XVII. ON THE DETERMINATION OF REVERTED PHOSPHATES.*

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In an investigation on the subject of reverted phosphoric acid, the first question that arises is, What is meant by this term? The curious phenomenon of a decrease in the amount of soluble phosphate in a superphosphate, and its reversion into a form insoluble in water, but soluble in the organic salts of ammonia, in weak acids and other reagents, has been attributed to several different causes.

According to the most common explanation,† it is due to the gradual interaction between the soluble or monocalcic phosphate formed in the manufacture, and the still undecomposed tricalcic phosphate of the original rock, this reaction resulting in the formation of the intermediate compound dicalcic phosphate.

Again, it has been noticed that this reversion is especially large when the amounts of iron and alumina present are considerable, and in such cases it has been attributed‡ to the formation of phosphates of iron and alumina having the solvent properties specified above.

Again, from experiments in our own laboratory, it has been found that this reversion is very noticeable in acid phosphates, which, after treatment with sulphuric acid, have been mixed with natural phosphates containing large amounts of carbonate of lime. The reaction that takes place between the monocalcic phosphate and carbonate of lime probably results in the formation of either the dicalcic or tricalcic phosphate. This latter salt, though insoluble in water, is readily taken up, on account of its fine state of division, by the reagents used for the estimation of reverted phosphates.

From these different explanations of the character of reverted phosphate, it is evident that the term is not capable of a strict chemical definition. It may consist in any given case of one or of several chemical compounds. The best definition that can be given is the general one condensed into the name itself. Reverted phosphates are those which, originally insoluble, but having been made soluble, have reverted or returned to the insoluble condition. They must now, however, be looked upon as :

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†Zeit. fur analyt. Chem. 10, Fresenius.

‡Zeit. fur analyt. Chem. 19, Z. Meyer.

(1.) Just over the border line that separates the soluble from the insoluble, lying very close to the soluble, and being brought back by a slight addition to the solvent power of water ; and, as

(2.) Widely separated and different in solubility from the insoluble form which they originally possessed. Like the flats lying just above the river's edge, they must be wholly covered by a slight rise in the water that affects the banks but little.

The object of the inquiry here described has been to establish the above distinctions, and to find a method of separation that shall in the actual analysis recognize them as nearly as possible. The course pursued has been that followed in similar inquiries :

I. An examination of the solubility of the different natural phosphates used in the manufacture of superphosphates.

II. An examination of the solubility of the different chemical compounds of which reverted phosphates have been found to consist ; and

III. An attempt based upon the results of these two inquiries to find the best method of separating these two classes.

In the examination of the natural phosphates, five different forms were taken as typical of all. These were :

1. *Apatite*, as type of the nearly pure tricalcic form in its most insoluble condition.

2. *South Carolina rock*, containing besides tricalcic phosphate, phosphates of iron and alumina, and carbonate of lime.

3. *Bone Ask*, the great organic source of phosphate.

4. *Navassa rock*, typical on account of its large percentage of iron and alumina ; and finally,

5. *Curacao phosphate*, as type of the island phosphates, notable for their peculiar mechanical condition and greater solubility in the organic salts of ammonia.

In examining the solubility of these natural phosphates, attention was first given to the effect of different relative proportions of phosphate and solvent. The standard method of Fresenius, Luck and Neubauer* was followed, using 50 cc. of citrate of ammonia solution, of sp. gr. 1.09, and made as nearly neutral as possible ; time, 30 minutes, temp. 35° C. Two series of experiments were made. In the first, one gram of substance was taken ; in the second, $\frac{1}{10}$ of a gram.

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*Zeit. fur analyt. Chem. 10.

	SERIES I.	SERIES II.
	P_2O_5 dissolved.	P_2O_5 dissolved.
Apatite	0 40 per cent.	1.54 per cent
South Carolina rock	2.00 "	6.60 "
Bone Ash	2.60 "	8.30 "
Navassa	2.65 "	10.10 "
Curacao	4.40 "	16.00 "

Comparing these tables, we see at once the fact that has been commented upon very frequently of late by German chemists as regards superphosphates, and to which special attention has been called within a few months by a printed letter of Dr. S. W. Johnson, in the case of Curacao phosphate, namely, that the percentage of phosphate dissolved increases very largely with the increase of solvent, or, what is the same, the decrease of substance taken for analysis. These tables show that this is true not only of reverted phosphates as found by the former, nor of Curacoa phosphate as shown by the latter, but also of all natural phosphates, including even the difficultly soluble apatite. This fact has a very important bearing upon the error involved in the determination of reverted phosphoric acid by this method, *i. e.*, an error as regards the strict separation of the reverted phosphates from the insoluble phosphates. Thus, supposing five superphosphates after the extraction of the soluble to contain no reverted phosphate, but to contain 10 per cent. of the above raw phosphates respectively, corresponding to about 3 per cent. of insoluble phosphoric acid, the citrate would attack these raw phosphates, and instead of the error being 0.04, 0.20, 0.26, 0.26 and 0.44 per cent. as would naturally be supposed from Series I, it would in reality be 0.15, 0.66, 0.83, 1.01 and 1.60 per cent. as shownby Series II. Thus, the superphosphates would be reported as containing these latter amounts of reverted phosphoric acid, when in fact they contained nore whatever.

This same fact of increased solvent power obtained by increasing the amount of solvent salt was shown to be true also of oxalate of ammonia, by treating 2 grams of Navassa rock and Curacao phosphate with 1, 5, and 10 grams of the salt dissolved in 100 cc. of water, at a temperature of 100° C. for 30 minutes.

SERIES III.

	1 gram.	5 grams.	10 grams.
Navassa, P_2O_5 dis.,	2.20	8.75	12.15
Curacao, " "	2.50	12.30	17.60

The influence of increase of temperature upon the amount of rock dissolved was shown by treating one gram of the different phosphates with 100 cc. of water containing four grams of oxalate at 20°C. and at 100°C.

SERIES IV.

	Apatite.	So. Car. Rock	Bone Ash.	Navassa.	Curacao.
At 20°C. P_2O_5 dis.	0.36 pr ct.	2. 25 pr ct.	2.72 pr ct.	2.85 pr ct.	5.51 pr ct.
" 100° " "	2.16 "	5.80 "	8.78 "	9.40 "	15 30 "

In performing the above experiments at 100°C. a strong odor of evolved ammonia was observed, and it was also found that the filtrates were decidedly acid in reaction. The importance of this and its bearing upon the subject will be better seen further on.

The results thus far given show very clearly the cause of much of the confusion that has arisen over the determination of reverted phosphates. This lies in the great facility with which the citrate and oxalate solutions attack the insoluble phosphate, especially when the proportion of solvent is increased or when the temperature of digestion is raised. Many chemists have been led by these difficulties to seek a better method. The suggestion has frequently been made that a weak or dilute acid be employed as a substitute for the organic salts of ammonia. Thus Grupe and Tollens* recommend the use of a $\frac{1}{4}$ per cent. of citric acid solution. The solvent power of this acid of $\frac{1}{4}$ per cent., also of oxalic acid of $\frac{1}{4}$ per cent. and $\frac{1}{10}$ per cent., also of hydrochloric acid of $\frac{1}{100}$ normal strength, upon the natural phosphates was examined. 100cc. of each of the above solvents were taken, the temperature of digestion was 40°C., time one hour. One gram was taken with each acid, and in addition also $\frac{1}{10}$ of a gram with the citric acid of $\frac{1}{4}$ per cent.

SERIES V

Acid employed—		Citric $\frac{1}{4}$ per ct.		Oxalic $\frac{1}{4}$ per ct.	Oxalic $\frac{1}{10}$ per ct.	HCl $\frac{1}{100}$ normal.
		1 gram.	$\frac{1}{10}$ gram.	1 gram.	1 gram.	1 gram.
Apatite.	P^2O^5 dis.	0.74 per ct.	2.70 per ct.	3.20 per ct.	1.08 per ct.	2 56 per ct.
So. Car. Rock.	"	2 80 "	11.40 "	8.75 "	2.68 "	4 25 "
Bone Ash.	"	3.80 "	11.80 "	9.23 "	4.15 "	3.85 "
Navassa.	"	3.30 "	14.00 "	9.96 "	3.50 "	4.15 "
Curacao.	"	4.20 "	19.80 "	9.12 "	4.00 "	3.35 "

Supposing a fertilizer to contain 10 per cent. of insoluble rock, the citric acid would make the reverted phosphoric acid 0.27 per

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*Berichte der deutsch. chem. Gesellschaft, 14, 754.

cent., 1.14 per cent., 1.18 per cent., 1.40 per cent., 1.98 per cent. respectively in excess of the actual amount present. The excess thus introduced would be considerably greater than that caused by the solvent action of the citrate of ammonia solution, *vide* Series II., and the claim made for the citric acid solution by Grupe and Tollens that it dissolves nearly the same amount of phosphate from different quantities of substance taken for analysis shown to be wholly unfounded as regards its action on raw phosphates. (Compare columns 1 and 2 above.)

The action of the different solvents upon the dicalcic and tricalcic salts was next studied. These salts were obtained by precipitation, and on analysis found to agree so closely with the theoretical composition as to show the admixture of traces only of other forms. After thorough washing they were mixed with about an equal weight of calcium sulphate, in order to imitate the conditions under which they are found in a superphosphate. These mixtures were then thoroughly air-dried. One gram of each was now treated with the different solvents, already employed, for 30 minutes at a temperature of 40°C. The mixture of the dicalcic salt contained 19.20 per cent. of P_2O_5, of the tricalcic salt 13.00 per cent.

SERIES VI.

Solvent.		$2CaO,P_2O_5$.		$3CaO,P_2O_5$.	
100 cc. $\frac{1}{4}$ per cent. citric acid, P_2O_5	dis. =	10.60 9.31	per cent.	10.26	per cent.
100 cc. $\frac{1}{10}$ " oxalic acid,	"	5.32	"	5 10	"
" $\frac{1}{100}$ normal HCl "	"	3 42	"	1.90	"
50 cc. cit. of ammonia sol.	"	19.20	"	13.00	"
50 cc. H_2O+1 gram oxal. ammo.	"	19.00 19.05	"	11.50	"

It will be seen from this table that the citrate solution dissolves both forms perfectly ; that the citric acid, though fairly successful with the tricalcic salt, dissolves only one-half of the dicalcic salt ; that the other acids, notably the mineral acid HCl, fall far below the citric in this respect. Special attention is called to the vigor of the weak solution of oxalate of ammonia. Though only one gram is used, it dissolves all but a trace of the dicalcic salt, and falls but little short of dissolving all the tricalcic form. In the original article of Fresenius, Luck and Neubauer, the weak acids were discarded on account of their inability to take up the reverted phosphate. This conclusion is corroborated by these experiments, with the additional objection proved by Series V., namely, the greater extent to which they dissolve the insoluble phosphate. They found also that oxalate of ammonia solution dissolved the dicalcic phosphate equally with the citrate salt, but abandoned its use on account of the vigor with which it attacked the raw phosphates. But they employed in their published experiments a very large amount of oxalate, six grams of the salt being taken. But it is here found that a much weaker solution of the oxalate is effective for dissolving the dicalcic salt. As to its solvent action upon the natural phosphates, a series of experiments proved that it was not as energetic in this respect as the citrate of ammonia solution, dissolving considerably less than the latter. On account of the many advantages possessed by an oxalate of ammonia solution over the citrate solution (1) as regards ease of preparing a perfectly uniform, neutral solution, (2) as to the greater facility of filtering and washing, and many others, many chemists urged and secured its adoption at the Cincinnati convention of agricultural chemists of 1881. But further experiments, to be described later, reluctantly compelled the conclusion that it cannot supersede the citrate of ammonia solution.

A series of experiments were now made upon a sample of acid phosphate, in order to compare the results obtained by the different methods, and to throw light, if possible, upon the causes of discrepancy. A sample made from Navassa rock was chosen on account of the large amount of reverted phosphate usually present in this class of fertilizers. The total phosphoric acid in the sample was 17.00 per cent., the soluble was 5.00 per cent., leaving 12.00 per cent. of reverted and insoluble. After thoroughly washing out the soluble, one gram was treated with 50 cc. of citrate of ammonia solution, and the directions of Fresenius carefully followed. Another gram was treated in exactly the same way, using however as a solvent 50 cc. of water containing in solution one gram of oxalate of ammonia. The following results were obtained:

SERIES VII.

	P_2O_5 dissolved.	P_2O_5 undissolved.
By citrate solution or "Washington method,"	6.10 per cent.	5.90 per cent.
By oxalate solution,	6.15 "	5.85 "

These two methods give results that are gratifying as regards their agreement. Subsequent experiments, however, showed conclusively that both were far from the truth.

Two grams of the same sample were now, after the extraction of the soluble phosphate, treated according to the method adopted by the agricultural chemists at Cincinnati, known as the "Cincinnati method." The two grams of residue were washed from the filter paper into a breaker with 100 cc. of water, containing in solution two grams of oxalate of ammonia. (This is the same amount of oxalate in proportion to the quantity of substance taken as is used in the above determination.) 400 cc. of water were brought to boiling, and the breaker, closely covered, now introduced into the boiling water, the lamp being at the same time removed. The temperature of the liquid in the beaker rose to about 70° C. in a few minutes, and then slowly sank during an hour to about 40° C. The beaker was quickly rotated at intervals. Two grams were treated in exactly the same manner, using however, instead of the oxalate solution 100 cc. of the citrate solution.

SERIES VIII.

	P_2O_5 dissolved.	P_2O_5 undissolved.
By oxalate of ammonia,	8.55 per cent.	3.45 per cent.
" citrate "	9.85 "	1.15 "

The point of interest connected with these results is the much larger amount of phosphoric acid dissolved by both the reagents as compared with that dissolved by them at the temperature of 35° C. continuous. This is especially the case with the citrate solution, the dissolved phosphoric acid rising from 6.10 per cent. to 9.85 per cent., an increase of 3.75 per cent. This increase can be explained in two ways only: (1) Either the insoluble rock present is dissolved to this increased extent, or (2) there is a form of reverted phosphate present that is not fully taken up by either of the citrate or oxalate solution at the lower temperature.

In order to ascertain if the former of these two explanations was the correct one, two separate portions of $\frac{2}{5}$ of a gram each of Navassa rock, containing 0.120 gram P_2O_5, and corresponding to 6 per cent. of insoluble phosphoric acid when calculated on two grams as used in the above analysis (which is just the amount of apparently insoluble acid left in Series VII.), were rubbed to a paste in a mortar and treated each with 100 cc. of citrate of ammonia solution, the one at a temperature of 35° C. continuous for one hour, the other at a temperature falling from 70° C. to 40° C. during an hour, as in Series VIII. The following amounts of P_2O_5 were dissolved, calculated as per cent. on 2 grams:

SERIES IX.

No. 1.	Phos. acid dissolved,	1.16 per cent.
No. 2.	" " "	1.59 "

The increase in phosphoric acid dissolved by the use of the higher temperature is found to be only 0.43 per cent. It is seen at once that this small increase cannot explain the large increase of 3.75 per cent. in the case of the acid Navassa, made from the same rock.

The second of the two possible explanations, viz.: The presence of a form of reverted phosphate not fully dissolved at 35° C., must therefore be the true one. The experiments already made show that this form can be neither the dicalcic nor tricalcic phosphates, as the citrate solution is a perfect solvent for these two forms at a temperature of 35° C. The only form left is the reverted phosphates of iron and alumina. A quantity of the mixed normal phosphates of iron and alumina, Fe_2O_3, P_2O_5 and Al_2O_3, P_2O_5, was now prepared by precipitation. A portion was mixed with a large quantity of calcium sulphate and dried to a powder at a temperature not exceeding 60° C. The remainder was dried at the same temperature without admixture. One gram of the first portion containing 4 per cent. of phosphoric acid was now rubbed to a paste in a mortar and then digested with 100 cc of the oxalate and citrate solutions, first at 35° C. and then at 70° C. to 40° C. for one hour.

SERIES X.

	P_2O_5 dis. at 35° C.	P_2O_5 dis. at 70° to 40°C.
Using oxalate of ammonia,	0.95 per cent.	3.25 per cent.
" citrate "	1.60 "	4.00 "

One gram of the unmixed portion containing on analysis 35.62 per cent. of phosphoric acid was now treated exactly in the same way, with results as follows:

SERIES XI.

	P_2O_5 dis. at 35° C.	P_2O_5 dis. at 70° to 40° C.
Using oxalate of ammonia	11.06 per cent.	26.50 per cent.
" citrate "	13.14 "	35.62 "

These two series of experiments prove the very important fact that neither the citrate nor oxalate solution will dissolve more than a small portion of the reverted phosphates of iron and alumina at the temperature of 35° C., and that even at the higher temperature of 70° C. to 40° C. the oxalate falls short of the perfect solvent power which must be required of it.

These results explain most clearly the great increase of phosphoric acid taken up in Series VIII. over that dissolved in Series VII. The acid Navassa under treatment contains a very large quantity of reverted phosphates of iron and alumina which are not dissolved at the lower temperature. They also explain why the citrate solution dissolves in 1.30 per cent. more than the oxalate, because of its more vigorous solvent action on these forms of reverted phosphates. One gram of these phosphates of iron and alumina, treated with 100 cc. of the citrate solution at a continuous temperature of 65°C. for 30 minutes, formed also a clear solution.

In order to ascertain the amount of solvent action of this method upon the different forms of raw phosphates, $\frac{1}{5}$ of a gram of each, corresponding to about 3 to 4 per cent. phosphoric acid when calculated upon two grams, was treated in the same manner as the above, temperature 70°C. to 40°C., using 100 cc. citrate solution.

SERIES XII.

	P_2O_5 dis.
Apatite	0.22 per cent.
South Carolina rock	0.61 "
Bone Ash	....
Navassa rock	1.09 "
Curacao	2.07 "

Comparing this table with Series II., dividing the results there by by ten, it is evident that at the higher temperature, only a small increase in the amount of insoluble rock dissolved is observed.

In this connection special attention is called to one point. Notice has been called to the fact that at 100°C. the oxalate solution loses ammonia and becomes decidedly acid in reaction. A solution of neutral oxalate, immersed in boiling water for one hour in an open beaker, acquired an acid strength of $\frac{1}{5}$ per cent. oxalic acid; 100 cc. of the citrate of ammonia solution treated for an hour in the same way acquired an acid strength of 1.2 per cent. citric acid. The energy with which these acid solutions attack the undecomposed rock present in a superphosphate is shown in Series V. It is on account of these facts that Fresenius uses a neutral solution of the citrate salt and adopts the low temperature of 35°C., and Luck* in a second paper dwells with great emphasis upon this point in answer to the criticisms of a French chemist. But as the higher

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*Zeitschrift fur anal. Chem. 14.

temperature is rendered indispensable on account of the presence of phosphates of iron and alumina in the great majority of superphosphates, this loss of ammonia and consequent acidity was prevented by digestion in a flask closed with a rubber cork.

The severest criticism upon the determination of reverted phosphates as an analytical process is the fact that when different quantities of substance are taken for analysis, different results are obtained. This most exceptional experience in chemical analysis, which is without a parallel in analytical determinations, requires a most careful examination, as this has done more than all else to cast discredit upon this analytical process. And yet it seems clear that this trouble can arise from only three sources :

(1.) Either the fertilizer under treatment has so large an amount of reverted phosphate present that when a large amount is taken for analysis the citrate is unable to take it all up, but is able to do so when a smaller amount is employed, or—

(2.) The citrate is an imperfect solvent for some form of reverted phosphate that may be present, either on account of the character of the latter, or on account of the method employed failing to dissolve it completely, the error showing more clearly as large quantities are taken for the analysis, or—

(3.) The discrepancy arises from the solvent action of the citrate upon the undecomposed rock present, a larger percentage of this being dissolved when smaller quantities are taken (*vide* Series I. and II.) The instances given by German experimenters, in the case of fertilizers containing 25 per cent. or more of phosphoric acid present as precipitated tricalcic phosphate, may be due mainly to the first of these causes. In such cases a smaller quantity must be taken, or it may be found that the higher temperature here recommended will so increase the solvent power of the citrate solution as to render this unnecessary. Whenever the phosphates of iron or alumina are present, it is evident from the experiments given that this discrepancy may be largely due to the second cause here assigned, namely, the method of the analysis, employing as it does the low temperature of 35° C. In order to ascertain whether the higher temperature of 70° C. to 40° C. will obviate the error from this second cause, 1, 2, 3, 4, and 5 grams of the above acid Navassa were treated each with 100 cc. of the citrate solution at this temperature, after the thorough washing out of the soluble phosphate.

SERIES XIII.

	P_2O_5 dissolved.	P_2O_5 undissolved.
Employing 1 gram substance	10.06 per cent.	1.94 per cent.
" 2 "	9.85 "	2.15 "
" 3 "	9.65 "	2.35 "
" 4 "	9.43 "	2.57 "
" 5 "	9.02 "	2.98 "

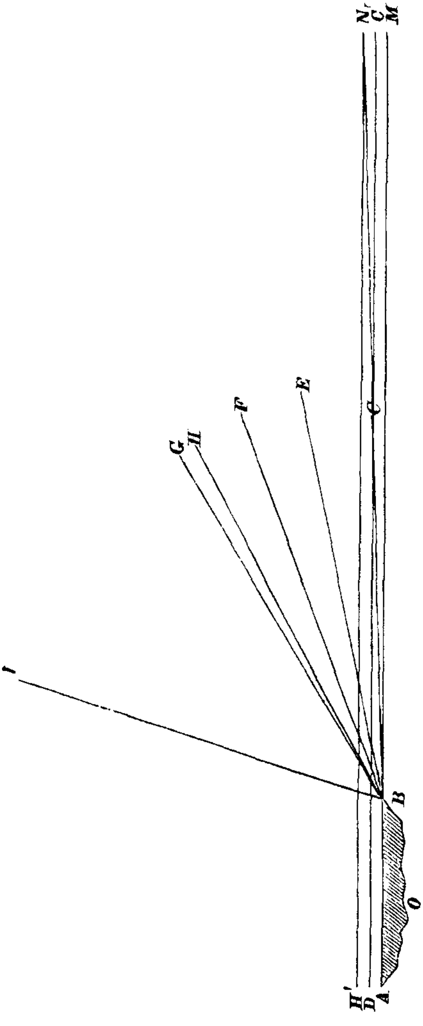
The very slight and uniform decrease of reverted phosphoric acid, about 0.20 per cent. for each additional gram taken, up to the 5 grams when the increase is a trifle larger, would certainly seem to show that every source of discrepancy but the third mentioned above had been obviated. When it is observed that in the last experiment 0.451 gram of reverted phosphoric acid is dissolved by the 100 cc. of citrate of ammonia solution at the temperature of 70° C. to 40° C., it certainly seems that nothing further could be desired as regards vigor of action upon the reverted forms. No other solvent suggested will approach the citrate solution in this important respect, when employed at the temperature here adopted.

But as regards the third cause of discrepancy it is very different. This cause lies in the very nature of things and cannot be overcome. No reagent can be found that will dissolve the strictly reverted phosphates and not affect the undecomposed rock present. Nor is it desirable that any such reagent should be found, nor would it be just to employ it in case it were possible to find it. The whole idea upon which the determination of reverted phosphates rests is that the solvent action of the liquids of the soil is stronger than that of pure water, and is closely imitated by the solvent action of the organic salts of ammonia. Now there is a certain percentage of the raw phosphates that will always be taken up by this increased solvent power, and this percentage is practically and with justice considered equal in value to and reported as reverted phosphate.

The only difficulty that now presents itself is to so fix the amount of substance taken for analysis that the solvent action of the citrate solution upon the undecomposed rock shall dissolve such a percentage of this as shall when reported as reverted phosphate be a fair equivalent of its agricultural value. This conception here stated will be best illustrated by the accompanying diagram. 2 grams of the five forms of raw phosphates were treated with 100 cc. of citrate of ammonia solution at a falling temperature 70° C. to 40° C. for one hour, also two grams of the reverted phosphates of iron and alumina containing 35.62 per cent. of phosphoric acid. The latter was dissolved to a clear solution.

SERIES XIV.

Apatite,	Phosphoric acid	dissolved,	0.60	per cent.
South Carolina rock,	"	"	2.62	"
Bone Ash,	"	"	3.15	"
Navassa,	"	"	3.75	"
Curacao,	"	"	7.50	"
Reverted phos. of iron and alumina,	"	"	35.62	"



In the diagram use is again made of the figure of speech previously employed. AOB is the river bed, representing the phosphates soluble in water, completely covered by the line AM, the height of which represents the solvent power of water. The line BC represents the flats or the reverted phosphates lying just above the water, and slightly rising, since the different forms possess different degrees of solubility. The line DC, DC' represents the solvent power of 100 c.c. citrate of ammonia solution at the temperature 70° C. to 40° C. The lines BE, BF, BH, BG and BI represent the banks rising at different angles on the different raw phosphates, Curacao, Navassa, Bone Ash, South Carolina rock, and Apatite here examined. These lines are all two inches in length, to represent the two grams of substance taken. All of BC falls below DC or becomes soluble in the citrate solution, $\frac{1}{4}$ of BE, $\frac{1}{8}$ of BF $\frac{1}{11}$ of BH, $\frac{1}{10}$ of BG, and $\frac{1}{70}$ of BI, calculating from 30, 30, 36, 27, and 42 percentages of phosphoric acid present in the five samples.

Now suppose one gram of the above substances be taken to 100 cc. of citrate solution. This proportion is the same as 200 cc. citrate solution to the 2 grams of substance taken in the diagram. The line DC will be raised to H'N, twice as far above the surface of the water. Twice as large an amount of reverted phosphates will be taken up, viz. BN, and at the same time nearly twice as large an amount of the raw phosphates as shown in the figure. Thus repeating Series XIV., using however one gram of substance, there were dissolved as follows:

SERIES XV.

Apatite,	Phosphoric acid	dissolved,	1.06	per cent.
South Carolina rock,	"	"		
Bone Ash,	"	"	5.20	"
Navassa,	"	"	6.20	"
Curacao,	"	"	11.50	"

Attention is called to the nature of Curacao phosphate as brought out in this connection. Since by successive treatments with citrate of ammonia solution, or by employing a very small quantity for analysis, as $\frac{1}{10}$ of a gram, nearly all of this can be brought into solution, many chemists regard its phosphoric acid as nearly all in the available form, and an analysis made by one chemist on the identical sample used in this work reports the presence of 18. per cent. of reverted phosphoric acid. But the whole course of experiments given in this paper shows conclusively that it differs from the other raw phosphates only in degree of solubility, and is very far removed as regards this property from the true reverted forms, being, as shown in the diagram, based upon Series XIV., only $\frac{1}{5}$ as soluble at the best as the latter, and only about twice as soluble as Navassa rock and bone ash.

It seems almost certain from the agricultural experiments described in the last edition of Johnson's "Agricultural Chemistry," on the use of finely ground phosphates, that all the phosphoric acid in such phosphates becomes ultimately soluble in the soil. The division of phosphates therefore into the three forms, soluble, reverted, and insoluble, will have reference only to the time required to render them available for plant use. Supposing, in the above diagram, that the solvent action of 100 c.c. of the citrate solution represents the solvent action of the liquids of the soil for a certain period of time, as *e.g.* one season, upon the forms of phosphate there represented, it is evident that all the soluble and reverted would be available the first season, that raw Curacao would all be rendered available in something over five seasons, the Navassa in eight seasons, and so on. The divisions, therefore, of soluble, reverted, and insoluble become indispensable as means of fixing commercial and agricultural values.

In conclusion, emphasis is laid upon the following points as brought out in this inquiry.

I. While the line of division between the reverted forms and the original insoluble forms of phosphoric acid may be sharply drawn in the case of an extremely insoluble phosphate, like apatite, in the case of the more easily soluble natural phosphates the two great classes overlap, one the other. Whatever solvent therefore is used for determining reverted phosphates the same will also dissolve a small percentage of the undecomposed phosphate that may be present; this percentage varying considerably according to the character of the insoluble phosphate. This percentage, representing as it does the comparative solubility which such insoluble phosphate possesses to the true reverted phosphates present, is justly considered as equivalent to an equal amount of the true reverted forms, and reported as such.

II. A slightly ammoniacal citrate of ammonia solution, alone of all the solvents that have been proposed, is a perfect solvent for all the forms of reverted phosphate, while at the same time not unduly dissolving the raw or insoluble phosphates present. Such a solution dissolves but a trace of the most difficultly soluble form of phosphate known, viz. apatite, and dissolves the other natural phosphates to a greater and greater extent as they approach in character the true reverted forms.

III. Neither the "Washington method" (method of Fresenius) nor the "Cincinnati method" can be relied upon to take up all the reverted phosphates that may be present.

IV. A modification of the method of Fresenius, consisting of the use of a higher temperature for the digestion, will meet all the requirements of the case, provided that the greatest care is taken to guard against acidity of the solvent and consequent excessive solution of the insoluble phosphates present. Whether the falling temperature of 70° C. to 40°C. as here explained, or a continuous temperature of 65° C. for 30 minutes, be used, there will be but slight if any differencee in the results, provided that the solution of citrate be slightly ammoniacal, and the digestion be made in a closed flask. To the use of *acid* solutions of citrate, either acid at the beginning or the digestion or becoming acid during its continuance, are probably due more than to any other cause, the discrepancies in this analytical process.

XVIII. THE CONTAMINATION OF THE NEW YORK WATER SUPPLY.

BY DR ALBERT R. LEEDS

In this journal (vol. III, 98,) I have given under the title "Relative purity of city waters in the United States," the analyses of the drinking waters of many of our large cities, as performed by the same methods, and as made upon samples collected at or near the same date. As a necessary deduction from these results, the drinking waters arranged themselves in a series, in which the Brooklyn water occupied the place of honor as the purest, the Boston water the lowest place, being the most foul. The New York water, No. VI, fell in the middle of the series. The water supplies (judged by the samples analyzed) of Brooklyn, Rochester, Philadelphia, Baltimore and Washington, were pronounced satisfactory. Those of New York, Newark, Jersey City, Hoboken, Cincinnati, Oswego, Wilmington (Del.) and Boston, were stated to be contaminated. There was no question as to the contamination of the Newark (Passaic) water (No. 7), because its impurities were established by a multitude of analyses. And with regard to the Croton water the evidence of contamination was found in the facts :

1st. That its various impurities exceeded the limits which are allowable in a pure drinking water. 2nd. That its composition approached very closely to that of the Passaic, of whose contamination there could be no question ; 3rd. That the water shed of the Croton contained sufficient sources of pollution to account for the figures obtained by analysis.

The results above summarized have been accepted without cavil, except in the case of the New York water supply. The pollution of the Boston water was so great that I could not credit my results without making a personal inspection of the sources of the Boston supply. This I did at a later season, and found not only were the first results more than confirmed but that the sources of pollution