REVERSION OF PHOSPHORIC ACID BY HEAT, TOGETHER WITH SOME OBSERVATIONS ON THE FINE GRINDING OF ANALYTICAL SAMPLES.

W. B. Phillips, Ph. D.

When manufactured phosphates are analyzed immediately after preparation, the percentage of phosphoric acid soluble in water is generally found to be higher than at any subsequent time. A portion of it becomes insoluble in water, but is soluble in some of the organic salts of ammonia; i. e., in the oxalate and citrate. To this phosphoric acid the term *reverted* is applied, signifying, as is well known, phosphoric acid which, though at one time soluble in water, has become insoluble in that liquid, and occupies an intermediate position between the original tri-calcium-phosphate of the crude material, and the tetra-hydrogen-calcium-phosphate of the manufactured product.

The change from soluble to reverted begins almost at the very moment of manufacture, and continues for an indefinite period, varying among other things with the raw material used, the quantity of acid employed, &c., &c.

It might be supposed that as this reversion begins when the product begins to dry, it was connected intimately with the process of drying. But it has been shown by Post (Chem. Industr. 1882, p. 217,) that it goes on even in samples enclosed in hermetically sealed bottles, and hence is not dependent on the loss of moisture, under ordinary conditions of temperature.

The limits of this paper will not allow me to enter at all into the discussion of the various causes of reversion. Among the more prominent ones are the presence of unattacked oxides of calcium, iron, and aluminum, and calcium sulphate and carbonate.

The object of this paper is to direct attention anew to the fact that a temperature of 100° C, maintained for varying lengths of time on the manufactured phosphates, causes a very rapid reversion.

The material used was a sample of an "Acid Phosphate" prepared under my personal supervision at the works of the Navassa Guano Company. It was prepared as follows :

Fine ground Charleston Rock	1,100 pounds.
Sulphuric Acid, 470 B	950 "

Several tons of it were made November 21st, 1883, and a sample of it was drawn by myself, November 22d. The sample was pulverized by hand as fine as possible, and analyzed at once.

Fifty grains of the sample were then taken and dried at a temperature of 90°-100° C. for two days. At the end of that time a sample was drawn, pulverized until it passed through a sieve of 100 meshes per square inch, and analyzed.

The drying was continued for eight (8) days longer, at the end of which time a sample was drawn, passed through a 100 mesh sieve, and analyzed.

Tabulating these results for convenience of reference we have :

	A	B	C
On a Dry Basis.	24 hours after preparation, pulverized by hand.	After 2 days at 90°—100° c. Through 100 mesh sieve.	After 10 days at 90°—100°c. Through 100 mesh seive.
Total Phosphoric Acid....	17.31 per cent.	17.13 per cent.	17.32 per cent.
Soluble " "	11.74 " "	10.59 " "	7.48 " "
Insoluble " "	3.32 " "	2.95 " "	2.85 " "
Reverted " " ...	2.25 " "	3.59 " "	6.99 " "
Available " "	13.99 " "	14.18 " "	14.47 " "

We have here a loss of 4.26 per cent. of sol. phos. acid in days, a loss of .47 per cent. of insol. phos. acid, and a gain of 4.74 per cent. of reverted. Ordinarily the loss of soluble is compensated by the gain of reverted, while the insoluble remains about the same. Post, in the article before referred to, claims to have found that in the course of six (6) months, in sealed bottles, some of the soluble becomes so insoluble as not to be dissolved by ammonium citrate at 90° C. But here it is shown that in ten (10) days at a temperature of 90—100° C, some of the originally insoluble phosphoric acid, viz: .47 per cent. has *become soluble in ammonium citrate at* 40° *C.*, that is, has changed to reverted ! But this loss of .47 per cent. of insoluble phosphoric acid is doubtless due to the very fine grinding of the dry samples. For the difference in insoluble phosphoric acid between the first and second analyses is .37 per cent., while the difference between the second and third is only .10 per cent. That is to say, the difference between the insoluble phosphoric acid in the sample pulverized by hand and the sample dried for two (2) days and then passed through a 100 mesh sieve, is .37 per cent. in favor of the finely pulverized. But the difference between the two finely pulverized samples after eight (8) days of drying is only .10 per cent.

That the ammonium citrate should dissolve more phosphoric acid from the finely ground sample is just what was to be expected. When sufficient sulphuric acid is added to the crude tricalcium phosphate to render *all* of the phosphoric acid soluble in water reversion does not appear to proceed as rapidly as when there is present some of the original undecomposed phosphate. But in this case, when using Charleston rock, it is very difficult to obtain a product which will dry in a reasonable time without the aid of artificial heat, or some carbonate as a dryer. Using artificial heat there is great danger of hastening reversion, and the same is true if some chemical "dryer" is used, to say nothing of the reduction of the content of total phosphoric acid in this latter case.

There is one point to which I wish to direct especial attention, and that is what I conceive to be the *necessity for fine grinding of the analytical sample.* Plants derive their food from the soil in solutions, and in these solutions the food is in a state of almost inconceivable fineness.

In estimating the value by chemical analysis of any plant food, we should, as far as practical, approximate to the degree of fineness to which the food must be reduced before the plant can use it.

Other things being equal, the finer we grind analytical samples before acting upon them with chemical reagents which in a greater or less degree represent the action of the soil the nearer do we approach to the methods of nature.

Laboratory of Navassa Guano Company,
Wilmington, N. C., Dec. 6th 1883.