PROPOSED METHOD

Carefully sample the lot of citric acid on hand, by grinding a sufficient quantity to get an average sample through a coffee or other suitable mill. Mix thoroughly, and weigh 7 g. into a liter flask. Dissolve in water, and dilute to mark. Pipette out 50 cc. or 0.35 g. of the citric acid, and titrate with $N/10$ caustic soda and phenolphthalein. If the acid is pure and uneffloresced, just 50 cc. of $N/10$ alkali will be required. Weigh 1850 g. of pure uneffloresced acid or its equivalent in acid value of effloresced or impure acid into a large bottle or carboy, and cover with 7 liters of cold water. Calculate the exact number of g. of anhydrous citric acid present. Run from a burette 25 cc. of concentrated ammonia into a 500 cc. flask containing cold distilled water. Dilute to mark and mix. Carefully measure 25 cc. of this solution and titrate with $N/2$ acid and methyl orange. Calculate the volume of concentrated ammonia necessary to neutralize the citric acid in the ratio of 1 of ammonia to 3.765 of anhydrous citric acid. (If a stock of approximately 10 per cent ammonia is on hand, it is perhaps preferable to use it instead of concentrated ammonia using, of course, a correspondingly suitable volume of water for the citric acid.) Add the carefully measured ammonia solution to the citric acid in the bottle or carboy, close immediately with a tightly fitting rubber stopper, and shake till the acid is dissolved; allow to stand tightly stoppered until cold, then shake again before removing the stopper. Bring to a gravity of 1.09 at 20° C. The volume of the solution should approximate 10 liters. The accuracy of the solution may be confirmed if desired, by analysis, using either the distillation method already described in this paper, or the method of Patten and Marti,¹ or that of Eastman and Hildebrand.²

It was suggested by one of my associates that we attempt to prepare the pure salt, tri-ammonium citrate, and determine the ratio of ammonia to citric acid in it. As anticipated it was found impossible to prepare, by evaporation and crystallization, but by adding to a solution of ammonium citrate made distinctly alkaline with ammonia, a large excess of strong alcohol, a salt was precipitated which on standing over night became beautifully crystalline. The supernatant liquid was filtered off, and the crystals washed thoroughly on the pump with a large excess of strong alcohol; the mass which was a felt of interlaced crystals, was dried quickly by pressure between blotting pads, and a portion dissolved in water; its reaction with corallin was distinctly alkaline, and an analysis of the solution showed the ratio of ammonia to citric acid to be 1 to 3.768. The remainder of the crystals left exposed over night to the summer temperature of the laboratory had entirely changed the nature of its crystalline structure, and a portion of it, when dissolved in water and tested with corallin, was decidedly acid to that reagent and upon analysis showed a ratio of 1 to 3.94. It is evident, therefore, that the normal salt is not entirely hypothetical, that it can be actually

prepared and dissolved in water, and its solution then shows an alkaline reaction to corallin and has very nearly the ratio of 1 of ammonia to 3.765 of citric acid.

There seems little reason to doubt that the neutral ammonium citrate solution which the A. O. A. C. has been prescribing since the date of its organization many years ago, and which able and conscientious chemists have ever since been earnestly trying to make exactly neutral, succeeding sometimes perhaps by accident, but usually only approximating it, was really intended to be a solution of the normal salt. This opinion was expressed by the writer in his report as Referee in the following words: "While the referee has a strong conviction that the only proper method of making the solution is by analysis and calculation of the exact quantity of ammonia and citric acid to be added to it, still he hesitates to urge it officially, as no work has yet been done by any other referee along this line, and because the referee is himself no longer an official chemist." In this opinion he has since been supported by those who have given the most earnest thought and painstaking experiment to the subject, as Patten and Marti, Eastman and Hildebrand and others.

The laboratory with which the writer is identified still makes its solution as prescribed by the A. O. A. C., approximating neutrality as closely as possible by the use of corallin, since that is still one of the legal and official methods, but the writer knows of other chemists who have already adopted the neutralization by analysis, and it is little wonder that under these conditions analyses for available phosphoric acid on tankages and bone meals, and fertilizers containing those ingredients should vary quite widely. Let us hope that the A. O. A. C. at their next meeting will conclude that the subject has been investigated long enough, and take some definite action at that meeting, or else appoint a small committee in whom they have confidence, with power to act in prescribing a method which shall be legal and official after a definite date.

McCANDLESS LABORATORY
ATLANTA, GA.

THE INFLUENCE OF FINENESS UPON THE AVAILABILITY OF BONE MEAL

By S. S. PECK

Received July 6, 1914

It has been thoroughly established that the availability of raw phosphate rock or of basic slag depends primarily on its fineness of subdivision. These two purveyors of phosphoric acid and bones or bone meal comprise the three forms in which insoluble phosphoric acid is supplied in fertilizers. In the case of basic slag, the phosphoric acid exists as a tetra-calcic or a four-lime phosphate. In phosphate rock and bones the phosphoric acid is combined with three parts of lime, and is known as tri-calcic phosphate, to which the general term of bone phosphate is applied.

As superphosphate, phosphoric acid is supplied in a form soluble in water. It is termed available not because after being applied to the soil it remains permanently soluble but because it is fixed in a finely divided

¹ THIS JOURNAL, 5 (1913), 567.

² *Ibid.*, 6 (1914), 577.

form and well distributed. From this it can be logically concluded that the finer the state of subdivision of rock phosphate, and the more thorough its distribution in the soil, the greater will be its availability to the crop. As a matter of fact, the latter condition is directly dependent on the former, since any given quantity of material can be more evenly distributed as its state of fineness increases. The influence of fineness in increasing yields has been demonstrated by the New York Agricultural Experiment Station,¹ and the University of Wisconsin Agricultural Experiment Station² has shown that thoroughness of mixing has a decidedly beneficial effect on plant growth.

Truog has published tests showing that the availability of raw phosphate rock is directly influenced by the simultaneous presence of fermenting organic material, this favoring the chemical and biological processes that give rise to carbon dioxide and other agencies which attack the fine rock and ultimately give the material a finer and more uniform distribution through the soil. For this reason the experimental data from phosphate rock experiments cannot be used in arriving at conclusions relative to bone meal action, since here the solvent action is influenced directly by the decomposition of the nitrogenous part of the bone particles, with the accompanying evolution of carbon dioxide and formation of nitric nitrogen. Experimental data, however, is not wanting on this point. The Berlin Agricultural Experiment Station has found that the finer bone meal is ground the better its utilization, coarse meal having but 66 per cent of the action of fine meal, when each contained the same phosphoric acid per cent. The importance of this condition has always been recognized. A hundred or more years ago when bones first began to be used in England, they were applied either unbroken, or later in coarse fragments, at the rate of ten or twelve hundred pounds to the acre. Afterwards, when bone meal came to be manufactured, 600 or 700 pounds of the meal per acre were deemed a sufficient dose, while later 100 or 200 pounds of superphosphate (in which a state of subdivision is reached that would be impossible by grinding) were found to produce the same effect on the same soils and crops.³

Storer⁴ says: "The fineness of the meal to which bones are ground is a very important consideration. Not so many years ago it was the custom to use crushed bones, . . . but there is no longer any question that fine meal is greatly to be preferred to that which is coarse. The finer the meal, so much the more readily will it putrefy and dissolve in the earth, so much the more quickly can the plants be fed by it, and so much the sooner and the more surely will the value of the crop be increased."

Voorhees⁵ also states in positive terms the necessity of fineness of division of bone meal. Many of the experiment stations in the United States attach different values to the phosphoric acid and nitrogen

in fine, medium, and coarse bone meal respectively, but do not in all instances agree in their definitions of these terms. In general, by fine bone meal is signified such as will pass through a sieve with circular holes one-fiftieth of an inch in diameter, and coarse such as will not. The New Jersey Agricultural Experiment Station uses values on this basis as follows: Fine bone meal—nitrogen 19 cents, phosphoric acid 4 cents per pound; coarse—nitrogen 15 cents, phosphoric acid 3.5 cents per pound.¹ The Kentucky Agricultural Experiment Station² defines fine bone meal as that which passes through a 25 mesh sieve, and medium as that which passes through a 6 mesh sieve, valuing the phosphoric acid from the former at 4 cents and from the latter at 3 cents per pound. Other stations, particularly that of California, no longer indicate valuations depending on the degree of fineness, since such a gradation is purely arbitrary; nevertheless, they insist on the necessity of such a condition.

There is a limit to which bone meal should be ground on three accounts: (1) When ground too fine to an impalpable powder, known as "floated bone," it is apt to be carried away by the wind when being applied; (2) in this condition it is extremely liable to putrefy, especially in moist air; and (3) there is a question whether its availability is raised for ordinary cultural purposes in a measure commensurate with its extreme fineness. In experiments with various crops, and using bone meal ranging from that passing a 60-inch sieve to that passing through bolting cloth, the New York Agricultural Experiment Station³ found that within the limits tested, fineness seemed to have little or no influence on availability.

Attempts have been made to measure the availability of raw phosphates by their solubility in various dilute solutions of acids, organic or inorganic, but it has not been found possible to duplicate or even approximately represent conditions in the field with laboratory tests. The solvent action of the soil is being exerted on the insoluble phosphates over a long duration of time, during which a part of the dissolved material is being gradually but constantly removed by the growing crop, and also probably suffering other alterations in character not possible to determine. It may be said that at the present time, there is no chemical method of determining this point in which absolute confidence can be placed.

It has already been stated that bacterial action with its consequent evolution of carbon dioxide and development of acids increases the solubility of rock phosphate, and that this condition exists in the decomposition of bone meal in the soils. In an endeavor to measure the availability of various grades of bone meal, this station has completed a series of tests in which attempts were made to answer the question of availability, and in which the decomposition of the organic matter of the bone was presumed to have a direct relation to the relative availability of the phosphate content.

¹ *Bulletin* 358, Feb., 1913.

² *Research Bulletin* 20, January, 1912.

³ B. H. Hite, *Bulletin* 80, West Virginia Experiment Station, April, 1902.

⁴ "Agriculture," Vol. I.

⁵ "Fertilizers," 1900, p. 73.

¹ *Bulletin* 259, September, 1913.

² *Bulletin* 168, December, 1912.

³ *Bulletin* 358, February, 1913.

EXPERIMENTAL WORK

For the purpose of these tests, a commercial bone meal was sifted and divided into four sizes. The sizes and analyses of each lot were as follows:

Number	State of division	Nitrogen Per cent	Phosphoric acid Per cent
1	Less than 40 mesh sieve.....	3.98	17.84
2	From 20 to 40 mesh sieve.....	4.34	22.28
3	From 12 to 20 mesh sieve.....	4.20	23.00
4	Greater than 12 mesh sieve.....	4.09	23.34

TEST NO. 1

This test was intended to measure the relative rates of ammonification of the nitrogen of the different sizes of bone meal. To Station soil representing 200 g. of dry matter placed in beakers enough of each grade was added to supply 200 mg. of nitrogen; to one lot no bone was added. The bone was thoroughly mixed, and then enough water added to bring the soil to two-thirds saturation.

The beakers and contents were weighed, and every two days during the test were again weighed and water added to replace that lost by evaporation. At stated times one series of each was analyzed for ammonia nitrogen by distilling the whole sample, thoroughly mixed and diluted with water, with recently calcined magnesia into $N/10$ acid. As the results of the fourth distillation showed a considerable drop in ammonia nitrogen, on the fifth and last test the residue from distillation was transferred to a graduated vessel, cooled, made up to the mark and filtered. In an aliquot of the filtrate, nitrate nitrogen was determined. The results are given in Table I.

Bone meal No.	Mgs. Ammonia Nitrogen				Mgs. after 18 days as		
	2 days	5 days	9 days	11 days	Ammonia	Nitrate	Total
Blank	0.28	0.14	0.14	0.14	0.14	2.1	2.24
1	5.46	12.88	6.72	4.20	1.8	29.32	31.12
2	1.96	4.48	2.10	2.38	3.08	13.40	16.48
3	1.40	3.92	3.92	0.98	1.12	10.8	11.92
4	1.26	2.24	2.10	0.28	1.26	13.4	14.66

Up to the fifth day, the rate of ammonia formation was greatest with the finest bone meal and least with the coarsest. On the ninth day a considerable drop in ammonia content is noticed in the lot with the finest material, which progressed until the 18th day. From the figures obtained for nitric nitrogen, this can be explained by the fact that nitrification had started in and was progressing rapidly. On the ninth day the three coarser materials showed practically the same state of ammonification. The final figures for nitrogen, ammonia and nitrate of the 18th day show that decomposition of the bone meal had taken place in the fine material to double the extent it had in the coarser; and that in the coarser materials there were but small and irregular differences.

TEST NO. 2

This test was a repetition of the previous one with the exception that the soil was kept at a moisture content equivalent to half saturation, and that nitric nitrogen as well as the ammonia was determined in each instance; except that in the first determination, only the ammonia was determined, nitrification not having in two days sufficient opportunity to make much difference, and at the last determination only the nitrates were determined. The results appear in Tables II, III, and IV.

TABLE II—AMMONIFICATION OF BONE MEAL—MGS. AMMONIA NITROGEN						
No.	2	4	7	10	14	17 days
Blank	1.40	2.31	0.70	0.84	0.70	1.26
1	8.47	9.80	12.32	7.42	1.26	2.38
2	7.42	9.94	8.68	5.18	0.70	1.96
3	6.09	10.08	12.74	4.76	1.12	0.98
4	5.18	8.12	10.22	2.24	0.70	1.26

TABLE III—NITRIFICATION OF BONE MEAL—MGS. NITRATE NITROGEN						
No.	4	7	10	14	17	21 days
Blank	4.20	4.20	4.62	4.62	4.20	3.08
1	3.92	4.54	9.24	20.30	17.92	24.64
2	3.22	4.76	10.64	14.70	14.98	15.40
3	3.08	2.10	7.70	9.66	15.56	14.70
4	3.08	2.24	9.94	9.94	13.30	14.40

TABLE IV—MGS. TOTAL NITROGEN AMMONIA AND NITRATE					
No.	4	7	10	14	17 days
Blank	6.51	4.90	5.46	5.32	5.46
1	13.72	16.86	16.66	21.56	20.30
2	13.16	13.44	15.82	15.40	16.94
3	13.16	14.84	12.46	10.78	16.54
4	11.20	12.48	12.18	10.64	14.56

In this test, the total water-soluble nitrogen at the end of the 17-day period showed a direct relation to the size of the bone meal; this may be said to hold true for most of the tests, the few irregularities occurring being only what may be usually expected in investigations of this character. It was thought, however, that these irregularities might be explained by the fact that the nitrate nitrogen as formed was accumulating to a much larger degree than usually obtained in nature (amounting to as high as 123 parts per million of dry soil), and perhaps the results would be more regular if the nitrate nitrogen formed were removed at intervals. With this in view, a new series of tests was carried out as follows:

TEST NO. 3—LYSIMETER TESTS

For this purpose, galvanized iron containers, with facilities for collecting the drainage, were filled with station soil. The lysimeters were 2 feet in height by eight inches in diameter, the bottoms being perforated and covered with coarse sacking, above which was one inch of animal charcoal, previously digested with acid and washed. Each lysimeter was given 40 pounds of soil. The analysis of this soil by the official acid digestion was:

	Per cent		Per cent
Loss on ignition.....	10.28	Potash.....	0.29
Insoluble residue.....	34.39	Soda.....	1.56
Iron oxide.....	24.96	Sulfuric oxide.....	0.16
Alumina.....	19.56	Phosphoric oxide.....	0.68
Manganese oxide.....	0.15	Chlorine.....	0.01
Lime.....	2.01	Nitrogen.....	0.21
Magnesia.....	5.35		

To each test where bone was added, sufficient was given to represent an application of 100 pounds of nitrogen per acre, amounting actually to 363.5 mg. per lysimeter. In addition to the bone tests, three were carried out with blood and fine ground phosphate rock (60 mesh), alone and together, to see if the effect of the decomposing action of the blood would render more of the phosphate rock soluble, and also to observe whether the presence of the phosphate rock would make any difference in the rate of decomposition of the blood. The blood supplied contained nitrogen at the rate of 100 pounds per acre, while the phosphate rock was equivalent in its phosphoric acid content to the fine bone meal. The plan of the tests was as follows:

LYSIMETER TESTS
0.3635 g. N per lysimeter (100 lb. N per acre)

No.	MATERIAL ADDED	Grams per lysimeter		Pounds per acre	
		Material	Phosphoric acid	Material	Phosphoric acid
1	(Blank).....				
2	Fine bone meal.....	9.133	1.629	2513	448
3	No. 2 bone meal.....	8.375	1.866	2304	513
4	No. 3 bone meal.....	8.655	1.991	2381	548
5	Coarse bone meal.....	8.888	2.068	2445	570
6	Blood.....	2.878		792	
7	Blood and phosphate rock.....	7.218	1.629	1985	448
8	Phosphate rock.....	4.340	1.629	1193	448

The materials were added by removing from the top of each lysimeter the surface two inches of soil, incorporating thoroughly the respective materials with half of this, replacing in the lysimeters and covering with the remainder of the soil. The bone, etc., was thus one inch below the surface and thoroughly admixed in the second inch. To each lysimeter 500 cc. of water were added, and further additions of water made when the surface of the soil was showing signs of dryness. After three weeks, and every three weeks thereafter, the lysimeters were flushed with 3 liters of water and the percolates analyzed. In the interim between irrigations small applications of water were made when the surface soil showed need of it.

In the analyses, nitrate nitrogen and lime were determined in large aliquots of the percolates, the whole drainage being measured and the results figured to milligrams removed. Por-

tions were concentrated and set aside for phosphoric acid determinations. In all, six percolations were completed, representing a total time of 18 weeks.

In the following tables will be found the amounts of nitrate nitrogen and lime removed at each irrigation.

TABLE V—NITRATE NITROGEN REMOVED (MILLIGRAMS)
Lysimeter number

Irrigation No.	1	2	3	4	5	6	7	8
1	49.0	56.2	52.7	52.0	62.3	69.4	67.2	91.2
2	23.3	41.2	37.1	33.2	33.7	97.6	81.9	40.5
3	18.1	27.8	24.9	21.1	18.8	90.4	95.7	19.7
4	13.0	20.5	20.3	18.6	16.6	31.4	45.8	9.8
5	17.9	29.0	22.1	22.1	23.0	22.1	27.3	19.4
6	13.6	25.5	20.2	22.5	22.0	17.1	17.3	14.9
Total	134.9	200.2	177.3	169.5	176.4	328.0	335.2	195.5

TABLE VI—CALCIUM OXIDE REMOVED (MILLIGRAMS)
Lysimeter number

Irrigation No.	1	2	3	4	5	6	7	8
1	47.2	53.5	19.0	44.1	45.3	48.6	53.4	63.6
2	54.7	70.2	37.8	66.1	58.1	85.5	86.3	80.6
3	64.8	79.1	38.8	71.8	67.3	111.6	116.6	95.8
4	61.4	70.0	39.8	73.8	69.3	77.1	94.2	70.4
5	58.4	62.2	46.8	61.3	46.9	66.8	22.2	121.4
6	50.1	36.4	40.0	61.0	58.3	41.1	94.8	82.1
Total	336.6	371.4	222.2	378.1	345.2	430.7	467.5	513.9

It will be noticed that in the first irrigation, the lysimeter to which phosphate rock only was added gave the highest returns for nitrate nitrogen, and of the bone meal tests, the coarsest ranked first in this respect. It is apparent that this discrepancy is due to an unequal condition of the soil at the time of being placed in the lysimeters, which was corrected after the first irrigation. In the following tables, the total amounts of the elements removed in the last five irrigations are reported in terms of pounds per acre:

TABLE VII—POUNDS OF ELEMENTS REMOVED PER ACRE
(CALCULATED ON SURFACE AREA OF LYSIMETER)

Lysimeter No.	Nitrate nitrogen		Lime		Phosphoric acid	
	Removed	Excess over check	Removed	Excess over check	Removed	Excess over check
1	23.6	...	79.6	...	4.39	...
2	39.6	16.0	87.4	7.8	6.4	2.1
3	34.3	10.7	55.9	...	5.2	0.9
4	32.3	8.7	91.9	12.3	5.4	1.1
5	31.4	7.8	82.5	2.9	6.0	1.7
6	71.1	47.5	105.1	25.5	5.2	0.9
7	73.7	50.1	113.9	34.3	8.1	3.8
8	28.7	5.1	123.8	44.2	5.0	0.7

From this table it again appears that the fineness of division of bone meal is a measure of its rate of decomposition in the soil, based on the formation of nitric nitrogen from the organic matter in the bone. It was thought that the amount of lime found in the percolates might give some indication of the rate at which the lime phosphate was dissolved within the soil, but the results are too irregular to allow any interpretation. This is partly caused by the fact that, as in lysimeter 6, where no lime was added, the rapid nitrification of the blood and the consequent nitrate nitrogen produced, made for an increase in the lime withdrawn from the soil itself. At the same time, it is interesting to note that the greatest amount of lime appeared in the test to which lime phosphate as phosphate rock was added, and in which the nitric nitrogen produced was less than in any other of the tests with the exception of the check. The phosphoric acid determination showed the greatest solubility in the case of the phosphate rock and blood test, and here the lime content is second in quantity to that of the rock alone. In the bone meal, the difference in results is within the limits of experimental error, but the fine bone shows a greater solubility than the coarser. The second size of bone showed a drop below the check in lime and was less in phosphoric acid than the two coarser bones; the lime drop is significant and points to some fault in the soil or its method of packing and nature of drainage, but the nitrogen transformation was apparently not affected.

While not germane to the question, it is nevertheless of interest to compare the results of the blood and rock tests with those

from the bone. Where the phosphate rock alone was employed, an increased nitrification of the soil nitrogen to the extent of 5 per cent is noted. With one exception, all the drainages from this test showed a higher nitrate content than the check. Of the nitrogen added as blood, 47.5 and 50.1 per cents were recovered in the period of 18 weeks as nitric nitrogen, while the best yield from the bone was 16 per cent. Nitrification of the blood nitrogen was accelerated by the addition of phosphate rock just as was the soil nitrogen, but to a lesser extent. More phosphoric acid was found in the test with blood alone than in the check, which points to a solvent effect exerted by the fermenting action of the blood on the soil phosphates.

TEST NO. 4

A final test was made with an attempt to measure the amount of phosphoric acid rendered soluble by bacterial action. In this test, quartz sand previously digested with acid and washed with water till free of acid was mixed with the various materials. Fresh station soil was shaken thoroughly with water, allowed to settle for twenty-four hours, and the sand tests moistened with the supernatant liquid. Two series were started, being allowed to stand three and five weeks, respectively. Five grams of the various sizes of bone meal were placed in 200 grams of sand. In two further tests, blood and phosphate rock or phosphate rock alone, were added, in amounts equivalent to the phosphoric acid and nitrogen content of the fine bone meal. At analysis, the contents of the beaker were transferred with water to a filter, and washed through paper until the runnings amounted to 300 cc. The entire filtrate was analyzed for phosphoric acid. In the case of the phosphate rock tests, the filtrate was very turbid. The results, therefore, do not express what was in solution, but represent material in so finely divided a condition that it passed through the pores of filter paper, and went into solution immediately on the addition of acid. The results were as follows:

TABLE VIII—PHOSPHORIC ACID DISSOLVED IN SAND TESTS
896.5 MG. OF PHOSPHORIC ACID APPLIED

	3 weeks	5 weeks	Total
Fine bone meal	4.0	3.4	7.4
No. 2 bone meal	2.2	3.8	6.0
No. 3 bone meal	2.6	3.7	6.3
Coarse bone meal	1.3	3.1	4.4
Phosphate rock	5.1	7.8	12.9
Phosphate rock and blood	7.5	11.1	18.6

It would appear from these tests that the phosphoric acid in fine bone meal is more available than that passing a 20 mesh sieve by 23 per cent, and almost 70 per cent more available than that passing through a 6 mesh sieve. The two intermediate sizes are about equal, and both superior to the coarsest. The phosphate rock gave, as was expected from the appearance of the filtrate, a considerably greater phosphoric acid content of the filtrate, which was augmented to an important extent by the decomposing action of the blood.

SUMMARY

The results of these tests, based on those from the fine bone meal as 100, may be seen from the following comparative tables:

TABLE IX—AMMONIFICATION IN TWO-THIRDS SATURATION

Days	2	5	9	11	18	Average
Bone meal Size No.	100	100	100	100	100	100
1	100	100	100	100	100	100
2	32	34	30	55	49	40
3	22	30	57	21	34	33
4	19	17	30	3	43	22

TABLE X—NITRIFICATION IN HALF SATURATION

Days	2	4	7	10	14	17	21	Average
Bone meal Size No.	100	100	100	100	100	100	100	100
1	100	100	100	100	100	100	100	100
2	85	92	71	92	62	77	57	77
3	66	92	83	62	34	75	54	67
4	53	65	64	60	33	62	52	56

TABLE XI—NITRIFICATION IN LYSIMETERS

Weeks Bone meal Size No.	6	9	12	15	18	Average
1	100	100	100	100	100	100
2	77	70	93	38	55	67
3	55	31	75	38	75	54
4	58	7	48	46	71	46

TABLE XII—SAND TESTS—WATER-SOLUBLE PHOSPHORIC ACID

1.....	100	3.....	85
2.....	81	4.....	60

CONCLUSIONS

I—The fineness of bone meal determines the rate at which its nitrogenous part will decompose in the soil to ammonia and thence to nitric nitrogen.

II—The solubility of bone phosphate is directly influenced by bacterial action, and an increased ammonia or nitrate decomposition may be held to indicate a more efficient phosphoric acid solvent action.

III—Since there is a limit to which bone meal can be ground to permit of its convenient handling, fine bone meal should possibly be defined as that which passes through a 50 mesh sieve.

IV—Since, however, it is not commercially practicable to prepare so fine a product without also including a considerable proportion of the very fine dust, a standard of fine bone meal of 65 per cent to pass a 50 mesh sieve, and at least 90 per cent of the remainder to pass a 25 mesh sieve is presented as one to which no reasonable objection can be offered by the dealers, and from which satisfactory results will accrue to the crops.

CHEMICAL LABORATORY, EXPERIMENT STATION
HAWAIIAN SUGAR PLANTERS' ASSOCIATION
HONOLULU, T. H.

A RAPID METHOD FOR THE DETERMINATION OF CAMPHOR AND OF CERTAIN ESSENTIAL OILS WHEN IN SOLUTION IN ALCOHOL

By W. B. D. PENNIMAN AND W. W. RANDALL

Received June 1, 1914

As the result of series of experiments carried out in this laboratory at intervals during several years, a method has been devised for the assay of spirits of camphor and of peppermint, and of the extracts of lemon, orange, peppermint, anise and nutmeg, which appears to be more rapid and much more accurate than any method with which we are familiar. The facts which form the basis of the method may be grouped under three heads, as follows:

1—Camphor and the several oils enumerated above are completely expelled from solution in alcohol, when these solutions are mixed with from four to ten volumes of a strong solution of calcium chloride.

2—The separated camphor or oil dissolves with the greatest ease in low-boiling gasoline, an operation with which alcohol, at least in the presence of such a calcium chloride solution, does not interfere.

3—Within certain fairly wide limits, the volume of the gasoline solution formed is exactly equal to the sum of the volumes of the gasoline itself and the solid camphor (or oil) which has been dissolved.

The method here described is by no means entirely new. Schmatolla¹ noted that when camphor dis-

solves in light petroleum oil, the volume-relation stated in "3" obtains. He employed a burette graduated in tenths cc. as a measuring apparatus, and weighed out the camphor spirit, which was later precipitated by means of saturated sodium chloride solution. We have secured better results by the use of calcium chloride solution, and prefer graduated milk bottles and the use of the centrifuge as means of accurate measurement of small quantities. Arnost¹ used a somewhat similar method to determine camphor in celluloid, correcting for alcohol dissolved. Chittick,² we have found since these experiments were made, used a method similar to ours for peppermint, precipitating the oil with water and, by means of a blank, correcting for alcohol dissolved. We have not found water a satisfactory precipitant, and believe that much time can be saved without decrease in accuracy by the use of pipettes and the avoidance of weighings.

The apparatus called for consists simply of several accurate full pipettes, a Babcock centrifuge, and one or more accurately graduated Babcock milk bottles. If the divisions on the neck of the bottle be from 0 to 10, then the graduated portion will contain just 2 cc. With a magnifying glass the volume of a column of supernatant solution in the neck of the bottle can be read with accuracy, probably to 0.008, perhaps to 0.004 cc.

As the volume of gasoline used should not be much less than, nor much more than twice as great as that of the camphor or oil to be dissolved (if the volume-relation mentioned under "3" is to hold good), it is well to work with such quantities that not much over 0.5 cc. of camphor or oil is to be determined. Thus we have found that 5 cc. of the alcohol solution serves well for strengths from 5 to 15 per cent; 10 cc. is probably better for 4 per cent solutions or anything weaker. The quantity of gasoline should in general be somewhat greater than that of the oil.

METHOD OF ANALYSIS

FOR STRENGTHS BETWEEN 7 AND 15 PER CENT—Pipette 5 cc. of the solution into the Babcock bottle; fill nearly to the neck with clear calcium chloride solution of sp. gr. 1.37; shake, add *exactly* 1 cc. of gasoline (b. p. 40° to 60° C.); shake, fill with the salt solution to near the top of the graduation; stopper tightly; shake violently, and whirl in the centrifuge at high speed for about five minutes. If now the salt solution is still cloudy, shake thoroughly, and whirl again. Read the menisci as in a milk-fat determination; *i. e.*, the lowest point of the lower meniscus and the extreme edge of the upper. For example, suppose the readings are 9.32 and 1.77; the column corresponds to 7.55 (= 1.51 cc.). Of this 5.00 (= 1 cc.) is gasoline, and 2.55 (= 0.51 cc.) is oil. Then $4 \times 2.55 = 10.20$ = percentage of oil in the extract.

FOR STRENGTHS LESS THAN 7 PER CENT—Use 10 cc. of the solution and a quantity of gasoline not more than twice that of the oil or camphor to be set free;

¹ *Apoth. Zeit.*, 16, 290; *Abstr. Chem. Centr.*, 1901, 1 (20), 1117; *J. Soc. Chem. Ind.*, 20 (1901), 756; Allen's "Commercial Organic Analysis" (new ed.), Vol. IV, p. 200.

¹ *Z. Unter. Nahr. u. Genussm.*, 12 (1906), 532; *Abstr. J. Soc. Chem. Ind.*, 25, 1169.

² *Proc. Assn. Am. Dairy, Food & Drug Off.*, 1913, p. 160; *Abstr. Chem. Abstr.*, 8 (1914), 1847.