by himself, but in daily use indestructable and properly compensated glass wedges have many advantages.

A METHOD FOR SEPARATING THE "INSOLUBLE" PHOSPHORIC ACID IN MIXED FERTILIZERS DERIVED FRON BONE AND OTHER ORGANIC MATTER FROM THAT DERIVED FROM ROCK PHOSPHATE.

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DURING the year 1895 the wholesale price of rough bone was about $19.50 per ton in the New York markets. Ground bone brought $22.75 per ton, and ground Charleston rock averaged $8.12½ per ton. After allowing for the value of the ammonia, the phosphoric acid purchased in bone still costs considerable more than the same amount purchased in mineral phosphates.

Estimating 3.75 per cent. of nitrogen in the ground bone, wholesale cost 12.3 cents per pound, there would be $9.23 worth of nitrogen per ton. This value would make the phosphoric acid in a ton of ground bone cost at wholesale $13.52, when the same amount approximately of phosphoric acid in ground rock costs about $8.12½ per ton.

This cheapness of mineral phosphates has led to their very general use by fertilizer manufacturers instead of bone as a source of phosphoric acid.

While the so-called Available Phosphoric Acid[1] of the two may be of equal value, it seems wrong to classify the phosphoric acid of mixed fertilizers insoluble in the ammonium citrate solution at the same price in the two. The Connecticut State Station's Report "Trade Value," of the organic phosphoric acid is (average) five cents per pound, while in the raw ground rock it is but two cents per pound.

It has been urged that there is no means of telling whether the "insoluble" phosphoric acid in mixed fertilizers was derived from minerals, or from bone and tankage. It was for

[1] That portion soluble in a neutral solution of ammonium citrate, sp. gr. 1.09, digested at 65° C. for thirty minutes.

this reason that the experiments herewith described were undertaken.

The method employed depends upon the difference in specific gravity between bone and other organic matter and the mineral phosphates. The following are the specific gravities of some of the more important compounds found in bone and in rock phosphates:

	Sp. Gr.
Bone and other organic matter, less than	2.0
Gypsum	2.3
Aluminum phosphates, above	2.3
Iron phosphates, about	2.6
Silica	2.65
Calcium phosphates	2.9 to 35.5
Fluorite	3.2

For the separation of the bone and organic matter from the mineral matter, a solution of mercuric iodide in potassium iodide was employed. This solution was first proposed by E. Sonstadt[1] in 1873, and elaborated by Thoulet[2] in 1878. The solution, as prepared by the writer, is as follows: Seventy-five grams of potassium iodide are dissolved in 350 cc. of warm water, and 100 grams of mercuric iodide added. The solution is filtered and evaporated in a porcelain dish over a water-bath, until a crystal of pure gypsum, sp. gr. 2.3, comes to the surface. The solution is then diluted at 15.5° C. until the gypsum is of the same density as the solution, scarcely floating or sinking. The solution is now at specific gravity 2.3, and should be diluted to specific gravity 2.26 according to the formula $V' = \frac{V(D-D')}{D'-1}$ where V is the volume of water to be added, V the volume of the solution, D its specific gravity 2.3, and D' the desired specific gravity 2.26. The specific gravity should be verified by use of the picnometer.

The separating solution should be placed in a small flask of about 100 cc. capacity, fitted up on the same plan as a wash bottle. The amounts given above will make about 100 cc. of solution.

1 *Chem. News*, **29**, 127.
2 *Compt. Rend.*, Feb. 18, 1878.

The tube for making the separation may be as elaborate as desired. A very good form is described by S. L. Penfield in the *American Journal of Science* for Dec. 1895. The following has given excellent satisfaction in these experiments. A glass tube, a broken burette for example, about one and three-tenths cm. internal diameter and twenty cm. long is connected by means of a short piece of rubber tubing, with a tube of similar diameter, closed at one end and about seven cm. in length. See Fig. 1.

The material to be separated is placed in the tube and fifteen or twenty cc. of the separating solution added, after which the tube is stoppered and shaken thoroughly. The sides of the tube are now washed down with more of the solution; after standing for five minutes, the bottom part or bucket should be tapped smartly to release any light portions carried down with the heavy material, and a jet of the solution blown against the matter floating at the top, to dislodge any heavy particles. The tube is then let stand till the solution is clear, all matter having gone to the top or bottom. This will usually take from forty minutes to an hour in finely ground mixed fertilizers or rock superphosphates.

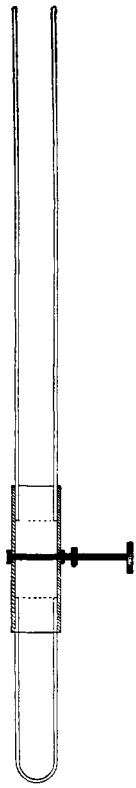

Fig. 1.

The rubber tube is now tightly clamped with a screw pinch-cock, separating the heavy material from the light. A beaker is placed beneath the tube, and the lower tube or bucket is removed, the fingers being encased in rubber finger-tips, as the separating solution cracks the skin. The tube and contents are brought on a dry filter and the liquid filtered back into the supply flask. Water is then used, the first washings being saved and evaporated down to a specific gravity of 2.26 again. The light portion is treated in a similar manner, care being taken to get all particles out of the tube at the last.

At first it was not supposed necessary to have any fixed specific gravity, but as will be seen by the following table, it is

important that the specific gravity should be somewhere about 2.26. The exact reason for this is not in the province of this paper to decide, but seems to be owing to the low specific gravity of the aluminum phosphates.

The plan of the experiments carried on was to take a fertilizer known to contain nothing but organic matter as a source of phosphoric acid, and a mixture of South Carolina and Florida phosphates, both the raw rock, and the acidulated product. These were analyzed and then mixed in different proportions and treated with the separating solution.

In the first experiment two grams of the mixture were treated with 100 cc. of the the neutral ammonium citrate solution (sp. gr. 1.09), and digested for thirty minutes at 65° C., shaking every five minutes. After filtering, the dried insoluble residue was separated as carefully as possible from the filter paper and treated as previously described. As will be seen by reference to the table following, this method, though most desirable, was given up owing to the large proportion of phosphoric acid left on the filter paper.

The next attempt was to treat the mixed fertilizer directly with the separating solution, and was also abandoned owing to soluble matter in the fertilizers which destroyed the separating solution.

These two experiments showed two things clearly, that the fertilizer cannot be treated with ammonium citrate solution before separating, and that the matter soluble in water must be removed before separating.

To obtain this latter end and expose the minimum amount of filter paper, the inner tube of a fat extraction apparatus was used, such as was described by Prof. S. W. Johnston.[1] These tubes are used by the Storrs (Conn.) Agricultural Experiment Station, and are made for them by Whitall, Tatum & Co., New York. The tube is about fifteen cm. in length and two and five-tenths cm. internal diameter, slightly contracted at one end, which has a rim so that a piece of filter paper reinforced on the outside with cheese cloth, can be tied on. (Fig. 2.) The method is as follows :

[1] *Am. J. Sci.*, **13**, 190, *1877*

Two grams of the raw or mixed fertilizer are transferred to the "extraction" tube and extracted with nearly 250 cc. of hot water, as for water soluble phosphoric acid determination. The tube and contents are placed in a drying oven, and when thoroughly dry the filter paper is taken off and all matter carefully removed with a spatula and brush. Any fine sediment adhering to the glass may be removed by a rubber tipped glass rod.

Fig. 2.

The material is now transferred to the separating tube and treated as before described.

The light portion and heavy portion are treated separately with ammonium citrate solution, and the insoluble phosphoric acid determined in the usual way. That in the "light" comes from bone, tankage or other organic matter, that in the "heavy" from minerals.

The following is a tabular statement of the results of the experiments:

Material.	Total P_2O_5.	Insoluble P_2O_5.
Prepared mixed fertilizers[1]	10.75	2.56
Mixed Florida and Carolina raw rock	27.51	24.36
Mixed Florida and Carolina dissolved rock	16.23	0.77

PERCENTAGE OF PHOSPHORUS PENTOXIDE FOUND IN THE HEAVY AND LIGHT PORTIONS AND LEFT ON THE FILTER PAPER.

No. of experiment.		Specific gravity.	Light.		Heavy.		Left on paper.	Total.	
			Theoretical.	Found.	Theoretical.	Found.		Theoretical.	Found.
	Treated with ammonium citrate before separating.								
1	Mixture A 1	2.46	1.28	1.79	12.18	8.33	2.66	13.46	12.78
2	Mixture B 2	2.46	1.28	2.02	0.39	0.43	0.44	1.67	2.89
3	Mixture A 1	2.46	1.28	1.83	12.18	8.33	2.66	13.46	12.82
4	Mixture A 1	2.35	1.28	1.52	12.18	9.68	2.66	13.46	13.86
5	Mixture B 2	2.35	1.28	1.66	0.39	0.49	0.44	1.67	2.59
	Separated before treating with ammonium citrate.								
6	Mixture B 2	2.22	1.28	0.93	0.39	0.70	trace	1.67	1.63
7	Mixture A 1	2.26	1.28	1.38	12.18	11.65	0.12	13.46	13.15

[1] Containing acidulated bone, tankage, dried blood, sodium nitrate and potassium sulphate.

No. of experiment.		Specific gravity.	Light.		Heavy.			Total.	
			Theoretical.	Found.	Theoretical.	Found.	Left on paper.	Theoretical.	Found.
8	Mixture C 3	2.26	1.28	1.63	6.28	6.03	0.06	7.56	7.72
9	Mixture B 2	2.26	1.28	1.18	0.39	0.65	trace	1.67	1.83
10	Mixture A 1	2.26	1.28	1.28	12.18	12.03	0.12	13.46	13.43
11	Mixture C 3	2.26	1.28	1.35	6.28	6.08	0.06	7.56	7.49
12	Mixture B 2	2.26	1.28	1.11	0.39	0.48	trace	1.67	1.59
13	Mixture A 1	2.26	1.28	1.24	12.18	12.07	0.12	13.46	13.43
14	Mixture C 3	2.26	1.28	1.15	6.28	6.09	0.06	7.56	7.30
15	Pre'd mixed fertiliz'r	2.26	2.56	2.51	....	....	trace	2.56	2.51
16	Dissolved rock.....	2.26	...	...	0.77	0.70	trace	0.77	0.70

1 Mixture A, 1.0 gram prepared mixed fertilizer.
" " 1.0 gram raw Florida and Carolina rock.
2 Mixture B, 1.0 gram prepared mixed fertilizer.
" " 1.0 gram dissolved Florida and Carolina rock.
3 Mixture C, 1.0 gram prepared mixed fertilizer.
" " 0.5 gram raw Florida and Carolina rock.
" " 0.5 gram dissolved Florida and Carolina rock.

Of the above analyses, the first five were tentative, the method and manipulation were experimental, and the results were unsatisfactory. They show, however, that a specific gravity of 2.46 or 2.35 is too heavy for the proper workings of this method, and that when treated with ammonium citrate solution before separation, at least twenty per cent. of the phosphoric acid is lost through the adherence to the filter paper.

The sixth analysis shows that a specific gravity of 2.22 is too light, and matter which should rise to the top sinks to the bottom. Nos. 7 to 14 show that the method as finally elaborated, is quantitative and apparently reliable and capable of being put into regular use as a method of testing the source of the insoluble phosphoric acid in mixed fertilizers. The attempt was made to treat first with ammonium citrate, and filter through the extraction tube above described, in order to expose less filter paper, but the solution would not filter at all.

No. 15 was a sample of mixed fertilizer containing acidulated bone, tankage, dried blood, sodium nitrate and potassium sul-

phate, and formed the source of the "light" phosphoric acid in the above experiments. When treated with the separating solution (after dissolving out salts soluble in water) everything rose to the top with the exception of a very small amount of some material, either calcium sulphate or silica, as there was no trace of phosphoric acid in it. The solution was perfectly clear in ten minutes.

No. 16 was the acidulated Carolina and Florida rock used in the above experiments. When treated with the separating solution, a small amount came to the top. There was, however, no trace of phosphoric acid in this portion. It took an hour for the solution to become clear, showing the presence of some substance, probably calcium sulphate and aluminum phosphates, of specific gravity but little higher than that of the solution, namely, 2.26.

The method of analysis were those of the Association of Official Agricultural Chemists.

SUMMARY.

The following method is proposed for separating the insoluble phosphoric acid in mixed fertilizers derived from bone, tankage or other organic matter, from that derived from mineral phosphates.

SOLUTIONS AND APPARATUS.

Separating Solution : Seventy-five grams of potassium iodide and 100 grams of mercuric iodide are dissolved in 350 cc. water and evaporated over a water-bath to a specific gravity of 2.26. This solution should be kept in a small flask arranged like a wash bottle.

Other solutions necessary to determine available and total phosphoric acid.

Separating Tube : Two tubes one and three-tenths cm. internal diameter, one seven cm. in length, closed at one end, the other twenty cm. long. These are connected by a piece of stout rubber tubing, so that the lower part or bucket, can be separated by a screw pinch-cock from the upper portion.

Extraction Tube : A tube two and five-tenths cm. internal

diameter, slightly contracted at one end, which has a rim over which filter paper and cheese cloth can be tied.

Other apparatus as for available and total phosphoric acid determinations.

Manipulation : Two grams of the substance to be examined are transferred to the extraction tube and washed with from 100 to 225 cc. of hot water, depending upon whether or not water soluble phosphoric acid is to be determined. Dry thoroughly, remove substance carefully, using spatula, brush, and rubber tipped glass rod, and transfer to a separating tube. Add fifteen to twenty cc. of the separating solution, shake thoroughly and wash down the sides of the tube with a jet of the solution. After standing five minutes tap the lower part or bucket smartly with the finger, to release any light portion carried down with the heavy, and stir up the matter on top with a jet of solution.

Let stand until the solution is clear, or for one hour, clamp the rubber tube, place a beaker under the bucket, which is carefully removed, the fingers being encased in rubber finger tips. Filter the solution back into the supply flask, wash thoroughly, saving the first washings for evaporation to a specific gravity of 2.26 again, and treat for insoluble phosphoric acid in the usual way. The light portion is treated in a similar manner. If desired, the heavy and light portions can be treated as for total phosphoric acid, thus determining all of the phosphoric acid derived from inorganic and organic sources respectively, except the water soluble.

MIDDLETOWN, CONN.

SOURCES OF ERROR IN VOLHARD'S AND SIMILAR METHODS OF DETERMINING MANGANESE IN STEEL.[1]

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VOLHARD'S method of determining manganese is generally considered a very accurate one; nevertheless, that the

[1] In this Journal, 18, 406, I omitted to state a precaution used, in the manner of performing Drown's sulphur method there described. The solution from the Troilius' bulb is heated to boiling (preferably with the previous addition of permanganate solution) before filtering into it the hydrochloric acid solution from the graphitic residue. This is to oxidize any sulphur that may be present as sodium sulphide.