18	4.23	23.5	327.2
Pepper (sili)	84.63	0.70	5.48	2.25	0.34	5.60	0.22	4.03	18.3	519.8
Sweet potato (camote)	84.20	0.42	1.15	1.98	1.90	10.25	0.35	20.45	87.0	505.2
Pechay (pechay)	92.97	0.34	1.00	1.26	0.79	4.64	0.22	20.00	100.0	262.9

Pasao (pasao)	80.61	0.44	5.07	2.77	1.81	9.30	0.22	4.33	19.7	630.1
Chinese mustard (mostaza)	91.30	0.31	2.06	1.10	0.80	4.43	0.22	10.58	48.1	304.9
Squash (calabaza)	89.45	0.34	4.07	1.87	1.16	3.11	0.35	8.61	24.6	326.0
Amargoso (ampalea)	81.94	0.13	2.30	2.06	0.75	16.82	0.22	9.57	43.5	796.0
Fern (pacó)	90.78	0.28	3.11	1.14	1.23	3.54	0.22	7.08	32.2	298.7
Cabbage (repollo)	91.86	0.28	2.03	0.79	0.91	4.13	0.35	17.26	49.3	278.6
Horse-radish tree (malungay)	76.67	1.10	7.30	2.14	1.75	11.04	0.12	1.64	13.7	854.3
Cowpea (sitao)	85.88	0.40	4.07	1.58	1.90	6.17	0.16	3.94	24.6	459.1
Coriander (unsuy)	90.82	0.41	2.17	1.38	0.79	4.43	0.20	9.22	46.1	308.7
Celery (kinchay)	92.72	0.32	1.65	1.56	0.86	2.89	0.20	12.00	60.6	215.0
Endive (escarola)	93.25	0.23	1.62	0.94	0.95	3.01	0.25	15.00	61.7	211.2
Garlic (bauang)	88.01	0.32	2.20	1.03	1.17	7.27	0.25	12.36	45.5	417.8
Parsley (peregil)	85.70	1.39	3.82	2.75	1.52	4.82	0.20	5.24	26.2	493.5
Leek (cuchay)	91.92	0.55	1.88	0.92	1.10	3.63	0.30	15.96	53.0	277.1
Pigweed (culitis)	83.35	1.71	3.98	2.44	1.53	6.99	0.07	1.75	25.1	608.7
Pigweed (colis maluco)	81.38	0.57	4.50	3.16	2.00	8.39	0.10	2.23	22.2	581.5
Young onion (cebuyas)	89.14	0.34	1.27	0.74	1.80	6.71	0.50	39.00	78.7	358.8
ROOTS.										
Sweet potato (camote)	71.20	0.52	0.65	0.91	1.35	23.37	0.14	21.55	153.9	1,033.2
Taro (gabi)	63.21	0.39	1.29	1.01	1.59	33.51	0.14	10.75	77.5	1,457.1
Yam (ube)	63.70	0.05	2.86	1.45	1.03	27.31	0.14	4.90	35.0	1,241.6
Chinese radish (rabano)	94.14	0.16	0.82	0.69	0.55	3.64	0.12	14.64	122.0	197.8
Pungapong (pungapong)	74.81	0.38	5.10	0.73	0.61	14.77	0.05	0.98	19.6	850.0
Yam bean (sincamas)	84.47	0.12	0.82	0.38	0.28	8.93	0.05	6.10	122.0	410.9
Carrot (carót)	86.36	0.23	2.26	0.80	1.27	9.08	0.15	6.64	44.2	486.3
Yam (tuguí)	67.49	0.19	1.50	1.07	0.95	18.80	0.15	10.00	66.7	850.0
Casava (camoting cahoy)	----------	----------	0.82	----------	----------	----------	0.05	6.10	122.0	----------
SHOOTS.										
Bamboo shoot (labong)	92.77	0.51	1.76	0.55	0.17	4.24	0.16	9.09	56.8	293.4
FLOWERS.										
Banana flower (puso nang saguing)	92.67	0.31	1.99	1.02	0.66	3.35	0.35	17.61	50.3	227.8
Caturay (caturay)	88.75	0.92	1.97	0.79	----------	----------	0.20	10.15	50.6	----------

[a] Edible portion only.

[b] Words in parenthesis are the names of vegetables as used by people in the markets of Manila.

[c] One peso Philippine currency equal 50 cents in United States currency.

CONCLUSION

The people should be taught the relative nutritive values of the various foods they are eating.

The work of the Bureau of Education in encouraging the establishment and cultivation of gardens should be furthered so that every household, wherever possible, will have a garden of its own.

A plant such as the soy bean should be introduced, in order that the people may have a food which eaten with their rice and camotes will give them a more nearly balanced diet.

IPEL, A COFFEE SUBSTITUTE: LEUCAENA GLAUCA (LINNÆUS) BENTHAM[1]

By HARVEY C. BRILL

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The use of *Leucaena glauca* as a substitute for coffee has recently been brought to our attention by the Philippine Bureau of Education. The supervising teacher of Bauang, La Union Province, reports that several of his teachers have used it instead of coffee with pleasant results.

Leucaena glauca (L.) Benth., known as *ipel,* or *ipel-ipel,* among the Tagalogs, is widely distributed throughout the Philippine Islands, although it is not native, having come originally from tropical America. Merrill[2] says of this species:

> A native of tropical America, now widely distributed in tropical and subtropical parts of the world; very abundant and widely distributed in the Philippines at low altitudes, the timber being used for house posts and for firewood. In Leyte the seeds are used by the natives as a substitute for coffee.

The Spanish name *Santa Elena* is in common use throughout the Islands, while the following names are used in the localities indicated: *Aghó* (Iloilo Province, Panay); *datels* (Leyte); *comcompitis* (Ilocos Sur); *adjog* (Negros); and *ipel* (Cavite, Pampanga, Rizal, Nueva Ecija). The last name should not be confused with "ipil," which is the name of one of our important timber trees, *Intsia bijuga* O. Kuntze. *Leucaena glauca* Benth. has attained considerable prominence because of its value as a reforestation crop.

About 40 per cent of the total land area of the Philippine Islands has become covered with grass to the exclusion of practically all other vegetation. Areas such as these are difficult to reforest, and are not cultivated, owing to the frequency of fires and the ease with which cogon—the dominant grass occupying these tracts—crowds out the other vegetation. Cogon possesses a dense mass of underground stems, which spreading throughout

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[1] Received for publication November 23, 1915.

[2] *This Journal, Sec. C* (1910), 5, 30.

the upper layer of the soil deprive it of nearly all the available moisture during the dry season. The removal of the grass for the purpose of reforestation is impracticable, because of the cost, and few trees are able successfully to compete with the cogon. Ipel, however, can thrive under these conditions, and owing to its habit of growing in thickets, soon chokes out the grass. Other trees can be successfully grown among the ipel. Indeed the presence of ipel is an advantage, since it serves as a shade to the young tree and raises the height at which the tree sends out branches.

While ipel is not so valuable a firewood as the *bacauans* (the mangrove trees), yet, in the growing scarcity of these and the demand for a quick-growing firewood for sugar centrals, etc., its value here will eventually increase.

Another factor worth considering is the improvement of the soil brought about by the cultivation of ipel. Since it belongs to the legumes, it possesses the property common to the members of this family of fixing the nitrogen of the air and making it available for plant growth. The shrub, or small tree, grows to a height of from 2 to 6 meters, in rare cases 10 meters, and bears thin, flat pods, from 12 to 18 centimeters long, within which are from fifteen to twenty-five small, shining, flattened brown seeds about 8 by 4 by 1.5 millimeters in dimensions.

These seeds when roasted and ground produce a reddish brown powder, having a color very similar to that of coffee and with an odor somewhat resembling the aroma of coffee. The odor of the infusion with water resembles the odor of coffee more closely than does that of the ground, roasted bean. This infusion is brown by direct light and has a deep green fluorescence by reflected light. It gives a violet color, but no precipitate with ferric chloride solution; with solutions of potassium-mercurio-iodide, potassium hydroxide, picric acid, iodine-potassium iodide, tannic acid, and Fehling it gives no precipitates. When warmed first with hydrochloric acid and then tested with Fehling's solution, it gives a precipitate of reduced copper oxide. Copper acetate produces a greenish brown, gelatinous precipitate with a dark green, supernatant liquid. Lead acetate gives a brownish yellow, gelatinous precipitate. The infusion is slightly acid to litmus and gelatinizes albumen.

Graham, Stenhouse, and Campbell proposed to take the density of different infusions of coffee and adulterants as a guide to the adulteration. They gave the following data for solutions made by treating the substance with ten times its weight of cold water, boiling, filtering, and then determining its density at 60° F.

TABLE I.—*Specific gravity of extracts of coffee and coffee adulterants.*[a]

Substance.	Specific gravity.	Substance.	Specific gravity.
Spent tan	1.00214	Carrots	1.01710
Lupine seed	1.00570	Bouka	1.01850
Acorns	1.00730	Black malt	1.02120
Peas	1.00730	Turnips	1.02140
Mocha coffee	1.00800	Rye meal	1.02160
Beans	1.00840	Dandelion root	1.02190
Neilgherry coffee	1.00840	Red beet	1.02210
Plantation Ceylon coffee	1.00870	English chicory	1.02170
Java coffee	1.00870	Yorkshire chicory	1.01910
Jamaica coffee	1.00870	Foreign chicory	1.02260
Costa Rica coffee	1.00900	Guernsey chicory	1.02326
Native Ceylon coffee	1.00900	Mangel-wurzel	1.02350
Brown malt	1.01090	Maize	1.02530
Parsnips	1.01430	Bread raspings	1.02630

[a] Blyth, Foods: Their Composition and Analysis, 6th ed. Charles Griffin & Co. Ltd., London (1909), 360.

The density of an infusion of ipel made and determined under these conditions is 1.00680. This density would place it between lupine seed and acorn in Table I and would serve as one means of identification. The roasted seed gave 24.4 per cent extract, soluble in water when treated in this manner. König[3] gives for coffee 21.12 per cent to 27.28 per cent. The ground, roasted seed when floated on strong salt water, cooled to a low temperature, in the course of a half hour sinks to the bottom of the cylinder. As it falls to the bottom, it leaves a trail of color. This color is not as intense as the color produced by chicory.

The analyses of the powder from the roasted and raw beans, along with that given by König[4] for coffee, are shown in Table II.

TABLE II.—*Analyses of ipel and coffee.*

[Numbers give percentages.]

	Ipel.		Coffee.	
	Raw.	Roasted.	Raw.	Roasted.
Moisture	14.80	8.13	10.73	2.38
Fat (ether extract)	8.68	6.95	11.80	13.85
Nitrogen	6.42	5.21	2.32	2.60
Sucrose	trace	trace	7.62	1.31
Nitrogen free material other than fiber	9.78	16.11	20.30	39.38
Crude fiber	22.29	22.18	24.01	18.07
Ash	4.20	4.37	3.02	4.65

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[3] Die menschlichen Nahrungs- und Genussmittel. 4th ed. Julius Springer, Berlin (1904), 2, 1072.

[4] Loc. cit.

The oils extracted from the roasted bean and from the raw bean have the indices of refraction and the saponification numbers given in Table III.

TABLE III.—*The constants of the oils of ipel and those of coffee.*[a]

	Index of refraction.	Saponification.
Ipel:		
Raw	1.4670	196.2
Roasted	1.4690	190.7
Coffee:		
Raw	1.4695	157.2
Roasted	1.4715	162.6

[a] König, loc. cit.

DISCUSSION

Ipel has no possibility of becoming of any great commercial value, but it has a local significance. Viewed in relation to the world's production of coffee, it is infinitesimally insignificant.

TABLE IV.—*Average annual production of coffee by continents. Years, 1906–1910.*

Continent.	Pounds.
South America	2,021,805,000
North America	384,138,000
Asia	92,818,000
Africa and Oceania	21,998,000

The properties of ipel are discussed here because of its local use as a coffee substitute or adulterant.

THE CHEMICAL PURIFICATION OF SWIMMING POOLS *

By George W. Heise and R. H. Aguilar

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TWO TEXT FIGURES

The purification of swimming pools has long been the subject of much study, and a vast literature has been developed concerning it. Many methods have been suggested, notably filtration, sterilization with ultra-violet rays, and the use of ozone, copper sulphate, liquid chlorine, and the hypochlorites of sodium, magnesium, or calcium. Although these methods, or combinations of two or more of them, have been found satisfactory under most conditions, great discrepancies exist in the results recorded. In spite of the fact that there are many factors influencing the purification of swimming pools, many experimenters have treated their particular problems as though they were of general application; hence has arisen much difference in opinion concerning the relative merits of different purifying agents, amounts necessary for efficient purification, methods of application, and the like. In many cases too little attention has been paid to important factors such as quality of water, temperature of pool, number of persons bathing, turbidity and the like to enable general conclusions to be drawn from the results of different workers. The treatment which is highly efficient for one water under certain conditions may fail utterly for a different water under slightly changed conditions.

Of the methods mentioned, the use of chlorine either as liquid chlorine or as a hypochlorite is probably the most widely practiced, and because of their cheapness and because of the ease with which they can be administered, hypochlorites are employed more than liquid chlorine.

The work here recorded was done (1) for the purpose of putting the swimming pools in Manila into a sanitary condition and (2) to study the factors influencing the chemical purification of swimming pools, with a view toward devising methods of chemical control. It is our purpose to discuss here only the chemical work done on this problem; the bacteriological work done in coöperation was performed by Dr. C. E. Gabel, of the Bureau of Science, and is recorded and discussed in detail separately.[1]

The three installations studied, which we shall designate as

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* Received for publication November 26, 1915.

[1] *This Journal, Sec. B* (1916), 11, No. 2.

I, II, and III, are of slightly varying depths and dimensions. Each of installations I and II has a capacity of about 200 cubic meters, and III has a capacity of about 225 cubic meters. Each is between 18 and 19 meters (60 feet) long, and has a depth of about 2.5 meters (8 feet) in the deepest portion. Installations I and II are situated indoors. Installation III, although covered by a roof and surrounded by a low, light wall of *sawale* (woven bamboo), is practically outdoors. Owing to building operations at III, the tank was not in continuous operation and foreign material fell into it, causing discrepancies in the results. These discrepancies, however, were not great enough to affect the general conclusions obtained.

The same water, direct from the Manila city supply system, was used in all three tanks. This is a river water, which is kept in storage for three days and treated, before it enters the city distribution system, with chloride of lime at a rate corresponding to an addition of 0.5 part of available chlorine per million parts of water.

As it leaves the pipes it is a slightly turbid water with a greatly fluctuating bacterial content. Its turbidity, due to very finely divided clay, varies from 7 to 15 parts per million, as measured by the United States Geological Survey turbidity-rod method. Its temperature, which shows slight variations at different seasons of the year, is usually between 27° C. and 30° C. A typical analysis of this water is shown in Table I.

TABLE I.—*Analysis of water from Manila supply system.*[a]

[Results expressed as parts per million.]

Total solids	154
Alkalinity (as $CaCO_3$)	100
Silica (SiO_2)	24
Iron and aluminium oxides ($Fe_2O_3+Al_2O_3$)	1.7
Calcium (Ca)	31
Magnesium (Mg)	6
Sodium (Na)	13
Potassium (K)	2
Normal carbonates (CO_3)	0–10
Bicarbonates (HCO_3)	100–120
Sulphates (SO_4)	14
Chlorides (Cl)	4
Nitrates (N)	0.046
Nitrites (N)	trace
Free ammonia (N)	0.03
Albuminoid ammonia (N)	0.116

[a] Analysis by V. Q. Gana, chemist, Bureau of Science.

The problem of maintaining a swimming pool in Manila in a sanitary and attractive condition is rather complicated. The water from the municipal supply is always slightly turbid, so that the bottom of a pool is generally invisible. This turbidity not only makes the pool unattractive and increases the danger from accidental drowning, but also militates against the action of disinfectants. The temperature (27°C. to 30°C.) is an added factor, as it is nearer the bacterial optimum than that of typical United States installations, and bacterial growth is correspondingly stimulated.

Obviously, filtration should be employed as a preliminary measure in the treatment of waters of the kind described; however, the lack of filtration facilities and the desirability of improving the sanitary condition of the local installations as rapidly as possible made it advisable to see what could be done with chemical methods of purification alone.

In the series of experiments here recorded, chloride of lime, copper sulphate, and sodium hypochlorite (antiformin) were used for purification. The first was either added as a uniform emulsion or was placed in a bag and dragged through the water until thoroughly leached out; the last two were added in water solution.

The chemical and physical tests consisted in daily determinations of turbidity, temperature, and chlorides and oxygen-consuming capacity, with occasional determinations of total solids, alkalinity, and near the end of the work of factors influencing the chemical decomposition of hypochlorites. With the exception noted, the water was changed at the beginning of each week, and chemicals were added to the fresh water. The analytical data secured are recorded in Tables II to VII, inclusive.

TABLE II.—*Daily variation in quality of water. No disinfectant added.*

[Results expressed as parts per million.]

Age of water in days.	Pool I.[a]			Pool II.[b]		Pool III.[c]		
	Chlorides (Cl).	Oxygen consumed (O).	Turbidity.	Chlorides (Cl).	Oxygen consumed (O).	Chlorides (Cl).	Oxygen consumed (O).	Turbidity.
1	5.0	1.10	13.5	5.7	1.42	4.8	1.65	--------
2	4.9	0.9	8.5	4.9	1.03	4.9	1.86	--------
3	4.7	0.83	--------	4.7	1.05	4.3	1.21	15.5
4	4.6	1.01	8.4	4.9	1.00	4.6	1.32	14.5
5	4.7	0.92	8.4	4.8	1.00	5.0	1.37	15.0
6	5.1	0.97	8.8	4.8	1.00	4.4	1.42	15.5
7	--------	--------	--------	4.6	1.11	--------	--------	--------

[a] Average temperature, 27.0° C. Total bathers, 200.
[b] Average temperature, 28.5° C. Total bathers, 159.
[c] Average temperature, 27.5° C. Total bathers, 79.

TABLE III.—*Variation in quality of water. Addition: 1 part of* $CuSO_4.5H_2O$ *per million parts of water.*

[Results expressed as parts per million.]

Age of water in days.	Pool I.[a]			Pool II.[b]		Pool III.[c]		
	Chlorides (Cl).	Oxygen consumed (O).	Turbidity.	Chlorides (Cl).	Oxygen consumed (O).	Chlorides (Cl).	Oxygen consumed (O).	Turbidity.
1	7.5	1.12	11.5	4.9	0.98	4.7	1.20	11.7
2	4.8	1.37	10.5	4.7	1.23	5.3	1.52	11.3
3	5.0	1.00	10.7	5.5	1.44	4.4	1.32	11.3
4	4.7	0.97	10.5	5.8	1.47	4.6	1.42	9.7
5	4.6	1.18	10.5	6.0	1.85	4.5	1.64	10.5
6	4.6	1.05	9.7	5.8	1.80	--------	--------	--------

[a] Average temperature, 28.5° C. Total bathers, 235.
[b] Average temperature, 27.5° C. Total bathers, 346.
[c] Average temperature, 28.5° C. Total bathers, 85.

TABLE IV.—*Daily variation in quality of water. Addition: 2 parts* $CuSO_4.5H_2O$ *per million parts of water.*

[Results expressed as parts per million.]

Age of water in days.	Pool I.[a]			Pool II.[b]		Pool III.[c]		
	Chlorides (Cl).	Oxygen consumed (O).	Turbidity.	Chlorides (Cl).	Oxygen consumed (O).	Chlorides (Cl).	Oxygen consumed (O).	Turbidity.
1	4.9	1.05	12.8	5.6	1.01	4.6	1.48	--------
2	4.7	1.10	13	5.7	1.08	5.5	1.67	20
3	4.8	1.20	12	6.0	1.15	4.4	1.53	12
4	4.9	1.09	13.5	5.5	1.22	4.5	1.68	--------
5	4.6	1.11	12.4	5.6	1.18	3.7	1.37	14
6	4.5	1.23	--------	5.8	1.34	4.1	1.37	13
7	--------	--------	--------	--------	--------	4.0	2.09	13
8	--------	--------	--------	--------	--------	4.2	1.84	10

[a] Average temperature, 28.0° C. Total bathers, 259.
[b] Average temperature, 28.0° C. Total bathers, 233.
[c] Average temperature, 28.5° C. Total bathers, 112.

TABLE V.—*Daily variation in quality of water. Addition: 0.5 part of available chlorine (from chloride of lime) per million parts of water.*

[Results expressed as parts per million.]

Age of water in days.	Pool I.[a]		Pool II.[b]		Pool III.[c]	
	Chlorides (Cl).	Oxygen consumed (O).	Chlorides (Cl).	Oxygen consumed (O).	Chlorides (Cl).	Oxygen consumed (O).
1	5.5	0.7	4.5	1.0	5.0	0.75
2	4.2	0.8	4.0	0.7	5.7	0.7
3	4.5	1.5	5.0	0.9	6.1	0.72
4	4.5	0.7	5.0	0.88	6.5	1.39
5	5.3	1.34	5.3	0.87	--------	--------
6	5.0	1.35	5.3	1.30	--------	--------

[a] Average temperature, 27.5° C. Total bathers, 424.
[b] Average temperature, 27.0° C. Total bathers, 298.
[c] Average temperature, 28.0° C. Total bathers, 70.

TABLE VI.—*Variation in quality of water. Addition: 1 part of available chlorine (from chloride of lime) per million parts of water.*

[Results expressed as parts per million.]

Age of water in days.	Pool I.[a]		Pool II.[b]		Pool III.[c]	
	Chlorides (Cl).	Oxygen consumed. (O).	Chlorides (Cl).	Oxygen consumed (O).	Chlorides (Cl).	Oxygen consumed (O).
1	5.3	0.74	4.5	0.85	7.1	1.51
2	6.0	1.24	5.8	1.15	5.9	1.21
3	6.8	1.02	6.3	0.95	7.1	1.36
4	6.5	1.00	6.2	1.11	6.7	1.18
5	6.0	0.97	6.0	1.72	6.5	1.29

[a] Average temperature, 28.0° C. Total bathers, 223.
[b] Average temperature, 27.0° C. Total bathers, 231.
[c] Average temperature, 28.5° C. Total bathers, 152.

TABLE VII.—*Variation in quality of water. Addition: 2 parts of available chlorine (from chloride of lime) per million parts of water.*

[Results expressed as parts per million.]

Age of water in days.	Pool I.[a]			Pool II.[b]		Pool III.[c]			
	Chlorides (Cl).	Oxygen consumed (O).	Turbidity.	Chlorides (Cl).	Oxygen consumed (O).	Chlorides (Cl).	Oxygen consumed (O).	Turbidity.	Total solids.
1	4.9	0.99	--------	5.3	1.21	6.0	1.49	16.0	155
2	6.8	1.31	13	5.4	2.23	7.2	1.56	10.1	164
3	6.3	1.54	15	5.5	1.52	7.9	1.72	10.1	167
4	6.8	1.90	10	5.8	1.51	7.9	1.78	12.5	160
5	7.1	1.34	10.5	6.1	1.44	7.7	1.86	12.9	162
6	7.2	1.30	13.5	6.2	1.84	7.6	1.46	10.5	170

[a] Average temperature, 28.0° C. Total bathers, 295.
[b] Average temperature, 27.5° C. Total bathers, 204.
[c] Average temperature, 28.5° C. Total bathers, 80.

When water was left untreated in the local swimming pools, the bacterial count invariably reached enormous figures about the second day, and organisms of the *B. coli* group were practically always to be found in 1 cubic centimeter water samples after the first day. The usual chemical analyses gave little indication of this state of affairs (Table II). A slight sedimentation occurred during the first day or two in which the water was used, leading to a decreased turbidity and corresponding fluctuations in oxygen consumption and chloride content. Differences during the week in total solids and alkalinity, if any, were too slight to be of significance; neither chlorides nor oxygen consumed showed the steady increase which might have been expected; turbidity, after the initial drop, remained practically constant.

The use of copper sulphate as a disinfectant both for public water supplies and for swimming pools has frequently been recommended.[2] For example, Thomas,[3] in a recent article, showed that a greater degree of bacterial purification had been effected in a swimming pool with daily additions of 0.4 part per million of copper sulphate than had previously been accomplished with a single addition of 2.5 parts per million of "hypochlorite" [0.8 (?) part of available chlorine], and concluded that the copper sulphate method was cheaper and more effective, and was further superior to hypochlorite treatment because it caused no odor and

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[2] For partial bibliography see Manheimer, *Publ. Health Report* (1915), 30, 2796.

[3] *Journ. Ind. Eng. Chem.* (1915), 7, 496.

was not irritating to the eyes. Unfortunately the author gives no data concerning the chemical quality of the water used nor the exact strength of hypochlorite employed. The water was filtered and refiltered, and alum was used as coagulant. As the author points out, the coagulation with alum and subsequent filtration removes the carbonates and bicarbonates which would otherwise hinder the action of copper sulphate.

Our results with copper sulphate show clearly the unsuitability of this method to a water high in substances which react with a copper salt. The test was conducted for two weeks, 1 part of crystalline copper sulphate per million parts of water being employed during the first week and 2 parts per million (with fresh water) during the second. In neither case was an effect on the bacterial content apparent after the first day, and long before the end of the week the colony count had reached an enormous figure, the copper sulphate seemingly exercising not the slightest inhibiting effect.

The chemical analysis of the water showed little or no variation (Tables III and IV). Upon addition of copper sulphate the turbidity of the water increased greatly, owing to interaction with the bicarbonates present and subsequent precipitation of hydroxides and carbonates of copper, calcium, or magnesium. This action would account for the removal of copper sulphate and its failure as a germicide in this series of tests. Owing to the turbidity resulting from its use and to the lack of efficient sterilizing action, it is apparent that, without filtration, the use of copper sulphate is not to be recommended for water similar to the one under observation.

A number of attempts were made to secure adequate purification with chloride of lime, different quantities being used each week.

The first attempt with chloride of lime was made with an addition of 0.5 part of available chlorine[4] per million parts of water. The effect on the bacterial content was apparent for only one day, after which the count was excessive and *B. coli* appeared. No better results attended the addition of 1 part per million, and only with an addition of 2 parts per million could an appreciable effect on the bacterial content on the second day be ascribed to the chemical added. After the second day the bacterial increase proceeded unchecked. In none of these cases was the effect on the chemical constituents great enough notice-

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[4] All hypochlorite used was analyzed with arsenious acid, using starch-potassium-iodide paper as indicator.

ably to affect the alkalinity or total solid content of the water (Tables V to VII).

It might be well to note parenthetically that although the last-mentioned concentration is far in excess of that generally employed for purification, there was no complaint from users of the pool, except in one case, where a few people complained of irritations of the eyes and of the mucosæ of nose and throat. In this instance it was shown that the trouble was due to careless and improper administration of the disinfectant, which allowed undissolved lumps to get into the tank. The odor was strong and persisted for days, but was not sufficiently disagreeable to be a real drawback to the use of hypochlorite.

The chlorination having failed to give the desired results, an attempt was made to study in detail the causes of the failure and to overcome the difficulties involved.

It was noticed that in general the city water showed no trace of "free chlorine" when it left the mains, as determined chemically by acidifying 200 cubic centimeter samples of water and adding a drop of methyl orange,[5] the presence of chlorine being indicated by the bleaching of the indicator. This result was rather surprising, since the water arrived at the swimming pools probably within three, almost certainly within five, hours after chlorination had taken place. Moreover, in spite of the relatively large additions of chloride of lime to the swimming pools, all trace of "free chlorine" was lost, usually within twenty-four hours.

A laboratory study of the decomposition of a clear (filtered) solution of chloride of lime added to (unchlorinated) city water gave the results indicated in Table VIII (fig. 1).

TABLE VIII.—*Decomposition of chloride of lime in water.*

Minutes.	Available chlorine in parts per million.
0	0.8
2	0.6
30	0.3
120	0.1 (?)

From the foregoing it is apparent that the chloride of lime lost its effective strength very rapidly and that in two hours its concentration had fallen below 0.1 per million. Just what is the minimum concentration of chlorine that will keep water free from dangerous organisms is not known; certainly it cannot be much less than the concentration mentioned above.

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[5] Winkler, *Zeitschr. f. angew. Chem.* (1915), 28, I, 22.

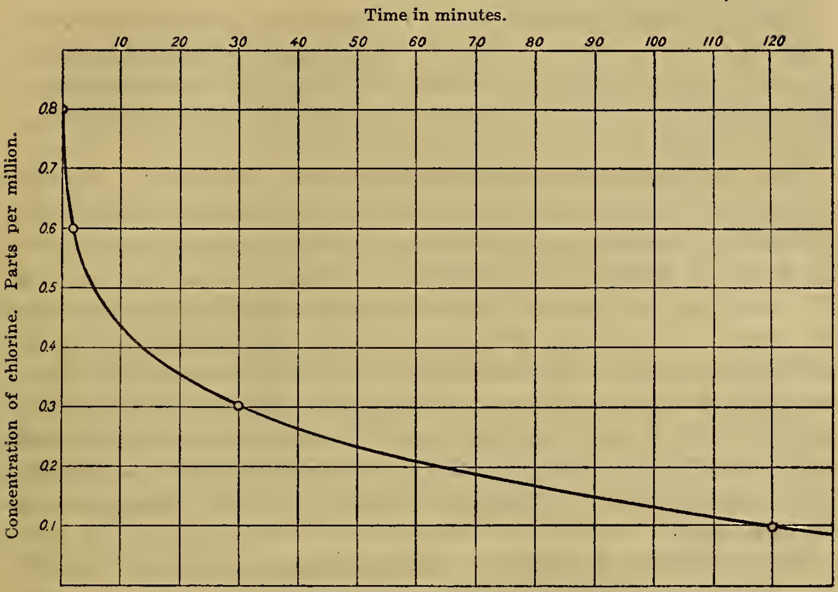

FIG. 1. Decomposition of calcium hypochlorite in water.

The destruction of hypochlorite must be due either to spontaneous decomposition or to interaction with substances dissolved in water. Hypochlorites decompose, even in the dark,[6] with measureable velocity. The reaction is greatly accelerated by light,[7] especially by the visible and ultra-violet rays, and by heat. The temperature of a bath, therefore, becomes a matter of no small importance in studying purification of water with hypochlorite, and the amount of daylight falling on a pool may greatly affect the rate at which hypochlorite disappears.

The interaction of chlorine with substances dissolved in water has been much studied in recent years.[8] The phenomenon is generally associated with a high organic content in water. A large amount of "free chlorine" disappears immediately, after which decomposition proceeds more slowly, but does not reach equilibrium for a long time. The amount of chlorine consumed appears to be dependent on the concentration in which it is added; the more hypochlorite added, the more will be decomposed in a given time. The reaction proceeds more rapidly at high temperature than at low.

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[6] Bhaduri, *Zeitschr. f. anorg. Chem.* (1897), 13, 385.

[7] Lewis, *Journ. Chem. Soc.* (1912), 101, 2371.

[8] Cf. Glaser, *Arch. f. Hyg.* (1912–13), 77, 165; Hairi, *Zeitschr. f. Hyg.* (1913), 75, 40.

Many substances are known [9] to affect the chlorine consumption, notably albumin and its decomposition products, urea, glycocol, peptone, asparagin, and the like. We have determined the chlorine-consuming power of a number of different substances, using the following method:

Two hundred cubic centimeter samples of water, or else the substances under examination dissolved in 200 cubic centimeters of distilled water, were placed in glass-stoppered bottles. To each sample a known excess of clear (filtered) calcium hypochlorite solution was added. The bottle was stoppered and allowed to stand at room temperature (30° C.) for two hours in the diffused daylight of the laboratory. After digestion with hypochlorite, 2 cubic centimeters of 10 per cent potassium iodide solution and 2 cubic centimeters of 25 per cent phosphoric acid were added to each sample, and the liberated iodine was titrated with 0.02N sodium thiosulphate solution, starch being used as an indicator.

The differences in chlorine consumption are shown in Table IX.

TABLE IX.—*Chlorine-consuming power of different substances.*

Substance.	Chlorine added.	Chlorine consumed.	Chlorine consumed per liter.	Remarks.
	mg.	*mg.*	*mg.*	
Distilled water	6.5	0.15	0.75	
Reservoir water (unchlorinated)	6.5	0.2-0.5	1.0-2.5	Varies from day to day.
Tap water (chlorinated)	6.5	0.2-0.6	1.0-3.0	Do.
Artesian well water	1.0	0.24	1.2	Bureau of Science well.
Sea water	6.5	0.75	3.75	From aquarium.
200 cubic centimeters distilled water:				
Plus 0.0025 gram oxalic acid	6.5	0.28	1.4	
Plus 0.005 gram oxalic acid	6.5	0.7	3.5	
Plus 1 cubic centimeter urine	6.5	4.4	22.0	
Plus 0.5 cubic centimeter ± sweat	6.5	5.6	28.0	
Plus 0.5 cubic centimeter saliva	3.4	2.0	10.0	

It is significant that the substances given off from the human body cause the consumption of relatively large amounts of chlorine. This emphasizes the necessity of personal cleanliness on the part of the users of swimming pools if the purification of tank water by means of chlorine is to be successful. A thorough bath with soap should be taken before the pool is entered to remove all body products so far as possible, not only to avoid introducing into the water substances noxious per

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[9] Cf. Elmanowitsch and Zaleski, *Zeitschr. f. Hyg.* (1914), 78, 473; Hairi, ibid. (1913), 75, 46.

se, but in order to prevent the destruction of the hypochlorites to which the purifying action is due.

There are, then, two distinct actions or effects: the first, the germicidal action of chlorine or hypochlorites; the second, the specific interaction between the chlorine and the substances in water. There is evidently a minimum concentration below which effective purification does not occur; if this is reached in a short time, purification will not be adequate or lasting in its effect. It thus becomes necessary to maintain at all times in the water of a swimming pool an excess of "free chlorine" sufficient to keep up effective purifying action.

With these conditions in mind, the purification of a swimming pool becomes a comparatively simple matter. A relatively small amount of hypochlorite will effectively purify the water, after which it becomes necessary to keep the bacterial content within safe limits by means of repeated additions of disinfectant. That this is true is evinced by the results obtained during a series of tests in which chloride of lime was used in quantities representing a daily addition of 0.5 part of "available chlorine" per million parts of water. Throughout this series the bacterial content was kept below 200 and no *B. coli* was found. In all cases the water remained in the pools for two weeks and was safe during the entire period. That there was no cumulative effect and that there was no large excess of chlorine at any time were shown by omitting chlorination for a single day, when the bacterial content immediately increased to dangerous proportions. Throughout the two weeks qualitative tests for the presence of free chlorine and quantitative determinations of the chlorine-consuming power were made, with the results listed in Table X.

At first the chlorine consumption remained almost constant, next it passed through a minimum, and then, as people used the pool, it rose rapidly. Evidently it takes more and more chlorine to produce a given effect as time goes on; and therefore it becomes advisable to change the water after the chlorine consumption reaches a certain maximum, although just where that maximum should be placed is a matter of conjecture. The efficiency of the purifying action was such that it is clear that the maximum was not exceeded during the first week, nor in the case of tank I even during the second week. Chloride of lime, therefore, will keep a tank clean and reasonably safe for ten days or two weeks, even under the unfavorable circumstances existing in Manila; and if the water be changed weekly, the danger of contamination is very slight.

TABLE X.—*Effect of daily additions of 0.5 part of available chlorine per million parts of water.*

[Results expressed as parts per million.]

TANK I.[a]

Age of water in days.	Turbidity.	Qualitative test for free chlorine.	Chlorine-consuming capacity.[b]	Chlorides (Cl).	Oxygen consumed.
1			2.5	5.6	0.75
2	8.4	Strong			
3	8.5				
4	9.5	Faint			
5	7.0				
6	8.7				
7	8.5	Faint			
8			2.8		
9	8.8		1.1		
10	8.1	Faint	1.05		
11	8.8	do	0.7		
12	8.5	do	1.0		
13	9.1	Very faint	1.0		
14	8.5	do		13.0	1.05
15					
16		Negative			

TANK III.[b]

1	10.5		2.5	4.4	1.42
2	8	Very faint			
3	11.5	do			
4	8.9				
5		Negative			
6	9.9		3.0		
7	9.1		3.0		
8			2.1		
9	8.3		3.1		
10	8.5		3.5	12.2	2.36
11					
12		Negative			

[a] Tank I was chlorinated daily at 9 o'clock in the forenoon; tank III at 4 o'clock in the afternoon; both were sampled at 6 o'clock in the afternoon and analyzed the following day.

[b] Two hundred cubic centimeter samples digested two hours at 30° C. with 6.5 milligrams available chlorine.

It was inadvisable to keep the water in the tanks for more than one week, for the additional reason that the amount of calcium chloride introduced might prove objectionable. In the cases under observation there was not the slightest complaint during the two weeks' run. The odor of chlorine was usually marked (even in some cases where it could not be detected chemically), but was not strong enough to be objectionable.

A second run of one week's duration in tank III, using the same daily addition of 0.5 part of chlorine per million parts of water, substantiated our conclusions throughout. In this run conditions were markedly improved, probably because of the partial cessation of building operations. There was generally a sufficient excess of chlorine in the pool to give a reaction with potassium iodide and starch in the presence of phosphoric acid. The bacterial count was low throughout the week. The chemical data secured are shown in Table XI.

TABLE XI.—*Effect of daily additions of 0.5 part of chlorine per million parts of water. Tank III.*[a]

[Results expressed as parts per million.]

Age of water in days.	Turbidity.	Qualitative test for free chlorine.	Available chlorine present.	Chlorine consumption.[b]
1	9.9	Positive		2.5
2	9	do		
3		do	trace	0.35
4	8.7	do	0.2	1.2
5	7.8	do	0.30	2.4
6	<7	do	0.35	1.75

[a] Chlorination occurred daily at 4 o'clock in the afternoon; the sample was taken at 6 o'clock in the afternoon and analyzed during the following morning.

[b] Two hundred cubic centimeter samples digested two hours at 30° C. with 3.5 milligrams available chlorine.

Although the results of turbidity measurements are somewhat conflicting, it is evident that there was a slight clearing of the water due to the addition of chloride of lime. In spite of the amount of disinfectant added, no bad effect on the swimmers was noted and no complaint was made.

A series (on tank I) was performed, substituting sodium hypochlorite (as antiformin) for calcium hypochlorite. Unfortunately a weak solution was used, so that bacteriologically the results left much to be desired; however, there can be no question that in proper concentration it would have given efficient purifying action. Sodium hypochlorite has the advantage that it introduces no calcium salts or irritating substances into water, and the results of this work indicate that, for Manila water at any rate, a large amount of clearing of water occurs. The chemical data secured are shown in Table XII.

TABLE XII.—*Effect of adding antiformin.*

[Results expressed as parts per million.]

Age of water in days.	Turbidity.	Qualitative test for free chlorine.	Chlorine consumption.[a]
1	8.5	Negative	
2	<7	do	
3	<7	do	1.0
4	<7	do	2.4
5	<7	do	2.8
6	<7	do	4.2

[a] Two hundred cubic centimeter samples digested two hours at 30° C. with 3.5 milligrams available chlorine.

In order to ascertain whether the quantity of disinfectant could be appreciably diminished without destroying the sterilizing efficiency of the hypochlorite, a final series was attempted, using daily additions of 0.25 part of available chlorine per million parts of water. It developed that, although tank I was kept sterile by this treatment, the bacteria count in tank III showed a rather alarming increase after about three days, in spite of the fact that tank I is used by more bathers than tank III. The building operations at tank III introduced disturbing factors; however, there can be little question that in this case light was the chief cause of the discrepancies noted. Tank III is built practically out of doors, and during the last week's run was open to the sky. The sunlight had sufficient accelerating effect on the decomposition of the hypochlorite to bring the available chlorine below the effective sterilizing strength in a short time.

The effect of additions of 0.25 part of available chlorine per million parts of water is shown in Table XIII. Chlorine consumption was determined by digestion both in the dark and in the diffused daylight of the laboratory. The differences noted in the two determinations give some indication of the marked effect of light.

It is doubtful if such high concentrations of hypochlorite as those used in Manila would be necessary under average conditions. In addition to the poor quality of the water, the added effects of excessive temperature (almost 30°C.) and of light must be taken into account. Even in the tanks under observation, where conditions were fairly uniform, each case required special treatment. Tank III, the best lighted, requires greater additions of chlorine to maintain an excess of disinfectant than does tank I, while in tank II, the most poorly lighted, the decomposition rate of hypochlorite is below that in the others. This furnishes explanation for the fact that the treatment with 0.5 part of chlorine, found necessary in tank III, was greater than the requirement for tank I, while the same treatment in tank II caused numerous complaints of excessive and disagreeable odor.

TABLE XIII.—*Effect of daily additions of 0.25 part of chlorine per million parts of water.*

[Results expressed as parts per million.]

TANK I.

Age of water in days.	Turbidity.	Qualitative test for free chlorine.	Chlorine present.	Chlorine consumed.[a]	
				Dark.	Light.
1	[b] 11	Positive	Trace	0.6	1.4
2	13	do	do	[c] 0.7	[c] 0.7
3	10	Negative	Nil	1.2	2.5
4	8	do	Negative	1.2	3.3
5	11	do	do	1.2	3.5
6	9	do	do	1.2	2.5

TANK III.

1	15	Negative	Nil	1.25	2.3
2	----------	do	do	[c] 2.3	[c] 2.3
3	----------	do	do	2.3	3.3
4	20	do	do	2.2	4.4
5	20	do	do	2.1	4.2
6	15	do	do	1.5	3.2

[a] Two hundred cubic centimeter samples digested two hours at room temperature with 2.8 milligrams available chlorine.

[b] Immediately after chlorination.

[c] Dull day.

In disinfecting municipal water supplies or sewage there is a certain quantity of contaminating material present; once this is destroyed or removed, there is usually no further influx of noxious matter. Glaser,[10] in contradiction of the findings of Grether,[11] concluded that a single addition of disinfectant is as efficaceous as the same amount added at intervals in smaller quantities. His results may be correct for ordinary water or for sewage, but it is obvious that different conditions obtain for swimming pools, where the contaminating substances are being continually added. In the latter case the periodic addition of chlorine in small quantities, but sufficiently great to effect puri-

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[10] *Arch. f. Hyg.* (1912), 77, 279.

[11] Ibid. (1896), 27, 189.

fication, is not only preferable, but even necessary, to provide adequate protection to people using the pool. The fractional addition has the further advantage that the objectionable features of high dosage (odor, irritation of mucosæ, and the like) are largely eliminated.

Obviously the water in a swimming pool should be as clear as possible, not only because clear water makes a pool more attractive and lessens the danger of accidental drowning, but also because it is more susceptible than turbid water to the disinfecting action of chlorine. Therefore water should be subjected to filtration, with or without coagulation, wherever practicable. Aside from its coagulating effect, the action of alum is beneficial in that it reacts with bicarbonated waters in such a way that the action of chloride of lime or copper sulphate is interfered with as little as possible.

The basic carbonates, which would otherwise form precipitates with copper sulphate or chloride of lime, preventing germicidal action in the case of the former by removing copper from the sphere of influence, and causing cloudiness of the water in both cases, are removed. The addition to tank III of 1 part of alum per million parts of water had the effect shown in Table XIV.

TABLE XIV.—*Effect of alum.*

[Results expressed as parts per million.]

	Turbidity.	Total solids.	Oxygen consumed.
Before addition of alum	14	164	1.51
Twelve hours after addition of alum	10	112	1.04
Reduction in percentage	28	31	31

An attempt was made to correlate the analytical chemical data with the biological, with a view toward establishing chemical methods of determining the state of purity of water in a pool. It must be admitted that little success was achieved. The oxygen consumption showed no traceable relation either to bacterial content or to chlorine-consuming power, and even the variation in chloride content failed to give reliable data on contamination. It may be that the intermittent settling and stirring up of the suspended matter which causes the high turbidity greatly influenced the analytical results; at any rate, differences noted were neither uniform nor great enough to justify conclusions. That a relation does exist is shown by the comparison between the number of bathers a week and the oxygen-consuming capacity at the end of the week, as shown in Table XV and fig. 2. The comparison was made only for tank I, as this is the installation on which the most reliable data concerning the number of bathers were obtained.

TABLE XV.—*Variation in quality of water, compared with number of bathers. Tank I.*

Week.	Series No.[a]	Average daily attendance.	Oxygen consumption (parts per million).[b]
First	4	70	1.34
Second	5	37	0.98
Third	6	49	1.32
Fourth	2	39	1.11
Fifth	3	43	1.17
Sixth	1	33	0.95

[a] As given in Tables II to VII.
[b] Average of readings of last two days.

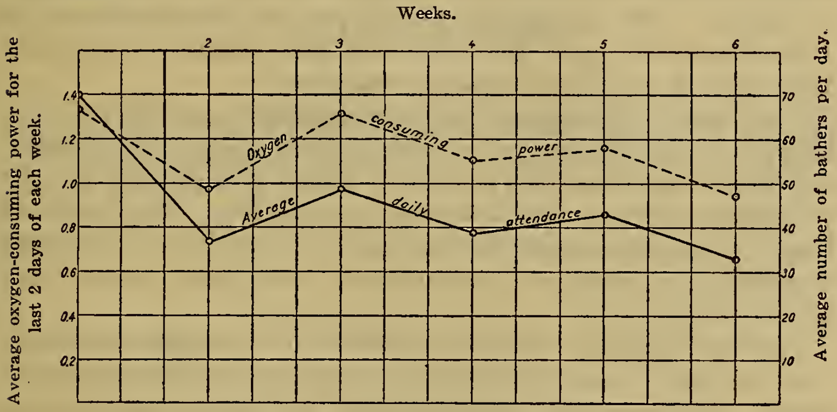

FIG. 2. Relation between oxygen consumption and number of bathers.

Therefore we may conclude that the most significant simple tests on the waters of swimming pools, in addition to the bacteriological examinations, are the determinations of available chlorine and of chlorine-consuming capacity. Once the quality of the water with respect to its chlorine-binding power has been established, it should be an easy matter properly to regulate the dosage. The qualitative test for chlorine is then enough for control purposes, as it shows whether a sufficient concentration of chlorine is being maintained and indicates any sudden variations which might be caused by occasional abnormal contaminations.

SUMMARY AND CONCLUSIONS

The chemical purification of swimming pools has been studied with special reference to the action of copper sulphate and chloride of lime.

The work was done on water that was turbid, high in bicarbonate alkalinity, and bacteriologically unsatisfactory.

Copper sulphate was found unsuited to a water of the type used.

As much as 2 parts per million of available chlorine, administered as chloride of lime and at a single dose, failed to keep the bacterial content of the water within safe limits due to the rapid disappearance of available chlorine from the water. It was only with daily additions of chloride of lime that adequate purification resulted. With this procedure, however, it was found possible to keep a pool bacteriologically clean for two weeks without change of water. There were noted no objectional features arising from the large quantities of disinfectant added (daily additions of 0.5 part of available chlorine per million parts of water). The advantages of the periodic administration of hypochlorites in small quantities over the addition of the same total amount at a single dose are discussed.

The factors influencing chlorine consumption and the chlorine-binding power of various substances were studied. The temperature of the water and the amount of light a pool receives greatly influence the decomposition rate of hypochlorites. Body products have an especially great binding power for chlorine, a fact that emphasizes the need of great personal cleanliness among users of swimming pools.

Determinations of dissolved chlorides or of oxygen consumption give little or no indication of the purity of swimming-pool water. The tests that apparently give the most information are determinations of available chlorine and of chlorine-consuming capacity.

In the purification of the water of swimming pools each case should be considered as a separate problem, since the procedure adapted to one may be entirely unsuited to another. Chemical study is as necessary as bacteriological to obtain the best results. The minimum quantities of hypochlorites necessary to maintain an excess of available chlorine should first be established by experiment, and these quantities should be administered at short, regular intervals. Once the dosage proper for ordinary circumstances is known, it becomes an easy matter to keep a pool in sanitary condition.

ILLUSTRATIONS

TEXT FIGURES

NOTE ON THE TIDAL VARIATION OF SPRINGS AND DEEP WELLS IN THE PHILIPPINE ISLANDS[1]

By George W. Heise

(From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila, P. I.)

Throughout the Philippines there are many springs, located near the coast, whose flow is greatly affected by the tides. Some of them, situated on the beach, are completely covered at high tide, so that to get water from them one is obliged to wade into the ocean and catch the fresh water as it issues from the sands. Many drilled wells show a great tidal variation in quantity of water. For example, the well at Bauan, Batangas, 90 meters deep, flowing 190 liters per minute at low tide, has a flow five times as great (950 liters) at high tide. Some, as in the case of several located at Iloilo, flow at high tide, but must be pumped at low water.

With all this variation in quantity of water, there is very little, if any, change in quality. This is quite to be expected, since the natural flow of subsoil water is toward the sea, generally under pressure great enough to prevent the admixture of sea water. A number of flowing wells in Iloilo, which yield brackish waters in quantities varying greatly with the tides, showed no appreciable change in quality, and because of their peculiar composition (high chlorine content and absence of sulphates and occasionally of calcium salts), entrance of sea water was practically out of the question.

A spring at Punta Oslob, Cebu, was described by Abella,[2] as follows:

> It emerges and flows over the beach in the zone which is alternately submerged and uncovered by the tides, and its waters, which are salty when the mouth of the spring is not covered by the sea, are, on the other hand, perfectly sweet when it (the spring) is covered at high tide. In consequence the inhabitants who use this water for drinking, await high tide to fill their 'bambones' (bamboo tubes) or jars, holding them in the whirl or eddy which the sweet water produces in the supernatant sea water.

Abella offers the suggestion that there may exist a cavity in the rocky structure of the beach in which water collects at high tide, discharging into the spring and contaminating the water at low tide.

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[1] Received for publication December 6, 1915.

[2] Rápida descripción * * * de la isla de Cebú. Madrid (1886), 87.

Correspondence with the district health officer of Cebu concerning the present status of the spring elicited the following information:[3]

> The spring in question is located at a distance of about 1 km. from the town of Oslob. It is found on the seashore which is rocky (covered with broken up particles of rock, not gravel), and slopes gradually toward the sea in such a way that at low tide the water recedes some 200 feet from the spring. Two big rocks mark the outlets of two springs separated from each other by a distance of about 30 feet * * *. One of these is situated further up from the sea and has its outlet in hollowed ground close to a big rock. Its flow is constant only at high tide, discharging only a small amount of water, and it completely dries up at low tide. Only when sea water mixes with it does the water becomes fresh, but soon gives a salty taste at the return of the tide. * * * About 30 feet from the spring above described, and further toward the sea, is another spring which has its outlet beneath a big rock. This is a much larger spring than its neighbor, discharging a large volume at high and low tide. * * * Being situated at a lower level than the former spring, it is completely covered with sea water at high tide to a depth of about four feet. It is impossible to obtain fresh water at this time, because the water of the spring can not rise up to the surface * * *. On account of their identical behaviour, these two springs probably represent two outlets of one and the same spring. * * * The water of the spring constitutes drinking water for the town of Oslob for years beyond memory, * * *.

Samples were obtained and analyses were made to ascertain whether or not this spring, or series of springs, really gave brackish water at low tide and fresh water only at high tide as reported, with the following results:

Sample No.		Chlorine, parts per million.
1.	Small spring at low tide	15
2.	Small spring, covered by tide	110
3.	Large spring at low tide	620
4.	Large spring at low tide (duplicate of No. 3)	610
5.	Large spring, covered by tide	840
6.	Large spring, covered by tide (duplicate of No. 5)	730

The greater salt content of the spring waters at high tide may well be accounted for by the unavoidable admixture of sea water in samples secured from below the surface of the sea.

Regarding these samples, a further letter from Doctor Cruz states:[4]

> The small spring, a sample from which was requested at low tide, was closely observed. It was noted to disappear completely at low tide, as was stated in previous report. It was, therefore, impossible to obtain a sample from it as was requested. However, at the return of the tide and just as it reaches the large spring, but not the outlet of the small one,

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[3] Letter of the acting district physician, Dr. Adriano Cruz.

[4] June 17, 1915.

water begins to ooze out from the latter, and sample forwarded you is taken from this at this time. Evidently the water (small spring) is not brackish as was reported, and neither is it so when covered by the tide. I must admit that * * * unusual weight has been given to tradition, current in the town of Oslob * * *.

There is, then, no reason to believe that the springs at the present time are really fresh at high tide and brackish at low tide, as had previously been reported. Perhaps the character of the springs has changed in recent years; perhaps the erroneous idea that the two springs were different outlets for the same water caused people to believe that the character of the water changed with the tide. This latter explanation seems most reasonable in view of the fact that at low tide the only available water (samples 3 and 4, from large spring) was brackish, while at high tide, the only accessible source (small spring) yields fresh water (sample 2).

MANUFACTURE OF LIME IN THE PHILIPPINE ISLANDS *

By L. W. Thurlow

(From the Bureau of Science, Manila, P. I.)

TWO PLATES

The status of lime manufacture in the Philippine Islands has always been far from satisfactory. In many sections lime is made in considerable quantities, but both the raw materials and the kilns employed usually prohibit production of a really good substance. Lime is often made from sea shells that are poorly cleaned and, consequently, yield an impure product. The kilns are frequently simply holes in the ground in which the limestone and wood are placed. In general, such arrangements are very wasteful in fuel and labor and make the cost of production of an inferior lime higher than it should be for a good one under proper conditions. However, in some cases these processes are more highly developed; a forced draft is sometimes used, and a fair product is obtained. Lime manufactured by crude methods is often satisfactory for ordinary construction work, but it is not at all suitable for chemical purposes, such as sugar manufacture. Since 1912 the demand for a better grade of lime has been so insistent that much has been imported into the Philippine Islands at considerable expense.

The investigations of lime manufacture now under way in the Bureau of Science were undertaken to encourage the local lime industry by pointing out the best deposits of limestone and the type of kiln best suited for the economical production of the material. The first kiln was too small to give results entirely comparable with commercial practice and owing to lack of funds was too lightly constructed to be permanent; but it gave fair results after a careful study of the details of its operation had been made. The lime produced was so far superior to that heretofore obtained in commercial practice in the Philippine Islands that it has been decided to present this report and to announce that a new kiln of greater capacity and improved design is practically completed, and experimental work will soon be carried on.

THE BUREAU OF SCIENCE EXPERIMENTAL KILN

The first experimental kiln at the Bureau of Science is shown on Plate I. It was cylindrical in shape and was constructed of

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* Received for publication December 1, 1915.

fire brick and cement. The smokestack shown in the illustration had been replaced by one 8 meters high by 40 centimeters in diameter before the tests described in this paper were undertaken. Considerable lime of excellent quality was burned in 1913 and 1914. This lime was used in the experiments of the Bureau of Science in the preservation of nipa sap for commercial production of sugar,[1] and a considerable quantity was sold to private individuals and to the Bureau of Supply.

The operation of the kiln, during the first two years, was primarily to obtain sufficient lime for experiments along lines entirely separate from the lime industry itself. Consequently no accurate data concerning the process were kept. In January, 1915, I was directed to run a series of tests on the kiln to determine the capacity, the fuel consumption per unit weight of lime, and other factors. Although the quality of the output of the kiln was well known, no study had been made of the cost of operation, and it was desired to know whether or not the kiln represented as great an advance in economy as it did in excellence of product.

A common practice in this kiln was to use pieces of limestone ranging from 5 to 10 centimeters in diameter. Under these conditions the stack did not always insure sufficient draft. A No. 2 Sirocco suction fan, driven at the rate of 500 revolutions per minute, was installed and proved very satisfactory. In one day the kiln was heated to the proper temperature, and on January 15, 1915, an experimental run was commenced. The kiln was fired at regular intervals—about four shovelfuls of Fushun coal per hour were thrown in at each door. The draft was controlled by a valve in the suction pipe at the top of the kiln. The results of the three-day run are recorded in Table I.

TABLE I.—*Results obtained from first run of kiln.*

Date.	Run.	Coal burned.	Lime produced.	Coal on lime.	Lime per kilo of coal.	Lime per hour.
1915.	*Hours.*	*Kilos.*	*Kilos.*	*Per cent.*	*Kilos.*	*Kilos.*
Jan. 15 to 16	12	190	293	64.8	1.54	26.8
Jan. 16 to 17	24	393	922	42.7	2.34	38.4
Jan. 17 to 18	15	331	645	51.3	1.96	43.0
Total	51	915	1,860			
Average				49.1	2.04	31.0

[a] The temperature of the flue gases was very high, probably from 400° to 500°.

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[1] See *This Journal, Sec. A* (1913), 8, 377.

The arrangement of the fan made it impossible properly to sample the flue gases on the first run, but this was corrected for the second run. The temperature of the kiln gases in a well-regulated kiln should not exceed 100°C. The temperature of the flue gases in our first run was much too high, and the loss from this cause represents at least 10 per cent of the coal consumed. In order to reduce this value, some changes were made in the kiln. To increase the efficiency of the preheating zone, the kiln was increased in height by 2.5 meters, and holes were made in one side of the kiln at intervals of 0.6 meter, from the grates to the top, so that, in case the kiln became clogged, iron bars could be inserted without interfering with the fire box.

The modified kiln is shown in Plate II. Because of the changes required in the kiln, and on account of other work, I was unable to continue the experiment for some time. On April 27 the kiln was charged for the second run. The charge consisted of 2,500 kilograms of rock, 10 centimeters in diameter. The results of this run are given in Table II.

TABLE II.—*Results obtained from second experimental run.*

Date.	Run.	Fuel burned.	Lime produced.	Coal or wood on lime.	Lime per kilo of coal.
1915.	*Hours.*	*Kilos.*	*Kilos.*	*Per cent.*	*Kilos.*
Apr. 28 to 29	24	[a]258	612	42.2	2.37
Apr. 29 to 30	(b)				
Apr. 30 to May 1	24	[a]464	1,086	42.7	2.34
May 1 to 2	24	[a]515	1,292	39.8	2.51
Total	72	1,237	2,990		
Average	24			41.3	2.42
May 2 to 3	24	[c]849	1,301	65.2	1.53

Date.	Lime per hour.	Gas analyses.			Temperature.
		Oxygen.	Carbon monoxide.	Carbon dioxide.	
1915.	*Kilos.*				*°C.*
Apr. 28 to 29	25.5	17.1	0.3	5.4	163
Apr. 29 to 30					
Apr. 30 to May 1	45.8	16.5	0.0	6.1	195
May 1 to 2	53.8	16.8	0.0	6.0	185
Total					
Average	41.5	16.8	0.1	5.7	181
May 2 to 3	54.3	19.8	0.0	1.1	204

[a] Coal.

[b] Kiln overdrawn—no lime.

[c] Wood used as fuel.

The second run was much more satisfactory. The temperature of the gas issuing from the stack was very greatly reduced with a corresponding decrease in the average coal consumption of 10.2 per cent. The average output of the kiln was increased to nearly 1 metric ton per twenty-four hours. The results of the gas analyses show an excess of air, admitted by the warped fire doors, which did a great deal to reduce the efficiency of the kiln. With properly fitted doors the coal consumption could easily be further reduced from 5 to 10 per cent.

Wood, consisting of thin strips of air-dried lumber and waste, was used on the last day of the second run. The amount of wood consumed is very small when it is considered that this wood has only about half the calorific value of coal. Wood is better adapted to lime burning than most coal, for it has a longer flame. The thermal conductivity of lime is very low, and the flame must surround the rock to give the best results. Where wood can be obtained, it is preferable, but in many places only coal is available. Information with regard to the value of Philippine firewood has been published by Cox.[2] The characteristics of some Philippine coals that are available for use in lime kilns are given by the same author.[3]

The kiln has served its purpose in demonstrating kiln requirements suitable for local lime burning and in forming the basis for the design of the new kiln.

[EDITOR'S NOTE.—Lime manufacture is more highly developed in some places in the Philippine Islands than the outline of processes in the first page of this report may indicate. For example, at Baguio large kilns are built of limestone and the fuel and rock are kept separate so there should be no contamination of the lime with ashes. The kilns require relining from time to time, because fire brick are not available. The kilns are not continuous, and there is considerable waste of fuel and labor.]

[2] Ibid. (1911), 6, 1–22.

[3] Ibid. (1909), 4, 211–229, and (1912), 7, 1–17.

ILLUSTRATIONS

PLATE I. FIRST LIME KILN BUILT BY THE BUREAU OF SCIENCE.

PLATE II. SECOND LIME KILN BUILT BY THE BUREAU OF SCIENCE.

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VOL. XI JULY, 1916 No. 4

THE STRIPPING AND THE ANALYSIS OF GALVANIZED IRON [1]

By GEORGE W. HEISE and AMANDO CLEMENTE
(From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila, P. I.)

INTRODUCTION

The extensive use of galvanized-iron products has led to the development of a voluminous bibliography on the manufacture, corrosion, testing, and stripping of zinc-coated iron. With the present increase in the price of zinc, from 10.10 pesos [2] per hundred pounds (about 45.36 kilograms) in July, 1914, to 37.50 pesos in January, 1916, the recovery of that metal becomes a problem of more and more importance.[3] It is the purpose of this paper to give a brief outline of various methods of analysis and stripping heretofore proposed, together with the results obtained in this laboratory.

When a shipment of galvanized-iron roofing is to be analyzed, so large a number of determinations is often necessary that a laboratory test should be extremely simple and rapid, as well as accurate. Although there are many factors, such as the purity and porosity of the zinc, influencing the durability of galvanized iron, in general, the most important factor is the thickness of the coating.[4] The amount of iron and other impurities in the zinc is generally small, and no serious error is involved even if they are included as part of the weight of

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[1] Received for publication March 25, 1916.

[2] One peso Philippine currency equals 50 cents United States currency.

[3] Juretzka, F., *Metall u. Erz* (1915), 3, 63 and 94.

[4] Walker, W. H., *Proc. Am. Soc. Test. Materials* (1909), 9, 431.

the coating, especially since the lack of uniformity in galvanized plate and the difficulty often encountered in getting sample pieces cut to exactly the same size make very concordant results out of the question. Therefore the determination of the amount of zinc and zinc-iron alloy per unit area is often relied upon for practical tests. Many quick methods have been developed to determine this factor. With these methods the zinc is removed by immersing the plated iron in a solution of the salt of some metal which will be replaced in solution by zinc, but not by iron, or else advantage is taken of the difference in solubility of zinc and iron in acids and alkalies.

The Preece test[5] employs a solution of copper sulphate into which a measured piece of zinc plate is dipped. Copper forms a spongy black deposit on zinc and a bright, hard deposit on iron; the number of one-minute immersions necessary to remove the zinc, shown by the first appearance of a bright red copper deposit, serves as a basis for calculating the thickness of the coating. The limitations of this method have been thoroughly discussed elsewhere.[6] Patrick and Walker[7] have suggested the use of basic lead acetate to replace the copper sulphate of the Preece test;[8] in this case zinc is dissolved and spongy lead is precipitated, while the iron remains unattacked.

Both acids and alkalies can be used to remove zinc from iron without appreciable attack on the latter. In this case, owing to the difference in potential of the two metals, the zinc in contact with the iron inhibits the solution of the latter, while the rapidity with which the former dissolves is increased. A simple method consists in dissolving the zinc from the iron by immersion in sulphuric acid,[9] determining the amount of iron in solution, and adding it to the weight of the remaining plate. The weight of the coating per unit area is calculated from the difference between the weight of iron and the original weight of plate. For certain concentrations of (dilute) sulphuric acid[10]

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[5] Walker, loc. cit.

[6] Walker, loc. cit.; Patrick, W. A., and Walker, W. H., *Journ. Ind. & Eng. Chem.* (1911), 3, 238.

[7] Loc. cit.

[8] It is interesting to note that had an ammoniacal, instead of a neutral, solution of copper sulphate been used, the Preece test would have lost many of its limitations. Although perhaps not quite so convenient as the lead acetate method, the use of ammoniacal copper sulphate solution (see experiment 25) gives reliable and concordant results.

[9] Burgess, C. F., *Electrochem. & Met. Eng.* (1905), 3, 19; Dudley, C. B., *Trans. Am. Soc. Test. Materials* (1909), 9, 441.

[10] Burgess, loc. cit., recommends the use of $\frac{2}{3}$ *N* sulphuric acid.

the attack on the iron of the base is so slight that it may be disregarded. Bauer[11] takes advantage of the frequently recorded[12] inhibitive effect of arsenic on the dissolution of iron in sulphuric acid to recommend the addition of arsenious acid to dilute (2 per cent) sulphuric acid in making the separation.

Hydrochloric acid is capable of similar utilization. The following analytical data (Tables II and V) show that concentrated hydrochloric acid can be used for stripping without appreciable effect on the iron of galvanized sheet, while Witt[13] recommends the use of dilute hydrochloric acid. Aupperle[14] suggests the use of concentrated hydrochloric acid (specific gravity, 1.2) with an addition agent, antimony trichloride ($SbCl_3$), to protect the iron. In this case the action is probably similar to the inhibiting effect of arsenious acid on the action of sulphuric acid.[15]

Alkalies also can be used. Walker[16] reports that the zinc of galvanized iron, exclusive of the zinc-iron alloy, may be removed quantitatively by dissolving in a hot caustic soda solution. The use of hot sodium peroxide solution is recommended by Meyer.[17]

There are several other stripping solutions mentioned[18] in the literature, although most of these do not yield sufficiently accurate results to serve in analytical methods, or have not been developed for analytical purposes.

EXPERIMENTAL PART

The first method to be tested in the present series of experiments was that of Meyer.[19] Briefly stated, this method con-

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[11] Bauer, O., *Mitt. kgl. Materialprüfungsamt* (1914), 32, 448.

[12] Millon, E., *Compt. rend. Acad. Sci.* (1845), 21, 37; Burgess, C. F., *Trans. Am. Electrochem. Soc.* (1905), 8, 165; (1906), 9, 199. For a possible explanation for this phenomenon see Watts, O. P., ibid. (1912), 21, 337.

[13] Witt, J. C., *This Journal, Sec. A* (1916), 11, 154.

[14] Aupperle, J. A., *Metal. Ind.* (1915), 13, 329; *Iron Age* (1915), 96, 132.

[15] Beneker, U. S. Patent 914,916 (March, 1909), uses dilute hydrochloric acid containing from 0.001 to 0.005 per cent arsenic as a cleaning or pickling bath for iron or steel.

[16] Loc. cit.

[17] Meyer, K., *Zeitschr. f. angew. Chem.* (1909), 22, 68; Serger, H., *Zeitschr. f. Untersuch. d. Nahrungs- u. Genussmittel* (1913), 25, 465.

[18] Broemme, E., and Steinau, R., U. S. Patent 1,042,315 (October, 1912). The use of alkali or alkaline earth bisulphates or bisulphites; the use of zinc chloride in slightly basic water solution; Weber, U. S. Patent 1,122,272 (December, 1914).

[19] Loc. cit.

sists in boiling weighed pieces of galvanized iron with sodium peroxide and water and determining the loss in weight. Typical analyses follow:

TABLE I.—*Analyses of galvanized iron by the Meyer method.*

Sample.[a]		Loss after treatment No.—		Coating in sample.[b]	Weight of coating.[b]	
No.	Weight.	I.	II.		Per square foot.	Per square decimeter.
	Grams.	*Grams.*	*Grams.*	*Per cent.*	*Ounces.*	*Grams.*
1	14.480	0.877	1.526	10.52	1.94	5.92
2	14.912	0.842	1.556	10.42	1.97	6.03
3	14.483	1.531	1.543	10.35	1.95	5.98
4	14.327	1.507	1.530	10.64	1.94	5.95

[a] Each sample was 5.08 by 5.08 centimeters (2 by 2 inches).

[b] Computed from loss of weight after second treatment.

The Meyer method gives concordant and reliable results. However, it was devised especially for the stripping of tin plate and is better adapted to that process than to the stripping of galvanized iron because of the relatively large amounts of zinc used for coating iron. Treatment with sodium peroxide must be repeated several times to insure the complete removal of the zinc coating from ordinary galvanized iron, so that the process becomes tedious.

Some of the experiments performed in the course of this study have little analytical or commercial value at present, but yield interesting information regarding the potentials of metals in various solution. We have divided them into two classes—namely, those in which the zinc has been dissolved by immersion in the stripping solution and those in which electric current has been used to aid or control the action.

Table II gives examples of stripping baths of the first class. For the tests enumerated, pieces were cut from a sheet of galvanized iron, which analysis had shown to be fairly uniform in composition. Therefore the results obtained may be considered comparable. As galvanized iron at best is of varying composition, differences of less than 0.1 per cent have little significance. A few tests by standard methods (Nos. 5, 16, etc.) are inserted for comparison.

TABLE II.—*Removal of zinc from galvanized iron by immersion.*

Experiment No.	Solution used.	Weight of sample.	Loss on immersion.		Remarks.
		Grams.	*Grams.*	*P. ct.*	
5	Sodium peroxide (Meyer method).	8.494	0.830	9.77	
6	Nitric acid (concentrated)	--------	--------	--------	Rapid and complete dissolution.
7	Hydrochloric acid (sp. gr. 1.2)	5.773	0.551	9.55	Loss after 30 minutes additional, 0.001 gram.
8	Hydrochloric acid (25 per cent by volume).	5.094	0.495	9.73	
9	Sulphuric acid (50 per cent by volume).	--------	--------	--------	Action is very slow, but iron is attacked.
10	Sulphuric acid (25 per cent by volume).	4.957	0.497	10.02	Action continues indefinitely.
11	Sulphuric acid (5 per cent by volume).	5.348	0.505	9.44	Loss after 80 minutes additional, 0.002 gram.
12	Sodium bisulphate (concentrated).	4.413	0.417	9.45	Loss after 18 hours additional, 0.002 gram.
13	Phosphoric acid (25 per cent by volume).	5.182	0.496	9.57	Loss after 60 minutes additional, nil.
14	Phosphoric acid (2 per cent by volume).	4.228	0.400	9.45	
15	Acetic acid (25 per cent by volume).	5.822	0.560	9.61	Required 24 hours for completion. Loss after 5.5 hours additional, 0.0025 gram.
16	Lead acetate	5.123	0.496	9.68	Loss after 90 minutes additional, 0.0015 gram.
17	Lead acetate plus sodium hydroxide.	5.027	0.468	9.30	Loss after 20 hours additional, 0.0015 gram.
18	Lead acetate plus acetic acid	4.705	0.428	9.09	Loss after 90 minutes additional, 0.0005 gram.
19	Lead nitrate	4.435	0.303	6.83	Deposit is hard and adherent.
20	Lead nitrate plus nitric acid	4.653	0.428	[a] 9.19	Action is slow.
21	Lead nitrate plus sodium hydroxide.	4.257	0.402	9.44	Deposit is not readily removed. Loss after 18 hours additional, 0.0035 gram.
22	Lead chromate plus sodium hydroxide.	--------	--------	--------	No action.
23	Cadmium nitrate	--------	--------	--------	Do.
24	Cadmium nitrate plus ammonium hydroxide.	4.159	0.398	9.57	Action is very slow; coating is hard to remove.
25	Copper sulphate plus ammonium hydroxide.	4.063	0.394	9.70	Action is very slow.
26	Copper sulphate plus tartaric acid plus potassium hydroxide.	3.953	0.381	9.64	Copper scale is readily removed by scrubbing.
27	Cobalt acetate	4.553	0.293	6.43	Reaction not completed at end of 10 days.
28	Cobalt acetate plus ammonium hydroxide.	2.669	0.255	9.56	Action proceeds with effervescence.
29	Chromium nitrate	4.549	0.467	10.36	72 hours required for completion, coating is hard and adherent, and iron is attacked.

[a] The iron base is attacked on continued immersion.

TABLE II.—*Removal of zinc from galvanized iron by immersion*—Continued.

Experiment No.	Solution used.	Weight of sample.	Loss on immersion.		Remarks.
		Grams.	*Grams.*	*P. ct.*	
30	Chromium nitrate plus sodium hydroxide.	3.684	0.356	9.68	72 hours required for completion; coating is hard and adherent.
31	Aluminium nitrate	4.629	0.458	9.89	
32	Aluminium nitrate plus sodium hydroxide.	4.259	0.068	1.61	Reaction not completed at end of 10 days.

The results in Table II, for the most part, are self-explanatory, yet some of them merit further attention.

Theoretically the removal of zinc from iron is easy, since the potential of the former is the higher in most solutions. In stripping with the metallic salts, it would seem necessary merely to find the salt of a metal whose potential, in any given solution, is lower than that of zinc and higher than that of iron. Practically, however, the manner in which the potentials of metals fluctuate in different solutions, the character of the metallic deposits formed, and other factors make the operation less simple.

Iron, cathodic to zinc in most acids, does not assume the passive state in contact with zinc; hence galvanized iron is completely destroyed in concentrated nitric acid (No. 6).[20]

The action of lead salts is interesting and peculiar. The precipitated lead from lead acetate in acid solution (No. 18) or in approximately neutral solution (No. 16) is crystalline in appearance, while that from a solution made alkaline with sodium hydroxide (sufficient to dissolve the precipitate formed) (No. 17) is velvety. The deposits obtained from lead nitrate solution (No. 19) are crystalline, but much harder to remove than those from lead acetate solution. The acidified solution of lead acetate (No. 18) did not attack plate so well as a nearly neutral solution (No. 16). A further peculiarity is the fact that a lead acetate or lead nitrate solution to which sodium hydroxide has been added (lead hydroxide) in sufficient quantity to redissolve the precipitate formed (sodium plumbite) will

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[20] However, the tin of tin plate can be completely removed by concentrated nitric acid, without affecting the iron base, although according to de la Rive [Gore, The electrolytic separation of metals. Van Nostrand & Co., New York (1894), 56], tin is electropositive to both zinc and iron in concentrated nitric acid.

strip zinc, whereas lead chromate dissolved in sodium hydroxide leaves galvanized iron unattacked.

Copper salts, which generally attack both zinc and iron, may have selective action in alkaline solution (Nos. 25 and 26). Ammoniacal and alkaline solutions of salts of other metals, such as aluminium (Nos. 31 and 32), cadmium (Nos. 23 and 24), cobalt (Nos. 27 and 28), and chromium (Nos. 29 and 30), have selective action, although the salts themselves have little or no such effect.

Of the cases mentioned, the precipitation of such metals as chromium, copper, lead, and aluminium from alkaline solution is of special interest because of the uncertain position of the metals in the complexes formed when their salts are dissolved in alkalies.

The fact that iron is generally attacked very little when it is used as anode in alkaline or oxidizing solutions has long been made the basis of methods of separation of metallic coatings from iron.[21] The separation is sufficiently complete and clean cut to serve as a rapid and accurate method of analysis of galvanized iron, as the results in Table III show. In the experiments here recorded, no particular effort was made to regulate the current. A voltage of about 3 and a current density of approximately 15 to 25 amperes per square decimeter were maintained, the stripping being completed in a few minutes. The galvanized iron was cut from the sheet used in the tests enumerated in Table II.

TABLE. III.—*Stripping of zinc from iron with the aid of an electric current.*

Experiment No.	Bath.	Sample.		
		Weight.	Loss.	
		Grams.	*Grams.*	*Per cent.*
33	Potassium chlorate, saturated solution	1.996	0.189	9.49
34		2.766	0.264	9.54
35	Potassium nitrate, saturated solution	2.300	0.217	9.43
36		2.229	0.213	9.53
37	Sodium nitrate, 30 per cent solution	4.055	0.393	9.69
38	Chromium nitrate, 20 per cent solution	2.601	0.274	10.53
39		2.455	0.263	10.72
40	Potassium hydroxide, 20 per cent solution	3.918	0.380	9.70
41	Sodium hydroxide, 20 per cent solution	4.454	0.422	9.47

Chromium nitrate allowed a slight although appreciable dissolution of the iron base. With the possible exception of the case of

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[21] Burgess, C. F., *Trans. Am. Electrochem. Soc.* (1903), 4, 31.

chromium nitrate, there was no noticeable attack on the iron base on continued passage of current.

The results of the foregoing experiments indicate that many of the methods enumerated are capable of being used for quantitative analyses; hence some of the more promising were studied in greater detail. For these experiments samples of the same galvanized iron (different from that used in the foregoing tests), cut with shears as accurately as possible into square of desired size, were used.

The results recorded in Table IV were obtained by making galvanized iron the anode in 30 per cent sodium nitrate solution.

TABLE IV.—*Stripping of galvanized iron with an electric current. Galvanized sheet anode, platinum cathode. Bath, 30 per cent sodium nitrate* ($NaNO_3$) *solution, except as noted; current, 0.7 to 1.0 ampere; voltage, 3 to 5; size of plate, 3.8 by 3.8 centimeters* (*1.5 by 1.5 inches*), *except as noted.*

Experiment No.	Sample.	Loss.		Weight of coating.	
				Per square foot.	Per square decimeter.
	Grams.	*Grams.*	*Per cent.*	*Ounces.*	*Grams.*
42	8.232	1.203	14.61	2.73	8.33
43	7.948	1.201	15.10	2.72	8.31
44	8.345	1.217	14.93	2.76	8.43
45	8.318	1.186	14.26	2.69	8.21
46	[a]33.175	4.650	14.02	2.64	8.07
47	[b]8.068	1.127	13.97	----------	----------

[a] This sample was 7.6 by 7.6 centimeters (3 by 3 inches).

[b] In a bath of 20 per cent sodium hydroxide

Only a few minutes were necessary completely to remove the zinc from the iron. There was no residual zinc on the stripped plate. The results obtained show as good agreement as could be expected, considering the lack of uniformity of zinc coatings, the size of the samples used for analysis, and the errors incident to cutting out squares with ordinary tin shears.

The presence of iron could always be shown in the solution after stripping had been accomplished. That this was not due to an appreciable extent to attack on the iron base is shown not only by the constancy of the results recorded for the thickness of the coating, but also by the constancy of the amount of iron removed in the different trials. Duplicate determinations fixed the amounts of iron from pieces of galvanized iron 3.8 by 3.8 centimeters (1.5 by 1.5 inches) as 0.046 and 0.048 gram, respectively. These figures are equivalent to losses of iron of 0.319 and 0.332 gram per square decimeter (0.105 and 0.109 ounce per square foot), with which the loss (0.11 ounce per square foot) recorded by Witt[22] for the same sample of galvanized iron when stripped with hydrochloric acid is in good agreement. There is always a layer of zinc-iron alloy formed when iron is galvanized by the "hot process," whereas little[23] or no[24] such layer is formed when iron is electroplated. Therefore it is evident that the iron found in the stripping bath was largely due to the zinc-iron alloy formed in the process of hot galvanizing.

As has been shown (Table II), sulphuric acid alone can be used for the analysis of galvanized iron with reliable results, provided the acid is used in proper dilution. However, acid strong enough to attack galvanized iron may be used successfully if electric current is used and the plate to be stripped is made the cathode.[25] That the iron is protected from attack by this method is shown by the data in Table V.

TABLE V.—*Stripping of galvanized iron with electric current; plate as cathode. Size of plate, 3.8 by 3.8 centimeters (1.5 by 1.5 inches), except as noted; bath, sulphuric acid; current, 0.75 to 1.5 amperes; voltage, 3.*

Experiment No.	Strength of acid by volume.	Sample.	Loss.		Weight of coating.	
					Per square foot.	Per square decimeter.
	Per cent.	*Grams.*	*Grams.*	*Per cent.*	*Ounces.*	*Grams.*
48	[a]2	7.979	1.081	13.55	2.44	7.45
49	[b]50	-----	-----	-----	-----	-----
50	20	8.285	1.155	13.94	2.61	7.96
51	20	8.230	1.135	13.79	2.56	7.82
52	20	[c]16.387	2.372	14.48	2.67	8.17

[a] Action is very slow, especially on side nearest anode.

[b] No appreciable action in thirty minutes.

[c] This plate was 3.8 by 7.6 centimeters (1.5 by 3 inches).

Analysis showed that iron was also dissolved in this process. The maximum amount determined in the solution was 0.047 gram. The agreement with our own previously recorded values

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[22] Loc. cit.

[23] Walker, W. H., *Journ. Ind. & Eng. Chem.* (1912), 4, 397.

[24] Bauer, loc. cit.

[25] Reed, C. J., *Trans. Am. Electrochem. Soc.* (1907), 11, 181, recommends the removal of mill scale from iron by making the iron the cathode in sulphuric acid.

(Table IV) for the same galvanized iron shows clearly that this iron was part of the zinc-iron alloy, not part of the iron base. However, as might be expected, the rate of solution of zinc is somewhat retarded by this process. The separation is completed in a very few minutes, and the iron base, so far as could be determined, is protected.

Finally a series of determinations was made, using different acids of varying concentrations. The results, which are self-explanatory, are given in Table VI.

TABLE VI.—*Stripping of galvanized iron with acids. Temperature, 30° C. Size of samples, 3.8 by 3.8 centimeters (1.5 by 1.5 inches).*

Experiment No.	Bath.	Sample.	Loss.		Weight of coating.	
					Per square foot.	Per square decimeter.
		Grams.	*Grams.*	*Per cent.*	*Ounces.*	*Grams.*
53	Sulphuric acid, 2 per cent, plus arsenic trioxide	8.128	1.015	12.48	2.30	7.03
54	Phosphoric acid, 25 per cent by volume	8.336	[a] 1.122	13.49	2.55	7.77
55	do	8.102	[a] 1.128	13.92	2.56	7.81
56	Hydrochloric acid (sp. gr., 1.19)	7.941	[b] 1.099	13.84	2.49	7.61

[a] No additional loss after reimmersion for one hour.

[b] Loss <0.002 gram after thirty minutes additional immersion.

In each case the removal of zinc is characterized by effervescence, which ceases entirely when the iron of the base is reached. Phosphoric acid reacts slowly, but the stripped iron can be left immersed for a long time without appreciable loss.

DISCUSSION

The experiments here enumerated,[26] aside from their possible application to analytical or commercial problems, are of interest in their bearing on the question of the potentials of metals in different baths and the replacement of a metal from its salts by another metal. That the replacement series of the metals differs not only in solutions of different substances in a given solvent, but also in solutions of the same substance in a constant solvent with factors such as change of temperature, pressure, concentration, magnetic influence, and the like is well known.[27]

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[26] The applicability of some of the methods enumerated above to the removal of tin from tin plate will be discussed in another paper.

[27] Cf. Gore, G., loc. cit.; idem, *Proc. Roy. Soc.* (1879), 30, 38; Christy, S. B., *Trans. Am. Inst. Min. Eng.* (1900), 30, 864.

A variation of the solvent[28] makes the subject still more complicated.

In this brief series of experiments there are several "reversals" of potential. Thus copper sulphate attacks both zinc and iron in aqueous solution, as might be expected from its position in the "electrochemical series," but on the addition of ammonia to solutions of certain copper salts, the copper apparently occupies a place above iron and below zinc. The same holds true for an alkaline copper sulphate solution (No. 26). Zinc replaces aluminium[29] (Nos. 31 and 32) from aluminium nitrate solution. The last reaction is retarded by the addition of sodium hydroxide.

Tzentnerschwer and Druckker[30] found that zinc reacts with solutions of cobalt chloride and cobalt sulphate, but only with very concentrated cobalt nitrate solutions. This is interesting in view of our experiments 26 and 27 with cobalt acetate. We have found that an ammoniacal solution of cobalt nitrate (like ammoniacal cobalt acetate No. 27) reacts very quickly with galvanized plate and gives a quantitative separation of zinc from iron.

The variation in the single potentials of zinc in different aqueous solutions has been studied in detail by Patten and Mott,[31] who found a difference of over 1 volt between the highest (+ 1.0 volt in KOH + KCN) and the lowest (— 0.08 volt in $KMnO_4 + K_2CrO_4$) values obtained. Other metals doubtless show equally great variations. Perhaps the fact that the potential of zinc is lowered in oxidizing solutions such as nitrate, chromate, or permanganate of potassium accounts for the failure of a solution of lead chromate in sodium hydroxide to attack galvanized iron.

SUMMARY AND CONCLUSIONS

Various methods of analyzing galvanized iron, or of stripping zinc from iron, have been studied and developed.

The separation of zinc from iron with phosphoric acid, sodium bisulphate, hydrochloric acid, or sulphuric acid is sufficiently rapid and complete to serve as a quantitative analytical

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[28] Gates, C. B., *Journ. Phys. Chem.* (1911), 15, 97; Ghosh, J. C., ibid. (1915), 19, 720.

[29] Preliminary experiments in this laboratory indicate that the potential of zinc is several tenths of a volt above that of aluminium in a normal sodium nitrate solution.

[30] Tzentnerschwer, M., and Druckker, Y., *Journ. Russ. Phys. Chem. Soc.* (1915), 47, 528.

[31] Patten, H. E., and Mott, W. R., *Trans. Am. Electrochem. Soc.* (1903), 3, 317.

method. Acetic acid gives accurate results, but the action is slow.

The separation can also be effected by the use of metallic salts, notably certain salts of lead, cadmium, copper, cobalt, chromium, and aluminium. The experiments with metallic salts give an indication of the changes in the potential of metals which occur in different liquids.

Stripping and analysis may be accomplished with the aid of the electric current, by making galvanized iron the cathode in sulphuric acid, or by making it the anode in concentrated caustic alkali solutions or in oxidizing solutions like sodium nitrate.

In the methods enumerated, the iron removed from the galvanized plate is largely that contained in the zinc-iron alloy present in the coating and is not due to corrosion of the iron base.

THE TESTING OF GALVANIZED IRON [1]

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TWO TEXT FIGURES

INTRODUCTION

There are four general methods for galvanizing [2]—namely, hot galvanizing, electrogalvanizing, sherardizing, and cowperizing. The essentials of each are briefly as follows:

Hot galvanizing.—This process was patented by Crawfurd [3] in 1837. The iron is first cleaned in dilute hydrochloric or sulphuric acid, washed in water, and then passed into a bath of molten zinc. The temperature is usually kept as low as possible to avoid too much volatilization of the zinc and too great a loss from alloying with the iron. Excess zinc is removed either by passing between rollers or by shaking or centrifuging. The process is economical in time, but wasteful in zinc. According to Turnbull [4] the distribution of zinc in a hot galvanizing bath is as follows:

	Per cent.
Coating on the articles	68
Dross	18
"Ashes"	12
Volatilized	2

Electrogalvanizing.—After being thoroughly cleaned, the iron is placed in a solution of a zinc salt and the zinc is deposited by electrolysis. The anode is usually lead or zinc. This process is extensively used for small objects, such as bolts and nails, and also for boiler tubes.

Sherardizing.—In this method the iron is cleaned and placed in a large iron drum which contains zinc dust. The drum is then heated to a temperature of from 260° to 315°C. The container should be air-tight, and most of the air should be removed

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[1] Received for publication November 24, 1915.

[2] See Sherard Cowper-Coles, *Electrochem. & Met. Ind.* (1908), 6, 189.

[3] Thorp's Dictionary of Applied Chemistry. Longmans, Green, & Co., London (1913), 5, 810.

[4] *Journ. Inst. Metals* (1914), 12, 301.

to prevent much of the zinc from oxidizing. The thickness of the coating depends on the time and the temperature.

Cowperizing.—The iron is placed in a drum made of wire netting and is treated with zinc vapor in an atmosphere of hydrogen. The reducing action of the hydrogen aids in keeping the zinc free from oxide and thus insures a good adhesion of the deposit. This process is especially suitable for coating articles which have threads or which require to be accurately fitted, because the zinc is evenly distributed.

Only the hot galvanizing and the electrogalvanizing processes are used in the manufacture of galvanized sheets. The present work has been done with sheets galvanized by the former method.

The question of galvanized sheets is of importance in the Philippine Islands. They are extensively used as a roofing material to replace nipa. They are light and, of course, not inflammable. About 80 to 90 per cent come from the United States and are bought under the specifications that for each 900 square centimeters there must be a minimum of 54.9 grams of coating (two ounces per square foot).[5] It seemed advisable to investigate various methods of determining the amount of the coating and to decide if possible which is the best with reference to accuracy and the time, labor, expense, and other factors of applying it.

In this connection the structure of galvanized iron is of interest. There is no sharp line of demarcation between the iron base and the zinc coating, but between the two is a series of zinc-iron alloys. The alloys nearest the iron base contain mostly iron. From this outward there are other alloys, each with a lower percentage of iron, till the zinc itself is reached. Warren[6] expresses the relationship very clearly when he says: "Zinc in galvanized iron exists in two states. (1) Part of the zinc forms an alloy with the iron (2) zinc adheres to this alloy mechanically."

Arthur and Walker[7] have made a study of the structure of galvanized iron by microscopic methods. They state that the

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[5] In the United States, tests on galvanized iron are reported in terms of ounces of zinc per square foot. In order that this paper may be easily compared with others on the subject, results are given in both systems of weights and areas.

[6] *Phil. Mag.* (1871), IV, 41, 132.

[7] *Journ. Ind. & Eng. Chem.* (1912), 4, 397; see also v. Vagesack, *Zeitschr. f. anorg. Chem.* (1907), 52, 30.

binding alloy is present even in iron that has been electrogalvanized or sherardized. In hot galvanized iron, crystals of $FeZn_3$ and $FeZn_7$ have been found.

VARIOUS METHODS OF TESTING

A number of methods have been published for determining the amount of zinc coating on galvanized objects. Among them may be mentioned the amalgamation method and the use of solutions of copper sulphate, sodium hydroxide, lead acetate, etc. The various tests may be divided into two groups:

1. The galvanized object is placed in a solution which will attack the zinc, but has little effect on the iron base. After a given period of time it is removed, cleaned of any loosely adhering substances, and again placed in the solution. The strength of the solution is known, and the temperature is kept within certain limits. When all the zinc is removed at any point, the test is regarded as complete, and the number of immersions are recorded.
2. All the zinc is removed. The weight per unit area or unit length is calculated.

A test of the second group is to be recommended whenever practicable. Such a test is now almost universally used for galvanized sheets and is well adapted to wire. Tests of the first group are usually applied to all irregular objects such as bolts and nuts. Specifications are written on that basis, and considerable work would be required to determine just how much coating should be found on all the various articles that are now galvanized and to rewrite the specifications. However, it seems likely that this will be done in time and that all tests of the first group will go out of use.

The amalgamation, or mercury, method seems to have been one of the earliest used. Warren[8] found that by putting a clean galvanized object into mercury all the free zinc was removed. The zinc, which was alloyed with iron, combined with mercury, also, in the ratio of 7:11. This new alloy could then be volatilized in a nonoxydizing flame and the zinc calculated and added to that previously removed. Of course, this procedure would not be satisfactory for routine work.

Sodium hydroxide solution is sometimes used for removing the zinc from galvanized iron. This method is not satisfactory because it is slow and because some of the zinc-iron alloys are not attacked.

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[8] Loc. cit.

The copper sulphate, or Preece, test is the one still in most general use for all galvanized articles except sheets. An outline of the method is as follows:

A strong solution of copper sulphate is shaken with copper oxide to neutralize any acid present and is then diluted to density 1.186 at 18.5°C. A galvanized article is placed in this solution for one minute and is then removed and cleaned. This operation is then repeated until a bright deposit of copper is formed on the iron base. In order to pass specifications, an object must withstand a given number of immersions. Many criticisms may be offered to this method as pointed out by Walker[9] and by Patrick and Walker,[10] who have studied it in detail. They state that since the zinc coating is not homogeneous and the zinc-iron alloys are less electropositive to the iron than is the zinc, the zinc does not go into solution at a constant rate of speed:

> Since the rapidity with which the zinc or zinc alloy will pass into solution, and an equivalent weight of copper be precipitated in its place, is a function of the difference of potential between the two metals, it will be seen that the rate of solution must of necessity change as we pass from the zinc to the alloy. The coating in the so-called sherardized iron and some kinds of electro-galvanized iron consists so largely of an iron-zinc alloy that any test or measurement based upon an assumed uniformity in rate of solution is liable to grave error and untrustworthy.

THE LEAD ACETATE METHOD

Patrick and Walker[11] devised the lead acetate method as a substitute for the Preece test. They recommended that it be used to determine the weight of zinc coating per unit length or area, but stated also that, even if it is used in the same way as the Preece test, it is more satisfactory. A solution is made by dissolving 400 grams of crystallized lead acetate in one liter of water. To this are added 4 grams of litharge to neutralize any acid present and to give the solution a slightly basic reaction. After filtering, the solution is ready for use. A piece of wire 7.6 to 15.2 centimeters (3 to 6 inches) long or a galvanized plate 5.08 by 5.08 centimeters (2 by 2 inches) is weighed and placed in a quantity of the solution for three minutes. The zinc goes into solution and a deposit of metallic lead forms on the plate or wire. The object is taken from the liquid, and the lead is removed. The operation is repeated until no more lead coating forms. The object is first washed in water and

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[9] *Electrochem. & Met. Ind.* (1909), 7, 440.

[10] *Journ. Ind. & Eng. Chem.* (1911), 3, 239.

[11] Loc cit.

then in alcohol, after which it is dried and weighed. Or the lead may be determined by dissolving in nitric acid and titrating with potassium dichromate.

COMMENTS ON THE LEAD ACETATE METHOD

In the original paper it is recommended that a square (5.08 by 5.08 centimeters), which should not vary more than 0.04 centimeter (1/64 of an inch) plus or minus, be used for the test. This is too small a piece to give accurate results under ordinary conditions. If two such squares are cut so that on each side of the first there is an error of plus 0.04 centimeter, and on each side of the second an error of minus 0.04 centimeter, the total error will amount to over 6 per cent. It is practically impossible to cut sheeting as accurately as this with ordinary shears, and a great many pieces are tested with errors much greater. Some of the pieces cut by power shears are not sufficiently accurate.[12] Another and more serious reason against the use of such small pieces is that they do not give a fair average of the composition of the material. Any variation in the coating is, of course, multiplied by thirty-six in calculating the results to the basis of 900 square centimeters.

That the variation in coating may be considerable was demonstrated by some tests made in this laboratory. The results are show in fig. 1. The maximum variation was 2.19 grams per 15-centimeter square, or about 12.3 per cent. This is equivalent to 8.76 grams per 900 square centimeters, or about 0.3 ounce per square foot. It is easy to see that had only the small squares been used a great error would have been possible, leaving out of consideration any inaccuracies in cutting. Nothing smaller than 15-centimeter squares should be used for testing galvanized sheeting, and when convenient 30-centimeter squares are to be recommended. All tests made in this work by the lead acetate methods have been with 15-centimeter squares, so that average results might be obtained. Such a procedure is satisfactory for experimental purposes, but would be too expensive for a laboratory where a great many tests are made.

Theoretically, to remove the zinc from a 15-centimeter square of galvanized iron containing 68.8 grams of zinc per 900 square centimeters, about 100 grams of lead acetate $[Pb(C_2H_3O_2)_2 \cdot 3H_2O]$ would be required. In practice, however, it has been found

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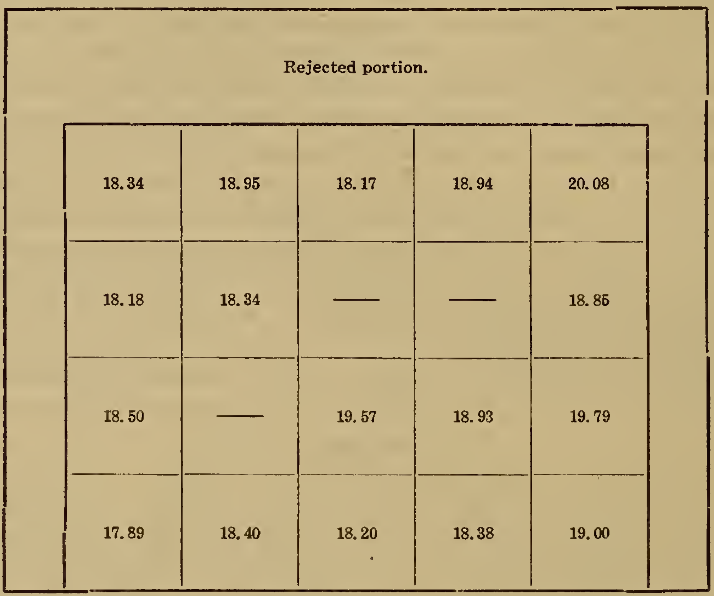
[12] These considerations are intended to apply to commercial testing only. Of course, for experimental purposes, it is possible to prepare squares having negligible variations in size, but this requires considerable time and is not practicable for routine work.

that considerably more than this amount is necessary, because the solution becomes exhausted long before all the lead has been removed. Three causes for this may be suggested.

1. The concentration of the lead ions is diminishing.
2. The concentration of the zinc ions is increasing.
3. The removal of the alloy layers is much slower than that of the zinc itself. As a result the reaction almost ceases unless there is a large excess of lead acetate present.

In order to determine the effect of each of these factors, the following experiments were carried out. One of the 15-centimeter squares was placed in a quantity of lead acetate solution containing the theoretical amount of lead necessary to replace the zinc, and although it was left for a number of hours, with frequent removals for cleaning off the precipitated lead, not all the zinc was removed. The action did not altogether cease, but was so slow that it was worthless. On analysis this nearly exhausted solution was found to contain 57.05 grams lead acetate per liter.



18.34	18.95	18.17	18.94	20.08
18.18	18.34	——	——	18.85
18.50	——	19.57	18.93	19.79
17.89	18.40	18.20	18.38	19.00

FIG. 1. A galvanized sheet was taken at random. A piece was cut 60 by 75 centimeters, rejecting the portion at the end and sides. This was then cut into squares 15 by 15 centimeters, and each was numbered so that its original position on the sheet might be known. The numbers in the diagram show the weight of coating in grams found on each square. The squares were cut accurately, so that the variation in results is almost entirely due to variation in the coating itself.

Another portion of lead acetate solution was subjected to immersions of fresh galvanized sheets until no more action could be noticed on the last one, even after several hours. The essential difference between this and the previous experiment was that in this case the solution was always acting on zinc rather than on any of the zinc-iron alloys. It might be expected that more of the lead could be removed. This was found to be true, for the analysis showed 2.62 grams lead acetate per liter.

A lead acetate solution which contains no zinc ions can be still more dilute and attack a galvanized surface. Some of the original solution was diluted to various concentrations with distilled water, and each was tried with a fresh piece of galvanized iron. A solution containing only 0.5 gram lead acetate per liter showed some action. This may be made clearer by summing up the results.

TABLE I.—*Minimum strength of active lead acetate solution under various conditions.*

Condition.	Lead acetate per liter. Grams.
Solution containing no zinc ions and acting on outer zinc coating	0.50
Solution containing zinc ions and acting on outer zinc coating	2.62
Solution containing zinc ions and acting on the zinc-iron alloys	57.05

These results indicate that each of the three factors mentioned above has its effect on rendering the acetate solution inactive. It is likely that the relative importance of each varies with the temperature, concentration of the solution, and character of the zinc-iron alloys. However, the net result is that more than the theoretical amount of lead acetate is required, and consequently the cost of each test is increased.

THE HYDROCHLORIC ACID METHOD

Hydrochloric acid[13] may be used for removing the coating from galvanized iron if the temperature and concentration are kept within certain limits. A solution made from one part

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[13] After the present paper had been completed, I received an abstract of a paper by Aupperle [*Metal Ind.* (1915), 13, 329; *Iron Age* (1915), 96, 132]. Aupperle uses hydrochloric acid having a density of 1.20, containing a small amount of antimonous chloride. The samples are cut 5.72 by 5.72 centimeters (2.25 by 2.25 inches). He objects to the Preece test, because of its unreliability, and to the lead acetate method, because of the long time required.

The results obtained in this laboratory show that if a lower density of acid is used no addition of any salt is necessary. The disadvantages of such small pieces have already been discussed.

(by volume) of chemically pure hydrochloric acid to one part of distilled water should be employed. Such a solution has a density of approximately 1.098 at 15.5°C. and contains 19.53 per cent acid. The temperature of the acid should never be higher than 45°C. A 15-centimeter square (or larger piece) of galvanized sheet is weighed, placed in the acid, and allowed to remain until perceptible effervescence ceases, which should require only two or three minutes. It is then removed and washed. If any zinc still remains, the sheet is again placed in the acid until this is dissolved, which usually requires only a minute or two. It is removed, washed in water, then in alcohol, placed in a drying oven for a few minutes, cooled in a desiccator, and weighed.

Preliminary tests convinced me several years ago that this is a very satisfactory method, but at that time no detailed investigation was undertaken. The fact that iron dissolves so readily in hydrochloric acid under some conditions would lead one to think that the acid was not suitable for this purpose. However, the present work shows that no iron (except, perhaps, a trace) other than that alloyed with the zinc goes into solution, provided the temperature and density of the acid are properly controlled.

COMPARISON OF THE LEAD ACETATE AND HYDROCHLORIC ACID METHODS

Preliminary experiments showed that in both methods some iron was removed from the sample. In the lead acetate method this iron comes entirely from the zinc-iron alloys, because the basic lead acetate solution does not attack the iron base. A number of tests were run to determine if the same thing was true with the hydrochloric acid. Variations had been noticed in results obtained by both methods, and it was desired to determine whether these were due to errors in the methods or to lack of uniformity in the coating itself. Consequently, in every case after the coating had been removed, the solution and all wash waters used in the operation were placed in a flask, made up to volume, and the iron and zinc were determined in an aliquot portion.

This operation was found to be much simpler in the hydrochloric acid than in the lead acetate solution. In the latter case the first analyses were made by simply pipetting off the solution from the metallic lead. This gave results which were incorrect. Approximately 50 per cent of the zinc had been absorbed by the metallic lead. It was found necessary first to decant the solution from the lead and then to heat the latter with sulphuric acid until it was completely disintegrated. After cooling, the mixture was added to the solution which precipitated all the lead as sulphate. The new mixture was then cooled, transferred to a 2-liter flask, and made up to volume. The lead sulphate settled completely, and portions of the clear solution were withdrawn and analyzed. The iron was precipitated with ammonia and determined gravimetrically. The zinc was determined by titration with potassium ferrocyanide.

In the hydrochloric acid solution it was only necessary to oxidize the iron with nitric acid, add some ammonium chloride, and then precipitate with ammonia.

Tables II and III show the results obtained by the two methods.

TABLE II.—*By hydrochloric acid method.*[a]

No.	Initial temperature.	Final temperature.	Total loss in weight.	By analysis.			Calculated to ounces per square foot.			
				Zinc (a).	Iron (b).	$\frac{b}{a+b}$.	Zinc by analysis.	Iron by analysis.	Total Zn+Fe by analysis.	Total loss in acid.
	°C.	*°C.*	*Grams.*	*Grams.*	*Grams.*	*Per cent.*				
1	31	45	17.6155	16.9289	0.7583	4.29	2.45	0.11	2.56	2.56
2	30	45	18.3519	17.5152	0.7757	4.26	2.55	0.11	2.66	2.67
3	30	45	19.4566	18.6183	0.7828	4.00	2.71	0.11	2.82	2.83
4	30	43	17.6164	16.9879	0.7583	4.29	2.46	0.11	2.57	2.56
5	30	44	17.7744	17.1068	0.7271	4.08	2.49	0.11	2.62	2.59

[a] The hydrochloric acid solution contained 19.53 per cent HCl (density, 1.098). A separate portion (400 cubic centimeters) was used for each sample. All samples were 15 by 15 centimeters and were cut from the same sheet, washed in benzol, dried, and weighed.

Column four shows the loss of weight suffered by each sample in the hydrochloric acid. These values multiplied by four give grams per 900 square centimeters. The acid solution was analyzed for iron and zinc. These results are shown in columns five and six. The last two columns show the very close agreement between the total zinc and iron determined by analysis and the total loss in acid.

TABLE III.—*By lead acetate method.*[a]

No.	Temperature.	Total loss in weight.	By analysis.			Calculated to ounces per square foot.			
			Zinc (a).	Iron (b).	$\frac{b}{a+b}$.	Zinc by analysis.	Iron by analysis.	Total Fe+Zn by analysis.	Total loss in lead acetate.
	°C.	*Grams.*	*Grams.*	*Grams.*	*Per cent.*				
1	30	17.3354	16.9007	0.5698	3.26	2.46	0.08	2.54	2.52
2	30	17.8257	17.3119	0.7217	4.00	2.52	0.10	2.62	2.59
3	30	18.4110	17.8625	0.6105	3.30	2.60	0.09	2.69	2.68

[a] Fifteen-centimeter squares cut from the same sheet as those used in the hydrochloric acid method were placed in 500 cubic centimeter portions of lead acetate solution. No appreciable rise in temperature took place.

It is evident that the results obtained by use of hydrochloric acid are accurate. The amount of iron dissolved, in terms of ounces per square foot, is a constant to two decimal places. Analytical results check those obtained by the acid method, and the amount of iron dissolved varies but slightly from that in the lead acetate. That slightly less iron is removed by the lead acetate may be explained by the fact that the acetate does not dissolve all of the zinc-iron alloys. This may also explain why the results of the iron determinations in the acetate solution are not so uniform as those in the acid solution. A square of galvanized iron which had been stripped in lead acetate was washed and then placed in hydrochloric acid for some minutes. On analysis it was found that both iron and zinc had been dissolved from the plate. However, it may be said that while the presence of the zinc is of experimental interest it was not present in sufficient amount seriously to affect the results.

EFFECTS OF CONCENTRATION AND OF TEMPERATURE

In using hydrochloric acid for removing zinc from galvanized iron, some attention must be paid to the concentration and temperature. Also it is obvious that an iron sheet should not be left in the acid longer than is necessary to remove the last of the zinc. These factors may be easily controlled, and the allowable range is so large that the test is perhaps the simplest of any yet published.

In deciding what strength of acid to employ in the work, the most important point is to have an acid that will remove all the zinc and as little iron as possible. Two other factors to be considered are the speed with which the acid dissolves the zinc and the rise in temperature caused by the reaction. Table IV shows the results obtained by using three different concentrations.

TABLE IV.—*Effect of acid concentration.*[a]

No.	Dilution of acid.	Density of acid.	Per cent HCl.	Volume of acid.	Initial temperature.	Final temperature.	Character of reaction.	Total loss (a).		Iron dissolved (b).		b/a.	Zinc dissolved.
								Per 900 square centimeters.	Per sq. foot.	Per 900 square centimeters.	Per sq. foot.		
				c. c.	*°C.*	*°C.*		*Gms.*	*Ozs.*	*Gms.*	*Ozs.*	*P. ct.*	
1	conc.	1.190	37.58	400	30.0	50.0	Violent	73.3449	2.67	4.1205	0.15	5.62	All.
2	1-1	1.098	19.55	400	30.0	41.5	Medium	73.3449	2.67	3.0217	0.11	4.12	Do.
3	1-3	1.052	10.55	400	33.5	40.0	Slow	71.1473	2.59	3.0217	0.11	4.25	Do.

[a] Each sheet was 15 by 15 centimeters.

The choice of the most satisfactory concentration is easily made. The action of the concentrated acid is too violent and results in dissolving some iron from the base. For that reason it may be eliminated. The other two concentrations are equally adapted to the work in that they both remove all the zinc with the minimum amount of iron. Since the 1.098 density acid acts more rapidly than the other and apparently has no disadvantage, it is considered the best. It is possible that an acid might be found some place between densities 1.098 and 1.190 which would act more rapidly without dissolving any more iron, but the former seems to answer every requirement. It is also possible that with some grades of galvanized iron it might be better to use a slightly weaker acid.

Having determined the best concentration of acid, it was next necessary to investigate the influence of temperature on the solution velocity of the iron base. Previous experiments had shown that if a 15-centimeter square of sheeting were left in the acid at room temperature for many minutes the loss in weight was negligible. This work was extended to include temperatures between 30° and 100°C. Each piece was left in the acid (at a given temperature) for twenty minutes, removed, washed in water and then in alcohol, and finally dried and weighed. The test was purposely made very severe to guard against any possible errors. Removal of zinc from a sheet does not require as much as ten minutes. No attempt was made to keep the temperatures exact by a thermostat, because such refinements are unnecessary in the actual tests. Fifteen-centimeter squares were used. The following results were obtained.

TABLE V.—*Effect of temperature on solution velocity of iron base.*

Strength of acid.	Temperature.	Loss in weight.	Loss.	Calculated to ounces per square foot.
Density.	*°C.*	*Grams.*	*Per cent.*	
1.098	30	0.0339	0.03	0.005
1.098	45	0.0494	0.05	0.007
1.098	60	0.0921	0.09	0.013
1.098	80	1.3256	1.26	0.193
1.098	100	6.1648	5.93	0.897

The temperature of the acid may run up to 60° without causing any appreciable error, but since there is no reason for such a high temperature, it is recommended that the solution be kept at 45° or below.[14]

CRITICISM OF AN ANALYTICAL METHOD SOMETIMES USED

Some chemists use an analytical method for determining the zinc, which is as follows:

A 30-centimeter square of the original material is weighed, and the weight is recorded. A few small pieces are then cut and weighed on an analytical balance, and the percentage of zinc is determined by analysis. The weight of the large square in grams is then multiplied by this factor to give grams of zinc in that area. Such a procedure is, of course, erroneous. The present work has shown that the galvanizing on one sheet 60 by 75 centimeters may vary as much as 8.76 grams per 900 square centimeters (fig. 1).

A SIMPLE AND RAPID METHOD FOR DETERMINING IRON

Any solution which will remove all the zinc from a piece of galvanized iron will also remove the iron in the zinc-iron alloy. If the zinc is then calculated from the loss in weight, there will be an error due to the iron that has been dissolved. This error is comparatively so small that it is usually disregarded. However, it is sometimes desired to correct it, and this may be accurately done by precipitating the iron with ammonia and weighing as the oxide.

The iron may be determined approximately by a much simpler procedure. The results are not so accurate, but are sufficiently so for most purposes. While the coating is being dissolved by the acid, the iron in solution is being reduced by the nascent hydrogen, and the rise in temperature aids the reaction. The tray in which the test is made should be nearly covered, with only a small outlet for the evolved gases. The minimum volume of acid should be used—about 350 cubic centimeters. As soon

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[14] In practice it is not necessary to use a separate portion of hydrochloric acid for each sample. In using any method for the first time, or in testing a brand of galvanized iron with which he is unfamiliar, it is well for a chemist to determine the alloyed iron and the loss in weight of the stripped sheet in the testing solution. For routine tests the hydrochloric acid is placed in a jar or crock which is large enough to accommodate one or more pieces of the galvanized iron (without touching each other). This same acid may be used for a number of samples until the action becomes too slow on account of the low concentration of hydrogen ions. The only necessary precaution is to observe the temperature from time to time and not allow it to exceed 45°C.

as the coating has entirely disappeared, the sheet is removed and rinsed, allowing the water to run into the tray. The contents of the tray are then rapidly transferred to a large beaker, containing from 400 to 500 cubic centimeters of recently boiled water and about 100 cubic centimeters of titrating solution.[15] The iron is then titrated with fifth normal permanganate (using a 100 cubic centimeter burette). The error in such a determination is probably due to the fact that a portion of the iron is oxidized by contact wtih the air before the titration is made and that the comparatively high concentration of hydrochloric acid present interferes to some extent with the end point. This determination requires less than five minutes, while the gravimetric method requires from one to two hours.

VARIOUS BRANDS TESTED

All results given above were obtained by tests on samples cut from the same large sheet of galvanized iron. This was done so that the samples might be as nearly uniform as possible and thus afford a sound basis of comparison. It was realized, however, that the method would be worthless unless it would give equally satisfactory results with products of various mills. Accordingly the test has been applied to five different brands of galvanized sheeting. Four of them were made in the United States and one in England. Two squares were cut from each sheet, properly cleaned and weighed, and the total loss in hydrochloric acid was determined. In each case, after the square was removed, the acid and washing were placed in a liter flask, made up to the volume and were analyzed for iron by the gravimetric method. The stripped squares were then placed in hydrochloric acid and allowed to remain for twenty minutes. They were removed, washed, dried, and reweighed.

It is evident that the iron dissolved from the base itself is negligible. This is true in all the results given in this paper as well as in a number of other brands which have been tested from time to time. The alloyed iron is nearly always less than the minimum variation of the coating between samples of the same sheet and can usually be neglected. It seems peculiar that the total alloyed iron per square foot for all the brands tested should be so uniform, when there is such a wide variation in total coating.

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[15] See Olsen, J. C., Quantitative Chemical Analysis. D. Van Nostrand Co., New York (1908), 319.

TABLE VI.—*Tests on various brands of galvanized iron by the hydrochloric acid method.*[a]

Brand No.	Total loss in weight. (a)	Iron dissolved with zinc. (b)	b/a.	Iron dissolved from stripped sheet.	Total loss per square foot.	Iron in coating per square foot.	Iron dissolved from stripped sheet per square foot.[c]	Initial temperature.	Final temperature.
	Grams.	*Grams.*	*Per cent.*	*Grams.*	*Ounces.*	*Ounces.*	*Ounces.*	°*C.*	°*C.*
1[b]	18.179	0.7826	4.29	0.035	2.56	0.11	0.005	31	46
	18.939	0.8036	4.26	0.034	2.67	0.11	0.005	30	45
2	17.790	0.8050	4.53	0.035	2.51	0.11	0.005	29	40
	18.880	0.8638	4.57	0.020	2.66	0.12	0.003	29	40
3	20.571	0.6210	3.02	0.043	2.90	0.09	0.006	29	40
	17.680	0.4724	2.67	0.030	2.49	0.07	0.004	29	42
4	11.259	0.5012	4.54	0.036	1.58	0.07	0.005	29	38
	13.170	0.5670	4.30	0.030	1.86	0.08	0.004	29	40
5	18.026	0.6608	3.63	0.059	2.54	0.09	0.008	30	41
	20.356	0.7350	3.61	0.089	2.87	0.10	0.013	30	43

[a] Density of the acid, 1.098.

[b] Brand used in all previous tests.

[c] At end of twenty minutes. The stripped sheets were placed in acid of the same density, at 30°. In this case the action was so slight that there was no appreciable rise in temperature. Each sample was 15.25 by 15.25 centimeters.

A study of Table VI reveals the following:

BETWEEN TWO SAMPLES OF THE SAME BRAND.

	Grams per 900 square centimeters.	Ounces per square foot.	Brand No.
Minimum difference in coating	2.9397	0.11	1
Maximum difference in alloyed iron	0.5944	0.02	3
Maximum difference in iron dissolved from stripped sheet[a]	0.1418	0.005	5

BETWEEN TWO SAMPLES OF DIFFERENT BRANDS.

	Grams per 900 square centimeters.	Ounce per square foot.	Brand No.
Maximum difference in coating	37.2480	1.32	3, 4
Maximum difference in alloyed iron	1.5256	0.05	2, 3
Maximum difference in iron dissolved from stripped sheet	0.2835	0.01	2, 5

[a] In all brands tested, except No. 5, this difference is negligible when temperature, concentration of acid, and time are uniform.

THE REACTION BETWEEN HYDROCHLORIC ACID AND GALVANIZED IRON

These measurements were made with the object of obtaining a clearer idea of just what happens when a galvanized sheet is subjected to the hydrochloric acid test. It is evident that the removal of the zinc is more uniform than with either copper sulphate or lead acetate solutions, because there is no metallic deposit to interfere.

As long as only the outer layer of nearly pure zinc is exposed to the action of the acid, the rate of solution should remain almost constant.[16] The surface exposed remains about uniform, and since the acid is present in considerable excess, the change in concentration is not great. The results show that this is true.

Manipulation.—A sheet of galvanized iron 7.6 by 30.6 centimeters was bent into the form of a cylinder and placed in a large beaker. The edges were suitably protected. The apparatus was fitted with a stirrer, and 1 liter of hydrochloric acid (density, 1.052) was rapidly poured in. At intervals of one minute 25 cubic centimeters of the acid were removed for analysis. Effervescence had apparently ceased by the end of the sixth minute, but the reaction was allowed to run ten minutes. After ten minutes the iron was removed and found by analysis to be free from coating.

Table VII shows the results. The iron was determined gravimetrically, and the zinc was titrated with potassium ferrocyanide. The results were calculated to total weight of iron and zinc dissolved in terms of ounces per square foot.

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[16] In a heterogeneous system, such as hydrochloric acid and zinc, the velocity of the reaction may be expressed by the equation $dx/dt = kO(a-x)$.
Here O represents the area of the exposed surface
a, the original concentration of the acid
x, the decrease in concentration of the acid caused by x equivalents of metal going into solution in the time t. [See Nernst, W., Theoretical Chemistry. Macmillan & Co., London (1911), 584.]

In the present work a large excess of acid was used, so that the concentration remained practically constant. It can be assumed that the total surface remains constant. Therefore, theoretically the right member of the equation becomes a constant, or $dx/dt = K$. This condition cannot be realized exactly, however, because of other factors which affect the velocity. In the first place no attempt was made to keep the temperature of the acid constant. In actual practice there is a rise in temperature, and it was desired to keep conditions as nearly similar as possible. Each zinc-iron alloy has its velocity constant and each has its velocity equation, $dx/dt = kO(a-x)$. Therefore, as the reaction proceeds and various alloys are exposed, it becomes more and more complex. The surface, O, for some of the alloys is not a constant because usually the entire surface is not exposed at the same time. While the outer coating of zinc is being dissolved, the reaction comes nearest to the theoretical.

TABLE VII.—*Zinc and iron dissolved from a sheet of galvanized iron, minute by minute.*

[Initial temperature, 30.5° C.; final temperature, 37.5° C.; volume of acid, 1,000 cubic centimeters; concentration of acid, 10.55 per cent HCl.]

Time.	Total zinc.	Total iron.	Zinc per square foot.	Iron per square foot.	$\frac{Fe}{Zn+Fe}$.
Min.	*Grams.*	*Grams.*	*Ounces.*	*Ounces.*	*Per cent.*
1	4.3280	0.0280	0.6102	0.0039	0.64
2	12.0812	0.0924	1.7034	0.0130	0.76
3	15.4214	0.1780	2.1744	0.0251	1.51
4	16.6165	0.5224	2.3429	0.0737	3.05
5	16.8109	0.5728	2.3703	0.0808	3.30
6	16.8109	0.6586	2.3703	0.0929	3.77
7	16.8245	0.6967	2.3723	0.0982	3.98
8	16.8278	0.7313	2.3727	0.1031	4.16
9	16.8502	0.7358	2.3769	0.1037	4.18
10	16.8998	0.7358	2.3828	0.1037	4.18

These values were used in plotting the solution velocities of the zinc and the iron against the time (fig. 2).

Discussion of results.—The iron in a hot-galvanized sheet is present as follows:

1. The spelter itself before being placed in the bath contains traces of iron.
2. The spelter is gradually contaminated with iron from the walls of the bath and from iron sheets or other articles that are passed into it.
3. Alloys are formed on the immersed sheet by the action of the molten zinc.
4. The base is, of course, nearly all iron.

The various steps in the action of hydrochloric acid on a galvanized plate may be clearly seen from the results. The acid at first comes into contact with the zinc, which contains only the iron present in the spelter when the sheet was placed in the galvanizing bath. The reaction is very rapid, and during the first three minutes 91.25 per cent of the total zinc present passes into solution. During the same period only 24.20 per cent of the total alloyed iron dissolves. During the next three minutes 8.22 per cent more of the zinc and 65.38 per cent more of the iron dissolve. The remainder of the time the reaction is very slow, only 0.53 per cent of zinc and 10.42 per cent of the iron being dissolved. The great variation of the percentage of iron in the total metal dissolved is given in the last column of the table. Still greater variation is observed if the percentages

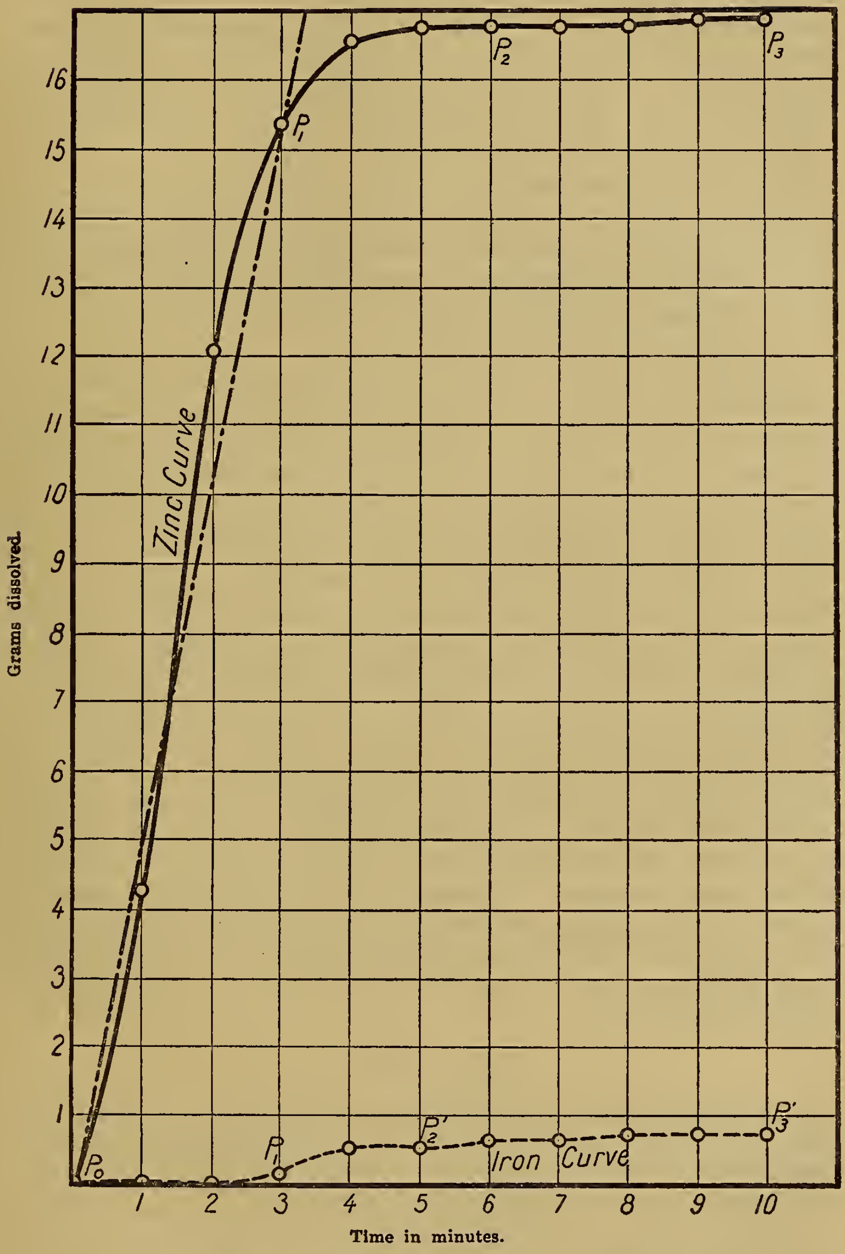

FIG. 2. Solution velocity of galvanized iron in hydrochloric acid.

are calculated separately for different minutes. For instance, during the first minute the iron is only 0.64 per cent of the total metal dissolved. During the fifth it is 20.29 per cent; in the seventh, 84.86 per cent; in the eighth, 91.32 per cent. This work seems to indicate that, in addition to alloys like $FeZn_3$ and $FeZn_7$, there may be a series high in iron and low in zinc, such as Fe_7Zn and $Fe_{11}Zn$.

On the zinc curve, from P_0 to P_1, the acid is dissolving the outer coating of almost pure zinc and the curve is nearly a straight line. From P_1 to P_2 the velocity falls off rapidly because the zinc coat has almost disappeared and the alloys are exposed. On the iron curve the maximum rise is between P'_1 and P'_2, or after the zinc is almost completely dissolved.

As has been stated, the iron dissolved during the first few minutes is due to the iron contamination of the molten zinc before the sheet is placed in the bath. It is true also that during that time the acid may have gone entirely through the outer layer of zinc at some point and started acting on one of the zinc-iron alloys. Therefore, if we know the amount of iron dissolved during the first stage of the reaction, or up to the point of the break in the zinc curve, P_1, we have a hint as to the value of the sheet to withstand corrosion. A high iron content would show that the iron contamination of the spelter is considerable, or that the zinc coating is thin in spots. Either condition would indicate that the sheet is of inferior quality. It is obvious that the outer zinc coating should be as uniform as possible, and that the purer it is, the better. On the other hand, a very small amount of iron removed during the first stage of the reaction would assure both the purity and the uniformity of the outer coating. I propose to investigate this question further and to attempt to determine the maximum percentage of iron that is allowable in a good quality of galvanized sheet under these conditions. Such a test would be simple to carry out, but important.

CONCLUSIONS

1. A hydrochloric acid solution gives satisfactory results for determining the amount of the coating on galvanized iron. Directions for its use are given. These include the concentration of the acid, the temperature, and the size of the test piece.

2. The accuracy and reliability of the test have been proved in a number of ways. It requires little labor and is rapid and inexpensive.

3. A convenient method is given for correcting for the alloyed

iron dissolved by the acid in case such correction is deemed necessary.

4. Measurements of the solution velocity of galvanized iron in hydrochloric acid have been made. The results indicate that the system of zinc-iron alloys is very complex. From the solution-velocity time curves, an approximate idea of the uniformity and purity of the zinc coating may be obtained.

5. In investigating the value of various methods for testing galvanized iron, it is necessary to know (*a*) how much iron is dissolved from the base and (*b*) whether or not any zinc in the form of zinc-iron alloys remains undissolved. Without these data it is impossible to get the proper basis of comparison.

ILLUSTRATIONS

TEXT FIGURES

COMMENTS ON THE ANALYSIS OF BABBITT METAL[1]

By J. C. Witt

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The analysis of Babbitt metal has always offered considerable difficulty to chemists, particularly those who are engaged in commercial testing. Although many excellent papers have been published on the subject, most of the methods given are either too long and involved for commercial purposes, or else they are not sufficiently accurate and reliable in the hands of the average analyst. There has been a wonderful advance in electrolytic analysis, and many of the methods now being published are along these lines. While this system is very close to the ideal with the right equipment, there are many laboratories doing general chemical work where the expense of installing suitable electrical equipment is hardly justified.

There is scarcely any other material which has so large a range of composition as Babbitt metal. The lead or the tin content may vary from 0 to 90 per cent, and there is often a great variation in the other elements present. Some of the varieties have special names, but as a rule the average consumer calls almost any white metal used for antifriction purposes a babbitt. Besides the metals actually called for in the formula, there are invariably impurities present which in some cases are in sufficiently large amounts to cause trouble in the analysis. Persons submitting such samples seldom seem to realize that while some samples are simple others are exceedingly difficult and cannot be completed without a great deal of labor if results are to be dependable.

An object of this paper is to point out that there is no general method that may be equally well applied to all samples. Many methods are published which show accurate results with one class of babbitts, but fail with others. Until a good general method is devised, the chemist must keep well in mind the limits of whatever method he may favor and be constantly on the alert to modify it to suit the circumstances, or to substitute a different one if necessary.

The present work has been done with babbitts having the

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[1] Received for publication September 9, 1915.

following composition: Lead, 85 to 90 per cent; antimony, 10 to 15 per cent; tin, 0 to 5 per cent; copper, 0 to 1 per cent. The methods of analysis which I have found most satisfactory and which are intended to apply to this class of alloys in particular are as follows:

ANTIMONY

The method of Walker and Whitman[2] for antimony, which is a modification of Low's[3] method, has been closely followed except for the changes which are noted. The method as given by them[4] is as follows:

> To 1 gram alloy in a 450 cc. Erlenmeyer flask, add 10–15 cc. strong sulphuric acid, and heat on hot plate until alloy is thoroughly decomposed. This is generally accomplished in about 30 minutes from the time fumes of SO_3 begin to be given off. Cool, add 200 cc. water and 20 cc. strong hydrochloric acid, boil to make sure that all SO_2 is driven off, cool and titrate rapidly with potassium permanganate which has been standardized against metallic antimony. The true endpoint is when a pink color shows after agitating the liquid, though this pink will very soon disappear.

In carrying out this method, difficulty is often experienced in obtaining a sharp end point, and some chemists have never used it to any extent on that account. However, a sharp end point can be obtained if the method is modified as follows: Use a 300 cubic centimeter Jena-glass Erlenmeyer flask for digestion and dilute to about 150 to 175 cubic centimeters. If after boiling the volume has decreased materially, add sufficient water to replace that which has been evaporated. Cool the solution thus obtained to about 5 or 10°C., and titrate as rapidly as possible, until the end point is nearly reached, then add two or three drops at a time, shaking the flask thoroughly. When a pink color flashes over the entire solution, the end point is reached. These precautions are necessary because the pink color at the end point is not permanent, as in the case of iron titrations, and unless the solution is kept cold and the permanganate added in some definite way for every determination, one is very likely to obtain erroneous results.

The permanganate solution should be standardized frequently. During the titration, if the hydrochloric acid solution is not sufficiently dilute, sometimes the odor of chlorine will be noticed,

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[2] *Journ Ind. & Eng. Chem.* (1909), 1, 520.
[3] *Journ. Am. Chem. Soc.* (1907), 29, 66.
[4] Loc. cit.

and the solution will become slightly yellowish. In this case it is best to throw out the determination and start a new one, using slightly less hydrochloric acid, because, under such conditions, the true end point cannot be obtained.

TIN

Walker and Whitman's method for tin has been closely followed, but slight modifications have been found helpful. Their method is as follows:

> Treat from 0.2–1 gram of alloy (do not use an amount of alloy containing more than 0.2 gram tin) in a 450 cc. Erlenmeyer flask with 10-15 cc. strong sulphuric acid, heat on the hot plate until the alloy is thoroughly decomposed, cool, add 200 cc. water, 30 cc. strong hydrochloric acid, and about 1 gram of steel turnings, heat and when reduction appears complete, but before the last particles of steel have dissolved, place a two-hole rubber stopper in the neck of the Erlenmeyer flask—one hole of the stopper should carry a tube reaching below the surface of the liquid, the other hole should carry the short arm of a bent tube, the long arm of which reaches nearly to the bottom of a 100 cc. Erlenmeyer flask containing a solution of sodium bicarbonate. This small Erlenmeyer is held on the bent tube by a cork which has a notch cut in it to act as a vent. Through the tube reaching below the surface of the liquid in the large Erlenmeyer pass a current of carbon dioxide, heat to boiling until all steel is dissolved, continue passing CO_2 and cool as quickly as possible; loosen stopper but let current of CO_2 continue, add cautiously some starch solution and titrate with $N/10$ iodine. It is necessary to absolutely exclude air and to standardize the iodine solution with pure tin. Results are accurate.

I find this method very satisfactory up to the point where the solution is boiled with 1 gram of steel turnings.

Walker and Whitman recommend the use of steel turnings for the reduction of tin, but give no details concerning the kind of steel or the size of the drillings which are best suited to the work. This is likely to give one the impression that any steel drillings which may be around the laboratory may be used. This is not true if it is desired to obtain the most rapid and most accurate results. Some steels are more suitable than others. For instance, a steel high in phosphorus is to be avoided. In general, a mild, open-hearth steel is best suited to the work. In order to complete the reduction in a comparatively short time, the steel drillings should be small and uniform in size. By using uniform drillings, the time of reduction is known within a very few minutes, and the work can be planned and carried out accordingly. The steel which I have found to give the most satisfactory results contained about 0.12 per cent carbon. The drillings were placed on a 40-mesh sieve, and only the portion passing the sieve was preserved for use.

The fine particles passing an 80-mesh sieve were rejected. A considerable quantity of these drillings was prepared and after thorough mixing was preserved for use in babbitt analyses. The uniformity of the drillings, both in size and composition, was a very helpful factor.

The troublesome part of this method for tin is in making the titration. The antimony compounds present have been reduced to metallic antimony, which is present as a black, flocculent precipitate. This is most troublesome with a sample which is high in antimony and low in tin, in which event it is usually necessary to allow the precipitate to settle after each addition of iodine before the presence of the blue color of the end point can be distinctly seen. Another disadvantage is that the precipitate is likely to conceal small pieces of undissolved steel, which would, of course, cause high results.

To avoid this remove the antimony by filtering the boiling-hot solution through a coarse filter paper and wash several times with hot water. If the solution is not filtered while very hot, lead chloride will crystallize out and interfere with the operation. Receive the filtrate in a 300 cubic centimeter Erlenmeyer flask, add 0.5 gram of steel drillings, and proceed with the method in the regular way. Cool the flask by placing it in a beaker of cold water, being careful to have a vigorous stream of carbon dioxide passing in order to compensate for the vacuum caused by the condensation of the steam in the flask. If a few flakes of antimony appear during the second reduction, they may be disregarded, since by removing the bulk of the antimony the object has been attained.

LEAD

Considerable difficulty was encountered in finding a method for the determination of lead which was accurate and at the same time sufficiently rapid for routine babbitt analysis. Most of the methods which I have tried from time to time failed in one of these two respects. A modification of the method used by Alexander[5] in the analysis of lead ores has given very satisfactory results. The following solutions are needed:

Ammonium molybdate, 4.25 grams per liter.
Acid ammonium acetate:
  Ammonia, 400 cc.
  Water, 450 cc.
  Concentrated acetic acid, 400 cc.
Tannic acid; one part of solid to 300 parts of hot water.[a]

[a] This solution should be made fresh whenever used.

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[5] *Eng. & Min. Journ.* (1893), 55, 293.

Chemically pure metallic lead or lead sulphate should be used for standardizing the ammonium molybdate solution. Weigh the lead with the sample and carry through in parallel. Place 1 gram of the alloy in a 250 cubic centimeter beaker and add 30 cubic centimeters of 1.20 specific gravity nitric acid. After the acid has boiled down to about 10 or 15 cubic centimeters, dilute with 30 to 40 cubic centimeters of water and boil the mixture for ten minutes. After allowing the precipitate to settle, decant the liquid through a filter paper to which has been added a little paper pulp and wash the filter two or three times with 1 per cent hot nitric acid. Treat the precipitate which remains in the beaker a second time with acid and water and filter as before.[6] After transferring the precipitate to the filter, wash it eight or ten times with dilute nitric acid, taking care to keep the volume of the filtrate and washings down to about 150 to 200 cubic centimeters. Evaporate very carefully to 20 or 30 cubic centimeters and cool. Add excess sulphuric acid and heat the mixture until the water has been expelled and white fumes appear. Dilute with 50 cubic centimeters of water and allow the lead sulphate precipitate to settle. Filter out the precipitate and wash thoroughly with very dilute sulphuric acid. Place the filter paper containing the precipitate in the original beaker and dissolve in 75 cubic centimeters of hot ammonium acetate solution and an equal volume of hot water. When the solution is complete, titrate with ammonium molybdate solution, using tannic acid as an outside indicator. It is very important that the lead solution should be almost boiling at the beginning of the titration to insure complete precipitation of the lead; otherwise it is easy to get a false end point and report wrong results. The standard is titrated in exactly the same way, and a blank is run on the ammonium acetate solution. To determine the value of the ammonium molybdate solution in terms of lead, the weight of the lead in grams, in the standard, is divided by the number of cubic centimeters of ammonium acetate solution used in the titration of the standard, minus the blank titration. This method seems long, but not much time

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[6] This second treatment with dilute nitric acid is very important and should never be omitted. Experiments have shown that after only one treatment with acid, considerable lead nitrate remains with the precipitate and cannot be completely washed out with dilute nitric acid.

It is also important not to evaporate the solution almost to dryness (as is done in the case of determining tin as stannic oxide), for not all of the lead will remain in solution. In case traces of antimony and tin go into solution, they do not interfere with the titration.

is required for the actual operations. I have never had much success in determining lead as chloride according to Walker and Whitman's method, or in determining it directly as sulphate as suggested by Demorest.[7]

COPPER

In many babbitts the copper content is less than 0.5 per cent. In this case a colorimetric method has been found to be sufficiently accurate. It is best to use as a standard a babbitt of known copper content. Weigh equal portions of the standard and sample and dissolve in a small quantity of nitric acid of 1.20 specific gravity. After diluting with about 10 cubic centimeters of water, neutralize with ammonia and add about 5 cubic centimeters in excess. After cooling, dilute the solutions to definite volume, 25 or 50 cubic centimeters, and filter into color carbon tubes having large diameters. By diluting as in the method of reading color carbons, the percentage of copper may be estimated. If a precipitate forms on diluting a solution of the sample or standard, it should be filtered out, using a dry filter, before making a final reading. If the copper exceeds 0.5 per cent, it may be determined by some modification of the cyanide method or the iodide method of Low.[8] The former is more satisfactory if the percentage of copper is low, while the latter is better for a higher percentage.

IRON AND ZINC

Iron is present in practically all babbitts, although usually the percentage is less than 0.1. To determine the iron, the filtrate from the lead sulphate may be utilized. Dilute this filtrate to about 300 cubic centimeters, heat to boiling, and saturate with hydrogen sulphide. If any precipitate is formed. filter and wash with hot hydrogen sulphide water. Partly evaporate the filtrate to expel the gas and boil with the addition of a few drops of nitric acid. Precipitate the iron by neutralizing with ammonia and determine as ferric oxide.

As a rule zinc is present in only small amounts—usually less than 0.1 per cent. It may be determined in the filtrate from the iron.

PREPARATION OF A STANDARD BABBITT METAL

The standardization of the various volumetric solutions mentioned above may be advantageously effected by the use of stand-

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[7] *Journ. Ind. & Eng. Chem.* (1913), 5, 842.

[8] *Journ. Am. Chem. Soc.* (1896), 18, 458.

ard babbitts. A set of several such standards corresponding in general composition to the samples usually submitted for analysis should be on hand and that one selected which closely corresponds to the composition of the sample. As is well known, it is difficult to prepare a babbitt which is sufficiently homogeneous to serve as a standard. As a rule there is considerable segregation of the materials present, but a standard was made for use in connection with this work which was satisfactorily uniform. Pure lead, antimony, tin, and copper were obtained and turned over to an expert in making alloys. The metals were mixed in the following proportions: Lead, 85 per cent; antimony, 12 per cent; tin, 2 per cent; copper, 1 per cent. The alloy was cast in the form of a small cylinder about 3.5 centimeters in diameter by 10 centimeters long. The samples were taken with a hack saw at various points in the cylinder and analyzed separately, in duplicate. The results showed the metal to be uniform. After preparing a quantity of the standard, uniform in fineness and composition, portions may be weighed with the samples and carried through the various operations. Especially in the tin and colorimetric copper determinations it is well to have both standard and sample as nearly as possible of the same composition.

GALVANIZED-IRON ROOFING IN THE PHILIPPINES[1]

By ANGEL S. ARGÜELLES

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INTRODUCTION

The great loss from fires in the Philippines due to the general use of readily combustible building materials has demonstrated the necessity of substituting noncombustible roofing for the ordinary nipa[2] thatch. Tile, slate, and asphalt are so utilized to a limited extent, but galvanized iron is by far the most widely used fire-proof roofing material. In towns of any importance practically all large buildings have galvanized iron roofs. The entire demand for this material is met by import, the following data showing the amount and value of galvanized iron annually brought into the Islands:

TABLE I.—*Quantity and value of Philippine importations of galvanized iron.*[a]

Year.	Quantity.	Value.
	Kilograms.	*Pesos.*[b]
1911	8,179,955	1,120,660
1912	10,095,640	1,344,024
1913	10,075,956	1,480,580
1914	10,520,233	1,540,622
1915	5,698,927	879,207
Total	44,570,711	6,365,293

[a] Data for this table were secured from the *Annual Rep. Bur. Customs for the year ended December 31, 1912* (1913), 117; ibid. for 1915 (1916), 97. These figures cover only corrugated sheets. In view of the fact that plain galvanized sheets are included under "all other sheets and plates" in the report, it is not possible to give exact figures for them. Import values for "all other sheets and plates amounted to ₱520,722 for 1914, of which probably 80 per cent are plain galvanized sheets.

[b] One peso Philippine currency equals 50 cents United States currency.

The value of this import gradually increased until it reached 1,540,622 pesos for 1914, but dropped to 879,207 pesos in 1915, a decrease largely due to the advance in price caused by the European war. In view of the material improvements going on in all sections of the Islands, an even greater demand for this roofing material may be expected in the future.

As a result of the great demand for corrugated galvanized sheets various brands of this material have been imported.

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[1] Received for publication July, 1916.

[2] The leaves of the nipa palm, *Nipa fruticans* Wurmb.

These have shown great variations in quality. There have been instances in which new sheets showed marked corrosion when brought from storage. Some brands failed completely after from two to five years of service, while some sheets put in place thirty years ago are in good condition and are still rendering satisfactory service. This striking difference in the behavior of old and certain modern corrugated galvanized sheets under actual conditions of weather exposure, together with the fact that the yearly import of this material represents a considerable financial outlay, led the Bureau of Science to study the various factors affecting the corrosion of galvanized iron and the problem of comparing old and modern galvanized-iron sheets.[3]

GENERAL CONSIDERATIONS

As is well known,[4] the durability of galvanized iron under normal service conditions depends on various factors, among them thickness, density, purity, continuity, toughness, and ductility of the coating and the purity of the iron base.

Of the factors mentioned above, thickness of coating is generally considered [5] the most important. It is true that to some extent zinc will exert a protective influence on iron with which it is in contact, even after the iron is exposed to ordinary corrosive action, but this influence is generally confined to a very limited area. Furthermore the oxidation products of zinc may be electro-negative to iron, so that corrosion would be accelerated instead of retarded. As zinc is removed at a rate depending on the conditions of service to which it is subjected, it is obvious that, other things being equal, the life of a galvanized sheet depends on the amount of zinc per unit area. Actual service tests bear out this view. The actual amount of zinc to be used to give the best service is dependent on economic considerations and on the physical character of the resulting plate. Manufacturers have claimed that a coating heavier than 4.88 grams of zinc per square decimeter (1.6 ounces per square foot) tends to flake off, the result being an imperfect, easily corroded sheet. This claim appears untenable, since the high spelter content of old sheets which have withstood long service exposure has amply

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[3] In recent years galvanized iron with an exceptionally pure iron base has been brought to the Islands. This has not been on the local market long enough to enable us to obtain comparative data concerning its durability under ordinary service conditions.

[4] Cf. Burgess, C. F., *Electrochem. & Met. Ind.* (1905), 3, 17; Walker, W. H., *Proc. Am. Soc. Test. Mater.* (1909), 9, 433.

[5] Walker, loc. cit.

demonstrated that a much heavier coating can successfully be applied.

In hot-galvanizing practice considerable difficulty is encountered in trying to attain high purity of spelter not only because the original spelter may contain such impurities as iron, lead, and other materials which will add impurities to the coating, but also because the iron sheets dipped in the molten bath are slightly dissolved, leading to the formation of zinc-iron alloys on the surface of the iron.

Very few data are available regarding the amounts of impurities permissible in spelter coating.[6] Cowper-Coles[7] stated of the impurities in the coating of hot-galvanized iron:

> It has been found that iron above 13% makes the zinc too brittle to bend. Lead up to 1% is harmless, but above 1.5% will not dissolve, and the excess collects and forms weak spots.

V. Vegesach,[8] W. Guertler,[9] and Arthur and Walker[10] have made elaborate studies of the complex zinc-iron alloys formed during the process of hot galvanizing. Cushman[11] has called attention to the fact that the use of zinc chloride or ammonium chloride as flux, sometimes in conjunction with hydrochloric acid, is a strong corrosive mixture and that small portions of the reaction products formed become embodied in the zinc coatings and tend to accelerate corrosion.

Porosity is a defect in zinc coating, since it accelerates the electrolytic corrosion of zinc in contact with iron and thus shortens the life of galvanized sheets under weather exposure. Although "hot galvanized" iron is generally free from pinholes and cracks, "wet galvanized" material, especially when thinly coated, is often extremely porous.[12] Increasing the thickness of the spelter tends to eliminate pinholes and thereby offers less chance for corrosion to start.

Toughness and ductility of coating are important factors, as they determine the resistance of galvanized iron to bending stress and abrasion.

In a well-galvanized sheet the iron base is rarely brought to test under weather exposure until after many years of service.

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[6] Burgess, loc. cit., 17.

[7] Industries and Iron (1898), quoted by Burgess, loc. cit.

[8] *Zeitschr. f. anorg. Chem.* (1907), 52, 30.

[9] Metallographie (1911), 353.

[10] *Journ. Ind. & Eng. Chem.* (1912), 4, 398.

[11] *Proc. Am. Soc. Test. Mater.* (1909), 9, 129.

[12] Walker, W. H., op. cit., 430.

Spellers[13] found that the base of galvanized roofing taken from Panama, which had seen service for over twenty-five years and was still in good condition, "proved to be steel, but a larger proportion is wrought iron, and often of inferior quality."

It is apparent that a well-coated sheet with an inferior iron base will last as long as sufficient spelter remains to prevent air and moisture from acting on the iron beneath. It is believed that a pure iron base, per se, does not greatly add to the durability of galvanized sheet in the absence of a liberal amount of coating. The outer layer of the iron base is no longer of original purity, being replaced by a series of iron-zinc alloy layers of different solution tensions. Under the action of weathering this in time offers a field for galvanic action between parts of different electrical potential, until the pure iron base itself is exposed and ultimately becomes corroded. In a corroding solution (Table IV) dezincked pieces from old iron sheets show no greater resistance to corrosion than modern sheets of very pure iron, although the former have given long and satisfactory service.

EXPERIMENTAL PART

The samples used for experimental purposes have been of two kinds: (1) Those that are known to have been under exposure to weather for thirty years and upward and (2) various brands of corrugated sheets recently introduced. The former were taken from roofs in the towns of Batangas and Lipa, representing seacoast and interior highland towns, respectively; the latter were unused specimens of representative brands obtained from the Bureau of Supply or in the open market. The old corrugated sheets were selected from houses whose ages are definitely known. Among the new galvanized sheets are included brands to which belong sheets known to have succumbed to corrosion in from two to five years.

AMOUNT OF SPELTER

Determinations of the quantity of spelter have been made of old corrugated sheets known to have been under weather exposure for more than thirty years. Whenever possible, the unexposed laps as well as exposed portions were analyzed to get a general idea of the amount of spelter originally present. The zinc was determined from pieces 7.62 by 10.16 centimeters (3 inches by 4 inches), these being large enough to give reliable results, yet small enough to enable the detection of marked local irregular-

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[13] *Proc. Am. Soc. Test. Mater.* (1909), 9, 440.

ities. On account of the presence of adhering dirt and films of zinc oxide and carbonate, the zinc was determined directly by precipitation as carbonate, ignition, and weighing as oxide. The results obtained are as follows:

TABLE II.—*Amount of zinc on old galvanized sheets.*[a]

[Flat sheet; all 22 gauge.]

Tracing No.	No. of sample.	Year placed under service exposure.	Weight of coating per—	
			Square decimeter.	Square foot.
			Grams.	*Ounces.*
1	1	1883	7.15	2.34
2	1-X	1883	8.33	2.72
3	2	1882	8.96	2.93
4	2-X	1882	11.02	3.60
5	3	1885	9.71	3.18
6	3-X	1885	9.98	3.26
7	4	1882	8.21	2.68
8	4-X	1882	8.69	2.89
9	5	1885	7.33	2.40
10	5-X	1885	8.42	2.76
11	6	1886	9.07	2.97
12	6-X	1886	12.63	4.13
13	7	1883	7.23	2.36
14	8	1882	8.89	2.91
15	8-X	1882	10.15	3.32
16	9	1884	8.78	2.88
17	[b]10	----------	9.71	3.18
18	[b]11	1880	10.47	3.43

[a] Samples marked X were taken from the unexposed lap of the sheets.
[b] Old sheets not continuously under service exposure.

For the determination of the weight of coating per unit area on modern, unused sheets, the following procedure was adopted:

Pieces of galvanized sheets cut accurately to 7.62 by 10.16 centimeters (3 by 4 inches) or 5.08 by 5.08 centimeters (2 by 2 inches) are cleaned, washed with alcohol and ether, and are dried and weighed, after which they are immersed in a sulphuric acid solution[14] (containing 3 per cent of the acid by weight) to remove the zinc. The complete solution of zinc is marked by the cessation of hydrogen evolution. By this process the iron base is attacked very little. After the reaction is completed, the iron is brushed, washed, dried, and weighed. The difference between the original weight and the weight after immersion in acid represents the zinc plus a small amount of iron and any

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[14] Burgess, loc. cit., recommends 0.66 *N*, or 3.2 per cent sulphuric acid.

lead or other impurity in the coating. The solution is reduced and titrated with 0.1 *N* potassium permanganate solution to determine the iron dissolved. The amount of iron found is subtracted from the weight of coating dissolved by the acid. The rest may be taken as zinc without appreciable inaccuracy.

Results obtained with new sheets of galvanized iron were as follows:

TABLE III.—*Amount of zinc spelter on modern galvanized sheets.*

[Flat sheet.]

Tracing No.	Sample.		Gauge.	Weight of coating per—	
	Brand.	No.		Square decimeter.	Square foot.
				Grams.	*Ounces.*
1	A	1	24	5.58	1.83
2	A	2	23	6.38	2.09
3	A	3	23	4.94	1.62
4	A	4	23	4.58	1.50
5	B	1	24	4.73	1.55
6	B	2	23	5.46	1.79
7	B	3	21	4.94	1.62
8	C	1	20	5.83	1.91
9	C	2	24	4.61	1.51
10	C	3	21	4.70	1.54
11	C	4	23	4.88	1.60
12	D	1	25	4.09	1.34
13	D	2	25	3.76	1.27
14	D	3	22	4.34	1.42
15	E	1	23	3.75	1.23
16	E	2	21	4.76	1.56
17	F	1	23	3.60	1.18
18	G	1	22	7.56	2.47
19	G	2	22	6.72	2.20
20	G	3	22	6.56	2.15
21	G	4	22	6.80	2.23
22	H	1	22	3.43	1.12
23	H	2	22	4.27	1.40
24	H	3	22	4.88	1.60
25	I	1	22	6.56	2.15
26	J	1	24	4.48	1.50
27	J	2	26	4.88	1.40

The data in the foregoing tables show that, with two exceptions, even the exposed portions of the old sheets had a heavier coating after thirty years of service than did the modern, unused sheets. The least amount of coating recorded for unexposed portions of old sheets was higher than the greatest determined for the new. The greater amount of zinc on the old as compared with the modern galvanized sheets doubtless explains to a great extent the marked inferiority of some of the latter. With the exception of brands G, A-2, and I, indicated in Table III, the greater number of samples of modern galvanized iron show less than 6.10 grams of coating per square decimeter (2 ounces per square foot). Sheets of two brands, "B" and "H," are definitely known to have failed in comparatively few years. It has been claimed that brand G gives satisfactory service. As for the rest of the modern brands very little information with regard to their durability is available. Actual weather-exposure tests over long periods of time will be necessary to determine this point, although it is fairly certain that those containing less than 6.10 grams of coating per square decimeter will not withstand the weather for a considerable length of time.

IMPURITIES IN THE COATING

The study of the impurities in the coating was confined to the determination of lead, of the iron alloyed with the zinc, and of the chlorides embodied in the spelter. The alloyed-iron determination presents considerable difficulty in view of the fact that part of the pure iron base is slightly attacked by 3 per cent sulphuric acid and that this attack differs widely with different samples of iron. To determine the extent of the solvent action of the acid, dezinced sheets of 7.62 by 10.16 centimeters (3 by 4 inches) were immersed in fresh standard acid at 30°C. for varying lengths of time. The results obtained are shown in Table IV.

TABLE IV.—*Solvent action of 3 per cent sulphuric acid on iron base.*

[Figures give number of grams per square decimeter.]

Brand.	Weight of sample.	Loss on immersion after—				
		5 minutes.	10 minutes.	15 minutes.	25 minutes.	35 minutes.
	Grams.	*Grams.*	*Grams.*	*Grams.*	*Grams.*	*Grams.*
4	37.0028	0.0328	0.0408	0.0491	0.0973	0.1369
F	35.4358	0.0164	0.0216	0.0309	0.0581	0.1276
H	38.1037	0.0116	0.0141	0.0302	0.0229	0.0363
G	40.4777	0.0093	0.0096	0.0098	0.0119	0.0138
I	38.4697	0.0094	0.0089	0.0150	--------	0.0124
8	33.1742	0.0111	0.0185	0.0167	0.0486	0.0337

The foregoing table indicates the variation in the solvent action of sulphuric acid which may be expected with different iron bases. In actual determination of the spelter the sheet is not allowed to stay in the acid more than five minutes after all the zinc has been dissolved, and when that point is reached, the acid solution is considerably weakened, so that the loss of iron is doubtless considerably lower than is indicated by the 5-minute or 10-minute immersion tests. However, the alloyed-iron determination is useful for purposes of comparison and is valuable, even though it may be more or less approximate.

The lead and alloyed iron found in the coating of some of the old and the modern galvanized sheets are shown in Table V.

TABLE V.—*Lead and alloyed iron*[a] *in coating of galvanized iron.*

A. ON OLD GALVANIZED SHEETS.

Brand.	Zinc per square decimeter.	Lead in coating.		Iron in coating.	
		Per square decimeter.	$\frac{\text{Lead}}{\text{Zinc}}$.	Per square decimeter.	$\frac{\text{Iron}}{\text{Zinc}}$.
	Grams.	*Grams.*	*Per cent.*	*Grams.*	*Per cent.*
1-X	8.33	0.0701	0.84	0.3081	3.70
2-X	11.02	0.0857	0.78	0.3132	2.84
3-X	9.98	0.0509	0.51	0.3316	3.32
4-X	8.69	0.0406	0.47	0.4623	5.32
5-X	8.42	0.0601	0.71	0.3040	3.61
6-X	12.63	0.0889	0.62	0.4591	3.64
8-X	10.15	0.0893	0.88	0.3375	3.32

B. ON MODERN GALVANIZED SHEETS.

A-2	6.36	0.0171	0.27	0.1982	3.12
A-3	4.91	0.0293	0.59	0.1926	3.92
B-1	4.71	0.0231	0.49	0.2302	4.88
C-1	5.80	0.0340	0.59	0.2293	3.59
C-2	4.58	0.0253	0.55	0.1822	3.98
D-1	4.07	0.0240	0.59	0.1811	4.45
D-3	4.31	0.0253	0.59	0.1475	3.42
E-2	4.74	0.0199	0.42	0.1287	2.72
E-1	3.71	0.0340	0.91	0.2032	5.48
F	3.58	0.0187	0.52	0.3730	10.42
G	7.51	0.0546	0.73	0.1768	2.35
H	3.41	0.0192	0.56	0.1731	5.08
I	6.50	0.0540	0.98	0.2272	3.49

[a] Dissolved in 3 per cent sulphuric acid.

Though no great accuracy is claimed for the analytical data on the amounts of iron alloyed with the zinc, they show clearly that the old sheets contained more iron in the coating than did the new; hence the better service of the old sheets cannot be ascribed to greater purity of coating, with respect to alloyed iron.

Although most of the modern galvanized sheets contained less lead per square decimeter than the old, the lead content, expressed as $\frac{\text{per cent lead}}{\text{per cent zinc}}$, was about the same for both, in no case exceeding 1 per cent. It is scarcely probable that its occurrence in either the new or the old sheets was a very important factor in determining durability. For the majority of the modern galvanized sheets the alloyed iron is considerably less in amount than for the old sheets, averaging about 0.2 gram per square decimeter for the former and about 0.3 gram per square decimeter for the latter. When calculated to $\frac{\text{per cent iron}}{\text{per cent zinc}}$ the greater number of both kinds of sheets give results ranging from 3 to 4 per cent. The maximum for old sheets was 5.32 per cent; the highest among the modern sheets were 10.42 and 5.48 per cent.

Tests for chorides in the sheets analyzed showed the presence of perceptible amounts in all cases, so that no difference in durability could well be ascribed to that cause.

IMPURITIES IN THE BASE

In recent years certain manufacturers have been using iron of exceptional purity, several brands analyzed in this laboratory showing only between 0.20 and 0.40 per cent impurities. So far as length of service of the galvanized sheets under investigation is concerned, the purity of the iron base has been a factor of minor importance and higher impurities than those found in modern sheets have not prevented long service.

PHYSICAL CHARACTERISTICS

With few exceptions, the modern sheets examined have been found to be free from physical defects, thus bearing out the observation made by Walker [15] on hot-galvanized ware in general They were, on the whole, fairly ductile, free from cracks and pinholes, and showed no marked brittleness. The old galvanized sheets have been found to be slightly less ductile, due to thicker spelter and to oxidation undergone during long years of weather exposure.

CORROSION OF UNUSED SHEETS

Considerable trouble has been experienced in the Philippines with unused sheets of imported galvanized iron which showed advanced stages of corrosion, either upon their arrival in Manila or after short storage periods. In some cases there was

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[15] *Proc. Am. Soc. Test. Mater.* (1909), 9, 436.

evidence of wetting by sea water, which, as is well known, is corrosive toward galvanized iron; in some cases sheets showed imperfections in galvanizing, such as pores, ragged edges, and buckles, which are conducive to the formation of centers of corrosion. There were sheets, however, that had imperfections yet which did not show corrosion, and there were cases of accelerated corrosion which imperfections in the coating and insufficiency of spelter did not explain. For example, in one instance galvanized sheets which had arrived apparently in good condition were stacked one over the other without shelter and were thus exposed to sun and rain for about three weeks. The majority of the sheets examined at the end of that time were in an advanced stage of corrosion. Some of the badly attacked sheets were covered by other sheets and were still moist. The average thickness of spelter was 6.41 grams per square decimeter (2.10 ounces per square foot).

There seemed to be but one fact to which the immediate cause of the damage may properly be attributed—that is, the continuous presence of moisture between sheets stacked one upon another, during exposure to weather. This explanation is borne out by the fact that sheets of the same brand that happened to be used for temporary roofs on sheds were in much better condition after nine months' exposure than the damaged sheets of even later arrival.

In a supplementary experiment six pairs of sheets were taken from different brands of the old and modern sheets. The edges were covered with paraffin, and the sheets were placed one on top of the other in pairs. The unexposed sides were kept moist by sprinkling with water once a day. In a few days signs of corrosion were noted and at the end of three weeks all sheets were in an advanced stage of corrosion.

Galvanized sheets undergo accelerated corrosion when the surface is kept moist either by actual wetting with water or by the presence of damp air. It is believed that similar conditions greatly contributed to the corrosion of sheets that arrived in damaged condition or which rusted during storage. The uniformly high temperature and humidity of most parts of the Philippines probably offer exceptionally favorable conditions for corrosion.

PAINT PROTECTION

The frequent failure of modern galvanized sheets in comparatively few years led to the necessity of applying paints, of which red lead, graphite, asphaltum, and oxide of iron are those most commonly used in the Philippines. A few paint-exposure tests were made, as follows:

A rusted galvanized sheet which had been washed with dilute hydrochloric acid to remove loosely adhering rusts and then washed with water and dried was coated with the following paints:

	Parts.
Primer:	
Sublimed blue lead	63
Linseed oil	32
Pure turpentine	5
Second coating:	
Bright red oxide of iron	85
Red lead	10
Zinc chromate	5

This paint has been exposed for three years and still renders good protection to the iron sheet. The same paint was applied on a new galvanized sheet, but it peeled off in less than a year.

A graphite paint was applied on a new galvanized sheet. After two years of weather exposure it shows slight peeling off in several parts.

Paint adheres better when it is applied after the surface of the galvanized sheets has undergone considerable oxidation, that is, after a year under weather exposure or when rusts begin to appear. When so applied, it undoubtedly increases the durability of the roofing. The use of paint for modern galvanized roofing is a necessity in the Philippines and will continue to be of immediate consideration to the consumer unless manufacturers put more spelter on their future output.

DISCUSSION OF RESULTS

It is apparent from the foregoing experimental results that the better service given by the old galvanized iron as compared with the modern product imported to the Philippines is accounted for by the greater amount of coating on the former. This conclusion is in accord with observations made by others elsewhere. For example, Van Gundy[16] noted that galvanized plate which had seen service of twenty or twenty-five years in Panama was better than plate which had been in service less than two years. Referring to the old galvanized sheet he said:

> Yet, even after this service, I found that it had three times as much zinc on it as the American manufacturers put on their plate, even the best in the market.

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[16] *Proc. Am. Soc. Test. Mater.* (1909), 9, 41.

Walker[17] found that a galvanized-wire fence carrying 3.9 per cent of zinc was still in good condition after four years of service, while another sample which carried 1.4 per cent was badly rusted in three years. He makes the following observations:

> In every instance where a very durable fence was found, the coating of zinc was relatively very thick; while on the other hand, the fences which showed marked corrosion in from one to two years proved to have almost no zinc on the iron, the zinc color being due to a layer of alloy alone.

In accordance with the conclusions of other observers, and from the results obtained, it is evident that in the manufacture of galvanized sheets the application of the "maximum amount of zinc consistent with the practical possibility of its manufacture"[18] should be striven for, if sheets are expected to render long service on exposure. Economic and physical considerations should be the limiting factors in deciding the minimum amount of spelter per unit area. In recent years the tendency among manufacturers to diminish the thickness of the spelter no doubt has had an important bearing on the durability of modern corrugated sheets.

Various standards of thickness of coating have been used, among them the following:

TABLE VI.—*Various standards of coating.*

Source.	Per square decimeter (flat).	Per square foot (flat).
	Grams.	*Ounces.*
Kidder, 1913 edition, p. 1439	7.63	2.50
American Civil Engineer's Pocket Book, 1913 edition, p. 393	16.58	5.44
Standard Specifications of the Isthmian Canal Commission for 1909	7.63	2.50
Trautwine, 1909 edition, p. 881	4.88	1.60
Altoona car roofing, *Proc. Am. Soc. Test. Mater.* (1909), 9, 441	12.21	4.00

The present work indicates that, for the Philippines at any rate, 7.63 grams per square decimeter (2.50 ounces per square foot) of spelter is the minimum coating for galvanized sheets which will ensure satisfactory service.

None of the other factors studied would account for the differences in durability noted between old and new galvanized iron. All sheets tested showed the presence of chlorides. The lead found in the old and modern sheets is approximately the

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[17] Ibid. (1909), 9, 43.

[18] Cushman, ibid. (1909), 9, 143.

same when calculated on the basis of spelter content, and probably in no case was it high enough to affect durability adversely. The iron dissolved by 3 per cent sulphuric acid assumed to represent the iron alloyed with zinc is approximately the same in the old and modern sheets when calculated on the basis of spelter content. Modern sheets are not inferior with respect to continuity and ductility of coating as compared with the old sheets. The iron body of modern galvanized sheets is of high purity and is equal or superior in quality to that of old sheets.

SUMMARY

The importantion of galvanized-iron roofing to the Philippines approximates 1,500,000 pesos in value annually. Many of the recently imported brands fail rapidly, while certain brands have given satisfactory service for over thirty years.

Of the various factors influencing the durability of galvanized iron which have been studied with a view toward accounting for the difference in behavior of old and modern sheets, it appears evident that the greater weight of zinc per unit area on the former accounts for the greater durability. The modern sheets were not inferior to the old product with respect to the presence of impurities in the coating or in the iron base or with respect to continuity, ductility, or toughness of coating.

For satisfactory service in the Philippines, galvanized iron should have a coating of not less than 7.63 grams per square decimeter (2.50 ounces per square foot).

The advanced corrosion often noted in the Philippines of sheets newly arrived or kept in storage probably finds explanation in the fact that galvanized iron corrodes very rapidly when continually kept moist either by actual contact with water or by the presence of damp air.

Proper paints, applied after the surface of sheets has become well roughened by exposure, will greatly increase the life of modern galvanized iron.

THE DETINNING AND ANALYSIS OF TIN PLATE[1]

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INTRODUCTION

Practically all the tin plate on the market is made by a hot-dip process—by immersing carefully cleaned sheet iron in a bath of molten tin. The coating formed by this process varies from almost pure tin at the outer surface of the plate to a tin-iron alloy rich in iron near the surface of the iron base. Often varying amounts of lead are used in the molten bath.

The removal of the coating from tin plate, both for the commercial recovery of tin and for analytical purposes, has been the subject of much study. Among the commercial methods the most important are the electrolytic detinning in alkaline solution,[2] the chlorine process,[3] and various modifications of these.[4]

In addition, a large variety of methods have been proposed, such as the mechanical separation of tin from tin plate by agitation of a mass of tin scrap with liquid air;[5] the treatment of the material with superheated steam,[6] whereby tin is fused and loosened by the formation of iron oxides; solution of tin in strong commercial hydrochloric acid, kept cold[7] to prevent the solution of iron; removal of tin by a solution of sodium plumbate;[8] or electrolysis in a bath of phosphoric acid.[9]

Many processes[10] have been recommended for the removal and determination of tin and lead in tin plate, among

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[1] Received for publication July 17, 1916.

[2] Keith, U. S. Patent 176,658 (1876).

[3] Cf. *Electrochem. & Met. Ind.* (1909), 7, 79.

[4] Skinner, R. P., German detinning methods, *Det. Ind.* (1914), 12, 236. Detinning industry, *Electrochem. & Met. Ind.* (1909), 7, 79.

[5] Phelps, W. J., U. S. Patent 952,351 (March, 1910).

[6] Wiltereck, H. C., German Patent 261,522 (February, 1912).

[7] Calmels, J. M., French Patent 448,004 (September, 1902).

[8] Ramage, A. S., *Met. & Chem. Eng.* (1911), 9, 219.

[9] Battle, A. E., Brit. Patent 14,514 (June, 1914).

[10] Cf. Serger, H., *Zeitschr. f. d. Untersuch. d. Nahrungs- u. Genussm.* (1913), 25, 465.

them the mechanical removal[11] of the tin after heating over a Bunsen flame; the digestion at boiling temperature with sodium peroxide,[12] the difference in weight before and after treatment serving as an indication of the amount of coating; the solution of the tin coating in 12.5 per cent hydrochloric acid[13] and subsequent precipitation of the tin as sulphide, heating, and final weighing as oxide; the solution in 10 per cent hydrochloric acid,[14] precipitation with ammonium sulphide, and heating, after certain precautions, with ammonium carbonate; and the heating of tin plate with dry sodium peroxide,[15] solution of the melt in water, acidifying with sulphuric acid, washing, heating, and weighing the precipitated oxide. I. H. Aupperle[16] suggests (1) the solution of the tin in hydrochloric acid, with certain precautions, and the final determination of tin by titration with iodine solution, or (2) the removal of tin with concentrated sulphuric acid and the determination of the iron in the solution, the tin being obtained either by difference or by direct analysis as above.

The above methods either give merely the amount of tin present or else the total amount of plate (tin, lead, and iron alloy in the coating). If the amounts of tin and lead are desired, additional processes are required.

Directions for a simple method for the determination of lead, as given by Serger,[17] are as follows:

Take 0.1 gram iron-free tin, carefully scraped from heated tin plate, decompose with 3 cubic centimeters of concentrated nitric acid on a steam bath, and evaporate to dryness three times. Add 10 cubic centimeters of water, allow to stand on a water bath for ten minutes, filter into a 100 cubic centimeter flask, and dilute to the mark with distilled water. Shake well, use 10 cubic centimeters in a large test tube, and add 10 cubic centimeters of fresh hydrogen sulphide water. Compare the color obtained with a standard made by adding 2, 5, 10, and 20 drops of a water solution, containing 0.16 gram of lead nitrate per 100 cubic centimeters (1 cubic centimeter=0.001 gram metallic lead) to 10 cubic centimeters of water and 10 cubic centimeters hydrogen sulphide water.

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[11] Serger, loc. cit.

[12] Meyer, K., *Zeitschr. f. angew. Chem.* (1909), 22, 68.

[13] Serger, loc. cit.

[14] Mastbaum, H., *Zeitschr. f. angew. Chem.* (1897), 10, 329.

[15] Angenot, H., ibid. (1904), 17, 521.

[16] *Metal. Ind.* (1914), 12, 327-328.

[17] Loc. cit.

For rapid, practical tests, where many examinations must be made to determine the quality of a large shipment of tin plate, simple determinations of the amount of coating per unit area will doubtless be found sufficient in addition to tests on uniformity of coating. Many of the procedures outlined are unnecessarily tedious.

In most of the foregoing methods the amount of iron alloyed with the tin is not determined, although it appears obvious that it is a factor having an important bearing on the quality of the resulting tin plate. A method which will first remove the coating, including the tin-iron alloys, from tin plate and which will enable the subsequent determinations of at least the tin and iron in the coating ought to yield more valuable information concerning the quality of tin plate than a determination of the tin only or of the tin and lead in the coating.

The work here recorded was done for the purpose of studying and developing methods of removing tin from plated iron without attack on the iron base, with special references to the analysis of tin plate.

EXPERIMENTAL PART

Different brands of tin plate were used in the work here recorded, but none of these contained lead. A sample of tin plate of uniform appearance and apparently good quality was cut into squares 5 centimeters on a side, cleaned with alcohol and ether, and analyzed according to the method of Aupperle,[18] the final titration for tin being made with iodine solution. The results with different squares were as follows:

TABLE I.—*Analysis of tin plate by Aupperle method (titration with iodine solution).*

No.	Weight of sample.[a]	Weight of tin.	Weight per unit area.		Tin in tin plate.
			Per square decimeter.	Per square foot.	
	Grams.	*Grams.*	*Grams.*	*Ounces.*	*Per cent.*
1	4.340	0.064	0.256	0.084	1.48
2	4.340	0.072	0.288	0.094	1.66
3	4.293	0.068	0.272	0.089	1.58
4	4.330	0.071	0.284	0.093	1.64
5	4.354	0.064	0.256	0.084	1.47
Average	4.331	0.068	0.271	0.089	1.57

[a] Size of plate, 5 by 5 centimeters.

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[18] Loc. cit.

When stripped by immersion in boiling sodium peroxide solution [19] samples of the same tin gave the following results:

TABLE II.—*Analysis of tin plate by the Meyer method.*

No.	Weight of sample.[a]	Loss after treatment.		Coating per unit area.	
				Per square decimeter.	Per square foot.
	Grams.	*Grams.*	*Per cent.*	*Grams.*	*Ounces.*
6	4.346	0.082	1.89	0.328	0.107
7	4.360	0.085	1.95	0.340	0.111
8	4.289	0.078	1.82	0.312	0.102
9	4.310	0.075	1.74	0.300	0.098
Average	4.326	0.080	1.85	0.320	0.1045

[a] Size of samples, 5 by 5 centimeters.

The Meyer method gives concordant and reliable results, but it is clumsy, because of the unavoidable and disagreeable spattering attendant on the use of sodium peroxide, and because long and repeated treatment is necessary to ensure complete removal of the coating.

The results obtained by this method are higher than those obtained by direct analysis of tin, the difference (about 0.05 gram) representing the amount of iron removed with the tin plate. That this iron is actually part of the alloy and is not due to attack on the base is shown by the fact that there was no further loss in weight on subsequent treatment with sodium peroxide.

Since iron is an insoluble anode in certain alkaline and oxidizing solutions, other metals can readily be stripped from it electrolytically.[20] For the work here recorded a 30 per cent solution of sodium nitrate was employed as stripping bath, and the plate was made the anode. As will be seen, the results obtained are comparable with those obtained with sodium peroxide. Comparable results were obtained with sodium or potassium hydroxide solutions, but with these the action was so slow that their use is not recommended.

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[19] Meyer, op. cit.

[20] Cf. Burgess, C. F., *Trans. Am. Electrochem. Soc.* (1903), 4, 31.

TABLE III.—*Analysis of tin plate by electrolysis.*[a]

A. IN A 30 PER CENT SODIUM NITRATE SOLUTION.

No.	Weight of sample.[b]	Loss after treatment.		Coating per unit area.	
				Per square decimeter.	Per square foot.
	Grams.	*Grams.*	*Per cent.*	*Grams.*	*Ounces.*
10	4.346	0.082	1.88	0.328	0.108
11	4.281	0.080	1.87	0.320	0.105
12	4.261	0.079	1.85	0.316	0.104
13	4.296	0.080	1.84	0.320	0.105
Average	4.296	0.080	1.86	0.321	0.105

B. IN A 20 PER CENT SODIUM HYDROXIDE SOLUTION.

14	4.337	0.072	1.66	0.288	0.094
15	4.292	0.078	1.84	0.302	0.102

[a] Voltage, 3.5; amperage, 0.7; time, about ten minutes.

[b] Size of samples, 5 by 5 centimeters.

This procedure offers an extremely simple and rapid method of analysis. Stripping is accomplished in a few minutes. There is no danger of attacking the iron of the base. The iron of the alloy removed from the plate is left in the bath in such form that it can be readily recovered as ferric hydroxide and can be determined quantitatively.

By reference to the results obtained in Table II it is evident that the two methods are strictly comparable.

In a study of the stripping of galvanized iron, we called attention [21] to a number of salts which would be replaced in solution of metals by zinc but not by iron. As zinc is generally electropositive to iron in aqueous baths, metals intermediate in the potential series to zinc and iron should form salts which strip zinc from iron. Such salts were readily found, among them a number which might have been expected to attack iron as well as zinc. To find salts which will strip tin from iron is more difficult, since tin is electronegative to iron in many aqueous solutions, and salts which dissolve the former might naturally be supposed to attack the latter.

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[21] *This Journal, Sec. A* (1916), 11, 144.

Basic lead acetate solution will strip zinc from iron,[22] but leaves tin plate unattacked. Lead acetate does not affect tin plate either in neutral or (acetic) acid solution, but lead acetate or other lead salts, in solutions made alkaline with sodium or potassium hydroxide, strip tin from plated iron very rapidly, depositing lead in a spongy, easily removed condition. The accuracy of the method may be judged by the tests made on samples of the same tin plate previously analyzed.

TABLE IV.—*Analysis of tin plate by immersion in alkaline lead acetate (sodium plumbite) solution.*

FIVE-MINUTE TEST.

No.	Weight of sample.[a]	Loss after treatment.		Coating per unit area.	
				Per square decimeter.	Per square foot.
	Grams.	*Grams.*	*Per cent.*	*Grams.*	*Ounces.*
16	4.285	0.078	1.82	0.312	0.102
17	4.214	0.076	1.80	0.304	0.100
18	4.221	0.072	1.70	0.288	0.094
19	4.325	0.073	1.69	0.292	0.096
Average	4.261	0.075	1.75	0.299	0.098

THREE-DAY TEST.

16	4.285	0.082	1.91	0.328	0.107
17	4.214	0.082	1.95	0.328	0.107
18	4.221	0.077	1.85	0.308	0.101
19	4.325				
Average	4.261	0.080	1.90	0.321	0.105

[a] Size of samples, 5 by 5 centimeters.

These data are again comparable with those obtained by the methods previously outlined. Concordant results are obtained, and unless great refinement is desired, the method is sufficiently rapid and accurate to serve as a reliable guide in the judgment of tin plate. Compared with the data previously recorded, the results obtained with alkaline lead acetate solution are a trifle low, showing that all of the tin-iron alloy is not removed immediately by this method. As a matter of fact, the lead solution does strip nearly all of the iron-tin alloy from the iron if the time of immersion is prolonged, the reaction being practically

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[22] Patrick, W. A., and Walker, W. H., *Journ. Ind. & Eng. Chem.* (1911), 3, 239.

completed after an hour or two. Doubtless the presence of much lead in a tin coating would lessen the accuracy and applicability of this method.

Other salts of lead yield similar results, but the reaction is by no means confined to lead salts. Aluminium nitrate, made alkaline with sodium hydroxide, will strip tin, although the action is extremely slow. A solution of copper sulphate and tartaric acid, made alkaline with sodium hydroxide, has a similar effect. Chromium nitrate solution attacks both tin and iron, but the same solution with enough sodium hydroxide added to make a clear liquid will dissolve only the tin. The data secured with typical solutions are given herewith, the tables showing the results obtained with two different samples of tin plate. Lead salts are the only ones listed to be recommended for analytical work.

TABLE V.—*Detinning by immersion.*

PLATE A.[a]

No.	Solution used.	Weight of sample.	Loss on immersion.		Weight of coating.	
					Per square decimeter.	Per square foot.
		Grams.	*Grams.*	*Per cent.*	*Grams.*	*Ounces.*
16–19	Lead acetate and sodium hydroxide	4.261	0.075	1.76	0.300	0.098
20	Lead chromate and sodium hydroxide	4.351	0.071	1.63	0.284	0.093
21	Chromium nitrate and sodium hydroxide	4.401	0.067	1.61	0.268	0.088
22	Aluminium nitrate and sodium hydroxide	4.321	0.065	1.52	0.260	0.085
23	Copper sulphate, tartaric acid, and sodium hydroxide	[b]1.224	0.022	1.79	0.303	0.099
24	Nitric acid, concentrated	4.272	0.069	1.61	0.276	0.090
25	do	4.299	0.066	1.54	0.264	0.086

PLATE B.[c]

26	Lead acetate and sodium hydroxide	5.202	0.064	1.23	0.248	0.081
27	do	5.314	0.066	1.24	0.256	0.084
28	Lead nitrate and sodium hydroxide	5.341	0.066	1.24	0.256	0.084
29	do	5.420	0.071	1.31	0.275	0.090
30	Lead chromate and sodium hydroxide	5.526	0.063	1.14	0.244	0.080
31	do	5.452	0.065	1.19	0.252	0.083
32	Aluminium nitrate and sodium hydroxide	5.374	0.071	1.32	0.275	0.090

[a] Size of samples, 5 by 5 centimeters, except as noted.

[b] Size of sample, 1.45 by 5 centimeters.

[c] Size of samples, 2 by 2 inches (5.08 by 5.08 centimeters).

Concentrated nitric acid will remove tin without attack on the iron base, although it will entirely destroy a piece of galvanized iron. Both tin and zinc are anodic to iron in concentrated nitric acid, and zinc is anodic to tin.

The experiments in the preceding tables are of interest, not only because of the apparent "reversals" of potential of tin, but also because of the fact that many of the reactions recorded took place in alkaline solutions in which the metals used (chromium, aluminium, lead, etc.) are generally thought to be part of the acid radicals.

AMOUNT OF IRON IN THE COATING

The amount of iron alloyed with tin depends on the temperature and purity of the plating bath and doubtless varies with different brands of tin plate. It is reasonable to suppose that it should be an important factor in determining the quality of tin plate and its resistance to corrosion. The various brands analyzed by us showed iron contents in the tin coating of about 0.05 gram per square decimeter.

SIZE OF SAMPLES TO BE USED FOR ANALYSIS

The analytical data previously recorded indicate the lack of uniformity of coating to be expected in commercial tin plate. Although errors are undoubtedly caused by failure to cut samples of tin plate accurately to squares of the required size, it is apparent that great discrepancies in uniformity of coating exist, even in samples cut from the same sheet. Obviously more concordant results would be obtained if larger samples were used, but in that case the analyst might easily fail to detect local defects in the coating. With the methods outlined, squares 5 by 5 centimeters, or at most 5 by 10 centimeters, should be ample for analytical purposes and should yield more reliable data than larger samples.

STANDARDS FOR TIN PLATE

The quality of a galvanized iron is determined chiefly by the thickness of the coating, since zinc, under ordinary service conditions, itself corrodes and inhibits the corrosion of iron even after the latter is exposed. Tin, on the other hand, frequently accelerates the corrosion of iron; its protective influence is mechanical. Uniformity of coating is, therefore, an essential requirement for good tin plate, and a test, such as the one devised by W. H. Walker,[23] for the detection of pinholes and

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[23] *Journ. Ind. & Eng. Chem.* (1909), 1, 440.

other inequalities in tin plate is of great importance in determining quality. Leaving out of consideration the question of the purity of tin plate, it is evident that specifications should require certain standards, both for thickness and for uniformity of coating.

Obviously the amount of coating necessary for good tin plate will depend, to a large extent, on the service to which it is subjected. The specifications for the United States Navy Department[24] call for 5 pounds of tin per 112 sheets 14 by 20 inches in size, corresponding to a coating of 1.123 grams per square decimeter (0.367 ounce per square foot). According to Serger,[25] a coating of 0.3 gram of tin per square decimeter of tin plate (that is, 0.15 gram per square decimeter of surface) is sufficient to make plate resistant to the corrosive influences to which canned goods are subjected, and no material which had given satisfactory service showed a smaller amount of tin. The few data at hand in the Bureau of Science tend to confirm the conclusion of Serger and indicate that the figures given by him represent the lower limit for good tin plate. For example, a certain shipment of tin cans corroded so badly during an eighty-day voyage from the United States to Manila that a large amount of the contents leaked out. The corrosion was entirely from the outside, the interior of the cans remaining bright and unspotted. There was no evidence of sea-water damage or undue corrosive influence. Upon analysis the cans were found to have a coating of 0.245 to 0.250 gram of tin per square decimeter.

SUMMARY

A number of methods of stripping tin plate without attack on the iron base have been studied. Of these, detinning by means of an electric current, making the plate the anode in a bath of sodium nitrate, and stripping by immersion in a solution of a lead salt made alkaline with sodium hydroxide (sodium plumbite) can be recommended for rapid and accurate analytical work.

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[24] No. 47 T 1 (February 15, 1912).

[25] Loc. cit.

REVIEW

Practical | Physiological Chemistry | [3 lines] | by | Philip B. Hawk, M. S., Ph. D. | [2 lines] | fifth edition, revised and enlarged | [4 lines] | Philadelphia | P. Blakiston's Son & Co. | 1012 Walnut Street | 1916 | Cloth, pp. i–xiv+1–638.

The great advances in physiological chemistry are very well illustrated by the numerous editions of books dealing with this phase of chemistry put out in their attempts to keep abreast of the subject.

The first edition of Hawk's Physiological Chemistry was published in 1907; the second in 1909; the third in 1910; the fourth in 1912, followed by reprints of this edition in 1913 and in 1915; and the fifth edition is copyrighted in 1916.

This last edition has been brought up-to-date by thoroughly revising and rewriting the preceding edition and by adding five new chapters. These chapters are: Chapter III on Nucleic Acids and Nucleoproteins, Chapter VIII on Gastric Analysis, Chapter XI on Intestinal Digestion, Chapter XVI on Blood Analysis, and Chapter XXVII on Metabolism. The system of including laboratory directions in the text and the use of black-faced type for the most important and reliable of these tests and methods are valuable features of this book. An examination of this latest edition impresses one with the important part given to the discussion of the function of enzymic activity in the everyday life of the human being.

The book is printed on good paper, is attractively and well bound, and is well printed. A number of errors have escaped the notice of the proof reader, as, *creatinine* has been used for *creatine* (page 508).

The book is excellent in subject matter and arrangement and is a valuable contribution to this phase of chemical literature, due to Doctor Hawk's wide experience and extensive knowledge of the subject.

H. C. B.

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AND THE INDUSTRIES

VOL. XI SEPTEMBER, 1916 NO. 5

PHILIPPINE PAVING-BRICK MATERIALS: A PRELIMINARY REPORT[1]

By J. C. WITT

(From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila, P. I.)

ONE PLATE AND 1 TEXT FIGURE

INTRODUCTION

One of the needs of the Philippine Islands is a cheap and satisfactory paving material for streets and roads. There are a number of imported products which give good service, but the cost of transportation prohibited their extensive use even before the present increases in freight rates. Imported paving brick has always been out of the question for this reason, but asphalt has been used from time to time. However, at present, high freight rates prohibit the further importation of this substance, and the supply on hand in Manila is being used only on repair work. As a result, the city must now depend almost entirely on macadam, which is the only class of paving that can at present be made on an economic basis from Philippine raw materials. Macadam is satisfactory for some purposes, but is, of course, not well adapted to heavy traffic. Paving of concrete alone or of concrete mixed or surfaced with bituminous substance, is used in some cities in the United States with various degrees of success, but unfortunately cement is another material which is not available for streets to any great extent. There is one mill in the Philippine Islands manufacturing cement from local raw materials, but the present output is not adequate to supply the cement for building purposes alone.

The area of each kind of paving in use in Manila (December

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[1] Received for publication June 2, 1916.

31, 1915) and the approximate cost per square meter are given in Table I.

TABLE I.—*Various paving materials in use on Manila streets.*

Kind of paving.	Area.	Original cost per square meter.	Annual maintenance per square meter.
[a]	*Sq. m.*	*Pesos.*[b]	*Pesos.*
Wood block	13,270	16.00	0.09
Stone block	35,370	not available.	very little.
Tar macadam	71,435	3.00	0.14
Macadam for—			
Heavy traffic	1,560,117	2.40	0.13
Medium traffic		2.00	
Light traffic		1.20	

[a] The information was obtained from the city engineer of Manila.
[b] One peso Philippine currency is equivalent to 50 cents United States currency.

Total length of improved streets and alleys, 192,446 meters.
Total paved area, 1,680,192 square meters.

The table shows that more than 92 per cent of all paving in Manila is macadam, and the percentage is increasing. The initial cost is low, but the high cost of maintenance prevents it from being an economical material.

ADVANTAGES OF PAVING BRICK

It is generally conceded that a vitrified-brick pavement will stand harder wear and give more satisfactory service for heavy traffic than any other except one of stone block. The cost of constructing a stone-block pavement is not excessive, and the maintenance is practically negligible for many years. However, such a pavement has a number of disadvantages. The edges of the blocks usually wear round, and a very rough street results. Such a pavement is hard on horses. Besides, it is noisy, and dirt settles in the cracks and cannot be removed by sweepers. The street is neither attractive nor sanitary when it is wet. In most large cities of the United States the stone-block pavement is confined to streets having only the heaviest traffic.

A brick pavement when properly constructed is very satisfactory. It wears smooth, offers little resistance to traction, and requires little maintenance.[2] Concerning the growth of the

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[2] Although a number of unsatisfactory brick pavements may be found in the United States, the difficulty with each is usually easy to find. As a rule the fault lies in the bricks themselves, in the foundation, or in the filler. In some cases the fault is with the traffic. This may have originally been too heavy for a brick pavement or may have greatly increased after the pavement was laid.

vitrified paving-brick industry in America, Blanchard and Drowne[3] say:

> The first piece of brick pavement in the United States was a short experimental section laid in Charleston, West Virginia, in 1870. This was followed by another experimental piece laid in Bloomington, Illinois, in 1875, and a few other sections laid from time to time, up to 1885, in different cities of the Middle West. The use of this kind of pavement then began to increase rapidly, and at the present time there are very few large cities in the country that do not have some of their streets paved with this material. A census taken of the permanent pavements laid in 1910, in the United States, showed that brick was one of the most popular forms of pavement, considering the number of cities that have used it. From this census it was found that while sheet asphalt was first from the standpoint of yardage in the 460 cities reported, brick was a close second. It is natural that the greatest yardage should occur in those cities throughout the Central States since this locality abounds with clay deposits suitable for the manufacture of paving brick and is devoid of road building stone.

Evidently what is needed in the Philippines is the local manufacture of some paving material, because it is unlikely that shipping rates will ever be sufficiently low to allow the importation of large quantities. The Bureau of Science has long considered paving brick to be well adapted to local conditions, and the possibility that it may be made from Philippine raw materials has led to the present investigation.

DIFFICULTIES TO BE OVERCOME

It is not an easy task to find a raw material suitable in every respect for making paving brick in the Philippines. In the United States various geological surveys have been made, and if one desires to install a brick factory, he can easily obtain information concerning the various deposits of clays and shales and their working properties, location, and available fuels. The points to be considered in such an investigation for the Philippines are:

Raw materials.—A clay or shale must be selected with the necessary properties to produce vitrified paving brick, either alone, or mixed with some other material. In case two materials have to be used, they must be located near each other.

Transportation.—The raw material must be in an accessible place where brick machinery can be installed and transportation to Manila can be had. On account of the lack of wagon roads in many undeveloped parts of the Islands and the comparatively

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[3] Blanchard, A. H., and Drowne, H. B., Text Book on Highway Engineering. John Wiley and Sons, New York (1914), 550.

limited kilometers of railroad, it is likely that only some locality near water transportation could be considered.

Fuel.—The high price of imported coal at present prohibits its use in burning brick. Therefore, if a factory is to be operated on an economical basis, it is desirable to locate it near a deposit of Philippine coal or other available fuel.

It would be very expensive to locate a large number of deposits and obtain samples for the investigation except in conjunction with other work. Thus far no systematic survey devoted exclusively to brick materials has been made. Most of the samples have been obtained at very little cost by members of the Bureau of Public Works and of the Bureau of Science who were in the field on other lines of duty. The Director of the former bureau has kindly sent a circular letter to all district engineers, requesting them to keep a lookout for shales and clays and to send samples of any promising material to the Bureau of Science.

RÉSUMÉ OF PREVIOUS WORK AT THE BUREAU OF SCIENCE

Systematic investigation of Philippine clays was started at the Bureau of Science by Cox.[4] According to the author, his object was—

> rather to show in a preliminary way the geological distribution and quality of clays on Luzon, than to pronounce on their economic value.

In the course of his work he examined more than thirty samples of clays, making chemical analyses and physical tests. Study of his paper clearly reveals the general character of the clays of Luzon. Some of the clays had already been used by Filipinos and Chinese in the manufacture of brick and pottery. The author says:

> The common clays of Luzon are already [1907] used in several places in the manufacture of brick and crude pottery. For example, the brick-kilns at Mandaloyon and the one near San Pedro Macati, on the Pasig River near Santa Ana, each of which employs from ten to twenty laborers, turn out from one to three thousand bricks a day per kiln. * * * No sand is added to it before molding, but the whole bank is broken down, mixed by the tread of carabaos, and used for the bricks. This makes the composition slightly different * * * but tests of the shrinkage and tensile strength show that its physical properties remain almost unchanged.

In his second paper[5] the same author says:

> This investigation was undertaken at the request of the Bureau of Education to enable it to choose a clay for use in the pottery school, the

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[4] Cox, Alvin J., *This Journal, Sec. A* (1907), 2, 413.

[5] Ibid., *Sec. A* (1908), 3, 377.

> building for which is now being erected in Santa Cruz. None of the clay deposits of Laguna Province have been thoroughly studied up to the present time and, therefore, I will first discuss those so situated that the stripping of the material would entail the least labor and the soil overlying could easily be disposed of. Such clays would be economical to use were they of high grade.

The work consisted in accurately locating a number of clay deposits and in examining their chemical and physical properties. It was found that—

> all of the high grade clays of Laguna Province are more or less mixed with clay of poorer quality. It is a question what percentage of the mixture is useful and whether the expense of sorting will not be so great that it can not compete with kaolin from other sources.

Adams and Pratt[6] give a report on the pottery industry in the Philippines up to 1910. This paper contains considerable information on the crude processes in use for making pottery, the general equipment, and other points of interest. The authors visited a number of potteries and brick factories.

> The usual type [of kiln] is a long semicylindrical structure built on a grade of about 10 per cent, having a chimney at the upper end and a door and hearth at the lower. There are also openings for firing along the sides of the kiln. They are constructed of volcanic tuff and common brick laid up and plastered over with mud. The fuel used is wood. A high temperature can not be obtained in these kilns and the semivitrified products from some of them are due to the low fusing point of the clays used. There is considerable shrinkage in burning, and when the clay fuses the sand used to prevent cracking comes to the surface, making the ware rough and pebbly.

A study of Philippine clays in relation to pottery manufacture has been made by Crowe,[7] of the Philippine School of Arts and Trades.

The papers mentioned above are the only ones published so far by the Bureau of Science in which the properties of Philippine clays are considered directly in connection with ceramics. However, papers have appeared on Portland cement raw materials[8] which deal with clays and shales.

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[6] Adams, G. I., and Pratt, W. E., *This Journal, Sec. A* (1910), 5, 143.

[7] Crowe, C. H., *Trans. Am. Cer. Soc.* (1912), 14, 723.

[8] Cox, Alvin J., Philippine raw cement materials, *This Journal, Sec. A* (1909), 4, 211.

Reibling, W. C., and Reyes, F. D., The efficiency of Portland cement raw materials at Naga, Cebu, ibid. (1914), 9, 127.

Pratt, W. E., Geological and field relations of Portland cement raw materials at Naga, Cebu, ibid. (1914), 9, 151.

PRESENT STATUS OF BRICK MAKING IN THE PHILIPPINES

Brick manufactured at a number of places in the Islands [9] is intended for building purposes only, and much of it is of inferior quality. Two of the factories visited may be briefly described here.

The factory near San Pedro Macati, mentioned by Cox,[10] is still in operation. The clay is obtained along the river near the plant. It lies near the surface, and very little labor is required to win it. The bricks are molded by hand by the soft-mud process. The workman throws a mass of the mud, about 30 centimeters in diameter, into a mold and cuts off the excess by means of a wire mounted on a frame. The clay is so sticky that the wet bricks are powdered with a black carbonaceous material, obtained by burning coconut husks, to facilitate handling and to prevent them from cracking during drying. A molder can make from one hundred to three hundred bricks per day. The bricks are allowed to dry from fifteen to twenty days in a large shed, where they are protected from the sun.

The kiln is very interesting and might be classed as a temporary, round, updraft kiln.[11] The front is permanent and is well constructed of masonry. Starting with this, for each burning, the bricks are built into the shape of a beehive and covered on the outside with clay. When the kiln is completed, it is from 3.5 to 4.5 meters high and from 6 to 8 meters in diameter. There is no grate of any kind, but a small wood fire is built on the floor of the kiln in a space left for the purpose at the time the bricks are placed in position. The combustion gases pass out through a small chimney and also through several small openings on the sides of the kiln. The fire is so small in comparison with the size of the kiln that a high temperature is never reached, and when the bricks are removed after two to three weeks, they have been little more than dried.

As a result, the product obtained is very inferior and could not be used in walls of any considerable height. Small pieces may be broken off with the fingers. However, the clay is a good material for making building brick when it receives the proper treatment. Some small test bricks were molded in this labo-

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[9] In 1903 there were 27 establishments, employing 954 persons, engaged in the manufacture of brick and tile. See Census of the Philippine Islands. Government Printing Office, Washington (1903), 4, 516.

[10] *This Journal, Sec. A* (1907), 2, 428.

[11] See *Bull. Oklahoma Geol. Surv.* (1911), No. 7, 81.

ratory by the stiff-mud process. When burned to only cone 02 (1,110°), they developed a crushing strength of 393 kilograms per square centimeter. A number of tests have been made on this clay; they are given in Tables III and IV. It seems obvious that the poor quality of the product made at the San Pedro Macati factory is due to the process of molding and to insufficient burning. The clay seems better adapted to the stiff-mud process. A view of the kiln, while in use, showing the permanent front, is given on Plate I. The small fire in the foreground furnishes the only heat for the kiln. One of the workmen stated that the fire is maintained at about the same intensity during the entire burning. Plate II shows the molding and drying room.

A building-brick and floor-tile factory is located on Cebu Island, about 600 meters north of Mabolo barrio. The clay used (Tables III and IV, clay 1) is in some respects superior to clay 2. Apparently it is molded by the soft-mud process, though I did not see the operation. The kiln is similar to a drawing shown by Adams and Pratt.[12] The shape somewhat resembles a truncated cone placed in a horizontal position. It is 26 meters in length. At the small end the height is 1.15 meters and the width 0.85 meter, inside measurements. At the large end the height is 2.20 meters and the width 2.30 meters, inside measurements. There are three fire boxes: one at the small end and two at the sides. Wood is used for fuel, and the kiln seems to be efficient. As a result of a better raw material and a more efficient kiln, the product is much superior to the San Pedro Macati brick.

CHEMICAL AND PHYSICAL TESTS

While the primary object of the present work is to find a suitable material for the manufacture of paving brick, it is also desired to obtain as much information as possible about Philippine clays in general. Consequently all clays that have been received have been tested, though in some cases it was evident that the material was not the one sought. A number of the samples appear to be excellent building-brick materials, though it is difficult to decide finally on a clay until full-size bricks have been molded and subjected, as nearly as possible, to the processes that are to be used in the manufacture.

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[12] *This Journal, Sec. A* (1910), 5, 145.

SOURCE AND DESCRIPTION OF SAMPLES

1. About 600 meters north of Mabolo barrio, Cebu. Brown; good working qualities.
2. Pasig River, near San Pedro Macati. Brown; sticky.
3. Laguna Province, on the shore of Laguna de Bay, between Lumbang and Pagsanjan. Gray; plastic.
4. Masbate, white clay; analysis corresponds closely to kaolin.
5. Calapan, Mindoro. Dark brown; contaminated with stone.
6. Camansi, Cebu. A brown shale.
7. Near Jaro River, about 3 kilometers from Iloilo. Dark brown; slightly contaminated with stone.
8. Rio Grande de la Pampanga, Matamu barrio, Arayat, Pampanga. Dark brown; contaminated with sand.
9. Bangued, Abra subprovince, Ilocos Sur. A light red clay.

The chemical analysis of each sample as received is given in Table II.

TABLE II.—*Analyses of clays.*[a]

[Numbers give percentages.]

Determinations.[b]	No. 1.	No. 2.	No. 3.	No. 4.	No. 5.	No. 6.	No. 7.	No. 8.	No. 9.
Loss on ignition	6.11	13.84	20.94	27.30	16.21	-------	13.45	10.72	14.56
Silica (SiO_2)	74.53	51.00	44.00	37.80	46.20	44.35	51.64	56.10	51.90
Alumina (Al_2O_3)	13.17	20.60	26.66	34.20	27.56	24.90	19.52	18.24	24.20
Ferric oxide (Fe_2O_3)	2.14	6.36	4.34	0.40	3.50	-------	6.06	6.92	7.14
Calcium oxide (CaO)	1.44	2.91	1.15	trace	2.80	11.37	4.14	3.74	0.54
Magnesia (MgO)	0.72	2.31	0.86	trace	2.50	2.59	3.74	2.64	0.79

[a] Most of these analyses were made by F. D. Reyes, inorganic chemist, Bureau of Science.

[b] Alkalies were not determined.

Methods of testing a raw clay.—There are a great many physical tests that can be applied to clays, but some of them are of doubtful value. In this work only those which are most important were chosen. In general, these are well known.[13]

Water of plasticity.—The clay is ground, put through a sieve having about 8 meshes per centimeter (20 per inch), and then mixed with sufficient water to give the right consistency. After a little experience this consistency can be determined by the working qualities of the clay. A small pat is made on a square of glass which has been previously weighed. The pat is dried at room temperature for several days and then for one day in an air oven at 105 to 110°C. It is removed from the oven and allowed to cool in a desiccator. The loss in weight is calculated to per cent on the basis of the dry weight. Clay of the same con-

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[13] I am indebted to Prof. A. V. Bleininger, of Ohio State University, for a number of suggestions, which have proved helpful in carrying out the physical tests.

sistency is used in making the other tests described here, and the method of drying is the same.

Drying shrinkage.—The clay is molded in the form of a bar 2.5 by 2.5 by 15 centimeters. Two parallel scratches, one near each end, are made with a pair of dividers. The distance between them is measured and recorded. After the bar has been dried, the distance is again measured and the shrinkage calculated on the basis of the dry weight.[14]

Slaking time.—A 2.5-centimeter cube is molded and dried; it is placed in a small wire basket and immersed in water. The time required for complete disintegration is recorded as the slaking time.

Tensile strength.—In making the tensile-strength determinations the Fox method[15] was followed, in general. The clay is mixed with water and is allowed to stand for a day or two. It is then rolled out in the form of a thick slab and cut into briquettes with a cutter similar to a biscuit cutter. The clay is forced into the molds and pressed into shape, and the excess is removed by a spatula. After drying for several days at room temperature, the briquettes are thoroughly dried in an air oven and then kept in a desiccator until broken. The width and thickness of each briquette at the narrowest point is measured before breaking and the results are calculated to tensile strength per unit area.

The physical tests on the raw clays are given in Table III.

TABLE III.—*Tests of clays in raw state.*

No. and source of sample.	Water of plasticity.[a]	Linear drying shrinkage.[a]	Slaking time.	Tensile strength.		Drying qualities at room temperature.
				Kilos per square centimeter.[b]	Pounds per square inch.	
	Per cent.	*Per cent.*	*Minutes.*			
1. Mabolo, Cebu	23.26	3.75	34	24.2	345	Very good.
2. Pasig River	45.96	10.87	62	12.2	176	Good.
3. Laguna Province	59.00	14.29	3	nil		Poor.
4. Masbate	59.97	9.09	65	nil		Do.
5. Mindoro	36.91	11.11	8	nil		Good.
6. Camansi, Cebu	30.96	10.05	13	21.7	308	Do.
7. Jaro River, Iloilo	37.46	13.21	6	5.8	83	Poor.
8. Pampanga	27.87	10.09	25	31.3	447	Good.
9. Abra subprovince	38.96	10.09	36	10.8	156	Do.

[a] Calculated to the basis of the dry weight. [b] Average of six briquettes.

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[14] See *Bull. Oklahoma Geol. Surv.* (1911), No. 7, 37.

[15] See *Bull. Ill. State Geol. Surv.* (1908), No. 9, 163.

Burning tests.—The change in porosity of clays with increasing heat treatment is an important factor in determining their value for paving-brick manufacture. This test is considered by many to be the best that has been so far devised. The test in this laboratory is, in general, carried out according to the method used by Purdy.[16] A number of small bricks, 2.5 by 2.5 by 5 centimeters, are molded and thoroughly dried. They are then placed in a kiln in a row parallel with a row of Seger cones.[17] As each cone fuses, the corresponding brick is removed from the kiln, allowed to cool slowly, and then marked with the number of the cone. The heating is usually continued until the fusing point of the clay is reached or the specimens begin to crack badly. The burning tests described here were made in a small gasoline muffle kiln.

The test bricks are weighed and placed on end in distilled water, with the upper surface exposed to facilitate the escape of air. After remaining overnight, they are boiled in water under reduced pressure for about six hours. They are then removed from the water and reweighed. The suspended weight is taken by weighing each specimen while suspended in water. From these data the porosity may be calculated.[18]

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[16] *Bull. Ill. State Geol. Surv.* (1908), No. 9, 141.

[17] It is customary to give temperatures in terms of Seger cones, although it is well known that the fusing points of these cones depend to some extent on the rate of applying heat and on various other kiln conditions. [See, for instance, The melting points of pyrometric cones under various conditions, Geijsbeek, S., *Trans. Am. Cer. Soc.* (1912), 14, 849.] However, since the cones and the test piece are subjected to the same heat treatment, they are in general use in ceramic processes. The approximate fusing points of the cones employed in this work are here given:

Cone No.	Temperature, °C.	Cone No.	Temperature, °C.	Cone No.	Temperature, °C.	Cone No.	Temperature, °C.
010	950	03	1090	5	1230	12	1370
09	970	02	1110	6	1250	13	1390
08	990	01	1130	7	1270	14	1410
07	1010	1	1150	8	1290	15	1430
06	1030	2	1170	9	1310		
05	1050	3	1190	10	1330		
04	1070	4	1210	11	1350		

[18] Percentage porosity $= \frac{W-D}{W-S} \times 100.$

Where, W=wet weight, D=dry weight, S=suspended weight.

TABLE IV.—*Porosity of clays at various cones.*[a]

[Numbers give percentages.]

Clay No.	Porosity at cone No.—										
	010.	09.	08.	07.	06.	05.	04.	03.	02.	01.	1.
1	35.04	-------	36.20	-------	35.84	-------	35.36	-------	27.85	-------	29.02
2	36.37	-------	35.88	-------	32.67	-------	31.25	-------	31.56	-------	28.41
5	-------	21.25	-------	19.49	-------	18.89	-------	20.76	-------	19.10	18.32
9	-------	36.15	-------	35.92	-------	34.22	-------	29.33	-------	28.41	-------

Clay No.	Porosity at cone No.—									
	2.	3.	4.	5.	6.	7.	8.	9.	11.	13.
1	-------	-------	3.13	-------	-------	10.96	-------	18.24	15.22[b]	-------
2	-------	-------	10.91	-------	-------	17.71	-------	([c])	-------	-------
5	-------	17.72	-------	13.77	-------	([d])	-------	([e])	-------	-------
9	28.21	-------	27.68	-------	27.11	-------	26.75	24.41	1.97	8.97

[a] Clays not given here did not show burning qualities suitable for these data.

[b] Specimen very soft at cone 11.

[c] Commences to soften at cone 7; fuses at cone 9.

[d] Cracks to pieces at cone 7.

[e] Commences to vitrify at cone 9.

DISCUSSION OF RESULTS OF PHYSICAL TESTS

The behavior of the clays in all the tests except porosity is as follows. All comments are based on the behavior of the small test bricks and pats. It is planned to carry on tests on full-size bricks made from all clays which show any promise as paving-brick material.

No. 1. This clay is one of the most favorable of those which have been tested in this laboratory. It is easily molded and dries without cracking or excessive shrinkage or distortion. When placed in the kiln, all of the specimens from cone 010 to cone 11 are in good condition. It commences to vitrify at about cone 4 and does not begin to soften until cone 11 is reached. Two test bricks burned at cone 4 showed a crushing strength of 880 kilograms per square centimeter. The clay burns to a medium dark red up to the point of vitrification and then becomes a dark brown. The raw clay briquettes show a strength of 24.2 kilograms per square centimeter.

No. 2. This material should produce good building brick under the proper conditions of molding and firing, although higher in water of plasticity and drying shrinkage than clay 1. It dries well without cracks or distortion. The test bricks are a dark red until vitrification begins, then become almost black. It is likely that this clay would cause trouble in a large kiln, because the vitrification range is so short. It commences to vitrify at about cone 4 and is completely fused at cone 9. The tensile strength is much lower than that of clay 1 (12.2 kilograms per square centimeter).

No. 3. All the physical tests made indicate that this sample is worthless for either building or paving brick. It has a very high shrinkage, poor drying qualities, and practically no tensile strength. The test bricks crack to pieces in the kiln.

No. 4. This clay is very plastic and could not be used for any class of ceramic work unless it was mixed with some inert subtance. The test bricks crack to pieces on drying.

No. 5. The drying qualities are good. It does not crack, but warps to some extent. It has practically no tensile strength. It begins to vitrify at about cone 1, but cracks to pieces at cone 7. It seems to have none of the qualifications of a paving-brick material, but could possible be used in making building brick. Its usefulness for this purpose would depend largely upon the extent of its contamination with stone. If this contamination continues very far back from the outcrop, the labor required to purify it would probably be prohibitive for building-brick manufacture.

No. 6. Carbonates are present in sufficient quantity in this material to prohibit its use if fired above cone 03. The test bricks fired below that temperature seem satisfactory for building brick. If building brick were made of this sample and burned in a kiln heated with coal, considerable care would be necessary to avoid too high temperatures. The test bricks break up at about cone 03 on account of the evolution of carbon dioxide and fuse completely at cone 05. The tensile strength is 21.7 kilograms per square centimeter. The working and drying qualities are satisfactory. Some of the test bricks soaked in water overnight showed no signs of cracking or disintegration.

No. 7. There is some contamination of stone in this material, and its drying qualities are poor. It appears worthless for either building or paving brick. The test bricks lose shape before reaching cone 1.

No. 8. The working behavior and drying qualities of this material are good. The tensile strength of the briquettes is exceptionally high (31.3 kilograms per square centimeter). It seems satisfactory for building brick if burned at about cone 05. It has too low a fusing point for a satisfactory paving brick if worked alone. Its high tensile strength leads me to believe that it could be advantageously mixed with some inert siliceous material.

No. 9. In most respects this is one of the best clays tested. Its working and drying qualities, tensile strength, behavior in the kiln, and color are excellent. It should produce a building brick, satisfactory in color and structure. It does not begin to vitrify until about cone 9. This would be a considerable advantage in making building brick, because the temperature would not have to be so carefully controlled as with a clay having a low fusing point. Unfortunately, however, the material could not be economically used for paving brick on account of the high temperature that would be necessary in the kiln.

Temperature-porosity data.—Of the samples tested so far, only Nos. 1, 2, 5, and 9 show burning qualities suitable for plotting temperature-porosity curves. The curves for these samples are shown on fig. 1.

Only one of them (No. 1) is apparently suitable for paving brick. Nos. 2 and 5 have short vitrification ranges, and No. 9 has a vitrification temperature too high for practical purposes. Clay 1 corresponds, in general, in chemical analysis and most of the physical tests to some materials now being used for paving-brick manufacture in the United States.

TABLE V.—*Chemical analyses and some physical tests of a number of clays used in the manufacture of paving brick in the central part of the United States.*[a]

Sample No.	Moisture.	Loss on ignition.	Silica (SiO_2).	Alumina (Al_2O_3).	Ferric oxide (Fe_2O_3).	Magnesia (MgO).	Calcium oxide (CaO).	Potassium and sodium oxides (K_2O, Na_2O).	Tensile str'gth of raw clay per square centimeter.	Linear shrinkage.	Water of plasticity.
	Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Per ct.*	*Kilos.*	*Per ct.*	*Per ct.*
1	0.50	8.18	60.89	16.40	8.20	1.61	0.55	4.15	5.038	2.10	14.40
2	0.27	3.54	68.50	16.98	5.77	1.71	0.99	2.97	4.023	0.90	13.40
3	0.81	7.02	58.35	18.09	6.14	2.03	1.20	4.58	12.503	5.82	19.60
4	1.02	10.45	55.18	19.22	8.19	1.67	0.56	2.85	9.094	3.25	15.23
5	0.60	10.09	54.37	23.61	6.14	1.61	1.58	2.78	22.586	3.60	13.35
6	0.43	7.97	57.09	19.07	7.92	1.91	0.80	4.69	7.529	3.30	16.30
7	1.29	8.08	58.42	25.05	3.04	1.52	0.46	2.30	10.025	4.50	13.40
8	0.68	4.86	63.41	18.61	5.82	1.16	0.41	3.60	8.527	3.30	13.00
9	1.06	5.95	58.57	20.40	7.40	1.37	0.63	3.27	4.996	3.00	13.30
10	0.02	8.00	55.51	21.81	7.66	1.63	0.56	3.56	5.032	3.20	13.20
11	0.83	9.40	55.02	20.35	6.26	1.70	0.87	3.64	9.071	2.70	17.20
12	0.79	4.39	56.29	20.32	7.90	2.01	0.48	4.46	9.882	4.20	16.60
13	3.05	6.70	60.31	19.11	6.14	1.73	2.73	1.44	9.208	5.00	17.70
14	0.86	5.14	63.42	16.24	6.62	1.87	1.64	4.83	8.634	1.94	11.80
15	1.49	7.01	56.25	18.79	8.02	1.33	2.39	4.60	14.174	5.50	16.50
16	1.57	5.08	68.15	12.89	7.52	0.59	1.02	2.93	13.062	4.20	14.40
17	0.98	6.75	62.70	16.95	8.98	1.47	1.17	3.03	9.865	4.60	16.50
18	2.55	6.66	58.62	17.74	8.48	0.98	1.26	3.92	8.526	3.70	16.40

[a] *Bull. Ill. State Geol. Surv.* (1908), No. 9, 285, 287.

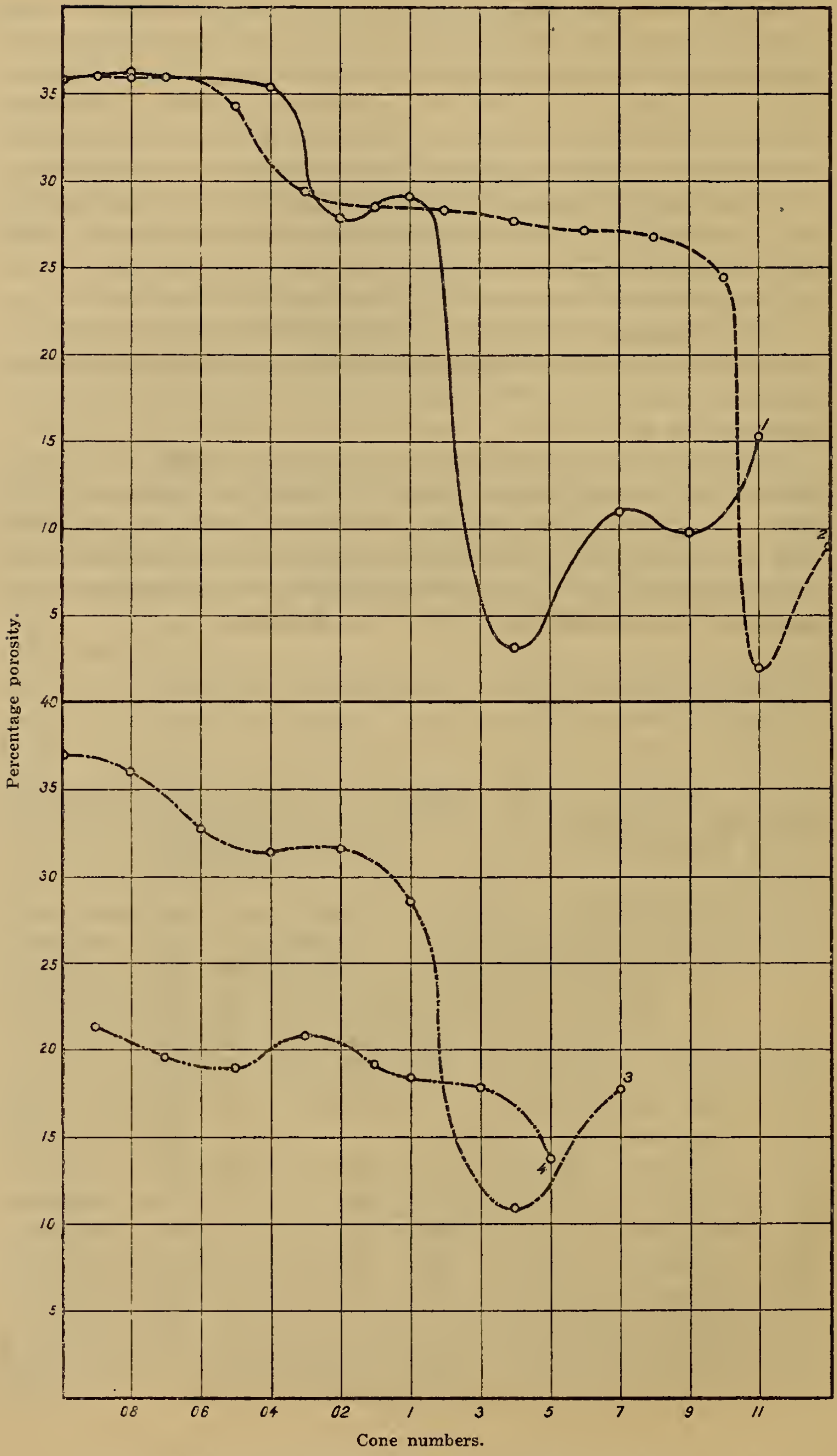

FIG. 1. Showing temperature-porosity curves for paving-brick materials. Curves 1, 2, 3, and 4 represent clays 1, 2, 5, and 9, respectively.

The geologic collection of the Bureau of Science contains many samples of clays and shales. Recently I have looked over these samples in a search for suitable paving-brick materials. The ones that show a lack of plasticity, or are too high in carbonates, have been given no further consideration. On other samples as much material as could be removed without destroying the specimens was taken and made into pats. Some idea of the working and drying qualities of the clays was obtained from these. Several of the more satisfactory pats were placed in a kiln to obtain some idea of their burning qualities. A list of the clays represented by these specimens and the locations of deposits as accurately as is known are given in Table VI. An effort will be made to obtain larger samples of the favorable materials.

TABLE VI.—*Samples of clays and shales in Bureau of Science geologic collection.*

[This includes only those which are plastic and which contain no carbonates.]

Location of deposit.		Material.	Appearance of raw-clay test pieces.	Probable value.
Town and province.	Additional information.			
Batan, Batan Island.	Entry No. 2, Bett's claim, between coal seams.	Shale	Gray	Very good.[a]
San Jose, Camarines	River north of Sabang.	do	Light brown, no strength.	
Colasi, Antique	Maralison Island	Kaolin	Gray, no strength	
Antique Province		do	do	
Los Baños, Laguna		do	White, no strength	
Angat, Bulacan	Maon Creek, pyrite veins.	Clay	Gray	Fair.[c]
Do	Mayapo	do	White, no strength	
Surigao Province	Eugenio's house	Shale	Brown	Fair.[c]
Isabela Province	Cagayan Nuevo mine	Clay	White, no strength	
Tagonton, Camarines	San Mauricio mine	Kaolin	do	
Magalang, Pampanga	San Agustin	Clay	do	
Paracale, Camarines	Trinidad mine	Kaolin	Light brown, no strength.	
Nagcarlang, Laguna		Clay	Light brown	Possible.[c]
Bucay, Abra		Kaolin	White, little strength	
Mindoro Province		Clay	Light brown, little strength.	
Batac, Ilocos Norte		do	do	
La Union Province	Cruz Mountains	Shale	Brown	Fair.[a]
Nasugbu, Batangas	East of town	Clay	White, no strength	
Matiquio, Laguna		do	Light gray, little strength.	
Alphonso, Palawan	Balabac Island	do	Reddish brown	Fair.[c]
Manito, Albay		do	Gray	Possible.[c]
Magpog, Mindoro		Kaolin	White, little strength	

[a] Vitrified below cone 7.

[b] Fused below cone 7.

[c] Did not vitrify below cone 7.

TABLE VI.—*Samples of clays and shales in Bureau of Science geologic collection*—Continued.

Location of deposit.		Material.	Appearance of raw-clay test pieces.	Probable value.
Town and province.	Additional information.			
Los Baños, Laguna	Alpha mine	Clay	White, little strength	
Santa Mesa, Rizal	Pasig River	do	Gray	Very good.[a]
Bulalacao, Mindoro	Mahohao River	Shale	Very dark gray	Very good.
Bannangan, Benguet	First hills on road to Baguio.	Clay	Light brown, little strength.	
Los Baños, Laguna		Kaolin	do	
San Remigio, Antique		Clay	Gray	Very good.[b]
Compostela, Cebu	Cotcot River	Shale	Brown	Fair.[c]
Tiwi, Albay	Tigaboc	Kaolin	White, no strength	
Bataan Province	Trail between San Jose and Mariveles; elevation, 106 meters.	Clay	Gray, little strength	
Cebu Province	Near Baliana	Shale	do	Possible.
San Fernando, Capiz, Sibuyan.	Mabolo	Kaolin	Gray, no strength	
Los Baños, Laguna		Clay	White, no strength	
Baguio, Mountain	Kelly's mine	do	Gray, little strength	Possible.
Bamaoto, Sabagan, Mountain.	Outcrop along trail	Shale	Gray, fair strength	Fair.
Placer, Surigao	Lagondola	Kaolin	White, very good strength.	

[a] Vitrified below cone 7. [b] Fused below cone 7. [c] Did not vitrify below cone 7.

BONDING QUALITIES OF PASIG CLAY

There is a large tuff quarry not far from the clay deposit on Pasig River (clay 2), and it was decided to investigate the properties of mixtures of the clay with pulverized tuff. The clay is not satisfactory for paving brick when used alone, but it seemed probable that the mixture of the two substances might be satisfactory. A large sample of the tuff was secured and ground to about 20 mesh. Some of the Pasig clay was dried and ground to the same fineness. The two were mixed in various proportions and from each mixture tensile-strength briquettes and some experimental bricks for fire test were made. Mixtures containing up to 70 per cent tuff exhibited very satisfactory working and drying qualities. The average tensile strengths of the various mixtures is shown in Table VII. All the briquettes were made in the same manner and carried through in parallel until broken.

TABLE VII.—*Bonding power of Pasig clay.*

Mix.		Tensile strength.	
Clay.	Tuff.	Kilos per square centimeter.	Pounds per square inch.
Per cent.	*Per cent.*		
100	0	12.2	176
80	20	8.0	115
70	30	9.2	132
60	40	8.3	118
50	50	10.5	149
40	60	10.5	151
30	70	10.2	147

It is surprising that the tensile strengths of all the mixtures were nearly alike. One might expect that the strength would be less with the lower percentages of clay, but the results obtained show that this is not the case. The general behavior of the various mixtures leads me to believe that most of them could be used in the manufacture of building brick; but unfortunately the results of the fire tests were such as to eliminate them from consideration as paving-brick materials. This is because the vitrification range is too short. In fact, the test pieces fused almost as soon as they commenced to vitrify. The disadvantage in making building brick from a mixture is the labor required to dry and pulverize the two materials.

SUMMARY

1. There is an urgent need, in the Philippines, for a suitable paving material for city streets. Imported materials are not generally available for this work on account of prohibitive freight rates.
2. The Bureau of Science is searching for a clay or a shale suitable for the manufacture of paving brick. Tests on nine samples have been completed.
3. The success of the undertaking depends, to a large extent, on coöperation in securing samples. If a sufficient number can be obtained, it seems likely that the right deposit may be located.

ILLUSTRATIONS

Plate I

Fig. 1. Kiln at San Pedro Macati brick factory.
2. Molding and drying room at San Pedro Macati brick factory.

TEXT FIGURE

Fig. 1. Chart, showing temperature-porosity curves for paving-brick materials.

PHILIPPINE LAKES

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ONE PLATE AND 2 TEXT FIGURES

INTRODUCTION

An incomplete list of Philippine lakes appeared in 1900,[1] and brief notes on different lakes have been recorded in various geographic and geologic studies of the Philippines, but these observations have not been assembled in collected form. The Bureau of Science recently received a request from a European geographic journal, compliance with which necessitated a compilation of the existing data with regard to lakes in the Philippine Islands. In order that the information brought together for this purpose might be made more widely available locally, it was prepared for publication in this Journal.

The origin of most of the lakes in the Philippines is closely related to volcanic and seismic activity. A number of smaller lakes occupy the craters of extinct volcanoes; others owe their existence to subsidence and differential vertical movement resultant upon volcanic activity or to the obstruction of drainage courses by lava flows and by fragmental volcanic ejecta. In the central valley of Luzon, along Cotabato and Agusan Rivers in Mindanao, and in other low-lying areas in the Archipelago, more or less permanent bodies of water are encountered which probably occupy abandoned portions of the courses of shifting rivers and low areas between the alluvial flood plains of adjacent, parallel streams.

Among the forty or more lakes which are known in the Philippines only three, namely, Laguna de Bay or Lake Bay in Luzon, Lake Bombon or Taal in Luzon, and Lake Lanao in Mindanao, stand out prominently because of their size or economic importance. On the other hand, because of the importance of fish in the diet of the average Filipino, districts in which lakes occur, even in the cases of small lakes in isolated regions, have always been better known to the people than the surrounding inland country.

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[1] El Archipiélago Filipino. Washington (1909), 2, 439.

LAKES OF LUZON

It will be convenient in description to group the lakes according to the islands upon which they occur and to take them up for discussion under these heads in the order of their importance.

LAGUNA DE BAY

The largest and most important lake on Luzon is Laguna de Bay. Lake Bay, the English equivalent for the Spanish name, has never come into general use, although the other lake names have been almost universally anglicized.[2] Laguna de Bay lies in the center of southern Luzon, immediately southeast of Manila. It is more than twice as large as any other Philippine lake, and excluding the area of Talim Island, it covers 930.7 square kilometers according to the Director of the Coast and Geodetic Survey. It is uniformly shallow, the deepest soundings recorded being 6.5 meters. The floor of the lake is level, and the immediate shores are low around most of the perimeter, but both east and west of the lake walls of tuff rise abruptly a short distance from the water's edge, and on the south the lake encroaches upon the foot of Mount Maquiling, an extinct volcano. The lake, whose surface fluctuates but seldom, rises more than 2 meters above sea level, receives drainage from numerous small streams on all sides, and is drained in turn by Pasig River, which cuts through the moderately low table-land of volcanic tuff on the west to Manila Bay. In outline Laguna de Bay is irregular; two rather slender but mountainous areas of flows, tuffs, and agglomerate—Jalajala Peninsula and Binangonan Peninsula with its southern continuation in Talim Island—protrude from the northern border dividing the northern half of the lake into three lobelike parts.

George I. Adams [3] reviews the various theories that have been advanced to explain the origin of Laguna de Bay. The early suggestions that it occupies a former crater or that it was formed through the subsidence of a volcano do not find general support. The idea that it was once an arm of the sea is generally accepted, but there is a difference of opinion as to the manner in which its impounding was accomplished. R. von Drasche [4] thought

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[2] The explanation of the persistence of the name Laguna de Bay is undoubtedly to be found in the anomaly which is involved in the term Lake Bay, because of the application of the English word "bay" to bodies of water other than lakes.

[3] *This Journal, Sec. A* (1910), 5, 103.

[4] Fragmente zu einer Geologie der Insel Luzon (Philippinen). Gerold's Sohn, Wien (1878).

that an eruption of Taal Volcano was responsible for the separation of the lake from the sea, while Becker [5] explained its isolation from the rest of the Central Plain of Luzon as the result of a slight undulation in surface. Adams [6] argues with considerable reason that the position of the lake marks a fault line which extends in a general north-south direction and that the escarpment of tuff to the west of the lake represents one face of a raised fault block which has retreated to the west through erosion. The elevation of the block on the opposite side of this fault separated the lake from Manila Bay, but was gradual enough to permit the erosion of the outlet through Pasig River.

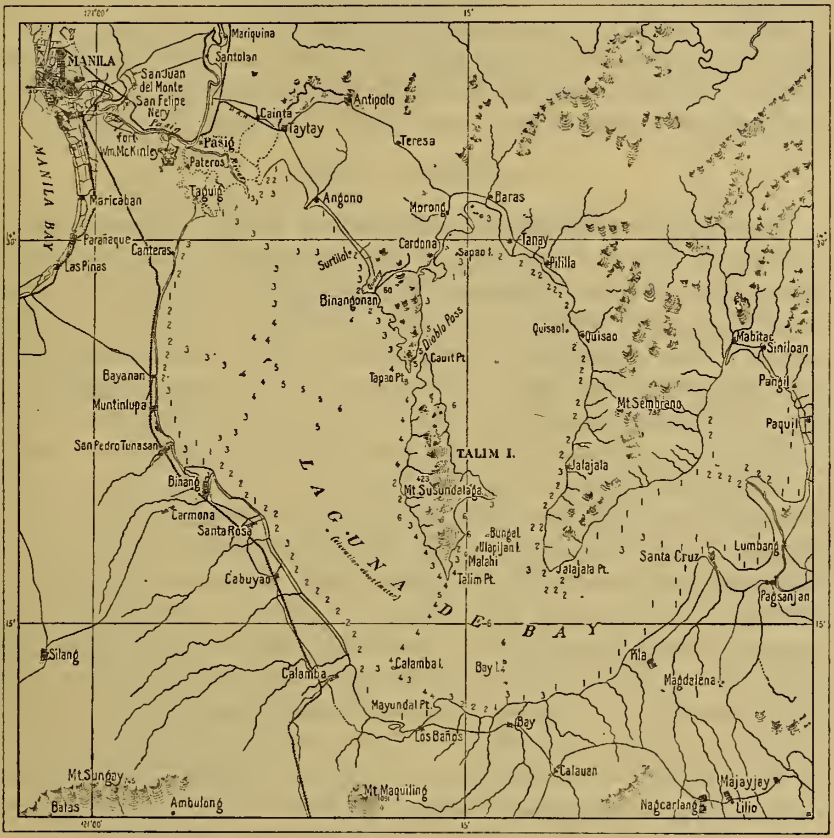

FIG. 1. Laguna de Bay, southwestern Luzon. (Depths and elevations are given in meters.)

It is said that the former town of Bay on the southern shore

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[5] Geology of the Philippine Islands, *21st Annual Rep. U. S. Geol. Surv.* (1901), reprint, 77.

[6] Op. cit., 97.

of the lake occupied a position which is now submerged, indicating subsidence in that region; likewise the lake is believed to be encroaching at the present time upon the land near Calamba on its southwest shore. To the north and northeast, on the other hand, there are considerable areas of low, flat country which were probably at one time a part of the lake floor, but have emerged through slow elevation.

Laguna de Bay is important as a waterway, and steamers ply constantly between Manila and the towns about its perimeter. It supports an extensive fishing industry, and there are rich agricultural communities on the low lands near its shores.

LAKE BOMBON OR TAAL

Taal Lake is situated in southwestern Luzon to the south of Laguna de Bay. It is roughly oval in outline, and the active volcano Taal forms an island some 25 square kilometers in area near its center; several smaller islands lie to the east of the volcano. Taal Lake has an area of 267.5 square kilometers and is comparatively deep; in its southeastern portion maximum soundings of 177 meters are recorded by the Coast and Geodetic Survey. In 1909 the surface of the lake was 2.13 meters above sea level; it varies only slightly from this mean altitude. Only small streams enter the lake, but the outlet, Pancipit River, which empties into the sea at Lemery about 8 kilometers southwest of the southern shore of the lake, has a flow of considerable volume. The land surrounding Taal Lake on the north and west slopes generally away from the lake as a center and is made up of nearly horizontal beds of water-laid volcanic tuff; walls of this material rise to an elevation of several hundred meters and closely encircle that part of the lake. On the southeast where the lake is deepest it washes the foot of Mount Macolod, an andesite peak which is 958 meters high. Elsewhere about the lake the shores rise more gradually.

Several early investigators acquiesced in the idea that Taal Lake resulted from the collapse of a volcanic cone. Becker[7] discusses this theory, but inclines to the belief that the lake was formed through an explosive eruption of a former great volcano, a gigantic predecessor of the modern Taal, rather than through collapse, the occurrence of which he considers improbable. The former existence of a volcano of great size on the site of Taal is argued by Becker and others from the presence of the abrupt walls surrounding the lake and the relatively high areas of tuff

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[7] Op. cit., 53.

to the north and west, which are taken to represent the outer slope of the old cone. Centeno calculated the height of this

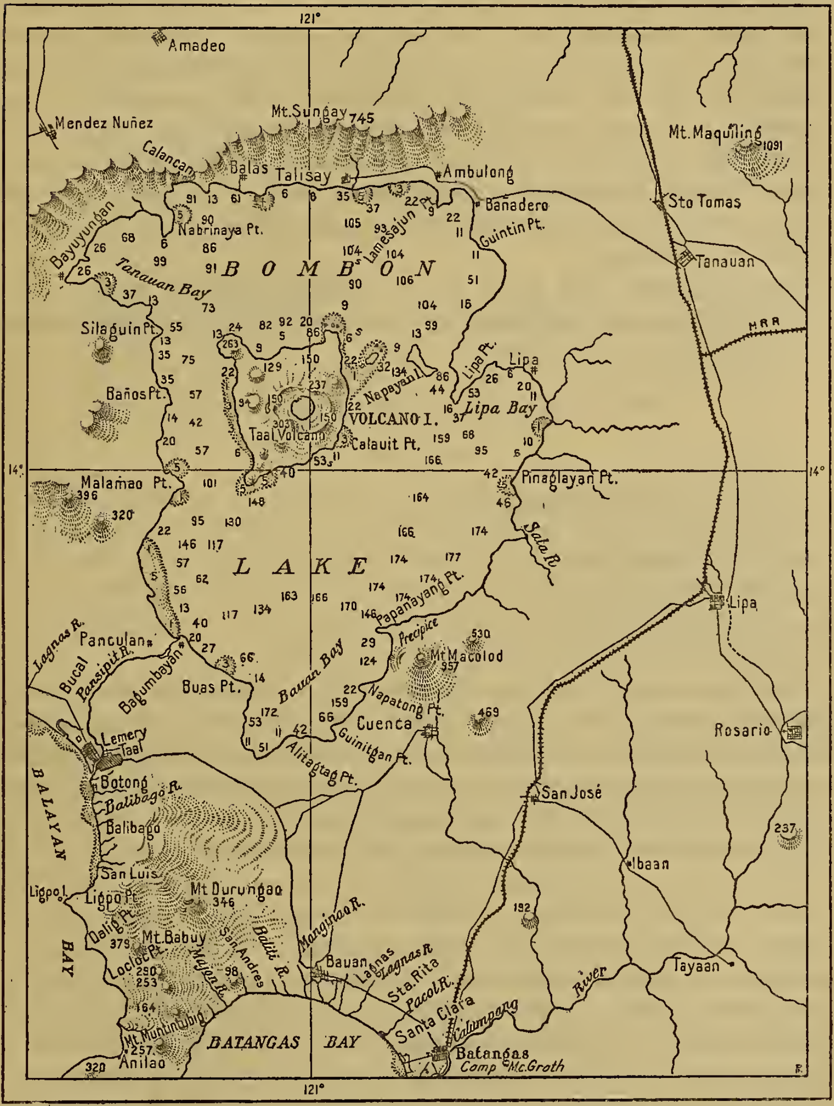

FIG. 2. Bombon, or Taal, Lake, southwestern Luzon. (Depths and elevations are given in meters.)

former volcano at 3,750 meters. Adams[8] points out that the volcanic tuff region which had been interpreted as part of the contour of the former cone is too nearly level to have been part

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[8] Op. cit., 102.

of a former cone and concludes that the elevation of the tuff could be explained more rationally as part of a raised fault block. Mount Macolod on the southeastern shore of the lake, which had also been considered as a part of the former volcano, Adams found to be an eruptive mass unlike the fragmental tuff on the other side of the crater and, therefore, not reasonably to be accepted as part of the old cone. He accounts for the lake as the result of peripheral faulting and subsidence around a volcanic center which contained a number of vents, as evidenced by historic eruptions in which activity manifested itself at several points in the lake.

The water in Taal Lake has a slightly brackish taste. The following analysis, published by Cox,[9] represents the composition of a sample taken in 1905:

TABLE I.—*Analysis of water from Taal Lake.*

	Parts per million.
Silica (SiO_2)	31.5
Iron (Fe) and aluminium (Al)	4.2
Calcium (Ca)	53.4
Magnesium (Mg)	49.4
Sodium (Na)	456.3
Sulphuric ions (SO_4)	191.3
Chlorine (Cl)	720.0

Volcano Island and the shores of Taal Lake formerly supported a large population of fishing and agricultural people, but since the eruption of Taal Volcano in 1911, when 1,335 people were killed, permanent habitations are not permitted on the island nor around parts of the lake perimeter.

In connection with Taal Lake the crater lake within the volcano should be mentioned. Prior to the eruption of 1911 the crater of Taal Volcano contained several small lakes of hot water, one of which was always boiling. After the eruption, however, a single lake about 1 kilometer in diameter occupied the crater. When the first descent into the crater was made following the eruption, the surface of this lake stood 70 meters below sea level,[10] but subsequently it rose until at the present time it is about at sea level. The water of this lake is hot (boiling at places) and highly mineralized as is shown by the following analysis by Cox.[11]

[9] *This Journal, Sec. A* (1911), 6, 96.

[10] Ibid. (1911), 6, 78.

[11] Loc. cit.

TABLE II.—*Analysis of water from crater of Taal Volcano.*

	Parts per million.
Silica (SiO_2)	710.8
Iron (Fe)	172.0
Aluminium (Al)	26.1
Manganese (Mn)	79.9
Calcium (Ca)	556.8
Magnesium (Mg)	909.3
Potassium (K)	237.4
Sodium (Na)	2,584.3
Lithium (Li)	none.
Sulphuric ions (SO_4)	2,732.0
Phosphoric ions (PO_4)	none.
Metaboric ions (BO_2)	small.
Arsenic ions (AsO_4)	small.
Chlorine (Cl)	6,024.3
Bromine (Br)	trace.
Iodine (I)	none.

LAKE BATO

Lake Bato, in southeastern Luzon, is a permanent body of water, roughly circular in outline, which is situated in the wide valley of Bicol River between Camarines and Albay Provinces. It is very shallow, and its surface stands only a few meters above sea level. Its area varies with the season and averages about 25 square kilometers. A great part of the surface is covered by vegetation, and the margins of the lake are low and marshy. Fish are abundant, and the lake is especially noted for the numbers of waterfowl which live in the vegetation-covered portions. It appears that Lake Bato was formed through slight elevation connected with Isarog Volcano, across the base of one slope of which the outlet of the lake, Bicol River, flows.[12]

LAKE BUHI

Lake Buhi, in the southern part of Camarines Province, is of peculiar interest because of the accounts of its origin, for this lake is alleged to have formed within historic times. It lies in mountainous country southeast of Mount Iriga, one of the several volcanic peaks which dominate the physiography of southeastern Luzon. The lake covers an area of 13 square kilometers and is irregular in outline. No soundings are recorded for Lake Buhi, but it is probably deep for its size; the surface is 75 meters above sea level.

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[12] Adams, Geo. I., and Pratt, Wallace E., *This Journal, Sec. A* (1911), 6, 457.

Lake Buhi is said to have formed during an eruption of Mount Iriga in 1641. As quoted by Jagor,[13] from Estado Geografico, the account is as follows:

> I was informed by the priests of the neighboring hamlets that the volcano (Iriga) until the commencement of the seventeenth century had been completely conical and that the lake (Buhi) did not come into existence until half the mountain fell in at the time of its great eruption. This statement I found confirmed in the pages of Estado Geografico "On the 4th day of January, 1641—a memorable day—for on that day all the known volcanoes began to erupt at the same hour—a lofty hill in Camarines inhabited by heathen fell in, and a fine lake sprang into existence upon its site. The then inhabitants of the village of Buhi migrated to the shores of the new lake, which on this account was henceforward called Lake Buhi."

A section of the otherwise nearly perfect cone of Mount Iriga, on the side next to Lake Buhi, has been removed, and great blocks and fragments that might well have been parts of the missing section are scattered across the valley below the lake. The outlet of the lake, which empties into Bicol River, flows across this fragmental material in a series of falls and rapids, and it seems probable that the stream has been obstructed by fragmental ejecta from Mount Iriga. Lake Buhi is certainly too deep, however, to have originated from the obstruction in the river. If the historic account of the origin is to be credited, there must have been at the same time a subsidence in the area now occupied by the lake.

OTHER LAKES OF LUZON

Among the lakes of Luzon that are yet to be described, those of larger area are fluctuating bodies of water which occupy swampy places and abandoned river courses in the low-lying river valleys. In the central valley of Luzon there are several lakes of this character, among which may be mentioned Candaba swamp in Pampanga Province close to the boundary with Bulacan Province; Lake Canaren in Tarlac Province near the boundary with Nueva Ecija Province; an unnamed swamp near Hagonoy, Bulacan; and another swamp near Bayombong, Pangasinan. Adams[14] accounts for Candaba swamp, which covers an area of some 50 square kilometers during flood season, as an area lying between the main channels of Pampanga and Quingua Rivers which has failed to receive sufficient sediments to build it up as rapidly as the adjacent portions of the delta region. A swampy area in Cagayan Province in northern Lu-

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[13] Reisen in den Philippinen. Wiedmann'she Buchhandlung, Berlin (1873), 109.

[14] Op. cit., 75.

zon, similar in character to the lakes of the Central Plain, is known as Lake Cagayan; it lies but little above sea level and is said to cover an area of more than 100 square kilometers.

Lake Paoay is situated in Ilocos Norte Province and is separated from the sea by a low, narrow barrier of wind- and water-borne sand. Its area, according to the Director of the Coast and Geodetic Survey, is 4.06 square kilometers and its maximum depth about 10 meters. No streams discharge into it or flow from it, and its level must be very nearly that of the adjacent sea.

A number of small crater lakes in southwestern Luzon should be mentioned to complete the list for this island. The volcanic region in which these lakes are found is marked by numerous cinder cones, and the lakes occupy the small craters around which these cones were built up. Thirteen such crater lakes are shown on Adams's reconnaissance map of southern Luzon, no one of which is more than 1 kilometer in its greatest dimension. They are most numerous immediately south of Laguna de Bay and are found as far west as the town of Nasugbu. A crater lake near the town of San Pablo has acquired a reputation locally as a point of scenic interest.

LAKES OF MINDANAO

Next to Luzon, Mindanao is of most importance in a study of Philippine lakes. Smith[15] enumerated thirteen lakes in his study of the physiography of Mindanao, and it appears that his list was not complete.

LAKE LANAO

Lake Lanao, in the Lanao upland region of central western Mindanao, is the second large lake in the Philippines and is the only large body of water at any considerable elevation. According to the Director of the Coast and Geodetic Survey Lake Lanao has an area of approximately 347 square kilometers and its surface is 700.4 meters above sea level. Its outline is irregular, but is slightly elongated from northeast to southwest. Soundings made in 1904 by engineers of the United States Army in the southeastern portion of the lake revealed a depth ranging from 78 to 112 meters; several harbors are utilized in the lake shipping, and depths of 2.7 to 4.6 meters are recorded for the water alongside. No soundings have been made in the center of the lake. The lake is drained by a single stream, Agus

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[15] *This Journal, Sec. A* (1910), 5, 356.

River, which flows north into Iligan Bay over a distance of 24 kilometers. Agus River is swift-flowing and forms an important cascade in Maria Christina Falls, where the water makes an uninterrrupted plunge through a vertical distance of 58 meters. No large stream flows into the lake.

Lake Lanao is a center of Moro population. Two American military posts are located on its shores, and there is considerable traffic across it. The Spanish Government maintained a small gunboat on Lake Lanao as a part of the military operations against the Moros.

Smith [16] believes that Lake Lanao was formed by the damming of a basin between two mountain ranges, by flows of lava, and by accumulations of wash. The lake shores rise abruptly on the south, but on the north there is only a gentle upward slope for some distance from the water's edge, followed by an abrupt drop of 50 meters or more to the north, making a terrace which Smith designated as the Keithley escarpment.

LAKE MAINIT

Lake Mainit, on Surigao Peninsula in northern Mindanao, is a fresh-water lake, roughly circular in outline, that covers an area of about 75 square kilometers. Montano estimated that its surface stood 40 meters above sea level; and Father Francisco de P. Sanchez, a Jesuit missionary who visited Lake Mainit in 1889, found its greatest depth to be 150 meters. The surrounding country is mountainous. The outlet, Tubay River, reaches Butuan Bay only after a long detour to the south.

Lake Mainit has been considered as a crater lake by some observers, and thermal springs occur around part of its perimeter, especially near the village of Mainit on its northern shore. Smith states that possibly it is a caldera. However, limestone is found on the eastern shore, a fact which would make it seem improbable that the lake occupies a former crater. Maurice Goodman crossed Lake Mainit during reconnaissance in Mindanao and it did not appear to him to be a crater lake, although he thinks it probable that volcanic activity may be responsible for its existence.

I visited Lake Mainit in March, 1915. It is a beautiful body of water surrounded by mountains, except on the northern side, where there is a wide border of rich, low-lying, agricultural land. The records of the Jesuit fathers show that the lake rose approximately 4 meters in 1891 and flooded some of the villages on its

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[16] Op. cit., 353.

northern shore. It is said to be subjected to fierce gales at short notice, and the native boatmen are wary about venturing upon it at certain seasons of the year. Fish are especially numerous in Lake Mainit, and immense colonies of wild ducks and other waterfowl make their home on its water. Crocodiles, also, are said to be especially numerous in this lake.

OTHER LAKES OF MINDANAO

The only other lakes in Mindanao that are of the same order of magnitude as Lake Mainit are swampy areas in the valleys of the larger rivers. In the valley of Mindanao River, inland from Cotabato, are three such bodies of water—Liguasan marsh, Libungan marsh, and Lake Butuan. Liguasan marsh covers an area of more than 100 square kilometers generally, but is subject to overflow during the rainy season; Libungan marsh is somewhat smaller. Lake Butuan covers an area of approximately 59 square kilometers and is from 3 to 6.4 meters deep, according to the Director of Coast and Geodetic Survey. These bodies of water are only slightly above sea level, and their surfaces are largely covered by aquatic vegetation. Smith[17] considers them to be remnants of a larger lake which formerly covered the intervening low country.

Lakes Dagum, Dinagat, and Linao and other adjacent smaller lakes occupy a swampy area in the upper valley of Agusan River in northeastern Mindanao. During flood periods these lakes become one body of water—always shallow (30 meters, maximum depth), but several hundred square kilometers in area. Their level is very little above that of the sea. They are said to have formed within historic times from subsidence or differential elevation following earthquakes. Such an origin is possible, since earthquakes are especially frequent and severe in Agusan Valley, but it is worthy of note in this connection that a large lake, Laguna de Mindanao, is shown on the upper Agusan on a map published as early as 1734.

Lake Leonard Wood lies north of Dumanquilas Bay in Zamboanga district at an elevation of 889 meters. The existence of this lake was first reported to the American administration by Captain C. C. Smith, Fourteenth Cavalry, United States Army, who explored it in 1904 in the course of an expedition from Misamis to Dumanquilas Bay. It is said to be like the figure eight in outline and 3 by 8 kilometers in maximum dimensions; its area is probably 20 square kilometers.

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[17] Op. cit., 356.

An unnamed lake about equal in size to Lake Leonard Wood is shown upon several maps of Mindanao near the head of Tagun River in Davao district, east-central Mindanao. The surrounding country is unexplored, and no details concerning the lake are available.

Lakes Munay, Dapao, and Nonugan are small bodies of water in the vicinity of Lake Lanao. Lake Munay has an area of 1 square kilometer and lies at an elevation of 700 meters; Lake Dapao has an area of 2 square kilometers and is 628 meters above sea level; Lake Nonugan has an area of 1 square kilometer and is 768 meters above sea level. According to Smith these lakes occupy local depressions on the surface of the basalt flows which cover the region in which they are found.

Smith observed two lakes, Malanao and Balut, near Cotabato and another, Lake Butig, in southeastern Davao, each of which seemed to him to occupy structural valleys, or synclines, in the locally folded sedimentary rocks. While these lakes are small and unimportant, they are worthy of note because of the unique origin ascribed to them. Nowhere else in the Philippines have lakes resulted from the folding of the bedded rocks.

A small lake called Majubdam was encountered by Father Sanchez on the slopes of Mount Maniayao above and to the north of Lake Mainit; its area is 0.1 square kilometer.

LAKES OF MINDORO

Lake Naujan, near the northeastern coast of Mindoro, is the only known lake on this incompletely explored island. Lake Naujan covers an area of about 70 square kilometers; in outline it is elongated from north to south, its surface dimensions being 7 by 14 kilometers. The Director of the Coast and Geodetic Survey estimates its elevation as 20 meters above sea level and its greatest depth as 15 meters. The outlet is to the north through Lumangbayan River. No large stream flows into the lake.

Lake Naujan is probably related in its origin to volcanic activity, although it does not appear to be a crater lake. The eastern shore is precipitous, but to the west the land rises gradually through vegetation-covered shallow water and swamps. The outlet has cut a fairly deep valley around the base of a hill which is probably of volcanic origin. Mr. A. L. Day, who spent a season on Lake Naujan collecting zoölogical specimens, found a number of hot springs and other evidences of solfatarism on its eastern margin.

LAKES OF NEGROS

In the mountains of the central part of southern Negros, west of the town of Dumaguete, are two lakes, the larger of which is called Lake Balinsasayao. These lakes lie side by side, and each is elongated in a north-south direction. Lake Balinsasayao covers an area of approximately 4 square kilometers, and the smaller lake is perhaps one half as large. Professor T. T. Crooks, of Siliman Institute, Dumaguete, has visited Lake Balinsasayao several times. He estimates its elevation at from 1,300 to 1,600 meters, and soundings taken by him reveal a maximum depth of 134 meters. The surrounding hills rise abruptly from the water's edge. The lake is well stocked with fish, and Professor Crooks recommends it as a pleasant, cool resort during the period from March to June.

LAKES OF LEYTE

There are several small lakes on Leyte Island, but there is little definite information concerning them. Lake Bito, near the eastern coast of central Leyte, is an expanded portion of Bito River. Its area is 1.2 square kilometers, and its surface is 3 meters above high tide according to the Coast and Geodetic Survey. Jagor found its greatest depth to be 13.3 meters. Adams [18] states that Lake Bito has generally been regarded as a crater lake, and while his own observations did not prove to him that the site was an old crater, he believes that the depth of the lake is greater than would be expected in the normal grade of the river.

Lake Danao is in the central portion of Leyte, 12 kilometers northeast of the town of Ormoc. Its area is the same as that of Lake Bito—1.2 square kilometers; it is at an elevation of about 500 meters and is elongated in form, lying between mountains. The outlet of Lake Danao flows into a smaller lake farther east, called Amandiuing. Lake Lunay, still smaller, is shown on older maps to the west of Lake Danao. Two small lakes lie to the south of Burauen in central Leyte. The water of one of these, Malaksan (sour), is acid and occupies part of a solfatara from which sulphur has been taken. Lake Jaruanan, the water of which is fresh, is a short distance south of, and somewhat larger than, Lake Malaksan.

Jagor states that Lake Jaruanan is 668 meters long, 330 meters

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[18] Op. cit., 340.

wide, and 21.7 meters deep. The greatest depth is near the southern shore, which is steeper than the northern shore. Maurice Goodman visited these two lakes while examining sulphur deposits in Leyte and found Lake Malaksan to be at an elevation of 375 meters and Lake Jaruanan, which he calls Lake Pangi, at an elevation of 350 meters.

LAKES OF SAMAR

Samar Island is very low lying for so extended an area, but while parts of the island are said to be swampy, lakes appear to be neither very numerous nor important. The island is not well explored, however, and inland bodies of water may well have escaped notice.

Lake Calbiga is the only lake shown on most maps of Samar. It lies a little south of the central portion of the island, covers an area of about 10 square kilometers, and drains to the west through Calbiga River. The lake is said to have the form of a caldera with high, steep shores and to be of unusual scenic interest.

Three other lakes, namely, Sompotoc, Ganoy, and Sampinit, are credited to Samar by El Archipíelago Filipino, but no information is given concerning their location or size.

LAKES OF PALAWAN

A single, small lake is recorded for Palawan by Randall A. Rowley, assistant professor of geology, University of the Philippines. This lake, known to the Filipinos by the name Mañ̃guao, lies a few kilometers inland from the town of Taytay on the east coast of northern Palawan. It is elongated in an east-west direction, is irregular in outline, and covers an area of approximately 5 square kilometers. Soundings taken at a time when the water stood 1 meter below high-water mark revealed a uniform depth of 6 meters. The lake drains to the southeast, the water escaping through the openings in a wall of vesicular or cellular basalt.

LAKES ON SMALL ISLANDS

There are a number of other small lakes distributed over the less important islands. On Pacijan Island, southwest of Leyte, there is a lake or swampy area 5 square kilometers in extent lying at, or slightly above, sea level. Its water is brackish and is probably contaminated with sea water. The small island Cagayan de Sulu contains three small lakes: Sapa, near the center of the island, with an area of 0.25 square kilometer, and Singuan and Ernestine, near the southern coast, with areas of 1 square kilometer each. The last-named lakes are circular in outline and might be supposed to occupy old craters. A third circular body of water, Jinata, has a restricted opening to the sea and is thus in reality a bay, although apparently related in origin to lakes Singuan and Ernestine. On Jolo Island are two lakes, Crater Lake and Siit Lake, each with an area of 1 square kilometer.

ILLUSTRATIONS

PLATE I

Part of Laguna de Bay, showing rice fields near the shore and the escarpment of tuff to the west.

TEXT FIGURES

FIG. 1. Map of Laguna de Bay, southwestern Luzon.
2. Map of Bombon, or Taal, Lake, southwestern Luzon.

Fig. 1. Kiln at San Pedro Macati brick factory.

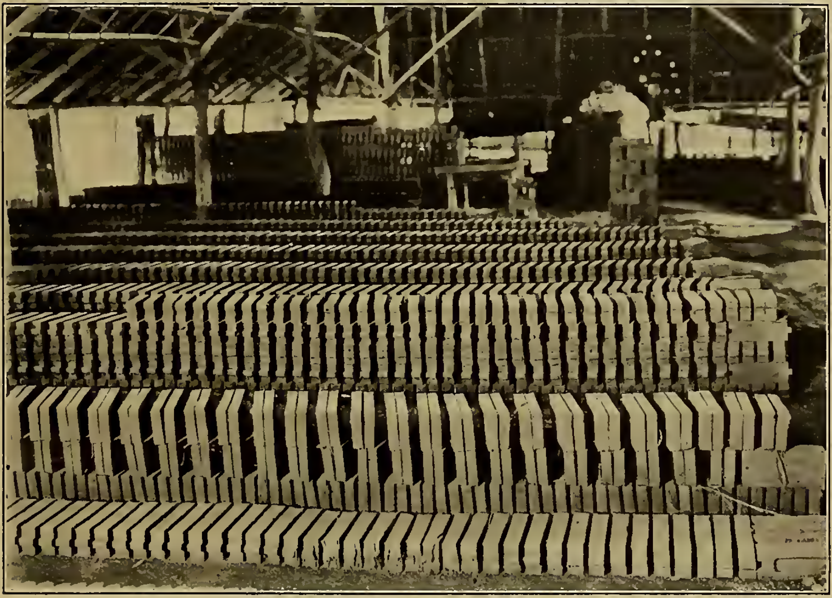

Fig. 2. Molding and drying room at San Pedro Macati brick factory.

PLATE I.

PLATE I. PART OF LAGUNA DE BAY, SHOWING RICE FIELDS NEAR THE SHORE AND THE ESCARPMENT OF TUFF TO THE WEST.

THE PALIDAN–SLIDE MINE

By V. E. LEDNICKY

(*From the Division of Mines, Bureau of Science, Manila, P. I.*)

In this day of scientific and economical mining a small mine is usually of little interest to the general public unless it has some unique or unusual features. The Palidan-slide mine is such a one. While actual mining in it is limited to small veins and shallow holes, it is unusual enough to be of interest to mining men or chance visitors who have the opportunity of seeing it.

In nearly all Spanish colonies are found remains of mining operations which distinctly bear the mark of the early settlers, but it is very seldom that a place is found where the Spaniards have allowed the use of old Indian methods without effecting changes. One of these places is in the mountainous regions of the Philippine Islands where the methods at present employed are known to have been used for at least five generations by the natives. The Spanish crown possessed the Islands for several hundred years, but it was not until 1850 that the first exploring expedition went into the land of the wild peoples "of a savage and ferocious character" to examine the wondrous copper deposits of the mountain region. A complete narrative of the trip has been translated by H. D. McCaskey[1] and is included in the description of the Mancayan-Suyoc region. No mention was made at that time of the gold workings by the Igorots, although gold ornaments and amulets were reported as being worn by the savages. Owing to the inaccessibility of the mines and the supposed danger from the inhabitants, the Spaniards stayed away from the northern mining district until 1865. As they were mainly interested at the time in the Mancayan copper, they ignored the gold mines, and the first reports of their entering Suyoc came some years later.

HISTORY

A brief history of the Palidan working was obtained through Mr. Charles Ambas, of Suyoc, who interrogated the natives. No definite dates were obtainable, as the Igorots divide their time vaguely into generations.

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[1] A preliminary reconnoissance of the Mancayan-Suyoc mineral region, *Bull. P. I. Min. Bur.* (1905), No. 4, 15–19.

The Suyoc Igorots have been miners for hundreds of years, and their old mine workings can be found in almost every part of the Suyoc district. There are workings all around the Palidan slide, but none is as large, although some of the veins mined before look more promising than the Palidan vein.

The Palidan vein was worked by at least four generations of Igorots before the coming of the Spaniards. It is possible that it was worked for a longer period, but the names of only four chiefs are remembered. They were Alaban, Gislang, Wasawas, and Witawit. The last, Witawit, was alive when the first Spanish military governor was put in charge of the district.

According to the history of the inhabitants, the first *comandante* attempted to take possession of the mine as soon as he saw it was valuable, but the Igorots objected. The case was finally taken to the governor-general, who ruled that owing to their long possession of the ground the Igorots were rightful owners and could not be removed. The comandante accordingly gave up his attempts to take possession and allowed the natives to work, but contrived to buy their gold at 10 pesos [2] per Mexican peso's weight (27.07 grams) of gold, a very profitable procedure which continued until the insurrection of 1895. The insurrectos took forcible possession of the property and compelled the Igorots to work throughout the season of that year. No record was kept of the gold extracted for the insurrectos, but it is probable that the amount was small.

After the American occupation the former Spanish comandante tried to obtain possession of the ground under the concession law, but his claim was disallowed. Meanwhile the Igorots continued working the ground.

In 1903, upon request of the leading Igorots, Mr. C. E. Petit staked out the ground under the American mining law for six Igorots and himself. The Igorots who signed the location notice were Congosan, Pig, Bayongosan, Madanis, Abalos, and Pagian. All of these are still working the ground with the exception of Pagian, who is now a prisoner in Hongkong.

The location of the property by the six Igorots and one American has not changed the local mining custom. The whole village still continues to regard the ground as common property and to work it as such. The real owners apparently have no more

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[2] One Mexican peso equaled about 40 cents United States currency. One peso Philippine currency equals 100 centavos, equals 50 cents United States currency.

right on the ground than any other inhabitant. It thus happens that the American partner has not realized anything from the ground, but this year he has leased his share for 15 ounces (466.5 grams) of gold, paid by contribution from all the workers. This custom of common ownership is peculiar in that only those Igorots from Suyoc or their relatives who are descendants of the old miners may work in the mine. There are many cases in which men or women living in Suyoc are not allowed to work with the rest. Some of them are married into families that work, but they themselves must stay out.

The Palidan slide is situated in the southwest corner of Lepanto subprovince, latitude 16° 50′ north, longitude 120° 55′ east, about 102 kilometers north from Baguio, within 1 kilometer of the Bontoc mountain road. It is an immense cavity, washed out around the Palidan and Cadangan ravines, approximately the shape of an inverted elliptical cone whose major axis bears north 60° east. The opening is approximately 620 meters long by 430 meters wide, and the vertex, or deepest point, is very close to the central edge of the northwest quarter of the ellipse at the point where the Candagan and Palidan ravines unite. This point is about 200 meters below the average rim of the slide. The sides dip very steeply from all directions, but in general the slope from the east is more gentle than that from the south or west. This is due, of course, to the greater distance from the outlet. At places the angle of dip is 80° from the horizontal, and in no place in the solid formation is it less than 20°.

The cavity is continually being enlarged by the heavy tropical rainfall, which washes away the soft material very rapidly. The Igorots aid nature in performing this work, as they make excavations in the sides and divert channels of water in order to wash off the surface material and to expose the rich stringers of gold ore.

The geologic formation of the slide is difficult to determine exactly. The lower part is composed of the solid dioritic base, which is found underlying all of the region.[3] The diorite shows rapid weathering on exposure, but is firm enough to form steep walls for the swift-flowing streams which cut through it. The rock of the upper portion seems to be the same diorite, very badly decomposed. It is so much altered that it is impossible to make any excepting megascopic examinations. It is porous

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[3] *Bull. P. I. Min. Bur.* (1905), No. 4, 37.

and is very highly impregnated with iron sulphides. The surface exposed to the air decomposes very rapidly and allows of excessive erosion.

The upper rock has been very heavily silicified in altering, and masses of a quartzose material are common. It shows a great network of little veinlets or stringers of quartz which are the results of a secondary infiltration into cracks and crevices, suggesting dehydration of a large mass rather than dynamic causes. These little veinlets of stringers are usually an indication of gold values.

Wherever the veins are wider, they present a banded structure of quartz and a bluish white kaolin known by the natives as "pitoc." A fibrous variety of gypsum, white in color and with a shiny luster, and fibers that are usually curved and transverse to the veins alternate at times with the kaolin. It is an indication of rich gold values and is very closely observed by the Igorots. Several kilograms of gold are said to have been removed from a single pocket in the gypsum.

Exposed in the slide are several rather prominent veins, which have been worked for gold by the Igorots. The most prominent of these, the Palidan and Cadangan veins, have produced the greatest amount of gold within the past few seasons. The gold occurs free in the ore in rather fine particles. The ore is very similar in color to the iron sulphide and is distinguished with difficulty by any one not well acquainted with it. The natives who have been handling the ore since childhood recognize the free gold at a glance, the rapidity with which they judge a piece of ore being almost unbelievable.

The mining season at Palidan lasts from one to six months, and from 40,000 to 80,000 pesos' worth of gold is recovered from the ground in that time. The miners start work immediately after one rainy season and continue until the next, when the ground becomes subject to slides and consequently dangerous. About two hundred men, women, and children are actively employed in the work. Of these, the majority are women, the rest are children, and a small number are men.

The method of working is that used in other countries known as "booming." In the smaller veins and in the beginning of the Palidan slide, dams have been built across gullies to form reservoirs, which are allowed to fill either with rain water or water from a small creek. As soon as the reservoir is full, the gate is opened and the flood of water is allowed to tear away the overburden from the vein. Between washings the native workmen place timbers or make such excavation as they consider necessary for more rapid cutting. The dams are usually built of sod, laid flat and reënforced with poles driven into the ground on either side.

The gate is unique and very efficient. It consists of a rough wooden frame several meters long and about half a meter wide set upright into the sod dam and luted into place with a very plastic clay. To the inside of the uprights and bottom of the frame are nailed strips, or cleats, against which the door is pressed by the force of the water.

The door itself is a thick, hewn pine board which fits loosely in the large frame. Its edges are beveled at an angle of about 60° to its face. The upper part of the door is tied to the top of the frame by a piece of bejuco to prevent its being carried away when the door is opened. To operate the reservoir, the door is placed in position with the wider face pressing against the cleats. With a pointed stick a long, water-soaked rope is forced around into the wedgelike crack left between the frame and the door. This seals the opening so effectually that scarcely a drop of water escapes. The pressure of the water tends to tighten the packing, and there is little danger of its coming out unexpectedly.

To open the gate against water pressure, the operator simply pulls out the rope packing and pries against the top of the board with a stick. The water pressure does the rest. It takes less than one minute to replace the gate after the water has run out.

In the Palidan slide the working has become so large and is so favorably situated that the rains of the wet season do most of the work necessary in washing off the overburden. As soon as the rainy season is safely over, the natives go into the slide and examine it for veins. Of late years they have worked on one vein about 2 meters wide with an enriched stringer not over 0.5 meter in width. They start in wherever this vein happens to be exposed most advantageously. In most places the vein is comparatively soft and can be worked out from the surface with hand bars. The latter are usually old drill steel obtained from Americans or mild-steel reënforcing rods which have been obtained from Chinese traders. The bit is sharpened into chisel shape about 6 millimeters wide, or else it is pointed like a gad. For greater convenience, and in order to make possible the utilization of short pieces of steel, the bar is inserted into a handle, a piece of pine with a knot on the end into which a socket for the bar is burned.

When rocks too hard for hand spuds are encountered, and when powder is not available, fire and water are used. This method is very efficient though slow. As the working is deepened, stulls are put in which achieve the double purpose of holding up the hanging wall and of serving as perches for the women ore sorters. The stulls are of pine, about 20 centimeters in diameter with regular head boards and wedges. They are furnished and put in by the men, this being the only work in which women do not seem to take a leading part.

In order to accommodate the one hundred fifty to two hundred persons, and for convenience in handling ore, the exposed vein is divided into sections which are worked by different sets of individuals. Each set has its preferred right in the section to which it is assigned and conducts mining operations to suit itself. This procedure allows for a diversity of opinions and leads to better mining. In each open stope the actual mining is done by a few men and women who wield the spuds, and who, of course, have first pick at any rich pockets of ore. They take turns at the face, so that all have an equal chance. Immediately back of the miners are the women and children. The hats the women wear serve a double purpose—as a protection against falling rocks and as ore baskets. They are made of bejuco and bamboo, with small, square bottoms and wide, flaring sides. They vary in width from 30 to 40 centimeters and are about 12 centimeters deep. The women and children catch the ore in their baskets as soon as it is broken down. They examine it once by the dim pitch-pine light, and if it is extra good, they cover it with another basket and send it to their relatives on the surface, who inspect and sort it more carefully. If it is nothing out of the ordinary, they pass it back to the woman next in line, who examines it and passes it back, this procedure being followed until it has been passed from hand to hand by the dozens of women packed in the stope.

What is left when it reaches the surface is given a final inspection and is dumped or saved.

The waste is thrown back into those parts of the stope which have been worked out and bulkheaded off from the rest of the stope, so that the actual open space is small and few accidents from caving take place. Since the ore is snatched away so rapidly, the miners are never in need of muckers, and as the appointed timbermen keep the stulls advancing with the face or bottom, the miner's task is an easy one. A white man could never work under the same conditions. The air inside is very stale, and the odors from the women packed in immediately back of the miners and the sooty smoke from the pine torches make it especially disagreeable. At times, when good ore is coming out, the women are so tightly jammed in the stope that it is necessary for the miner to walk out over their shoulders.

In case of an exceptional strike it is customary for the women to fight and pull each other's hair to get advantageous positions. Fortunately no one has ever been killed in one of these fights. The women and children are very expert in hand picking, and can tell almost at a glance whether or not the specimen is of value. They look for free gold after moistening the rock with their lips. Although hundreds of pieces are examined in this way almost every day, there seems to be no transmission of communicable diseases nor sickness resulting from swallowing so much earth.

The fine ore that is discarded and all the sulphide wash are concentrated and reconcentrated several times before they are allowed to escape to the river below. The concentration is carried on in shallow, oblong depressions in the hillside, about 1 meter long by 0.5 meter wide, into which a tiny stream of water is delivered by a small flume made of straight, grooved pine trees. The woman operator works the ore back and forth in the depression until all the gangue has been washed out, leaving only rich sulphides. She keeps the latter in a basket for further treatment at home.

The depressions which serve as concentrators are located on the hillside, one above the other, the one below taking the tailings from the one above and so on. The tailings are concentrated at least six times before they are turned into the river, so that the actual residual gold content is then very small.

The rich ore and the concentrates are taken home and there ground in a native mill, then panned in a bark pan, smelted, and finally sold. The crusher is a large, flat stone, usually of diorite, about 0.5 to 1.5 meters long, with a depression hollowed out in the center. After being broken by hammering between two stones, the ore is placed in this hollow and is crushed down so fine that it would pass a sieve having 40 meshes per centimeter (100 meshes per inch). The muller, or rubstone, weights 15 to 20 kilograms and is usually of the same hard stone as the bottom.

The ore is always well mixed with water, and the rubbing is a direct pushing and pressing such as is used in washing clothes on a washboard. The fine ore is collected in an earthen pot and is then panned.

The pan is a piece of bark about ½ to ⅔ meter long by ⅓ meter wide. About 6 centimeters of the sides are bent up and held in position by two pieces across the top near the ends. These pieces also serve as handles. The action in panning is very similar to that of the belt vanner. The native places the pan with ore on it in a small tank of water whose depth is just sufficient to cover the top of the crosspieces. By grasping a crosspiece in one hand and lifting, a current of water is caused to pass over the ore and wash off the lighter material. With the other hand the operator returns the mineral to the head of the pan and again lifts. The motions are regulated to a nicety, and the separation is very cleanly made. In order to separate the gold from the rich sulphides, a slight side shake and roll are given the bark pan. When handled by a skillful manipulator, the gold seems to travel up and away from the sulphide. The tailings are carefully saved and panned over in the rainy season when mining is impossible. Some observers have reported that the natives bury the tailings and expect the gold to come back to them. This belief is easily explained by the fact that the sulphides oxidize very rapidly after being once ground and no doubt release some gold that is coated by the iron sulphide. The fine-gold pannings are melted with a small amount of lead in a wide clay crucible somewhat similar to a scorifier. The melted product is poured and is then placed in another clay dish with a covering of salt and given a chloridizing roast. When this is done properly, the gold has a very pure appearance, although in reality it is only about 700 fine. I was unable to ascertain if this chloridizing was done with the deliberate intention of deceiving the purchaser or merely to improve the appearance of the product. Since the method of buying after comparison on a touchstone has been adopted, chloridizing has become obsolete.

The Igorots have many curious superstitions in regard to mining, and very great faith is placed in their religious offerings to the "anitos," or spirits. These religious observances take the form of *cañaos*, or feasts, at which *tapuy*, a liquor made from fermented rice, is drunk and animals are killed and eaten.

If a low-grade rock is encountered in mining, it is customary to hold a cañao to improve it. If a rich pocket is struck, a stop must be made and a cañao of thanksgiving is held. Meanwhile some Igorots, not quite so superstitious as the rest, may slip down into the mine and steal the ore, leaving just enough to keep the others somewhat appeased. Whenever a theft is discovered, some one must be punished. More cañaos are necessary, and curious trials to determine the culprit are held.

The women remain continent during the mining season, and never wash their bodies so long as the vein is producing, for fear that the gold will disappear. If it thunders, the Igorots must perform a cañao, and if any cloth is burned near the mine, they will not work until the proper anito has been appeased. They burn nothing but pitch in the workings; a lighted candle taken into the mine would create much excitement.

About 60,000 pesos in gold are produced yearly out of Palidan. Most of this, or about 45,000 pesos' worth, is sold to buyers, who use the old Spanish custom of buying by the old Mexican peso weight (28.34 grams). Ordinarily about 20 to 30 pesos are paid per peso weight of gold. By taking advantage of natives who are forced to sell in order to give cañaos, unscrupulous buyers are able to get a large fraction of the output at an even lower figure. The remainder of the gold not sold outright is made into jewelry or buried under the houses until needed.

Good miners are known to take out several hundred grams of dust in a single season. These are, of course, expected to give larger cañaos, so they remain practically as poor as the rest.

ERUPTION OF BULUSAN VOLCANO[1]

By J. P. Goldsberry
(*From the Division of Mines, Bureau of Science, Manila, P. I.*)

INTRODUCTION

The first news of the eruption of Bulusan Volcano was a telegram received January 21, 1916, by the Director of the Weather Observatory in Manila and sent by the municipal presidente of Irosin. This telegram, dated January 20, stated that Bulusan Volcano was in a state of eruption, beginning January 18 at 2 o'clock in the morning, with action continuing, accompanied by the pouring of ashes, landslides of fire, and ejection of mud and also heavy rains and strong winds.

On the day received, the Director sent a message to the presidente of that municipality requesting more detailed information in regard to seismic disturbances, the nature of the ashes, whether hot or cold and the quantity, the direction of the wind, the effect upon the vegetation close to the crater, the gases evolved, and the location of the mountain.

In answer to the requests made, the Director received on January 23 a second telegram, dated January 22, from the presidente of Irosin containing the following information:

> Cold ashes fell. Smoke issued during first forty-five minutes. Eruption continues to date, but with less ashes. Direction of ashes is southwest due to winds from the northeast. Radius of ashes from the crater is 25 to 30 kilometers. One remarkable quake occurred on the 18th at 4.00 a. m. Vegetation up to the crater is alive. The river from the volcano is heavily charged with ashes. Little fire comes out. Subterranean noises are almost continuous, but in general almost imperceptible. Thickness of ashes on the town at the close of the first day of the eruption was 0.5 centimeter. During the afternoon of January 21 there were intense waves of sulphur fumes during the first 8 hours. On January 22 from 8.00 to 9.00 a. m. great noises were heard nearly every 15 minutes. After the last noise the atmosphere about the volcano became clear and the top of the volcano was visible. The distance from the town to the crater is about 15 kilometers.

TRIP TO SORSOGON

The trip to Irosin is best made by boat to Bulan, and hence by automobile to Irosin, a distance of 21 kilometers, although there are foot trails from both Juban and Bulusan. Until recent washouts in the road, there have been four auto trucks

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[1] Received for publication March 27, 1916.

plying between Bulan and Irosin, taking in rice, fish, and other supplies, and returning with hemp and copra for Manila.

The road to Irosin follows a general northeast course, crossing first about 8 kilometers of coastal plain deposits, and then by a series of grades it winds up over the divide and down into Irosin Valley. The divide consists of a chain of andesitic and basaltic hills trending northwest-southeast and forming the western limit of what Adams and Pratt[2] have designated as the third division of the Southeastern Cordillera of Luzon.

IROSIN

Irosin, including its barrios, is said to have about 12,000 people. It is situated at the foot of Mount Bulusan and forms a semicircle around the base. Aneroid readings place its elevation at from 50 to 60 meters above sea level. Being almost surrounded by mountains, it is well protected from baguios, although during the recent rainy season (November to February) floods occurred which carried out most of the bridges and caused much damage to the roads.

Arriving in Irosin in the afternoon of the 28th, I could see no confusion, and except for a small amount of fine volcanic ash in sheltered places, there were no remnants of the eruption. As the summit of the mountain was surrounded by heavy clouds, it was not possible to tell whether or not activity had entirely ceased.

1916 ERUPTION

I obtained much of the data concerning the events of the eruption from Mr. S. B. Chestnut, district school supervisor, who was in Irosin during part of the eruption. His information was supplemented by that of two Filipino school-teachers and the municipal officers. Older residents of Irosin remember the eruptions of 1886 and 1894, but very little reliable information could be obtained.

On Tuesday, January 18, about 2 o'clock in the morning, rice planters heard a faint noise, felt a slight quake, and then noticed "smoke" issuing from the volcano which settled into the valley. Ashes began to fall. No incandescence could be seen from Irosin, but people in Mombon, a barrio about 3 kilometers northwest of Irosin, claim to have seen "fire." Most of the ashes fell shortly after the initial eruption, then a small amount fell for a period of three days. All together Irosin received about 1

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[2] Adams, G. I., and Pratt, W. E., *Phil. Journ. Sci., Sec. A* (1911), 6, 455.

centimeter and Mombon about 1.5 centimeters. An odor said to resemble "gunpowder" was detectable. Reports had come from Patag, a barrio 3.5 kilometers east of Irosin, that 0.25 meter of ash had fallen, but upon investigation the thickness of ash was located in stream eddies and had been carried down from the mountain by water and not by wind.

Wednesday, January 19, was a clear day. White clouds of steam and sulphur vapor came from the volcano, seemingly from a vent near the top. Late Tuesday night or early Wednesday morning the people claim to have felt a long-continued quake which was not violent.

No disturbance was noticed on January 20 or 21, but between 7 and 8 o'clock in the morning of January 22, loud noises were heard, followed by light and dark "smoke." A small stream of milky water, which appeared the size of an arm, could be seen pouring from the crater. These disturbances are said to have continued for a period of from three to four hours, although some claimed to have heard noises during the afternoon. After the 22d no disturbances occurred except in the minds of some, who felt earthquakes and heard noises every evening. Clouds kept the mountain hidden for the following seven days.

RECONNAISSANCE ABOUT IROSIN

The day after my arrival at Irosin (Saturday, January 29) it rained during the entire morning, but about 2 o'clock in the afternoon the weather cleared and the volcano became visible.

The mountain rises from Irosin Valley to a height of about 1,500 meters. From my viewpoint the slopes appeared symmetrical and moderately steep. The summit seemed to be truncated and serrated. Small erosion gullies could be traced down the flanks and resembled the ribs of a fan. The vegetation appeared green to the top. A small crater could be seen on the southwest side, a short distance below the top, from which rolled a small spiral of white vapor. The mist, rising in the small gullies, gave some of the people the impression that the flanks were dotted with numerous small vents. The clouds soon surrounded the mountain, obscuring the view, and more showers followed.

I had decided that the first clear day I would try to make a trip to the top of Bulusan. Sunday morning it was raining at daybreak, so I spent the day in making a trip to Mombon, a barrio about 3 kilometers to the northwest of Irosin, to see the hot springs in that vicinity, after which I returned to Irosin and hence west to the divide between Irosin Valley and the

Bulan coastal plain in order to examine and get specimens of a so-called conglomerate which is exposed on the east side of the divide. It is not a water-laid deposit but a flow breccia or a volcanic conglomerate, containing igneous pebbles and bowlders, more or less rounded, in a matrix of igneous rock. I have not studied the rock under the microscope, but macroscopically the pebbles and bowlders appear to be andesite inclosed in a matrix of scoria. The andesite being more resistant stands out in relief in the exposures of the conglomerate.

TRIP TO THE CRATER OF BULUSAN

I had planned to make an attempt to reach the top on Monday if the weather permitted. A start was made about 8 o'clock from Patag barrio. The trail up to the last house, a height of 765 meters, was good. From the last house to the cogon grass, the guide had previously brushed out a trail for Mr. Elmer, a botanist from Manila. The green vegetation stopped at 1,010 meters, and the cogon grass stopped at 1,260 meters. This cogon appeared dead, but showed no signs of sintering. On the south slope much of it was covered by sand and gravel, which had been carried down recently by water and landslides.

The crater was reached at 12.30, after four hours of almost steady climbing. The aneroid gave an altitude of 1,450 meters at the crater's rim, which is from 10 to 15 meters down on the flank; however, the atmospheric conditions were so changeable that readings were not very reliable.

On the rim of the crater is a small, irregular vent whose long dimension trends north 20° west up the slope. There are three openings: the largest, 10 by 4 meters, and two small crevices, measurable in centimeters. From all of these vents there was a steady rush of steam and sulphur dioxide (SO_2) vapor. Around the orifices there were being deposited fine crystals of sulphur. In this type of sulphur formation, which is designated as the "solfatara type," crystals of sulphur are formed from sublimation. The formation of "solfataras" was formerly thought to be due to the reaction of gases, namely, hydrogen sulphide (H_2S) and sulphur dioxide, in which water and free sulphur were formed according to the reaction

$$2H_2S+SO_2=2H_2O+3S$$

but Brun[3] has shown that this reaction cannot take place in nature.

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[3] Brun, A., *Chem. Zeitg.* (1909), No. 15, 29, quoted by Hunt, W. F., *Econ. Geol.* (1915), 10, 544.

The sulphur is probably derived from pyrite (FeS_2) contained in the igneous rock. In the loose material on the slopes which has been recently carried down by water and by landslides, there is much basalt, which is conspicuous on account of the shining crystals of pyrite which are disseminated throughout the mass. When pyrite is heated with a free access of air, it evolves sulphur dioxide and gives a residue of iron oxide (Fe_2O_3) with 2 to 3 per cent sulphur, but when heated in an incomplete supply of air or in a closed retort, it volatilizes, and upon passing into a condenser or coming in contact with a cool surface, the vapor condenses as flowers of sulphur.

When pyrite burns, a considerable amount of heat is generated which in ores containing over 35 per cent of sulphur is sufficient in the burning of pyrites in the manufacture of sulphuric acid (H_2SO_4) to maintain combustion after it is given an initial start. It is well known that the oxidation of pyrite in coal seams has generated sufficient heat to fire them. In the Panama Canal Zone, during the construction of the canal, carbonaceous shales containing pyrite were heated to the point of combustion by oxidation of pyrite, and smoke issuing from vents caused much alarm to the workmen. The heat generated by pyrite oxidation is a very plausible explanation for the local heated conditions of the rocks as exhibited by numerous hot springs and minor volcanic eruptions.

A rivulet of water, formed by condensation of water vapor, trickled from beneath a large rock resting on the rim of the crater, but disappeared in the loose sand and gravel within a few meters.

On the west rim of the crater, toward the upper end, there is an indentation in the rim about 5 meters long, which resembles a lip and has resulted by the recent pouring out of water. It is through this so-called spillway that the small stream of milky water, discernible from Irosin during the eruption, flowed from the crater.

The crater wall is made up of loose, heterogeneous material comprising volcanic ash, yellow sand, gravel, and bowlders. One large bowlder (3 meters in diameter) is balanced on the west edge of the crater awaiting future rains to wash out its infirm foundation, when it will crash down the mountain side, causing much anxiety in Irosin.

CAUSES OF THE ERUPTION

It seems very improbable that the eruption of Bulusan was the after effect of some great earth movement, because the one or possibly two shocks felt were of such small magnitude as not to be perceptible at the Gubat, Legaspi, or Manila stations. I was informed by Mr. Chestnut that there had been a small amount of steam given off for several years before the eruption, which together with the existence of numerous hot springs in that vicinity indicates conclusively that the rocks are hot. That water poured from the crater and much steam was evolved would seem to involve the fact that this rainy season was a long and exceptionally heavy one.

The explanation which appears the most plausible, and the one that takes into consideration the observed facts, is that the large amount of water from the heavy and long-continued rainy season percolated through the beds of porous strata and encountered the hot rocks, and more steam was generated than could be evolved by the old vent, with the result that an explosion took place in which the old vent was widened and volcanic ash derived from the crater walls was thrown into the air and carried a distance of about 25 kilometers by the strong southwest winds. Not having seen the crater previous to the eruption, I cannot be certain of an enlargement of the old vent, but observations substantiate the belief.

I do not believe that the ash was derived from molten lava by the explosion of inclosed gases, because one would expect to find coarser fragments of vesicular lava (bombs and lapilli) scattered on the slope.

The incandescence accompanying the eruption can very easily be explained by static electricity, the particles of ash becoming electrified by friction and discharging in the moist atmosphere.

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THE PHILIPPINE
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DATURA ALBA [1]

By HARVEY C. BRILL
(From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.)

In connection with a survey of the medicinal plants of the Philippine Islands the Bureau of Science has had occasion to examine the various portions of the plant *Datura alba* [2] for its alkaloid content and to investigate the effects of drying on its content.

Table I describes the condition of the material when examined, the methods of drying and extracting, and the results.

TABLE I.—*Description of material, methods of drying and extracting of Datura alba, and results obtained.*

Description of material.	Method of drying.	Method of determining.	Total alkaloid.[a]
			Per cent.
Mature seeds	Sundried	According to Autenrieth[b]	[c]0.405
Do	Washed in water and then dried on a board in the shade.	do	[c]0.461
Do	Partially dried in shade; finished in large flat dish in sun.	do	[c]0.504
Do	Partially dried in shade; finished on paper in sun.	do	[c]0.561
Do	Dried on gas range in 4 hours	do	0.351
Green leaves	Not dried	Modification of Autenrieth	0.375
Stems	do	do	0.440

[a] Calculated to dry weight.
[b] Autenrieth-Warren, Detection of Poisons. P. Blakiston's Son & Co., Philadelphia, Pa., 4th ed. (1915), 293.
[c] The average of several determinations.

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[1] Received for publication September, 1916.

[2] For a discussion of its occurrence and use in the Philippine Islands and references to the literature pertaining to it, see Bacon, *This Journal, Sec. A* (1906), 1, 1019.

TABLE I.—*Description of material, methods of drying and extracting of Datura alba, and results obtained*—Continued.

Description of material.	Method of drying.	Method of determining.	Total alkaloid.
			Per cent.
Flowers	Not dried	Modification of Autenrieth	0.450
Immature fruit	do	do	0.409
Pods from preceding.	do	do	0.022
Nearly mature fruit.	do	do	0.325
Mature seeds	do	do	0.537
Mature fruit	do	do	0.380
Mature pods	do	do	0.076
Green leaves	Ground and then dried at 90–100° C.	According to Autenrieth	0.243
Stems	do	do	0.183
Flowers	do	do	0.248
Immature seeds	do	do	0.248
Immature fruit	do	do	0.275
Pods from preceding.	do	do	0.081
Mature seeds	do	do	0.393
Mature fruit	do	do	0.038
Mature pods	do	do	0.327
Green leaves	Dried in steam oven. Allowed to remain for several days after becoming dry.	do	0.108
Do	do	do	0.114
Stems	do	do	0.032
Flowers	do	do	0.171
Immature fruit	do	do	0.131
Mature fruit	do	do	0.175
Mature seeds	do	do	0.266
Green leaves	do	10 grams material treated with 50 cc. H_2O and 0.5 cc. HCl and warmed on steam bath, filtered, evaporated to small bulk, and treated as in preceding.	0.069
Flowers	do	do	0.205
Immature fruit	do	do	0.160
Mature fruit	do	do	0.198
Mature seeds	do	do	0.217
Immature fruit	do	10 grams material in 50 cc. alcohol, evaporated to dryness at low temperature after being made acid, and then treated as above.	0.134
Do	do	Same as above except made alkaline with NH_4OH.	0.052
Do	do	Same, except made acid with HCl.	0.147

TABLE I.—*Description of material, methods of drying and extracting of Datura alba, and results obtained*—Continued.

Description of material.	Method of drying.	Method of determining.	Total alkaloid.
			Per cent.
Immature fruit	Dried in steam oven. Allowed to remain for several days after becoming dry.	10 grams material in 50 cc. H_2O acidified with HCl and heated, filtered, extracted with fuller's earth, and filtered.[d] Extract made alkaline and treated as preceding.	0.094
Green leaves	Dried in desiccator over KOH	According to Autenrieth	0.406
Flowers	do	do	0.489
Mature seeds	do	do	0.589
Mature pods	do	do	0.067
Green leaves	Dried in air on floor of room. Time about two weeks.	do	0.234
Stems	do	do	0.251
Immature fruit	do	do	0.262
Immature fruit. This fruit had become somewhat moldy.	do	do	0.222
Green leaves	do	By use of fuller's earth, see above.	0.210
Stems	do	do	0.208
Immature fruit	do	do	0.231

[d] Japanese fuller's earth used in this extraction and the plant material used were given to us by Mr. Dean C. Worcester. For discussion of the use of hydrous aluminium silicate in the extraction of alkaloids, see Lloyd, John Uri, *Journ. Am. Phar. Assoc.* (1916), 5, 381.

DISCUSSION OF RESULTS

The flower heads of *Datura alba* grown in China are reported[3] to contain 0.485 per cent of alkaloid calculated as hyoscine. A. R. K. Dohme[4] states that the fresh parts in general contain more than the dried parts; that the stems contain the most alkaloid, the seeds next, then the leaves, and the roots least of all. I have found the various parts to range in the following order: Mature seeds, flowers, stems, immature fruit, and leaves. These experiments show that prolonged drying and heating at high temperatures cause a loss of the alkaloid; that the alkaloid is more readily extracted from the material by alcohol in an acidified suspension than in either a neutral or alkaline; and that a possible commercial method is to grind the raw material finely, treat it with hot acidified water, and then treat this extract with fuller's earth. By extracting this earth with alcohol after

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[3] U. S. Dispensatory, 18th ed., 1290.

[4] Ibid.

it has been made alkaline, a concentrated solution of the alkaloid in alcohol can be made. The alkaloid is somewhat soluble in neutral water. The fuller's earth used in these experiments was not very active. It enabled me to extract from 66 to 90 per cent of the alkaloid by using relatively large quantities of the earth. A more active variety should be used in order that the bulk may be kept small. This active variety can either be obtained from Professor Lloyd or prepared by the methods described[5] by him. He was able to secure practically complete absorption by the use of eight parts of the hydrous silicate to one part of the alkaloid.

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[5] *Journ. Am. Phar. Assoc.* (1916), 5, 381.

SOME PHILIPPINE TANBARKS [1]

By Vicente Q. Gana

(From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila, P. I.)

As far as I am aware, mangrove bark, camanchili bark, and alum are the only tanning materials utilized in the Philippine Islands at present. The blending of different barks is not being practiced here, and until more is known of the tanning qualities of the available materials, it will not be possible for the Filipino tanners to produce combination tannages like those used in Europe and in the United States.

At present the mangrove swamps, which constitute 2 per cent of the public forests of the Philippine Islands, or 207,200 hectares,[2] are considered the most important source of Philippine tan material, not only on account of the abundance of the mangrove trees, but also because of the fair amount of tannin in the bark. The tannin content and the tanning qualities have been already investigated.[3] The bark, when used [4] alone, produces a leather which is harsh and dark red in color; it is almost unsalable. Cox [5] found that the available heating value of the combustible matter [wood − (water + ash)] in the air-dried bark of six species of mangrove averages 4,625 calories. Although these results were obtained from fresh bark and not from spent tanbark, it is obvious that the waste material should be found useful in steam and power production at the tannery.

Camanchili (*Pithecolobium dulce* Bentham) bark comes next in importance and is used to some extent by the majority of Filipino tanners. It has little coloring matter and produces a dull, light brown leather. Due to the presence of nitrogenous compounds [6] an infusion of the bark very soon ferments and develops a disagreeable odor.[7] In using camanchili bark in a warm climate, antiseptics should be added to the infusion to check excessive fermentation.

With the object of rendering more materials available to the

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[1] Received for publication May, 1916.

[2] *Bull. P. I. Bur. Forestry* (1911), No. 10, 17.

[3] Bacon, R. F., and Gana, V. Q., *This Journal, Sec. A* (1909), 4, 205. Williams, R. R., ibid. (1911), 6, 45.

[4] Ibid. (1911), 6, 45.

[5] Cox, Alvin J., ibid. (1912), 7, 8.

[6] Ibid. (1915), 10, 366.

[7] In France a root bark of *Quercus coccifera*, called "garoville," has the same disadvantage.

tanning industry, the Bureau of Science has undertaken this investigation of the barks of some of the common trees of the Philippine Islands that may have tanning properties. The results obtained with the following barks have already been published.[8]

Common name.	Botanical name.
Cateban and ulayan.	*Quercus* sp.
Balinghasay.	*Buchanania arborescens.*
Pagsahinging.	*Canarium villosum.*
Calamansanay.	*Nauclea calysina.*
Ligas.	*Semicarpus accuminatissima.*
Sacat fruits.	*Terminalia nitens.*

The present work deals with the barks of the following trees:

Common name.	Botanical name.
Pine.	*Pinus insularis.*
Narra.	*Pterocarpus vidalianus.*
Palo maria.	*Calophyllum inophyllum.*
Alibangbang.	*Bauhinia malabarica.*
Pili.	*Canarium luzonicum.*
Oak.	*Quercus* sp.
Acacia, raintree.	*Enterolobium saman.*
Bulak, kapok.	*Ceiba pentandra.*
Tuba.	*Jatropha curcas.*
Bignay.	*Sporosa* sp.

Of the above list, the acacia, or raintree; kapok, or cotton tree; tuba; and bignay contain little or no tannin.

Although some of the others are low in tannin, their great abundance renders them of value to the tanner, especially in localities where there is no other tanning material. The chemical analyses of the barks are given in Table I.

TABLE I.—*Chemical analyses of some Philippine barks.*

[Numbers give percentages.]

Tree.	Moisture.	Calculated to dry basis.			Color of the infusions.
		Total extracts.	Tannins.	Nontannins.	
Pine, *Pinus insularis*	15.5	6.6	3.8	2.8	Wine red.
Narra, *Pterocarpus vidalianus*	15.1	41.9	30.7	11.2	Deep wine red.
Palo maria, *Calophyllum inophyllum.*	10.2	16.9	11.9	5.0	Wine red.
Alibangbang, *Bauhinia malabarica.*	12.4	22.8	9.5	13.3	Do.
Pili, *Canarium luzonicum*	11.3	11.2	7.8	3.4	Wine red with yellow tinge.
Oak, *Quercus* sp	10.5	22.4	17.9	4.5	Deep wine red.

[8] *This Journal, Sec. A* (1915), 10, 349.

The reactions of the infusions with some reagents indicate that the extracts of pine and palo maria are similar in quality, notwithstanding the difference in quantitative analysis. The same qualitative similarity is found in the extracts of narra and pili barks. The qualitative tests are given in Table II. The action of the various infusions on delimed sheep skin is shown in Table III.

TABLE II.—*Reactions of the infusion of the barks with reagents.*

Bark.	Reagent.			
	Concentrated sulphuric acid.	Boiling diluted sulphuric acid.	Bromine water.	Ammonium ferric alum.
	Liquid.	*Precipitate.*	*Precipitate.*	*Precipitate.*
Pine	Yellowish brown or violet.	Reddish orange; difficultly soluble in alcohol and in boiling water.	Brown	Greenish black.
Narra	Yellowish brown.	Red; soluble in alcohol and in boiling water.	do	Reddish black or black with violet tinge.
Palo maria	Brown	Red; difficultly soluble in alcohol and in boiling water.	do	Greenish black.
Alibangbang			Whitish	Greenish brown.
Pili	Yellowish brown.	Reddish brown; soluble in alcohol and boiling water.	Brownish yellow.	Brownish black or very dark brown with violet tinge.
Oak	do	Red; difficultly soluble in alcohol and in boiling water.	do	Green to bluish black.

TABLE III.—*Tanning effects of infusions of Philippine barks on delimed sheep skin.*

Bark.	Leather produced.
Pine	Satisfactory leather, of reddish tan, with firm texture and good grain. Tanning is slow.
Narra	Satisfactory leather, nut brown, with full, firm texture and good grain.
Palo maria	Satisfactory leather, similar to pine-tanned leather in color, texture, and grain.
Pili	Satisfactory leather; yellowish brown, firm texture, and good grain. Tanning is slow.
Oak	Light reddish brown leather, somewhat loose in texture and harsh in grain.

Like the bark of the majority of the Coniferæ[9] the bark of the Philippine pine (*Pinus insularis*) is low in tannin content.[10] However, the good quality of the leather produced and the availability of pine trees make it commercially important. The area of the pine forest is estimated at 518,000 hectares,[11] or 5 per cent of the public forest of the Philippines. The collection of bark should be easy, as the tree is used for lumber and at present the bark is waste. Whitford states that there is little doubt that, if fires were kept off, the pine (in the absence of broad-leaved competition) would quickly seed the entire area, for its reproduction is very rapid.

Pinus insularis has been investigated, but no work has been done on *Pinus merkusii,* which occurs in Mindoro[12] in pure stands and in open groves scattered throughout the grasslands, southwest of a high mountain mass. The samples used in this work were collected in the vicinity of Baguio, Benguet, by the Bureau of Forestry. They were 60 centimeters wide and 1.5 centimeters thick. The outside surface was dark gray, grooved, and scaly. This epidermal layer resembled cork; it contained no tanning principles. The inner surface was brownish and somewhat fibrous or woody.

Narra.—The bark of the narra tree has a fairly high tannin content and produces good leather. However, the timber is so widely scattered that it is doubtful if it will ever be available for tanning.

Pili.—The bark of this tree is suitable for tanning purposes and produces a satisfactory yellowish brown leather. However, it is not likely that this bark will be available on a commercial scale, because the tree produces valuable nuts and high-priced resin.[13] It is not abundant, nor is it systematically grown, and its propagation should be encouraged. The sample of bark collected in Ambos Camarines by the Bureau of Forestry was 2

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[9] Procter's Principles of Leather Manufacture (1903), 246.

[10] Barks containing 3 to 15 per cent of catehol tannins are used in Styria, Austria, and in Russia. *Pinus cembra,* which grows in the Alps and which contains 3 to 5 per cent tannin, is used in Tyrol. The *pin sauvage* of France contains from 4 to 5 per cent. Hemlock bark, obtained from the hemlock fir which is abundant in the northern and western parts of the United States and in Canada, forms the staple tanning material of the United States [H. G. Bennett, Manufacture of Leather (1914), 136]. It contains from 8 to 11 per cent of tannin with much phlobaphenes.

[11] Whitford, H. N., *Bull. P. I. Bur. Forestry* (1911), No. 10, 17.

[12] Ibid., 31.

[13] Clover, A. M., *This Journal, Sec. A* (1907), 2, 1–40.

millimeters thick; it was brown with white and gray cuticle. The inner surface was brown, brittle, and easily ground.

Palo maria de la playa.—The bark of *Calophyllum inophyllum* is suitable for tanning purposes. The species is more abundant than camanchili, and the trees are larger. It is widely distributed in the Philippine Islands, occupying a prominent place in the beach forests. The sample of bark taken at Pasay beach was 15 millimeters thick. It was brown with a decided yellow tinge and was divided into distinct ridges, many of which were broken into irregular, rectangular plates by cross fissures; the inner bark was pink or yellowish with concentric lines of a darker color.[14]

Oak.—According to Mr. E. D. Merrill,[15] botanist, Bureau of Science, there are about twenty-five species of Philippine oaks which grow at high altitudes in the mountains. The sample obtained by the Bureau of Forestry at Limay, Bataan, was 11 millimeters thick. The inner surface was dark red. The outer surface was lightly grooved and covered with a thin gray epidermis which contains no tannin. The bark is brittle and is easy to grind.

SUMMARY

At present only mangrove and camanchili bark are used for tanning in the Philippine Islands. A greater variety of barks is needed.

The Benguet pine and palo maria produce barks that can be used on a commercial scale. The latter surpasses camanchili in quality and availability. The barks of narra, pili, alibangbang, and oak were also studied. With the exception of the last two barks, all produced a leather with full, firm texture and good grain.

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[14] It has been pointed out by the Director of Forestry that while palo maria is much more abundant than camanchili the trees are widely scattered and the collection of bark from trees felled for lumber would be difficult and expensive. (EDITOR.)

[15] *This Journal, Sec. C* (1908), 3, 317.

POSSIBILITIES OF GULAMAN DAGAT AS A SUBSTITUTE FOR GELATIN IN FOOD[1]

By ALBERT H. WELLS

(*From the Laboratory of Organic Chemistry, Bureau of Science, Manila, P. I.*)

The seaweed *gulaman dagat,* a species of *Gracilaria,* is found growing throughout the Philippine Archipelago. During the first quarter of the year it is brought in to a limited extent by fishermen and is marketed as a food product. As a food it is used in two ways: (1) Washed free from salt water and boiled and eaten as a salad and (2) sun-bleached, dried, and marketed as a cheap substitute for gelatin. Its use and manufacture has not been exploited, and at present the local consumption is exceedingly small, due principally to the fact that a purer and whiter product has already been established in the market and is obtainable at a nominal price. This product is the Japanese gulaman, which is extensively used as agar-agar.

An investigation has been made with regard to the food value of gulaman dagat and to determine whether or not it could be used as a suitable substitute for gelatin. A food gelatin should stand tests showing a high percentage of purity and should be clear, only faintly colored, and quite odorless. It should have an excellent congealing strength.

A specimen of the seaweed was collected and identified as a species of *Gracilaria* by Mr. E. D. Merrill, botanist, Bureau of Science. After washing, boiling in water, and straining, the extract was cooled to a translucent greenish jelly. Another portion was washed free of salt and other foreign matter and was treated in the cold with very dilute acetic acid, after which it was washed, and dilute ammonia was added. It was again washed, and the residue was boiled for some time and strained through a suitable cloth. The extract was concentrated, and the jelly was dried. Three grams of the dry substance, made

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[1] Received for publication October, 1916.

in the manner described above, gave a strong jelly when treated with 300 grams of water and then boiled and cooled. This jelly had a higher melting point than true gelatin, thus resembling the gelose prepared by Payen[2] from *Gelideum corneum.* Another jelly having a dilution of 1 : 300 gave a firm jelly, having almost the consistency of ordinary gelatin as prepared for the table. This preparation melts in the mouth. However, it would seem that the ratio of 1 : 275 more nearly approximates the proper ratio for a jelly from gulaman dagat to be used as a food.

Gulaman dagat differs chemically from gelatin in that it is not an albuminoid. Gelatin contains approximately 17.9 per cent nitrogen, while gulaman dagat shows less than 1 per cent. It is equally low in all nutritive substances.

Analysis of the dry, prepared substance shows the following composition as compared with Japanese gulaman.

TABLE I.—*Analysis of gulaman.*

	Philippine.	Japanese.
	Per cent.	*Per cent.*
Moisture	16.00	19.60
Ether extract	1.20	1.08
Protein (N× 6.25)	4.20	4.23
Hydrolizable carbohydrate expressed as starch	35.39	29.65
Ash	4.00	2.90

Analysis of a firm jelly prepared in the laboratory showed the following:

TABLE II.—*Analysis of jelly from gulaman dagat.*

	Per cent.
Moisture	99.37
Ether extract	0.10
Protein	0.10
Ash	0.04
Starch	none
Carbohydrate by difference	0.39
	100.00

Many seaweeds after boiling yield a gelatinous extract which sets to a jelly. Table III shows the composition of various British algæ compared with that of gulaman dagat and the Japanese gulaman. Some of these are used as food and medicine.

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[2] Allen's Commercial Organic Analysis. P. Blakiston's Son & Co., Philadelphia (1914), 8, 622.

TABLE III.—*Comparison of gulaman with various seaweeds used for like purposes.*

	Water.	Nitrogen in dry substance.
	Per cent.	*Per cent.*
British algæ:[a]		
Chondrus crispus, bleached	17.92	1.534
Do	19.79	1.485
Chondrus crispus, unbleached	21.47	2.142
Do	19.96	2.510
Gigantina mamillosa	21.55	2.198
Laminaria digitata (dulse tangle)	21.38	1.588
Rhodymania palmata	16.56	3.465
Porphyra laciniata	17.41	4.680
Sarcophyllis edulis	19.61	3.088
Alaria esculenta	17.91	2.424
Japanese gulaman	19.60	0.806
Philippine gulaman dagat	16.00	0.800

[a] Thorpe's Dictionary of Applied Chemistry (1913).

It is evident that a jelly made from gulaman dagat would be of no appreciable value as a nutritive product. But it seems possible that gulaman dagat could be used in place of gelatin in food where a substance possessing only the physical qualities of gelatin is required. In other words, it could act as a carrier for flavors and fruit juices.

The suitability of gulaman dagat for agar-agar as a substitute for the Japanese gulaman has been worked out by Dr. H. Windsor Wade, bacteriologist, Bureau of Science. The physical characteristics of the extract were briefly noted by comparing them with those of ordinary agar-agar.

Extracts were made by soaking in cold water, boiling for considerable periods, and after rubbing through wire gauze filtering off the soluble portion through cheesecloth. Soaking the dried material, which is entirely filamentous, caused it to swell to two or three times its original bulk, the effect being apparently the same after two hours as after twenty-four hours. Using a proportion of 4 per cent of dry weed and replacing the water as evaporated, the extract obtained solidified on cooling and could be cast in the form of cakes which, with care, might be handled without breaking.

In order to compare the surface strength of this jelly with that of ordinary agar-agar of known concentration, a simple apparatus was devised with which the sustaining power of the uninjured surfaces of blocks of uniform size could be determined in terms of grams weight. Table IV gives the results obtained by averaging several tests. These figures are, of course, of value simply for comparison, since they apply only to the conditions of the experiment.

TABLE IV.—*Crushing pressure for agar-agar blocks.*

Emulsion No.	Agar-agar.	Room temperature, 28°C. (average of 3 tests).	Incubator temperature, 37°C. (average of 2 tests).
	Per cent.		
1	1.5	40-45 (?)	37
2	1.75	55.5	58.5
3	2.0	66	[a] 60
4	2.25	74	[a] 65
5	2.5	94.5	89.5

[a] Optimum.

Specimens 3 and 4 are particularly useful for bacteriological work; number 2 might be somewhat soft for use in planting water.

When the same test was applied to the gulaman extract, it was found that the surface strength was very slight, amounting to no more than from 5 to 8 grams. When, after prolonged boiling, the whole was passed through a sieve—in itself a very laborious process—and reboiled, the filtrate when cold gave pressure readings of but 9 to 10 grams. In addition to being very soft when cold, it appeared that an extract of this concentration, when still hot, was not freely fluid, but was stiff enough to interfere somewhat with cloth filtration.

With the intention of obtaining constant concentration of the extract, a quantity of the rubbed-through extract was dried to constant weight at incubator temperature. This gave a dark, hard, rather brittle material.

Upon attempting to redissolve this dried material, it was found that soaking for twenty-four hours restored a fragment approximately to its original size, but that even after this length of immersion, boiling rapidly for fifteen minutes effected only partial solution.

It was concluded that since the somewhat gelatinous extract of gulaman dagat resembles ordinary agar-agar, but does not have a similar peculiarly marked solidifying power, does not melt so freely, and is not so fluid when melted and solidified at a higher temperature, it is not suitable for use in bacteriological work.

SUMMARY

Gulaman dagat, a seaweed of the genus *Gracilaria* and found throughout the Philippine Islands, was investigated.

The conclusion was reached that it might serve as a substitute for gelatin where only the physical properties of gelatin are important, but that it is unsuitable for use in bacteriological work, owing to its low crushing pressure.

THE EFFECT OF SULPHIDE ON CEMENT[1]

By J. C. WITT
(From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila, P. I.)

ONE PLATE AND 1 TEXT FIGURE

There has long been an opinion among cement users that no materials containing sulphur compounds should ever be utilized in making concrete.[2] Cases of failure have been reported which were attributed to sulphur compounds in some of the materials used or to sulphur compounds which came into contact with the finished construction.[3] According to Ljamin,[4] calcium sulphide, which is often present to a small extent in cement, has relatively little effect, though Kremann and Potts[5] mention potassium sulphide as an accelerator for the hydration of cement. There are so many factors, any one of which may be responsible for a failure, that it is often difficult to place the blame unless considerable research is carried on. It is known that cinders from certain sources are not satisfactory for concrete. This has been attributed to the sulphur in the coal burned. It is likely that some of the failures said to be due to sulphur compounds are caused by other agents, and vice versa.

A frequent source of sulphur compounds in concrete is the water used in mixing. In this case they are more uniformly distributed through the concrete than if present in the sand or aggregate. For these reasons the sodium sulphide used in the present work was added in the form of solutions. In most cases, where trouble is experienced from the presence of sulphur in the water used, it is likely that it is due to a mixture of several compounds. We might expect to find hydrogen sulphide, soluble metallic sulphides, sulphates, and possibly sulphites. It is obviously impossible to attempt the solution of a problem of this nature unless the effect of each substance is studied separately. It is our intention to carry on work along many of these lines. Work on the effect of sulphate on cement and

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[1] Received for publication May 10, 1916.

[2] This does not refer to the addition of a reasonable amount of gypsum to the cement for controlling the set.

[3] Borrowman, G., *Journ. Ind. & Eng. Chem.* (1912), 4, 405. Desch, C. H., The chemistry and testing of cement. Edward Arnold, London (1911), 75.

[4] Ljamin, N., *Journ. Soc. Chem. Ind.* (1902), 21, 972.

[5] Kremann, R., and Potts, H. E., The application of physicochemical theory to technical processes and manufacturing methods. D. van Nostrand Co., New York (1915), 161.

concrete is at present under way. There seems to have been little research done along these lines, except in studying the effect of various amounts of gypsum used in the manufacture of cement, especially where the concrete is subjected to the action of sea water. Many of the papers appearing in current journals are accounts of failures of concrete rather than the results of constructive research.

The general subject of the effect of sulphur compounds on concrete may be subdivided as follows:

1. The effect of sulphur compounds present in concrete which is exposed to normal conditions.

Borrowman[6] is of the opinion that sulphides and sulphates in cinders are sometimes largely responsible for failures of cinder concrete.

2. The effect of sulphur compounds present in concrete which is exposed to abnormal conditions, such as contact with sea water.

In some countries the idea is prevalent that a higher percentage of sulphuric anhydride is permissible in a cement used for ordinary construction than in one used for construction which is exposed to sea water. For example, France,[7] Japan,[8] and Argentina[9] have two specifications for sulphuric anhydride—a lower one for sea-water construction, and a higher one for ordinary construction.

3. The effect of sulphur compounds in liquids or gases which come into contact with concrete.

Rohland[10] reports the failure of a smokestack constructed of reënforced concrete, lined with bricks. The mortar between the bricks was made with a cement which was supposed to be acid-resisting. Sulphur compounds in the flue gases are blamed for the failure. The same writer[11] cites a case in which gases containing sulphur compounds had an injurious effect on the concrete in a tunnel. Sulphates in soil caused the failure of a concrete flower pot, according to Sartori,[12] and hydrogen sulphide in the waste water from a brewery caused considerable damage to a concrete sewer pipe.[13]

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[6] Loc. cit.

[7] *Ciment* (1912), 17, 213.

[8] *Mitt. Zentralstell. Ford. Deut. Port. Zem. Ind.* (1912), 1, 167.

[9] Ibid. (1912), 1, 305.

[10] Rohland, P., *Feuerungstechnic* (1914), 2, 360.

[11] *Beton u. Eisen* (1914), 13, 341.

[12] Sartori, A., *Chem. Zeitg.* (1915), 39, 957.

[13] Heyer, ibid. (1916), 40, 102.

Renezeder[14] has carried on some experiments on the effect of sodium sulphide solutions on briquettes. He placed a number of briquettes, of both slag and Portland cement, in sodium sulphide solutions of various concentrations. Other briquettes of the same kind were kept in water for comparison. The test pieces were broken at the end of one, three, six, and twelve months, respectively. The briquettes which had been immersed in the sulphide solution were all weaker than the ones which had been kept in water. However, the writer states that if a briquette is kept in water for the first several weeks, and then placed in sulphide solution, no bad effects are noted.

The present work was undertaken in an effort to obtain data on the following points:

> The concentration of sulphide which may be present in water used in making concrete, without causing any injurious effects.
>
> The effect of sulphide solutions of accurately known concentrations on the setting time and tensile strengths of various cements.
>
> Any chemical reactions which take place.

Since it was desired to make the work as comprehensive as possible, five barrels of cement, each of different brand, were purchased in the open market for the work. The brands chosen represent a wide range in method of manufacture and in composition. The contents of each barrel were thoroughly mixed. Samples of sufficient size to make the usual physical and chemical tests were taken, and the remainder was placed in large tin cans with tightly fitting covers and preserved until used. The five brands of cement will be referred to in this paper as A, B, C, D, and E. The chemical analyses are given in Table I; the physical tests, in Table II.

TABLE I.—*Chemical analyses of cements.*[a]

	A.	B.	C.	D.	E.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Loss on ignition	2.50	2.80	1.50	2.40	2.00
Insoluble residue	0.30	0.60	0.30	0.80	0.45
Silica (SiO_2)	21.10	20.00	22.50	18.80	18.95
Alumina (Al_2O_3)	8.76	8.86	7.58	9.18	9.52
Ferric oxide (Fe_2O_3)	1.42	1.34	1.12	1.12	1.38
Calcium oxide (CaO)	63.10	63.00	63.00	64.10	63.80
Magnesia (MgO)	1.26	1.34	1.74	1.12	1.80
Sulphuric anhydride (SO_3)	0.67	0.86	1.34	1.34	1.24
Potassium and sodium oxides (K_2O, Na_2O)	0.93	1.16	0.87	1.16	0.87

[a] Analyses by Francisco Peña, inorganic chemist; Bureau of Science.

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[14] Renezeder, H., ibid. (1907), 31, 237.

TABLE II.—*Physical tests of cements.*[a]

Brand.	Fineness.		Specific gravity.	Soundness (five hours, in steam.)	Initial set.	Final set.	Tensile strength (neat). Kilos per square centimeter.[b]				Tensile strength (mortar). Kilos per square centimeter.				Tensile strength (neat). Pounds per square inch.				Tensile strength (mortar). Pounds per square inch.			
	Passing 200-mesh sieve.	Passing 100-mesh sieve.					1 day.	7 days.	28 days.	60 days.	1 day.	7 days.	28 days.	60 days.	1 day.	7 days.	28 days.	60 days.	1 day.	7 days.	28 days.	60 days.
	Per cent.	*Per cent.*			*Hrs. min.*	*Hrs. min.*																
A	87.6	99.0	3.12	O. K.	5 15	9 6	24.8	41.8	48.1	47.3	7.0	16.8	23.4	25.3	353	595	685	673	100	238	333	360
B	81.6	99.0	3.10	O. K.	3 55	6 40	23.6	43.5	45.7	45.7	7.0	17.5	21.7	22.8	337	617	651	649	100	248	308	325
C	89.6	99.0	3.16	O. K.	4 32	7 16	23.2	41.2	47.8	45.3	9.3	19.8	26.7	30.1	330	586	679	644	133	282	380	428
D	85.6	98.6	3.10	O. K.	4 26	7 4	24.5	44.5	50.7	47.5	8.7	20.8	28.8	30.9	348	633	722	677	124	294	409	441
E	88.2	99.0	3.10	O. K.	4 14	6 36	27.3	44.2	51.3	50.6	10.8	23.2	28.5	29.1	388	628	731	720	154	331	407	414

[a] All physical tests were made in accordance with the specifications given in circular No. 33 of the United States Bureau of Standards.

[b] Each result represents the average of six briquettes.

PRELIMINARY WORK

An aqueous solution of hydrogen sulphide first suggested itself as the best source of the sulphide radical for the investigation, because it contains no metal which could cause complications. However, the idea was soon abandoned, for it was evident that sufficiently high concentrations of sulphide could not be obtained in such a solution, especially at the high average room temperature in Manila (30° C.). Therefore a soluble metallic sulphide (sodium sulphide) was chosen as being better suited for the work.

A sufficient quantity of sodium sulphide was obtained and analyzed. It was found to contain:

	Per cent.
Sodium (Na)	18.83
Sulphur as sulphate (SO_4)	0.34
Sulphur as sulphide (S)	11.93

After analysis, a quantity of this salt was dissolved in water to make a strong stock solution. The exact concentration of this solution was determined by analysis, and other solutions were made by dilution. The strength of each solution is given in terms of grams sulphur as sulphide per liter.

A cement which develops faults only after a considerable time has elapsed is worse than one which gives trouble in mixing. A cement which is quick-setting, or which is unsound in the boiling test, is, of course, rejected at once, while one which is satisfactory in the preliminary tests, but ultimately develops objectionable features, is not only valueless but dangerous, in that it may cause failure of the concrete in place.

Some former work[15] had shown that cement is very sensitive to the influence of sodium sulphide. With some of the solutions of higher concentration employed at that time, a number of cements set so rapidly that briquettes could not be molded. Therefore in this work setting time tests were made first. The results are given in Table III.

TABLE III.—*Effect of various concentrations of sodium sulphide on the setting time of cements.*[a]

Sodium suphide added.		Initial set.					Final set.				
Sulpur (as sulphide) per liter of solution.[b]	Sulphur (as sulphide) per gram of cement.	A.	B.	C.	D.	E.	A.	B.	C.	D.	E.
Grams.	*Per cent.*	*H. m.*	*H. m.*	*H. m.*	*H. m.*	*H. m.*	*H. m.*	*H. m.*	*H. m.*	*H. m.*	*H. m.*
0.00	0.00	5 15	3 55	4 32	4 26	4 14	9 6	6 40	7 16	7 4	6 36
0.02	0.0004	6 50	6 2	6 25	5 32	4 22	17 10	13 55	13 55	14 29	9 55
0.11	0.0022	9 31	5 41	6 24	5 31	4 30	22 37	14 8	16 47	14 9	11 50
0.21	0.0046	6 56	5 59	7 11	6 39	4 33	14 39	12 4	12 7	12 24	8 53
0.43	0.0095	5 21	5 39	6 6	5 46	2 55	12 6	11 39	11 45	12 9	9 8
1.06	0.0233	5 54	5 2	5 37	4 54	2 51	12 32	11 17	11 20	11 39	8 11
2.13	0.0469	5 58	5 5	5 26	4 5	2 1	15 6	11 42	7 16	6 50	6 16
2.96	0.0651	5 38	5 46	5 8	3 35	1 1	14 16	9 11	6 58	6 35	5 21
5.93	0.1305	4 13	4 40	4 07	1 16	0 44	7 26	8 35	6 27	6 34	4 46
10.00	0.2200	1 42	4 44	4 44	1 3	0 35	5 38	7 49	7 49	3 1	3 5
20.00	0.4400	1 19	2 57	2 57	0 58	0 29	4 48	6 12	6 42	3 37	2 59

[a] Soundness tests were made, and each was found to be satisfactory.

[b] The concentrations of the solutions are given in terms of sulphur (as sulphide) per liter. The sulphate was determined, but was negligible.

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[15] Unpublished results obtained by Witt, J. C., and Baptie, J. A.

A study of Table III reveals that considerable change in both the initial and final set is caused by the sodium sulphide. The setting time is retarded by an addition of a small amount of sulphide, but is accelerated after a certain amount has been reached. For instance, with brand A the initial set is retarded from five hours and fifteen minutes to nine hours and thirty-one minutes, with the addition of 6.11 grams sulphide per liter; however, with the addition of 20 grams per liter, it is accelerated to one hour and nineteen minutes. The final set goes from nine hours and six minutes to twenty-two hours and thirty-seven minutes and then to four hours and forty-eight minutes, with the corresponding concentrations of sulphide. The table shows that brands A and E are the most sensitive to the effect of the sulphide; the former has the greatest range in setting time, while the latter shows the quickest initial and final set of all, that is, a sodium sulphide solution may either accelerate or retard the set, depending on the concentration. In every case the acceleration is greatest at some point between 0.02 and 0.21 gram per liter. As the quantity of sulphide becomes greater, the retarding influence increases until equilibrium is established. In most cases this point is between 0.43 and 5.93 grams sulphide per liter. The accelerating effect is supreme from this time on, and in general, the setting time is decreased with each increase in sulphide. However, after the concentration of 5.93 grams per liter is reached, further additions cause relatively small changes.

EFFECT OF HYDROGEN SULPHIDE

An experiment was carried on to determine whether or not the effect of sodium sulphide shown in the above experiments is due entirely to the sulphide radical or is partially attributable to the sodium present. To decide this, a solution of hydrogen sulphide was made by passing the gas into distilled water. Alliquot portions were removed and analyzed. The solution was found to contain 0.91 gram of sulphur per liter, present as sulphide. Setting time and soundness tests were made on the five brands of cement with this hydrogen sulphide solution. The results are similar to those obtained with the sodium sulphide solution having a sulphide concentration most nearly corresponding to that of this solution. All the soundness tests were satisfactory. The time of initial and final sets are given in Table IV.

TABLE IV.—*Effect of a solution of hydrogen sulphide on setting time of cements.*

Brand.	Initial set.						Final set.					
	Water only.[a]		Sodium sulphide. S= 1.06 grams per liter.[a]		Hydrogen sulphide solution. S= 0.91 gram per liter.		Water only.[a]		Sodium sulphide. S= 1.06 grams per liter.[a]		Hydrogen sulphide solution. S= 0.91 gram per liter.	
	Hrs.	*min.*	*Hrs.*	*min.*	*Hrs.*	*min.*	*Hrs.*	*min.*	*Hrs.*	*min.*	*Hrs.*	*min.*
A	5	15	5	54	5	7	9	6	12	32	8	52
B	3	55	5	2	4	7	6	40	11	17	7	35
C	4	32	5	37	4	51	7	16	11	20	8	13
D	4	26	4	54	3	37	7	4	11	39	6	27
E	4	14	2	51	2	14	6	36	8	11	5	49

All soundness tests were satisfactory.

[a] These results were taken from Table III for the sake of comparison.

It is possible that in some of the higher concentrations of sodium sulphide solutions the sodium may have some influence, but for reasons already stated, a comparison with hydrogen sulphide cannot be made.

TENSILE STRENGTH TESTS

From the results given in Table III, the concentrations of the solutions for making the tensile strength specimens were decided on. A solution containing as much as 20 grams of sulphide per liter in some cases renders the cement quick-setting and causes trouble in making the briquettes properly. Therefore, to avoid any abnormalities in the briquette molding, it was decided to use no solution stronger than 10 grams per liter. The number of briquettes to be made with each cement and each solution was very large; consequently the number of solutions was limited to four. A stock solution was accordingly made to contain approximately 10 grams per liter. Portions were withdrawn from the stock bottle and diluted to give ½, ⅒, and 1/100 of the original. The exact strength of each solution (by analysis) was as follows:

Solution 1 contained 9.70 grams sulphur, as sulphide, per liter; 2, 4.80 grams; 3, 0.97 gram; and 4, 0.097 gram.

Neat briquettes were made for the periods one, seven, twenty-eight, sixty, one hundred twenty, and one hundred eighty days; and for one, two, three, and five years. Mortar briquettes (one part cement to three parts Ottawa standard sand) were made for the same periods, except the one day. This paper covers only the results obtained during the first sixty days. The other briquettes are properly stored and will be broken when due. The results so far obtained are given in Table V.

TABLE V.—*Effect of sodium sulphide on the tensile strength.*[a]

NEAT CEMENT.

	Brand.	Kilos per square centimeter.					Pounds per square inch.				
		Solution.					Solution.				
		Water.	4	3	2	1	Water.	4	3	2	1
1 day	A	24.8	21.5	21.1	10.8	13.3	353	307	300	155	190
	B	23.6	28.8	27.3	23.9	18.4	337	411	388	340	262
	C	23.2	28.9	28.5	24.9	23.9	330	412	407	355	341
	D	24.5	23.5	21.7	15.1	17.9	348	335	308	214	255
	E	27.3	23.5	23.9	15.6	18.9	388	334	340	222	268
7 days	A	41.8	41.2	35.4	21.1	18.9	595	586	506	300	268
	B	43.5	43.7	40.8	33.3	32.3	617	622	579	475	460
	C	41.2	40.5	40.0	32.3	30.4	586	577	568	461	433
	D	44.5	41.3	39.0	32.7	38.9	633	587	554	467	553
	E	44.2	44.9	42.9	31.9	36.5	628	638	609	456	519
28 days	A	48.1	45.1	38.6	40.3	27.4	685	642	548	573	391
	B	45.7	42.9	42.2	39.8	34.7	651	611	599	567	495
	C	47.8	44.4	42.5	31.7	28.8	679	632	605	452	410
	D	50.7	50.9	46.0	44.3	41.2	722	726	655	630	584
	E	51.3	51.6	45.3	41.4	37.9	731	736	645	588	539
60 days	A	47.3	42.5	38.0	39.4	28.4	673	606	542	560	406
	B	45.7	43.5	40.8	40.1	36.8	649	618	581	569	526
	C	45.3	46.7	47.4	35.3	28.1	644	666	676	503	400
	D	47.5	48.1	45.1	40.8	41.1	677	685	642	581	584
	E	50.6	47.4	42.3	41.5	36.1	720	676	602	589	516
MORTAR.											
7 days	A	16.8	14.8	12.2	16.5	5.2	238	209	174	234	74
	B	17.5	16.4	16.2	12.2	10.1	248	233	230	174	145
	C	19.8	17.8	17.5	12.2	11.8	282	253	248	174	168
	D	20.8	16.9	16.9	11.3	10.1	294	239	240	162	144
	E	23.2	18.6	26.2	12.6	10.9	331	265	374	179	157
28 days	A	23.4	20.5	16.6	16.9	8.7	333	292	237	240	124
	B	21.7	19.7	18.2	17.7	15.4	308	280	258	252	218
	C	26.7	25.0	21.4	10.8	17.6	380	357	305	155	251
	D	28.8	24.1	23.2	16.6	15.8	409	343	329	237	226
	E	28.5	22.5	21.4	19.7	15.9	407	319	304	279	227
60 days	A	25.3	21.1	22.5	19.9	18.2	360	299	320	283	258
	B	22.8	28.1	26.8	20.4	18.3	325	399	382	290	259
	C	30.1	22.4	20.4	14.3	10.9	428	318	290	205	157
	D	30.9	26.9	24.5	20.3	18.6	441	383	348	288	265
	E	29.1	24.2	24.6	18.7	17.6	414	344	351	267	249

[a] Each result shown is the average of six briquettes.

A comparison of the results reveals that there is a considerable decrease in strength, caused by sulphide solutions. In general, this decrease seems to be approximately proportional to the concentration of sulphide in the solution used. It is also apparent that brands A and E are again most affected by the sulphide. The broken briquettes appear normal in every respect except in color; there is no swelling, cracking, nor distortion. Table V shows that the average loss in tensile strength caused by using a given sulphide solution in place of water is greatest with the cement highest in iron.

CEMENT HIGH IN IRON CONTENT

In order to determine how far the relationship between iron content and tensile strength might hold, briquettes were made from two other samples of cement much higher in iron. These were designated as F and G. Sample F was a brand of cement different from any other used in this work. It contained 3.44 per cent iron oxide (Fe_2O_3). There was no cement of still higher iron content available, so sample G was made by grinding iron oxide to pass a 100-mesh sieve and by intimately mixing a given weight with a portion of sample F. This added iron oxide could not be considered as a part of the cement, but was present as a foreign substance. The experiment was carried on with the object of determining whether or not there was any relation between the effect of iron which was an integral part of the cement and iron which was added to the finished product.

The tensile strengths of samples F and G are shown in Table VI.

TABLE VI.—*Effect of sulphide on cement high in iron content.*

Sample.	Total ferric oxide (Fe_2O_3) in dry cement.	Tensile strength.[c]										Setting time.	
		Kilos per square centimeter.					Pounds per square inches.						
		Neat.			Mortar.		Neat.		Mortar.				
		1 day	7 days	28 days	7 days	28 days	1 day	7 days	28 days	7 days	28 days	Initial.	Final.
	Per cent.											*Hrs. min.*	*Hrs. min.*
F[a]	3.44	29.6	48.1	42.9	17.3	28.0	423	685	611	247	398	2 47	5 15
F[b]		15.3	23.9	23.2	14.3	17.6	218	341	330	204	250	2 2	5 24
G[a]	8.63	24.1	38.7	41.2	19.7	24.5	343	550	586	279	348	3 59	5 41
G[b]		12.6	20.4	18.3	11.6	15.5	180	291	261	162	221	2 47	6 42

[a] Gauged with water.

[b] Gauged with solution 1.

[c] Each result represents the average of three briquettes.

Soundness tests were made with both water and solution 1. All were satisfactory.

The results show that the relation between iron content and loss in tensile strength continues for sample F, although the relative loss is not so great as with the five cements previously tested. Apparently the added iron oxide in sample G has little effect as far as the sulphide is concerned, but causes a lowering of the tensile strength as any foreign substance is likely to do. The fact that the added iron is not so finely divided nor so uniformly distributed as that originally present no doubt partly accounts for the difference in behavior.

PERCENTAGE LOSS IN TENSILE STRENGTH

It is evident that in comparing the loss in tensile strength with the iron content of the cements and with concentrations of the sulphide solutions, the percentage loss should be the true basis of comparison. Accordingly Tables VII and VIII have been prepared. Table VII shows the percentage loss in tensile strength for the cements of various iron content when gauged with the sulphide solution having the highest concentration (No.1). Table VIII shows the percentage loss in tensile strength of brand A when gauged with sulphide solutions of various concentrations. This brand has the highest iron content of any of the cements studied in detail. The values given in these two tables may be taken in general as typical of the tensile strength results, although some of them are not so regular. This can be understood by remembering that a great many factors other than the iron content and sulphide concentration influence the strength of these briquettes. In general, the relation between percentage loss in tensile strength and iron content is not so well established with the mortar briquettes as with the neat briquettes.

TABLE VII.—*An example of variation of percentage loss in tensile strength with the iron content.*

Brand.	Iron oxide (Fe_2O_3).	Tensile strength in kilos per square centimeter.[a]		Tensile strength in pounds per square inch.		Loss in tensile strength in kilos per sq. cm.	Percentage loss.
		With water.	With solution No. 1.	With water.	With solution No. 1.		
	Per cent.						
D	1.12	50.6	41.2	722	584	9.4	18.58
B	1.34	45.7	34.7	651	495	11.0	24.07
E	1.38	51.3	37.9	731	539	13.4	26.12
A	1.42	48.1	27.4	685	391	20.7	42.62
F	3.44	48.1	23.9	685	341	24.2	50.31
G	8.63	38.7	20.4	550	291	18.3	47.29

[a] All briquettes were made of neat cement and broken at the end of seven days. Brand C shows irregular results, and since it has the same iron content as brand D, the results have been omitted here.

TABLE VIII.—*An example of variation in percentage loss in tensile strength with concentration of sulphide.*

Solution No.	Sulphide per liter.	Tensile strength.[a]		Loss in tensile strength.	Percentage loss.
		Per square centimeter.	Per square inch.		
	Grams.	*Kilos.*	*Pounds.*	*Kilos.*	
Water only		41.8	595		
4	0.097	41.2	586	0.6	1.43
3	0.97	35.4	506	6.4	15.31
2	4.80	21.1	300	20.7	49.52
1	9.70	18.9	268	22.9	54.78

[a] All briquettes were made of neat cement (brand A) and broken at the end of seven days.

The variation in percentage loss in tensile strength is also shown in fig. 1.

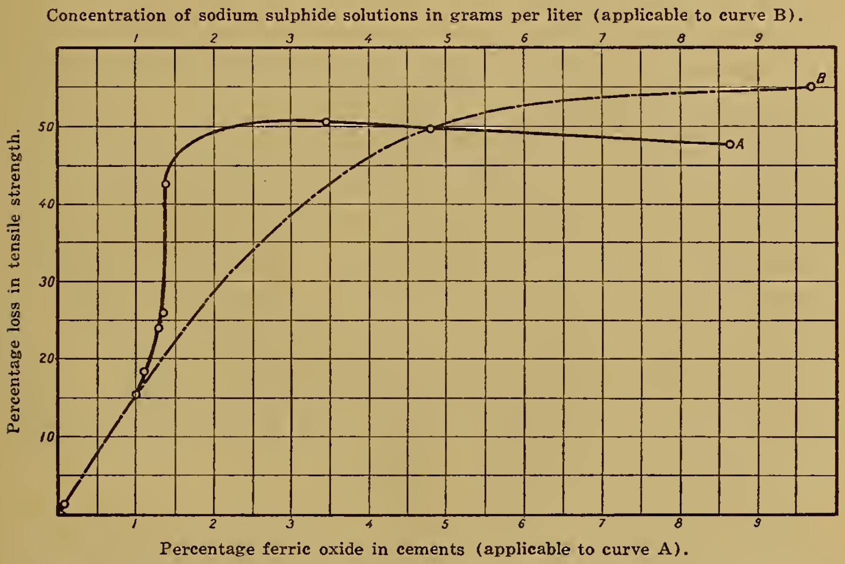

Fig. 1. Examples of variation of percentage loss in tensile strength with the iron content of cements (curve A and with the concentration of sulphide solutions (curve B).

A STUDY OF THE CHEMISTRY INVOLVED

In preparing the test pieces after the solutions of higher concentrations had been reacted, it was noticed that there was an abnormal rise in temperature and that the mixture turned green. Some of the cements showed these characteristics in a greater degree than others. The color was much lighter when the briquettes and pats were dry—becoming light bluish green. It seemed very likely that the production of color was connected with the effect of the sulphide on cement and, accordingly, an effort was made to determine its cause. The briquettes, in a measure, retained the green color even until the time of breaking, but is was noticed that the color was more intense in the interior than on the surface.

The distribution of the colored areas is shown in Plate I. Broken briquettes were selected at random, ground square on an emery wheel, and photographed while wet. The section shown is at the point of fracture. The briquettes were broken at the end of twenty-eight days, and were gauged with solution No. 1, containing 9.70 grams sulphide per liter. The upper two are neat briquettes, and the lower two, mortar briquettes. Nos. 1 and 3 contain no sulphide; they were photographed simply for comparison. It is interesting to note the irregular distribution of the color in the mortar and the fairly uniform distribution in the neat cement.

The boiling pats lost the color on the upper surface, which was exposed to the steam, but the surface which remained next the glass plate and the interior retained the color. In order to demonstrate that the color was not produced by the action of the sulphide on the steel trowels, or on some foreign substance about the mixing table, some of the cement was mixed with a sulphide solution, where the mixtures came in contact with nothing but a glass plate and a porcelain spatula. The color appeared as before. Since iron is the only element present, in any quantity, which is known to give a dark-colored sulphur compound, it was believed to be involved in the reaction. This idea was strengthened by the fact that de Koninck and Ledant[16] report the formation of a bright green on treating iron salts with sodium or potassium polysulphide. The first effort to determine the factors in the reaction was as follows:

Brand E, which is one of the most sensitive of the cements under consideration to the influence of sulphide, as shown in both the setting and the tensile-strength test, was chosen for the preliminary work. Accurately weighed 5-gram duplicate portions of the cement were placed in beakers. Ten cubic centimeters of a sulphide solution, the analysis of which was known, were added; after thoroughly mixing, hot water was added and the mixture was stirred. After settling, the cement was separated from the supernatant liquid and washed until the wash water showed no further tests for sulphide. The filtrates and

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[16] De Koninck, L. L., and Ledant, M., *Zeitschr. f. angew. Chem.* (1891), 202.

washing were allowed to cool and were made up to definite volumes. Alliquot portions, equivalent to 1 cubic centimeter of the original sulphide solution, were removed and titrated with ammoniacal zinc chloride solution. Some of the original sulphide solution was titrated at the same time, so that the change in the concentration of the sulphide in the two solutions could be calculated. The results are shown in Table IX.

TABLE IX.—*Analysis of sulphide solution before and after contact with cement.*

Solution.	Zinc solution required per cubic centimeter of sulphide solution.	Sulphur as sulphide per cubic centimeter.	Sulphur as sulphide removed by cement.
	cc.	*Grams.*	*Grams.*
Original	27.10	0.0422	
After mixing with 0.5 gram cement	25.37	0.0396	0.0026

Although the green color caused by adding the sulphide solution to the cement appeared almost immediately, the above results show that only 6.16 per cent of the sulphide was removed from solution, either by oxidation or by the formation of an insoluble compound. Considerable calcium and a trace of magnesium went into solution. (Further test indicated that the presence of the sulphide did not increase the solubility of the calcium hydroxide.) The results were verified by mixing some cement of known sulphate content with sulphide solution and allowing to stand overnight. On analysis it was found that there was a slight increase in sulphate.

The preliminary experiments were carried out in contact with the air, and it seemed likely that this might account for some of the oxidation that took place. Moreover it was noticed that the carbon dioxide in the air interfered by converting some of the dissolved calcium hydroxide into carbonate. Consequently the next experiments were made in an atmosphere of hydrogen.

Five hundred cubic centimeters of water were placed into each of two 750-cubic centimeter Erlenmeyer flasks. The flasks were fitted with reflux condensers, and the water was boiled from one to two hours to remove the air. The flame was then removed, and a stream of hydrogen was passed through the water until it had cooled to room temperature. Two 5-gram portions of freshly ignited cement were then weighed and placed in small glass capsules. One of the capsules was added to the first flask while a stream of hydrogen was passing, so that no air entered the flask, and immediately a solid rubber stopper was placed in the neck. To the other capsule containing the cement 2.5 cubic centimeters of sulphide solution were added from a burette, after which the whole was added to the second flask, observing the same precaution as before. After shaking vigorously to break up any lumps, the two flasks were placed in a mechanical shaker and violently agitated for twenty-four hours. Fifty cubic centimeter portions were withdrawn, while a stream of hydrogen was passing, and the sulphate was determined. The results indicated that a very small amount of the sulphide was oxidized.

According to Desch,[17] ferrous sulphate may be formed in a cement by the action of a sulphide, provided ferrous iron is present. He says:

> Calcium sulphide, CaS, is often present to a very small extent in cements, and is then derived from the reducing action of the fuel on calcium sulphate contained in the raw materials or formed, in a stationary kiln, from sulphur compounds in the fuel. Calcium sulphide is more characteristic, however, of blast furnace slags. If the cement contains ferrous iron, this is converted into the green ferrous sulphide which is generally considered to be objectionable from its liability to undergo oxidation accompanied by expansion of volume.

While ferrous sulphate may be formed in some cements under the above conditions, I believe it is not frequently formed in quantities sufficient to cause trouble—certainly not in any of the cements studied in the present investigation. The green color produced by sodium sulphide solution is misleading because it suggests the presence of ferrous sulphate, whereas various tests have shown that no appreciable amount of this compound is formed.

REACTION BETWEEN IRON OXIDE AND SODIUM SULPHIDE

With the object of obtaining further information on the formation of the green color, ferric oxide was treated with 10 per cent sodium sulphide solution. After a few minutes the mixture commenced to darken; on warming on the hot plate the red color disappeared entirely, and an examination showed that the particles had become coated with a dark film. To study the reaction further, weighed portions of ferric oxide were treated with known volumes of the sulphide solution. Blanks containing no iron were run for comparison. Each was made up to a definite volume, and portions were removed for titration. The results

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[17] Loc. cit.

are given in terms of grams sulphur, as sulphide, per cubic centimeter of sodium sulphide solution.

Sulphur per cubic centimeter—	Gram.
In original solution	0.0460
In blank after warming	0.0240
After warming with iron oxide	0.0090

The ferric oxide, therefore, removed 0.0150 gram sulphur from each cubic centimeter of solution. The total iron present was 0.3500 gram. The total sulphur removed was 0.1500 gram.

It was apparent that not all of the ferric oxide had been attached by the sulphide. The film which formed around each small particle protected the interior, and the action stopped as soon as mechanical equilibrium (*Mechanisch Labil*[18]) was established.

The black substance was insoluble in the sulphide solution and was filtered out with the unconverted oxide for the purpose of examining its composition. However, on attempting to wash it with water, it produced a dark green, slightly turbid solution. More of the substance has been prepared, and its behavior has been studied. The results indicate that it is a colloid. The substance may be precipitated by a number of electrolytes, among which are sodium sulphide, calcium hydroxide, and sodium sulphate. On this basis both chemical and physical tests point to the following explanation:

When cement is gauged with a sodium sulphide solution, the sulphide acts with the iron in the cement and forms a colloid, which may be percipitated by dissolved calcium hydroxide or by excess sodium sulphide present. Some of the calcium hydroxide is removed from solution by adsorption, and possibly some is directly precipitated by the sodium sulphide. This is no doubt largely responsible for the decrease in tensile strength. It is in harmony with the work of Renezeder[19] previously mentioned. After a cement briquette has fully hardened, the sulphide solution cannot reach a sufficient amount of the iron to cause any noticeable effect, except after a long period of time, although it does react with the iron at the surface.

CONCLUSIONS

While the results of this investigation are not directly applicable to every cement on the market, they may serve as a

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[18] Vide Cox, Alvin J., *Zeitschr. f. anorg. Chem.* (1904), 40, 174.

[19] Loc. cit.

guide in predicting the effect of a sulphide solution on a given cement.

1. The setting time of a cement is greatly modified by the presence of sodium sulphide. With low concentrations the set is retarded, but after reaching a maximum, further additions accelerate the set. In general, the cements highest in iron content are most sensitive to this influence.

2. There is a decided decrease in tensile strength.[20] The percentage loss varies with the concentration of the sulphide and with the iron content of the cement. The briquettes appear normal in every other respect, except in color. There is no cracking nor distortion of any sort.

3. In most cases sulphide may be present in concentrations up to 1 gram per liter without causing the tensile strength to fall below United States Government specifications.

4. Certain results indicate that a colloid is formed by the action of sodium sulphide on the iron in the cement.

5. Based on the results of both chemical and physical observations, the following explanations of the decrease in tensile strength are offered:

(*a*) The precipitated colloid forms films of inert material through the cement and interferes with the cohesion.

(*b*) When the colloid is precipitated a portion of the dissolved calcium hydroxide is removed from solution. Since the latter substance is a very important factor in the strength of cement, it is to be anticipated that the strength will be lowered, when some of it is removed.

6. It is probable that a number of other factors influence the effect of sulphide on cement. Among these may be mentioned the fineness of the cement, the temperature at which it is mixed, the percentage of water used, and the amount of dissolved calcium hydroxide.

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[20] The only specimens yet broken are those during the first sixty days.

ILLUSTRATIONS

TEXT FIGURE

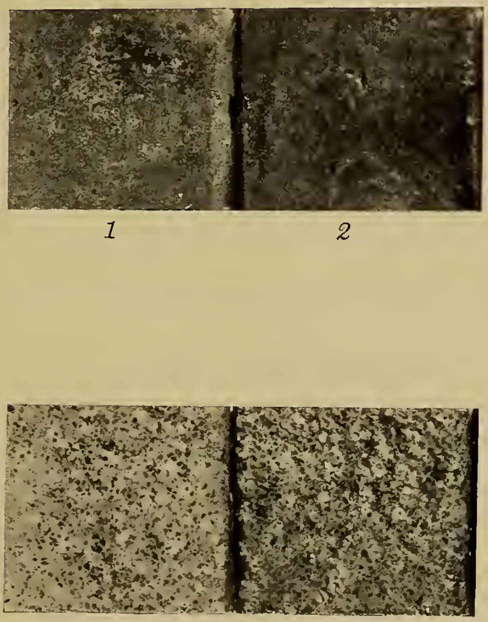

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PLATE I. COLORED AREAS IN BRIQUETTES CAUSED BY PRESENCE OF SODIUM SULPHIDE.

NOTE ON THE BLACHER METHOD FOR THE DETERMINATION OF HARDNESS IN WATER[1]

By A. S. Behrman

(*From the Laboratory of General, Inorganic, and Physical Chemistry, Bureau of Science, Manila, P. I.*)

Because of the large amounts of free carbon dioxide and sodium chloride often found in Philippine waters, a study was made of the influence of these substances in the determination of hardness of water by the Blacher method,[2] as such data are not available in the literature. Attention was also directed to certain details of manipulation. Briefly summarized, the results of this study were as follows:

1. *Effect of free carbon dioxide.*—The presence of large amounts of free carbon dioxide causes incorrect results in the determination of temporary hardness, as well as an indistinct end point, with correspondingly incorrect results, for the "total hardness." Satisfactory results were obtained with concentrations as high as 28 parts of free carbon dioxide per million, and it is possible that even this figure might have been exceeded without introducing any great error, though no attempt was made to find the exact limiting concentration possible. Twenty-five parts per million may be regarded as a safe maximum. Even with very high initial concentration, aspiration of five to ten minutes was sufficient to bring the quantity of free carbon dioxide below this limit.

2. *Removal of carbon dioxide.*—Boiling the solution for from five to ten minutes to remove carbon dioxide, as advised by several investigators, before titrating with potassium palmitate, was found to have no more beneficial effect than aspiration for five minutes.

3. *Effect of salt.*—Sodium chloride in the amounts normally found in natural waters has no effect on the results. Concentrations varying from 10 to 2,000 parts per million of chlorine were employed, without perceptibly affecting the end point.

4. *Dilution of very hard water.*—If the total hardness (as

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[1] Received for publication October 2, 1916.

[2] Blacher C., Grunberg, P., and Kissa, M., *Chem. Zeitg.* (1913), 37, 56–8.

calcium carbonate) is much over 250 parts per million, it may be found convenient to dilute a water sample with distilled water to prevent the heavy precipitate from obscuring the end point. A 100 cubic centimeter sample may be diluted to at least 500 cubic centimeters with distilled water, without appreciably affecting the end point.

5. *Distinction of end points.*—An effort was made to distinguish the three end points mentioned by Herbig,[3] namely, a very faint red, followed by a light red, followed by an intense red, the last of which, Herbig states, is the one to be used in almost all cases, particularly in waters high in magnesium. With solutions containing only calcium, the first two end points lie very close together, so that either could be taken as the true end point and give results well within the limits of experimental error. With solutions containing considerable amounts of magnesium, the first end point was reached long before a value corresponding to the true end point was obtained. Additions of potassium palmitate after the second end point had been reached produced deepening of the phenolphthalein coloration, apparently corresponding simply to successive transformations of additional amounts of indicator. No sharp transition point was observed, so that the third end point mentioned by Herbig could not be located.

By taking the second end point, mentioned in the preceding paragraph, very satisfactory results were obtained, whether the hardness of water was caused by calcium or by magnesium, singly or combined. Determinations made in a considerable number of both artificially prepared and natural waters, checked by gravimetric determinations, showed an average variation of 2 to 3 per cent from the true calcium and magnesium content—a degree of accuracy comparable with that obtained by J. Zink and F. Hollandt,[4] and by E. Nochmann.[5]

Using these data as the basis of any deviation from Blacher's original procedure, the method as finally adopted is as follows:

A 0.1 *N* potassium palmitate solution is prepared, according to the method given by Herbig[6] for potassium stearate, by the neutralization of palmitic acid in alcoholic glycerol solution. This solution is standardized against a saturated solution of calcium hydroxide.[7]

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[3] Herbig, W., *Farber Zeitg.* (1913), 24, 98–101.

[4] *Zeitschr. f. angew. Chem.* (1914), 27, 1, 439.

[5] *Pharm. Zentralh.* (1914), 55, 436–7.

[6] *Farber Zeitg.* (1913), 24, 113–4.

[7] Blacher et al, loc. cit.

The acidity of the sample (due to free carbon dioxide) is first determined with sodium carbonate in the presence of phenolphthalein. If the amount of free carbon dioxide is found to be over 25 parts per million, a fresh 100 cubic centimeter portion is aspirated from five to ten minutes and is used for the remaining determinations. If the acidity is less than 25 parts per million, aspiration is unnecessary. The 100 cubic centimeter portion is then titrated with 0.1 *N* sulphuric acid,[8] using one drop of dimethylamidoazobenzene (butter yellow) as indicator. From this titration is obtained, as usual, the "bicarbonate alkalinity," which may also be taken as a measure of the "temporary hardness"—in both cases, of course, making proper allowance for the normal carbonates.

A few drops of 0.1 *N* sulphuric acid are added in excess, and the solution is aspirated for five minutes. One cubic centimeter of phenolphthalein solution (1 per cent) is then added, followed by 0.1 *N* alcoholic potassium hydroxide until a slight phenolphthalein coloration can be noted in the yellow produced by the dimethylamidoazobenzene. Titration is then made with 0.1 *N* potassium palmitate solution. The end point taken is not the first faint pink which is observed, but the first intense pink—an end point which can be determined without difficulty after a little practice. From the volume of solution used in the titration the total hardness, expressed in parts per million of calcium carbonate, is calculated.

It is believed that the degree of accuracy and the rapidity of this determination make the method as outlined above very desirable for the determination of hardness in a commercial laboratory. The calcium may be separately determined and the magnesium obtained by difference, thereby eliminating the tedious gravimetric determination of the latter.

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[8] Sulphuric acid was employed in place of hydrochloric (as recommended in Blacher's original communication), because of the possible applicability of the former in the form of sodium bisulphate in field work.

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