

THE COLORIMETRIC DETERMINATION  
OF THE  
FORMS OF INORGANIC PHOSPHORUS IN SOILS

by

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## I N T R O D U C T I O N

Since the first extensive use of mineral phosphate fertilizers in the latter part of the 19th century many sporadic attempts have been made to devise means of estimating the available phosphorus in soils. The complexity and fineness of division of soil materials have always prevented the separation and study of pure soil phosphate particles. These considerations, together with the minute quantities present, have frustrated the petrographic identification of many phosphates that might be present in soil. Such conditions have necessarily limited the number of ways in which the problem might be approached.

One of the most valuable "implements" that has been devised for studying phosphates is the extremely sensitive colorimetric method of determination of phosphorus. Since its first analytical use in 1920 ( 4 ) a number of modifications have been suggested, but it will suffice at this time to stress the sensitivity, rapidity and convenience of the method which admirably adapt it for practical use. It was believed a technique, which would give an estimate of the different forms of phosphates in soils, could be devised from this method.

The possibility of using such a method lay in the fact that different compounds possess different rates of solubility,

amorphous substances generally being more soluble than crystalline materials. This is especially true if one employs for different periods of time extractants maintaining unlike pH values. By using extractants of unlike pH values and for individual periods of time it should be possible to gain sufficient information to allow of estimating the relative proportions of each form of phosphorus present. It was felt that if this could be done, it would, no doubt, help to explain many exceptions in crop responses when compared with the indicated phosphorus needs of soils by existing methods. It would also remove the objection which many soil scientists have had to the use of the extraction methods (15), (16), (3), (11), (5) for determining available phosphorus, - their empirical nature.

The method in most common use (16) calls for extracting the soil for one half hour with sulfuric acid buffered at pH 3 - empirically assuming that this duplicates the feeding power of crops within one season. This assumption probably is based upon the correlations which have been obtained with crop responses. Even if the method did duplicate the feeding powers of crops, it would tell us little about the phosphorus changes and transformations taking place in soil. Consequently this method must inevitably give place to one throwing more light upon the natural forces governing phosphorus

availability.

These considerations together with a long felt interest in soil phosphorus have prompted the present investigation of the possibilities of devising an extraction method for estimating the forms of inorganic soil phosphorus of immediate use to plants.

## S T A T E M E N T O F T H E S I S

### Objective

To devise an extraction method of classifying and estimating inorganic soil phosphorus.

### Plan

(1) Well buffered acid extractants were developed which might be used to extract any soil without a change in their pH values.

(2) Experimental work was conducted to prospect the possibility of a classification and estimation of phosphate materials upon the basis of their rates of solution in these solvents.

(3) Solubility studies were made on pure amorphous phosphate materials and upon representative crystalline phosphate minerals.

(4) A simple extraction procedure was then formulated upon the basis of these rates of solution.

(5) Concurrently with this investigation, samples of twenty-two Maryland soils representative of three soil provinces, seven series and twelve types, were tested in pot experiments with tomatoes and millet in order to secure an index of their responses to phosphorus applications.

(6) These samples were then analyzed by the technique devised and a direct relation between the contents of phosphorus found and between crop responses was found to exist.

(7) To substantiate the extraction method some leaching studies were conducted to show the distinguishing power of the extractants used and to throw light on the possibility of exchangeable phosphorus.

(8) The phosphorus fixing power of hydrous oxides of iron and aluminum was investigated by the technique devised.

(9) As an indication of the fate of soluble phosphates applied to Maryland soils fixation studies were conducted.

(10) A final discussion and summary of the findings is given.

#### E X P E R I M E N T A L

In this investigation extracting solutions were developed which were highly buffered at the respective pH values of 2 and 5. These were adopted after testing them on pure phosphate materials. From these studies a procedure was selected which it was thought would differentiate between the easily soluble,



slightly soluble and more difficultly soluble phosphate materials. Twenty-two Maryland soils were tested by this procedure. As a check upon this method crops were grown upon these soils in the greenhouse to determine their actual responses to phosphorus.

### Extractants

Previous to the initiation of the present investigation proper, some preliminary studies were carried out ( 6 ): First, to learn something of the effect of varying the pH of the extraction medium in the Truog-Deniges method (10), and secondly to try to devise suitable extractants with higher buffer capacities. In the extraction of basic soils with the regular extractant the reaction of this medium changes. This condition has reduced the reliability of the method on soils of unknown carbonate contents. As a result of these early studies it was found that the most suitable buffer for the usual sulfuric acid medium was potassium acid sulfate. A .3% solution of this salt gave a well buffered extractant with a pH of just under 2. The actual pH value was 1.95. Soils were extracted which had as much as 10% of calcium oxide added to them with a change of only .35 pH. Since this first use of this extractant it has been highly recommended by other workers ( 8 ). It is employed in the present investigation and is spoken of as the pH 2 extractant.

One of the motives in the early work arose from the belief

that the reaction of pH 3, used in the regular method, was too acidic to best duplicate the extracting or feeding power of plants. An extractant was developed, therefore, with a pH value of 4.0 by adding 20 grams per liter of sodium sulfate to .001 N. sulfuric acid. This solution was as well buffered as the regular extractant. Upon further **thought**, stimulated by the work of McGeorge and Breazeale ( 9 ), it appeared that even this extractant was too acidic. A further one was therefore developed with a pH value of 5. This is a buffered solution of acetic acid. It contained 3.6 cc of concentrated acetic acid and 19.04 grams of sodium acetate per liter. The pH values of this extractant prepared in this way ranged between 4.98 and 5.02. When used to extract soils to which 20% calcium oxide had been added the pH value of this extractant changed only .30 pH. This extractant has been used to estimate amorphous phosphates in the method to be reported.

### Solubilities

Following the development of suitable extractants, the next step was to employ them to obtain solubility data upon pure amorphous and crystalline phosphate materials. These compounds were treated in very much the same manner in regard to the amount used and the time of extraction, as though they were soils containing the respective materials. It was believed

that the results obtained in this way would be comparable to actual soil extractions.

fineness of materials.

As the rate of solution of a material must depend upon its surface, an effort was made to assure a uniform surface area for all materials studied, by passing them through a one hundred mesh sieve and rejecting that part passing a two hundred mesh sieve. All materials studied in this investigation were treated in this way with the exception of cacoxenite. As the amount of this material was very limited it was passed through a one hundred mesh sieve only.

extraction period.

It was found early in this study that the time of contact between the extracting solution and the material to be extracted was very important. In the method for "Readily Available Phosphorus" (16) the sample is shaken for one-half hour before filtering. With a group of ten samples, filtration of about 200 ml is finished in 40 to 45 minutes from the time the extracting solution is added to the soil. As the pure phosphate materials contained much less colloidal material than soil, the extract of these materials filtered more rapidly. In order that the filtration would end at the same time, or the time of contact would be the same as for a soil, filtering was not started until thirty-eight minutes after adding the pH 5 solution, although shaking was for only one-half hours time. It

was found that this period of extraction would take all the phosphorus from tricalcium phosphate, manganese phosphate, and most of the phosphorus from tertiary magnesium phosphate. This is shown by the data in Table 2. It was therefore adopted as the initial or short time extraction period. A continued shaking with the pH 5 solution was then needed in order to give an increased solution of amorphous aluminum and iron phosphates in addition to these calcium, manganese and magnesium phosphates. Two and one-quarter hours was found satisfactory for this purpose as is shown in the table. Three hours was selected as the time for the pH 2 extraction. This time limit was selected because of the following considerations. First, the extraction is nearly as complete at this point as it will go within reasonable time as evidenced in Table 1. Secondly, this is a convenient period of time for completing a set in four hours. By using these periods of time for the three extractions it would be possible to finish one complete run easily in one-half day.

weight used.

Initial samples of materials were 5.5 milligrams in amount in order to give a reading of 300 - 400 ppm for soluble phosphorus when 400 cc of extracting solution is used. The reason for choosing this uniform concentration was the desire to have data which would be comparable to that obtained in the

extraction of low phosphorus soils. Maryland soils contain about 400 ppm. of total phosphorus, a content similar to that found in some earlier analytical experience with Saskatchewan soils. Similar phosphorus contents have been reported for the soils of Greece (1 ). Again the use of small samples greatly facilitated work on rare phosphates. Heck ( 7 ) has also used this concentration extensively. When such small samples are used, very accurate weighing must be done. In this work the weighings were made upon a balance very sensitive to one-twentieth milligram and with weights standardized by the Bureau of Standards. Some idea of the accuracy of the weighings is supplied by the data reported in Table 1. of the appendix on the analysis of pure phosphate materials using 5.5 milligrams of each. It is felt that these weights were more accurate than the reading of the color intensity due to the depth of the blue color.

#### Extraction Method

On the basis of the solubility data obtained the following procedure was formulated for extracting soils to determine the forms of phosphorus.

#### procedure.

Weigh out three 2 gram samples of each soil and place in separate 750 cc Erlenmeyer flasks. Add to two of each set of three flasks 400 cc of the pH 5 extractant. An equal volume of the pH 2 solution is added to the third flask of each soil. In order that each soil sample may be placed in contact with

extracting solution at the same time, it is desirable to have the solutions measured out ready to add to the respective flasks. After noting the time, stopper and place in an end over end shaker. While the flasks are shaking prepare for filtering through either 12.5 cm No. 40 or 11 cm No. 41 Whatman filter papers. One half hour after extractants were added remove one of the pH 5 extraction flasks for each soil and filter, catching the filtrate in a 250 - 300 cc Erlenmeyer flask. The first 25 - 30 cc should be discarded. Remove funnels from the receiving flasks at 45 minutes, using only that filtrate which will run through in this time. Aliquots of the filtrates are used for the regular colorimetric phosphorus determination ( 16). Remove the remainder of the pH 5 flasks at the expiration of two hours and filter, removing funnels at 2 1/4 hours. Determine phosphorus in the usual way. Terminate the shaking of the pH 2 extractions at 2 3/4 hours and filter, removing funnels at 3 hours. Determine phosphorus in the usual way.

It is believed that the first pH 5 extraction dissolves all amorphous and simple crystalline phosphates of calcium, magnesium, and manganese together with a small fraction of amorphous iron and aluminum phosphates. It may also be assumed that the second pH 5 extraction obtains all this phosphorus together with an increased proportion of the phosphorus present as amorphous iron and aluminum phosphates. It is to be further postulated that the pH 2 extraction gives a total estimate of the soluble amorphous and simple crystalline phosphates together with the apatite group of phosphorus minerals. This separation will be discussed later.

### Leaching Studies

To substantiate the findings of the extraction method upon Maryland soils leaching studies have been carried out.

An improved apparatus set up after Russell (14) was employed. The dropping tubes were made of capillary tubing to allow of greater precision in the control of rate of flow. They were adjusted to drop 200 cc of extractant every 4 hours. Readings were made upon each 200 cc separately. Some interesting results which support the extraction data were obtained in the experiment and are reported in Tables 9 - 12.

### Crop Indexes

In preparation for the investigation of the significance and truth of the method by pot experiments, large samples of twenty-two typical Maryland soils which had not been fertilized or cultivated within ten years were obtained in the fall of 1932 \*. After screening and mixing, the samples were air dried and stored until spring. Equal volumes of each soil were weighed into replicate half gallon glazed porcelain jars. An application of 100 mesh superphosphate was added to each jar at the rate of 1000 pounds per acre. The superphosphate was mixed with sufficient of each soil to supply the mixture with 400 ppm of the "available" phosphorus. This mixture was placed in the jars as a uniform layer one and a half inches below the surface and about three-eighths of an inch thick. This arrangement prevented loss of phosphates by leaching and by spattering

\* They were selected with the aid of Mr. H. B. Winant.

of rain when the jars were taken outside the greenhouse. In addition it somewhat controlled the local concentrations.

To avoid potassium, nitrogen and calcium being too limiting, an application of potassium nitrate at the rate of one hundred fifty pounds per acre and the same amount of calcium nitrate were applied in mixed solution to each jar. This was applied in two treatments at an interval of two weeks; the first coming four days after setting out the tomato seedlings. All pots received equal amounts of water applied daily except during cloudy weather.

In each pot of soil, excepting soil numbers 2, 5, 7, 8, 9, 11, 13, 16, 18, 19, 20, 21, and 22, on which only millet was seeded, was placed one tomato plant and several millet seeds. These tomato plants were carefully selected for their uniformity of size and shape. The tomatoes were allowed to grow until the millet began to head. Then the entire plant was removed and weighed. The millet was allowed to mature after thinning to a uniform number of plants per pot. Further crops of tomatoes on fresh soil were grown on numbers 5, 7, 8, 16, 18, and 19 in 1934. The tomato yields are reported in grams per soil, and the millet in grams of seed produced. These data are reported in Table 5. As some of the millet grown in the pots with the tomatoes was unsatisfactory, very little weight was placed on the millet yields obtained following the tomato plants. No



millet yield is reported for soil number 6 because part of the millet heads were destroyed by rodents. The growth responses on some of the soils due to the phosphorus treatment are very great. Only one soil, number 11, gave no response to the phosphorus application. These growth responses are illustrated for some of the soils by Plates I to VI.

The twenty-two Maryland soils used in this study were analyzed by the procedure recommended for determining the different forms of phosphorus in soils. The data obtained by these extractions are reported along with the pH values in Table 4. It can be noted from this table that there is very little phosphorus obtained by the first extractant. The large part of the phosphorus is obtained by the pH 2 extractant. The data obtained by this analysis support the crop response data, as they show very little available phosphorus for plant use.

#### D I S C U S S I O N

In order to facilitate the understanding of the extraction method adopted for this study, the nature of the phosphorus compounds in soils is here explained. Since it was impossible to separate these compounds from the soil for study, the pure phosphorus compounds and minerals are discussed as to their importance and solubilities. Following this a method to estimate the forms of phosphorus in soils is advanced. The

contents of phosphorus obtained by this method are compared with crop yields.

### Compounds to be Determined

Soil authors usually ascribe to apatite the most important position among the different phosphate materials comprising the inorganic phosphates of soils. In addition to this mineral the simple phosphates of calcium, magnesium, iron and aluminum are usually listed. To the list should also be added manganese and titanium phosphates and several of the phosphate minerals that are of sufficient occurrence in nature to make them of likely occurrence in soils. Of these we will consider cacoxenite, dufrenite, strengite, vivianite, fisherite, variscite, and wavelite as representative of the crystalline iron and aluminum phosphates. In all there are forty odd crystalline phosphate minerals that have been recognized ( 2 ), any of which may exist in certain soils in traces. The method devised separates only the materials named on the basis of their respective solubilities. It is shown in Table 3 that apatite is practically dissolved by the pH 2 reagent in three hours, but that it is almost insoluble in the pH 5 reagent, if first leached with water. Apatite was previously found to be appreciably soluble at pH values of 3 and 4. It is felt that the crystalline phosphates of iron and aluminum such as dufrenite and wavelite, might also have been

less soluble in the pH 2 solution if they had first been leached with water. This effect is clearly demonstrated in the case of vivianite (Table 3) for which results are given for both "leached" and "unleached with water" previous to the extraction.

It is a striking fact that although all leading soil investigators agree that apatite is the parent mineral of soil phosphorus, no quantity of it has ever been identified in soil. Fry (12) in a petrographic investigation of 45 representative American soils identified apatite only twice and then only in traces. In data given in Tables 6 little phosphorus of the apatite group was found in Maryland soils by the method reported. It is reasonable to suppose, therefore, that parent materials more soluble than apatite - those soluble at pH 5, will have been still more completely removed from the average soil of any maturity. Figures from leaching studies shown in Tables 9 - 12 substantiate this view. In order to devise a simple practical method, vivianite and other equally soluble materials were not considered as being present in normal soil. It is admitted, however, that they may be present in traces. This possibility is illustrated by a sample of vivianite obtained by the National Museum (origin unknown) at the site of one of the new government buildings in Washington. It is assumed in this study, however, that all the phosphorus

obtained from the soil at pH 5 represents that present in the form of amorphous phosphates of secondary origin, formed during weathering and biological activity.

#### Leaching and Extracting Results

The results secured by the continued leaching studies on the amorphous aluminum and iron phosphates and on soils, Tables 9 - 12, indicate that these phosphates possess a similar solubility to that of some of the phosphates of the soils. This substantiates the belief that a part of the phosphorus exists in these soils as aluminum and iron phosphates. Another very definite indication of this is the dwindling of the parts per million of phosphorus to nothing soon after all the aluminum phosphate had been leached and before all the iron phosphate had been removed. This is strong evidence that the phosphorus extracted from soil by the pH 5 solution comes from the amorphous phosphates - largely aluminum and iron phosphates in the soils. These data indicate that much of the soil phosphorus might come from aluminum phosphate. It is believed, however, that more iron phosphate would be extracted from the soil than is shown by the data obtained from the extracting and leaching of the pure compounds, as the natural iron phosphates of the soil are thought to be in a finer state of division.

As the pH 2 leachings on these soils gave high initial amounts of phosphorus following a previous leaching with the

pH 5 solution, it is believed a new form of phosphorus was being dissolved. This is substantiated by the fact that the pH 2 leaching, even though continued for a long period of time, did not decrease the phosphorus yields below a certain minimum value. These facts suggest that the phosphorus obtained in the initial pH 2 leachings came from apatite and from adsorbed phosphorus. The phosphorus obtained by the long continued leaching appeared to be coming from the more insoluble crystalline forms of iron and aluminum phosphates.

A study of the data obtained in the extraction of these soils (Table 4) revealed the fact that for several of them there was twice as much phosphorus extracted by the pH 5 solution in 2 1/4 hours as in 3/4 hours. It was apparent, therefore, when compared with the extraction of the pure phosphate materials, that there was very little of group A phosphorus (easily soluble calcium, manganese and inorganic phosphates) present in some of these soils. The extraction and leaching data (Tables 9 - 12) also show that only one-half of the amorphous aluminum and iron phosphates, group B, are obtained by the pH 2 extractant in 3 hours. It was roughly indicated by these data that 1/11 of the amorphous aluminum and iron phosphates was obtained by the first pH 5 extraction. In addition a study of these data discloses the fact that only half the phosphorus of the apatite group is recovered in

an extraction at pH 2 for 3 hours. These conditions have supplied a basis for developing algebraic expressions for calculating the amount of each of these groups of phosphorus in the soil.

### Scheme of Separation

The total phosphorus which can be extracted by leaching at pH 2 within reasonable time, can be divided into three groups: A, B, and C. The A group is comprised of amorphous and finely divided crystalline phosphates of calcium, magnesium and manganese. The B group is composed of amorphous phosphates of iron and aluminum. And the C group is composed of adsorbed phosphorus and of apatite. The following is a simple way of expressing these separations using the letters to signify the respective groups of materials:

(I) pH 5 for 45 minutes gives  $A + B/11$

(II) pH 5 for 2 1/4 hours gives  $A + B/5.5$

(III) pH 2 for 3 hours gives  $A + 6B/11 + C/2$

These algebraic expressions make the estimation of the amount of phosphorus present in each group very rapid. By subtracting the reading for extraction I from the reading of extraction II a value equal to  $B/11$  is obtained. From this B, or the total content of amorphous iron and aluminum phosphates, may be determined. A, or the content of amorphous and finely divided crystalline phosphates of calcium, magnesium and manganese is found by subtracting the value for  $B/11$  from

the reading for extraction I. Having obtained values for A and B it is a simple matter to calculate C from the reading for the third extraction.

The amounts of the A, B, and C forms of phosphorus in these twenty-two Maryland soils was calculated by the proposed algebraic formulae from the extraction data given in Table 4 and are reported in parts per million in Table 6. There was considerable variation in the three kinds of phosphorus for these soils. The soils having the lowest amounts of A and B phosphorus gave the greatest crop responses. As the total content of these two forms is not large for most of the soils they should respond to phosphorus treatment. The soils which gave the smallest increase for phosphorus fertilization contained the largest amount of group B phosphorus. This is taken as evidence that considerable of the amorphous aluminum and iron phosphates are available to plants.

Since the extraction and leaching data have shown that these different groups of phosphates have individual rates of solubility it is only natural to expect that they should supply the phosphorus to the growing plants at different rates. One of the objects of the pot experiments was to determine these differences in nutritional values. If these values can be estimated there should be a correlation between the phosphorus groups and the crop responses. A preliminary study of the analyses of the soils showed that group A phosphorus alone did

not place the soils in the order of their phosphorus needs when compared to crop responses. The addition of phosphorus contained in both A and B groups and the arranging of each resultant in increasing order gave better correlation with crop yield. This agreement was not as good as was expected. In order to produce a better correlation it was thought that if the group B phosphorus was multiplied by a factor instead of using the total there would be a better agreement. It was found that using 6/11 of B group showed a slightly closer relationship between plant growth and phosphorus needs. This is shown by the data in Table 7.

In column one of this table the soils giving the greatest returns for phosphorus treatment head the list. Soil number 13 gave the greatest response and number 11 the least. In the second column the soils are arranged according to the amount of phosphorus contained in the A and B groups. This is the amount of phosphorus which is thought would be supplied by these groups to the plants. Indirectly, then, one would expect the soils with the smallest amounts of these forms of phosphorus to give the greatest phosphorus returns. In the third column is the amount of phosphorus obtained by adding A group and 6/11 of B group. This total for the B group in this table only corresponds to the amount of phosphorus obtained by the extraction at pH 2. It is evident from a study of this table that there is not a perfect correlation. This is believed to be due to the fact that some of the group C phosphorus was being utilized by the plants. In order to evaluate



the nutritional value of the group C phosphorus, various fractions of the C group have been used for addition to the A + 6/11 B total. Three of these fractions are given in Table 8.

Before discussing these results the method of determining final crop response indexes is here explained. It was evident that on soils, which gave small yields in spite of the addition of plant foods, there were other limiting factors. For the maximum crops on these soils the same total amount of potentially available phosphorus was not, therefore, required. Phosphorus did not become as limiting on these soils as it should have, if the plant had consumed the normal amount of phosphorus. This fact must be allowed for if close correlation with crop responses is to be expected. This is not an easy thing to do, for this effect will express itself in more than a direct relationship. It is more likely to approach a square or cubic relation as phosphorus becomes absolutely insufficient in the upper yield ranges. In this study this influence is corrected for as though it were a direct relationship, in the belief that at least this much correction is perfectly justified. The average yield of tomatoes with fertilizer is taken as 150 grams for six pots and the average yield of millet is taken as 6 grams for 2 pots. On a soil yielding only 2 grams of millet on two pots the per cent increase for phosphorus is multiplied by 6/2. Similarly if the yield is 8 grams the per cent increase is multiplied by 6/8. The same method of

correction has been applied to the tomato yields, which have supplied most of the final indexes used. In effect these corrections only reduce the amounts of potentially available phosphorus required, to the same level on each soil. To save space the crop increases in the last two columns of Table 8 are reported in hundreds of per cent e.g. If a value is given as 5.2, this is really 520 per cent.

The use of the fraction  $1/10$  for the C group phosphorus as given in Table 8 places soils number 15, 16, 19, 17, 7, 3 and 33 out of the order indicated in crop responses, while multiplying by  $1/40$  misplaces soils 13, 19, 7, 5, 18, 20, 6, 22 and 10. But using  $1/20$  as the multiple arranges the soils in practically the identical order indicated by the crop responses. It should be noted that the pH values of soils 18 and 20 as given in Table 4 may account for their relatively high response. Other factors were also instrumental in the case of soil number 1, a Portsmouth loam. Its low content of calcium and high acidity probably helped to give it a higher response than it should have. Although the use of the fraction  $1/20$  gives a good agreement, it is possible that slightly different multiples would give a better one. It is believed then that approximately  $1/20$  of the apatite group phosphorus and adsorbed phosphates in the soil are potentially available for plant use in one season.

The data obtained in these studies substantiate the work

of Fry on 45 United States soils (12) in that only a few parts per million of phosphorus in the form of apatite were found in virgin soils. This suggested that the group C phosphorus was, in part, composed of adsorbed phosphorus. In order to determine if this was the case, some supplementary experiments were carried out. The work of Roszman (13) showed that phosphorus adsorption is governed by the pH values of the medium. Pure hydrous oxides of aluminum and iron were prepared and treated with sufficient of the concentrated phosphorus standard solution of Truog (16) to give them a content of 4000 ppm adsorbed. When 20 mg samples treated in this way were extracted with the pH 5 extractant for 2 1/4 hours none of this phosphorus was recovered. The pH 2 extractant, however, in the three hour period took 2,600 ppm of phosphorus from the hydrous oxide of aluminum and about half this amount from the hydrous oxide of iron. In the method reported in this paper adsorbed phosphorus will therefore be reported in the same fraction with the apatite group. A slight change in the proposed procedure would allow of accurate differentiation of apatite and adsorbed phosphorus.

In conclusion it is fitting to mention fixation studies conducted on eight of these Maryland soils. Of these, Manor loam number 16 had the highest fixing capacity. The application of 400 ppm of phosphorus to this soil in the form of superphos-

phate was 50% recovered by a three hour extraction at pH 2. The phosphorus had been in contact with the moist soil for a year's time. On the basis of the leaching data summarized in Table 12 one is justified in saying that no appreciable part of the phosphorus applied would go over into completely unavailable crystalline phosphates within this period of time. These studies brought out the fact that the decreased solubility of phosphorus was due to the formation of amorphous aluminum and iron phosphates and to the adsorption of phosphorus by hydrous oxides of aluminum and iron. Data reported show that both these forms of phosphorus remain slowly available.

#### C O N C L U S I O N S

(1) Sufficiently buffered suitable acid extractants have been developed for use on any soil.

(2) Solubility studies of the solvent action of these reagents upon pure phosphate materials have indicated that these reagents might be used to estimate the more soluble materials.

(3) The findings of the extraction method have been substantiated by leaching studies.

(4) A scheme of estimation has been drawn up to estimate the following classes of materials.

- A. Amorphous and finely crystalline phosphates of calcium, magnesium and manganese.
- B. Amorphous phosphates of iron and aluminum.
- C. Phosphorus adsorbed by hydrous oxides and that present as apatite.

(5) Pot experiments have been conducted on twenty-two representative Maryland soils to obtain their response indexes to phosphorus applications.

(6) These soils have been analyzed by the technique devised and a high degree of agreement between analysis and crop responses found to obtain.

(7) Studies made of the action of the extraction reagents upon the phosphorus adsorbed by hydrous oxides of aluminum and iron showed that the proposed procedure estimates these forms and that they are all available in time.

(8) Fixation studies on some of these soils indicate that phosphorus is fixed as amorphous aluminum and iron phosphate and as phosphorus adsorbed upon hydrous oxides of aluminum and iron.

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TABLE I.

The Effect of Time Upon the Amount of Phosphorus Extracted at pH 2 Expressed in ppm.

Soil Studied	Time in Hours				
	.25:	.75:	2.25:	3 :	6
Sassafras Si. L. #4	12	15	19	22	
Keyport L. #10	28	47	49	46	
Elkton Si. L. #12				23	27
Hagerstown Si. L. #14				7	9
Manor L. #16				45	45
Portsmouth L. # 1				127	155



Table 2.

The ppm. of Phosphorus Extracted  
From Phosphorus Materials by pH 5 Solu-  
tion During Different Periods of Time.

Material	: Mg. per : :400 cc.Of: : extract	:The Phosphorus extracted by different times of contact					
		:3/4 hr.:	:1½ hr.:	:2 1/4 hr.:	:3 hrs.:	:3/4 hr.*:	:2 1/4 hr.*
		ppm.	ppm.	ppm.	ppm.	ppm.	ppm.
Aluminum Phosphate		5.1		19.0			
		20.4		80.0			
		5.1	9.0				
		5.5	11.0			24.0	
		50.0	31.0		127.0	97.0 **	
	100.0			390.0			
	10.0	32.5		51.5		47.5 126.0	
Ferric Phosphate		5.8		12.5			
		23.2		30.0			
		5.8	4.0				
		5.5	4.0			8.0	
		50.0	25.0		38.0	35.0	
	100.0			114.0			
	10.0	10.0		13.5		10.5 14.0	
Tricalcium Phosphate		2.0		155.0			
		8.0		730.0			
		4.9	400.0				
Tertiary Magnesium Phosphate		4.3	260.0				

\* Data on 200 meshed phosphate.

\*\* Without shaking.

Table 3.

The ppm. of Phosphorus Extracted From Phosphorus Minerals by pH 5 and pH 2 Solutions

Material Studied	: The phosphorus extract-:The phos-		
	: Mgs. of:ed by the pH 5 solution :phorus ex-	: samples:with different times of :tracted by	: per :contact :the pH 2 solu-
	: 100 cc.:3/4 hr.:2 1/4 hrs.:3 hrs:tions in 3 hrs.		
	: ppm.	ppm.	ppm.:
<b>Apatite:-</b>			
(a)U.S.D.A. # B 15	: 5.5	: 1.25	: 1.5 : 360.0
(b)Same H <sub>2</sub> O leached	: 5.5	: 0	
(c)Quebec	: 5.5	: 1.5	: 400.0
(d)Same H <sub>2</sub> O leached	: 5.5	: 1.0	
(e)Russia	: 5.5	: .5	: 365.0
(f)Same H <sub>2</sub> O leached	: 5.5	: 0	
(g)Chlorapatite	: 5.5	: 2.0	: 2.0 :
<b>Vivianite:-</b>			
(a)Penn.	: 5.5	: 8.0	: 285.0
(b)Same H <sub>2</sub> O leached	: 5.5	: .7	
" "	: 50.0	: 13.0	: 19.5 :
(c)Australia	: 5.5	: 15.5	
<b>Dufrenite:-</b>			
(a)Virginia	: 5.5	: 0	: 0 :
	: 20.0		: 5.3
(b)England	: 5.5	: .5	: 7.0
<b>Cacoxenite</b>	: 5.5		: 5.5
<b>Strengite</b>	: 5.5	: 0	: 1.5
<b>Variscite</b>	: 5.5	: 1.8	: 10.5
<b>Wavellite:-</b>			
(a)Arkansas	: 5.5	: .2	: .2 : 5.0
(b)Columbia	: 5.5	: .7	
<b>Fischerite</b>	: 5.5	: 2.0	
<b>Titanium Phosphate</b>	: 5.5	: 17.0	
<b>Manganese Phosphate</b>	: 5.5	: 360.0	
<b>Rock Phosphate:-</b>			
(a)Florida	: 5.5	: 23.0	
(b)Curacao	: 5.5	: 80.0	
(c)Wyoming	: 5.5	: 5.0	

Table 4.

The Phosphorus Obtained by the Proposed  
Extraction Method on Twenty-Two Maryland Soils

Soil Studied		Phosphorus Extracted in ppm.			
No.:	Type	: pH	: pH 5 : 45 min.	: pH 5 : 2 1/4 hrs:	: pH 2 : 3 hrs.
1	Portsmouth L.	4.2	8.0	8.0	125
2	Sassafras L. S.	4.5	1.0	1.0	6
3	Elkton L.	5.2	4.75	6.25	27.5
4	Sassafras L.	6.1	3.25	5.25	22
5	Sassafras Si. L.	5.7	2.25	3.0	23
6	Sassafras S. L.	6.2	2.0	4.0	28.5
7	Sassafras Si. L.	5.3	2.25	2.87	23
8	Keyport Si. L.	4.7	5.5	9.0	25
9	Elkton Si. L.	4.5	2.5	3.12	14.5
10	Keyport L.	6.0	3.5	7.0	45.5
11	Sassafras S.	5.5	7.0	14.0	190
12	Elkton Si. L.	4.7	2.87	3.12	23
13	Manor L.	5.0	2.0	2.0	18
14	Hagerstown Si. L.	6.0	.5	1.0	6.5
15	Manor L.	6.0	2.25	2.25	12
16	Manor L.	5.0	2.0	2.0	28
17	Frankstown Si. L.	5.5	1.25	1.75	14
18	Frankstown Si. L.	8.0	4.0	4.0	40
19	Hagerstown S. L.	7.0	3.25	3.31	18.5
20	Frankstown Si. L.	8.5	6.75	7.5	37
21	Hagerstown Si. L.	6.5	.5	1.0	7
22	Sassafras Si. L.	6.3	6.75	8.00	34

Table 5.

The Total Yield and Per Cent Increase of  
Tomatoes and Millet on Twenty-Two Maryland  
Soils with and Without Phosphorus Treatment

No.	Soil	TOMATOES				MILLET			
		No. of pots	Treatment			No. of pots	Treatment		
			No P. gms.	P. gms.	In- crease %		No P. gms.	P. gms.	In- crease %
1	Portsmouth L.	6	35	78.5	124	6	17.5	9.8	- 79
2	Sassafras L. S.					2	.16	1.09	545
3	Elkton L.	2	25	68	172	2	5.32	3.07	- 73
4	Sassafras L.	6	86	106	23	6	11.58	12.64	9
5	Sassafras Si. L.	4	24.5	98.5	300	2	4.06	1.96	107
6	Sassafras S. L.	6	54.2	102	88	6	--	--	30
7	Sassafras Si. L.	4	3.0	27	800	2	7.04	5.29	- 33
8	Keyport Si. L.	4	28.5	44.5	56	2	8.26	9.53	15
9	Elkton Si. L.					4	3.05	9.64	216
10	Keyport L.	6	70.2	76	8	6	7.32	8.74	18
11	Sassafras S.					2	2.42	2.22	- 9
12	Elkton Si. L.	6	24	65.5	173	6	5.18	3.81	- 36
13	Manor L.					4	--	16.76	∞
14	Hagerstown Si. L.	6	6.5	146	2,146	6	3.14	7.2	130
15	Manor L.	2	2	52	2,500	2	.50	6.48	1196
16	Manor L.	4	4.7	51.5	1,000	6	8.63	14.10	63
		6	--	182.3	1,000	6			
17	Frankstown Si. L.	6	17	139	815	6	7.85	2.67	-194
18	Frankstown Si. L.	4	9.5	69.5	630	2	2.12	7.07	234
19	Hagerstown Si. L.	4	6.3	64.5	920	2	.58	5.86	918
20	Frankstown Si. L.					2	.80	5.86	630
21	Hagerstown Si. L.					2	1.16	14.13	1123
22	Sassafras Si. L.					2	7.31	11.20	53

Table 6.

The Total Content of Easily Soluble (Group A), Slightly Soluble (Group B), and Less Soluble (Group C) Forms of Phosphorus in the Twenty-Two Maryland Soils Calculated from the Extraction Data and Using the Proposed Algebraic Formula.

No.	Soil Type	:The ppm. of Phosphorus in Group		
		A	B	C
1	Portsmouth L.	8.0	---	234.0
2	Sassafras L. S.	1.0	---	10.0
3	Elkton L.	4.25	16.5	28.5
4	Sassafras L.	1.25	22.0	17.5
5	Sassafras Si. L.	1.5	8.3	34.0
6	Sassafras S. L.	--	22.0	33.0
7	Sassafras Si. L.	1.63	6.8	35.3
8	Keyport Si. L.	--	38.5	4.0
9	Elkton Si. L.	1.87	6.8	17.9
10	Keyport L.	--	38.5	49.0
11	Sassafras S.	--	77.0	216.0
12	Elkton Si. L.	1.87	2.8	45.7
13	Manor L.	2.62	--	34.0
14	Hagerstown Si. L.	--	5.5	7.0
15	Manor L.	2.25	--	19.5
16	Manor L.	2.0	--	52.0
17	Frankstown Si. L.	.75	5.5	20.5
18	Frankstown Si. L.	4.00	--	72.0
19	Hagerstown Si. L.	3.2	.7	29.8
20	Frankstown Si. L.	6.0	8.3	53.0
21	Hagerstown Si. L.	--	5.5	8.0
22	Sassafras Si. L.	5.5	13.8	42.0

Table 7.

Arrangement of Soils in the Order of Their A + 6/11 B Phosphorus Content and Their Response to Phosphorus Treatment.

<u>Soil Numbers in Order of :</u>		
<u>Crop</u>	<u>: Content of</u>	<u>: A + 6/11 B</u>
<u>Response</u>	<u>: A + 6/11 B</u>	<u>: Phosphorus</u>
	<u>: Phosphorus</u>	<u>: in ppm.</u>
13	2	1.0
2	13	1.0
15	16	2.0
14	15	2.25
21	14	3.0
16	21	3.0
19	19	3.6
17	17	3.75
7	18	4.0
20	12	4.12
18	7	5.33
12	9	5.57
5	5	6.0
9	1	8.0
6	20	10.5
1	6	12.0
3	22	13.0
22	4	13.25
4	3	13.25
8	10	21.0
10	8	23.0
11	11	42.0

Table 8.

The Arrangement of Soils in the Order of Phosphorus Contained in Groups A + 6/11 B + 1/20 C and the Crop Response to Phosphorus Treatment.

Phosphorus in ppm. Contained in Groups A + 6/11 B plus			Soil Numbers in Order of		Crop Yields	
1/10 C	1/40 C	1/20 C	Phosphorus Groups	Crop Response	Weighted	Original
2.0	1.3	1.5	2	13	∞	∞
5.0	1.8	2.6	13	2	30.0	5.4
4.0	2.75	3.3	15	15	25.0	25.0
3.4	3.1	3.3	14	14	24.0	21.0
3.4	3.2	3.4	21	21	24.0	11.0
7.2	3.3	4.8	16	16	10.0	10.0
6.6	3.0	5.2	19	19	19.1	9.0
5.8	4.25	5.5	17	17	8.0	8.0
8.9	6.43	5.8	7	7	8.0	8.0
6.0	5.1	5.9	12	20	6.0	6.0
7.8	5.92	6.1	9	18	4.3	4.3
9.6	6.9	7.7	5	12	3.8	1.7
12.0	5.8	8.0	18	5	3.0	3.0
15.8	11.33	12.7	20	9	2.8	2.2
15.3	14.7	13.6	6	6	1.3	.88
15.9	13.0	13.8	3	1	1.24	1.24
15.25	13.69	14.0	4	3	1.22	1.7
16.8	13.6	15.1	22	22	.6	.5
33.0	14.0	20.0	1	4	.36	.23
23.2	23.0	23.0	8	8	.36	.36
25.9	22.2	23.4	10	10	.2	.2
74.0	50.0	58.0	11	11	---	---

Table 9.

Results of Continuous Leaching Studies  
on Pure Phosphates and on Maryland Soils.

Leachates of 200 cc.; timing 4 hrs.; pH 5

(Begun November 21, 1933)

Number of Leachate	Material							
	Aluminum phosphate : 10 mg.	Ferric phosphate : 10 mg.	Titanium phosphate : 10 mg.	No. 6 Sassafras S. L. : 10 gms.	No. 10 Keyport L. : 10 gms.	No. 11 Sassafras S. : 5 gms.	No. 12 Elkton Si. L. : 10 gms.	No. 19 Hagers-town Si. L. : 10 gms.
1	70.0	22.0	100.0	20.5	9.0	29.0	7.5	16.0
2	55.0	11.0	61.0	15.0	10.0	31.0	4.5	16.0
5	56.0	8.5	29.0	7.5	8.0	19.0	5.5	5.0
10	34.0	9.0	24.0	5.0	7.5	16.5	6.0	2.5
15	33.0	7.0	7.0	5.0	7.0	14.0	6.0	2.0
20	29.0	7.0	14.0	3.5	6.5	13.0	6.0	2.0
25	27.0	7.0	9.5	3.0	5.5	9.5	5.5	1.5
30	21.0	7.0	9.5	3.0	4.5	8.5	4.5	1.5
35	18.5	6.5	20.5	3.0	5.0	9.0	4.0	1.5
40	17.0	7.0	9.5	2.5	5.0	8.5	3.5	1.0
45	13.5	8.0	7.5	2.5	4.5	7.5	3.5	1.0
50	10.5	7.0	11.0	2.5	3.0	5.5	3.0	1.0
60	2.5	6.0	5.0	1.5	3.0	4.0	1.5	.5
70	.5	6.0	10.0	1.0	2.0	2.5	1.5	.5
80	.0	5.0	8.0	1.0	2.0	3.0	1.5	.0
90		5.5	9.0	.5	1.0	3.0	1.5	.0
100		5.0	7.0	.0	.5	.5	.0	
120		5.0						

N. B. - Summary table, for full data see appendix.



Table 10.

The ppm. of Phosphorus Leached from the  
Five Maryland Soils by pH 2 Solution After  
Previous pH 5 Leaching

Leaching: Number	Phosphorus extracted from soils				
	No. 6	No. 10	No. 11	No. 12	No. 19
	Sassafras : S. L.	Keyport : L.	Sassafras : S.	Elkton : Si. L.	Hagerstown : Si. L.
	ppm.	ppm.	ppm.	ppm.	ppm.
1 - 4	31.0:36.0	64.0:62.0	95.0 :90.0	30.0:30.0	20.0:
5 - 8	17.5:16.5	41.0:40.0	8.5 :12.0	5.0: 5.0	21.0:
9 -12	7.0: 7.5	24.5:24.5	5.0 : 5.0	3.0: 3.5	16.5:
13 -16	5.0: 3.5	20.0:20.0	3.0 : 3.0	2.0: 1.5	12.5:
17 -20	4.5: 5.0	12.5:11.5	1.75: 1.25	1.75: 1.25	10.0:
21 -24		9.0: 9.5			8.5:
30 -60					4.0:

Table 11.

The ppm. of Phosphorus Extracted  
from Three Maryland Soils by Continuous  
Leaching with pH 2 Solution

<u>No. 19- Hagerstown Si.L.:No. 12- Elkton Si.L.:No. 10- Keyport L.</u>					
<u>Leaching :</u>	<u>Phos-</u>	<u>:Leaching :</u>	<u>Phos-</u>	<u>: Leaching :</u>	<u>Phos-</u>
<u>Number :</u>	<u>phorus</u>	<u>:Number :</u>	<u>phorus</u>	<u>: Number :</u>	<u>phorus</u>
	<u>ppm.</u>		<u>ppm.</u>		<u>ppm.</u>
1	160.0	: 1 - 2	150.0	: 1 - 2	264.0
2	56.0	: 3 - 6	12.5	: 3 - 6	98.0
3	42.0	: 7 - 10	9.0	: 7 - 10	30.0
4	30.0	: 11 - 14	1.5	: 11 - 14	14.0
5	29.0	:		: 15 - 18	13.5
6	26.0	:		: 19 - 22	12.0
7	24.0	:		: 23 - 26	9.0
8	20.5	:		: 27 - 30	5.5
9	19.5	:		:	
10 - 13	11.5	:		:	
14 - 17	9.5	:		:	
18 - 21	8.5	:		:	
22 - 25	8.0	:		:	
26 - 29	7.5	:		:	
30 - 33	6.0	:		:	

Table 12.

The Total ppm. of Phosphorus Leached from Pure Phosphates and Five Maryland Soils by pH 5 and pH 2 Solutions.

Materials	:Weight: : of : :Sample: : Gms. :	Phosphorus obtained by leaching		
		pH 5	pH 2 : after : pH 5 :	pH 2
		ppm.	ppm.	ppm.
Aluminum Phosphate	.010	1393	--	
Ferric Phosphate	.010	760	288	
Titanium Phosphate	.010	1294	572	
Sassafras S. L. #6	10.0	275	268	
Keyport L. #10	10.0	393	676	1250
Sassafras S. #11	5.0	754	452	
Elkton Si. L. #12	10.0	322	164	390
Hagerstown Si. L. #19	10.0	136	392	590

PLATES I - VI.

PLATE I.

30 day growth of tomatoes on  
Hagerstown Si. L., No. 19, with  
and without application of super-  
phosphate.

PLATE II.

Growth of millet on Manor L.,  
No. 13, with and without super-  
phosphate.



Plate I.

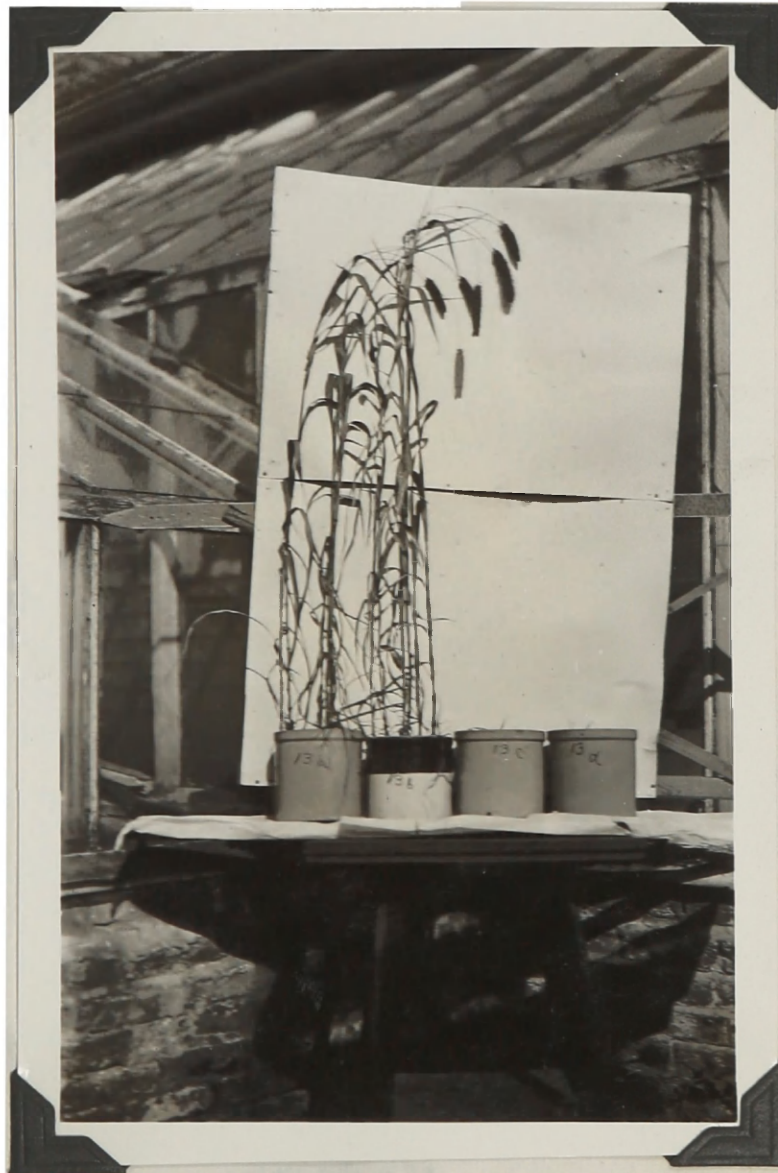


Plate II.

PLATE III.

30 day growth of tomatoes on  
Sassafras Si. L., No. 7, with and  
without application of superphos-  
phate.

PLATE IV.

Growth of millet on Elkton L.,  
No. 3, and on Portsmouth L., No. 1.  
Pot X received superphosphate; pot  
Y received no phosphorus.



Plate III.



Plate IV.



**PLATE V.**

**30 day growth of tomatoes on  
Manor L., No. 16, with and with-  
out superphosphate**

**PLATE VI.**

**30 day growth of tomatoes on  
Frankstown Si. L., No. 18, with  
and without superphosphate.**



Plate V.



Plate VI.

## A P P E N D I X

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RAPID COLORIMETRIC DETERMINATION  
OF TOTAL PHOSPHORUS IN SOILS \*

The advantages of time saving and convenience in the colorimetric method used for "more readily available phosphorus" ( 6 ) were particularly impressed upon the author during analytical work in Saskatchewan as being adaptable for total phosphorus. However, in the normal fusion or extraction for total phosphorus there are several substances brought into solution, which interfere with the use of this colorimetric method. An investigation has been made of the possibility of devising a convenient method of extraction which would give an extract free of interfering substances. Such a technique has been worked out and is here reported together with comparative data obtained by volumetric methods.

Procedure:-

After a large number of trials of fluxes and extractions the following procedure was adopted for the colorimetric method.

Fuse one gram of soil with 5 grams of a mixture of four parts sodium carbonate and one part potassium carbonate in a nickel or iron crucible. Transfer the fusion from the crucible to a beaker using a minimum of distilled water with heating. After breaking up the lumps, decant the liquid upon a 12.5 cm. No. 40 Whatman filter. Then thoroughly pulverize the residues with a rubber tipped policeman and wash upon the filter, rinsing out the beaker two more times. Wash the filter with a fine stream of distilled water thoroughly five times, allowing it to empty completely each time. Make the filtrate up to 250 cc. and take a 5 cc. aliquot for color development.

\* This work was begun under Dr. Wiley in the Chemistry Department.

In the colorimetric method 6 ppm. of iron, or 20 ppm. of titanium, or 700 ppm. of silicon will interfere with the proper development of color ( 6 ), ( 1 ). In the case of silicon, interference is avoided in the above technique with the use of very small aliquots. The main problem in the determination was the removal of iron and titanium. To separate these elements the carbonate fusion was employed. Tests of the method on two soils of known phosphorus were found to give good agreement with the known analyses.

To ascertain the accuracy with which this method might be used on Maryland soils, samples of seven types representing three soil provinces were analyzed by standard volumetric methods and then by this colorimetric technique. The results of these analyses are given in Table 1. The volumetric methods were those employed by the U. S. D. A. ( 5 ) and a modification of the official magnesium nitrate method. This latter method was developed by Professor Truog and as it has never been published is given here with his permission:

Procedure:-

Fuse 4 grams of soil with 6 grams of magnesium nitrate. Pulverize fusion and digest with 12 cc. conc. nitric acid in a 100-150 cc. erlenmeyer flask boiling moderately until loss of acid gives mixture a thick consistency (about 20 minutes). Shake to avoid caking and do not allow to go to dryness. Transfer the mass to a graduate using as little water as possible, make up to 50 cc. Filter and take 25 cc. of filtrate for determination. Add 12%  $\text{NH}_3$  until permanent yellow color or slight precipitate forms. Add sufficient more  $\text{NH}_4\text{NO}_3$  solution (1/2 gram per cc) to give 5 grams in all and finally 4 cc. of conc. nitric acid and shake. Heat on steam bath to  $58^\circ\text{C}$ , add 10 cc. of ammonium molybdate with shaking; stir vigorously maintaining at  $58^\circ$  for 5 minutes; then reduce to  $40^\circ$  for 1/2 hour and not over 1 hour. Filter and wash with pure water and titrate as usual.

Table 1.- The Percentage of Total Phosphorus Obtained on Eight Maryland Soils by the U. S. D. A., Magnesium Nitrate and Colorimetric Methods.

Soil Analyzed	: U.S.D.A. : :Method - : :Per Cent :	MgNO <sub>3</sub> : :Method - : :Per Cent :	:Colorimetric Method : :Increase : :Per Cent: : :Over MgNO <sub>3</sub> : : Method :
Manor Loam #15	.0328	.0398	.0436 10.3
Elkton Silt Loam #12	.0238	.0265	.0314 5.4
Hagerstown Silt Loam #14	.0228	.0288	.0331 6.6
Sassafras Loam #4	.0395	.0428	.0455 6.3
Keyport Silt Loam #8		.0363	.0368 1.4
Portsmouth Loam #1		.1625	.1531 - 5.9
Manor Loam #16		.0480	.0530 10.4
Sassafras Silt Loam #5		.0368	.0375 7.1

It is to be noted that there is better agreement between the magnesium nitrate and the colorimetric method than between the two volumetric procedures. The colorimetric figures on the whole are slightly high. Most workers agree that a magnesium nitrate fusion does not completely break down all mineral aggregates and that phosphorus within them would not be completely recovered. Furthermore the colorimetric method may be used in the presence of the maximum amount of vanadium to be expected in soil without interference ( 3 ), ( 4 ), ( 5 ). In related work the author has found that 1 ppm. of vanadium in the form of ammonium metavanadate may be present in the standard without serious effect

but that greater amounts progressively reduce the color developed - 10 ppm. reducing it 25%. For these reasons the magnesium nitrate method might give lower results than this colorimetric method.

To demonstrate the variation to be expected between replicates when using the colorimetric method, readings for the first four soils are reported in the following table.

Table 2.- Replicate Readings by the Colorimetric Method.

Soil Analyzed	:	Replicate readings in cc. on separate extracts *			
Manor Loam #15	:	34.5	35.	35.	35.
	:	35.5	35.	34.	35.
Elkton Silt Loam #12	:	25.	25.5	25.	25
	:	25.	25.5	25.5	25.
Hagerstown Silt Loam #14	:	27.	26.	26.	27.
	:	27.	27.	26.	26.
Sassafras Loam #4	:	36.	36.	36.	36.
	:	36.	38.	36.	37.

\*Blank correction made for 2.5 cc. for chemical impurities, etc.

Following the initial work the method was tried on different phosphate materials. Tennessee Brown Rock Phosphate (U. S. D. A. Sample # B14) was analyzed by the colorimetric method. In this determination 29.00% of  $P_2O_5$  was secured as against the known 33.74%. The reason for this difference was not apparent, especially since one of the previous soils analyzed had received heavy applications of lime apparently without interference. The possibility of calcium having

interfered through the precipitation of tricalcium phosphate was investigated, however. Two and four per cent of lime were added to one gram samples of the Sassafras Loam previously analyzed. The phosphorus values obtained from both of these limed samples were 7% low, suggesting that the calcium contents of rock phosphates might be the explanation of the low colorimetric results obtained on them. If this were the case it might be possible to find a solvent that would not dissolve sufficient calcium carbonate to remove the phosphorus from the solution.

In "prospecting" for such a solvent for dissolving the fusion, solution in normal sodium hydroxide was tried on fusions of the above mentioned phosphate. This gave a  $P_2O_5$  content of 32.9%. The blank, however, was too high to make certain the validity of the results. As a result, a tenth normal sodium hydroxide solution was employed to take up fusions of this phosphate and also of a sample of Florida pebble phosphate (U. S. D. A. sample #910). The  $P_2O_5$  content obtained in the fusion of sample B 14 was 31.5% as against a known phosphorus content of 33.74%. On sample #910 the  $P_2O_5$  content was 30.3% as against a known 31.09%. The greatest variation in these comparisons, 6.6% is not far beyond the range of accuracy of the colorimeter used.



Following the determinations on phosphate rock, tenth normal sodium hydroxide was used as the solvent for fusions of limed samples of the Sassafras loam. With this solvent the addition of lime did not depress the phosphorus value as it had with the water solvent. These findings seemed to substantiate the idea that it was calcium that was interfering in the analysis of phosphate rocks. The sodium hydroxide "takeup" was tried, therefore, upon samples of the eight soils previously analyzed, to see if it would change the readings on these acid soils. The resultant figures were identical with those given by the water solvent, further substantiating the method. The sodium hydroxide solvent was therefore adapted for this method.

Some further work has been done to determine whether a fusion might not be employed which would require less heat and would be more easily removed from crucibles. Fusing with sodium hydroxide was tried, since it would effect nearly the same separation. This fusion eliminated these difficulties but gave slightly lower figures on the rock phosphates. The B 14 gave 29.8% and the 910 gave 27.5%  $P_2O_5$ . The addition of half a gram of silica ( 2 ) did not increase the values in the determinations.

The Manor loam, #16, and the Sassafras silt loam, #5, samples were analyzed using this fusion, and very slightly lower figures were obtained than by the first two methods of fusion. An

addition of 4% of lime did not change the figures for these soils. As a result of this work it appeared that sodium hydroxide and sodium bicarbonate fusions would be less desirable than the carbonate fusion, although easier to make. The carbonate fusion followed by taking up in a solution of sodium hydroxide is the method recommended.

### Summary

A colorimetric method for total phosphorus determination in soils was developed. Briefly this consists of fusing with alkali carbonate, dissolving with .1N sodium hydroxide and estimating the phosphorus colorimetrically. This method is sufficiently accurate for all practical purposes. The principal advantages of the method are: the elimination of the need for expensive equipment & the use of fuming acids, the small opportunity for personal error, and the saving of half the time usually required.

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COLOR STANDARD FOR COLORIMETER

For use in a Kennicott-Campbell-Hurley colorimeter the regular standard is unsuitable. This instrument, with a slight modification, allows one to place a tube of a turbid extract beneath the standard and thus overcome shade of color difficulties. It is also the most rapid instrument available. These considerations have prompted Dr. Russel at the University of Nebraska to devise a more permanent standard that would not coat this colorimeter.

The one he developed consists of a .2 normal solution of boric acid adjusted to pH 7.8 with sodium hydroxide and colored with sufficient brom thymol blue and brom cresol green in equal proportions to equal the color of the standard. A very close match is obtainable in this way. This standard remains permanent for at least a whole day after adjustment with the regular standard and need not be renewed for a month or two. The author found the addition of 3 - 4 % of alcohol, to prevent the growth of moulds, greatly lengthened its life. This standard and colorimeter have been used in this work.

MOLYBDATE REAGENT FOR USE AT pH 5

To provide for the right reaction for color development, when using the pH 5 extractant described in this thesis, a special molybdate reagent is necessary. Sufficient additional sulfate ions have to be present to combine with sodium ions. In the table below this matter is investigated. The regular standard was made up in the pH 5 extractant, using molybdate reagents with acid concentrations varying slightly from the regular 280 cc. per liter.

Molybdate Reagent

H <sub>2</sub> SO <sub>4</sub> Present in Molybdate Reagent	:	Standard Reading
330 cc. per liter	:	57 ppm.
350 " " "	:	55 "
370 " " "	:	51.5 "
390 " " "	:	50 "
410 " " "	:	47.5 "

The regular standard reads 50, but a blank with the pH 5 reagent is 1.5 ppm. higher than with water. Three hundred and seventy cubic centimeters of sulfuric acid per liter is therefore very close to the correct amount. This concentration has been used in this work.

The Per Cent of Phosphorus Contained  
in some of the Phosphate Minerals Used  
in the Solubility Studies.

Phosphate minerals		: Phosphorus
		: per cent
Apatite	(Quebec)	17.88
Vivianite	(Pennsylvania)	10.74
"	(Australia)	7.35
Wavelite	(Arkansas)	3.48
"	(Columbia)	5.0
Dufrenite	(Virginia)	12.5
"	(England)	5.07

DESCRIPTION OF THE TWENTY-TWO MARYLAND SOILS STUDIED

No.:	Soil	Location			Cropping History	
	Type	Farm	Address	Topography	Vegetation	Treatment
1	Portsmouth L.	Jarrell	Ridgely	depression	brush sumac	never farmed
2	Sassafras L. S.	Atkins	Salisbury	south slope	pasture	not fertilized in 10 years
3	Elkton L.	Church	Cordova	north slope	bush	not farmed
4	Sassafras L.	Church	Cordova	flat	grass	never fertilized
5	Sassafras Si. L.	Price	Centerville	flat	grass	never tilled or fertilized
6	Sassafras S. L.	Talbot-West	Cordova	northwest slope	grass	never fertilized
7	Sassafras Si. L.	Morris	Chestertown	flat	woods	never fertilized or tilled
8	Keyport Si. L.	Harris	Centerville	West slope	woods	never fertilized or tilled
9	Elkton Si. L.	Jarrell	Ridgely	northwest slope	bush	not fertilized recently
10	Keyport L.	Jarrell	Ridgely	northwest slope	edge of woods	not fertilized recently
11	Sassafras S.	Jarrell	Ridgely	northwest slope	sedge grass	not fertilized recently

DESCRIPTION OF THE TWENTY-TWO MARYLAND SOILS STUDIED -(Cont'd)

No.:	Soil	Location			Cropping History	
	Type	Farm	Address	Topography	Vegetation	Treatment
12	Elkton Si. L.	Princess Anne	Princess Anne	flat	field	uncultivated in 2 years
13	Manor L.	Garrett	Manchester	10% east slope	Wood lot	not farmed in 40 yrs.
14	Hagerstown Si. L.	Corderman	Hagerstown	10% west slope	permanent pasture	never fertilized
15	Manor L.	Shriver - East	Sykesville	1% north slope	bush	not cultivated in recent yrs.
16	Manor L.	Shriver - Midway	Westminster	3% west slope	bush	not cultivated in recent yrs.
17	Frankstown Si. L.	Downey	Downsville	5% east slope	pasture	manured but not fertilized
18	Frankstown Si. L.	Mercer	Frederick	5% south slope	grass and weeds	never fertilized
19	Hagerstown Si. L.	Cunningham	Chewsville	2% north slope	permanent pasture	fertilized 12 yrs. ago
20	Frankstown Si. L.	King	Frederick	roadside	grass	not fertilized recently
21	Hagerstown Si. L.	Oaks	Hagerstown	5% east slope	permanent pasture	never fertilized
22	Sassafras Si. L.	Bryan	Chestertown	1% east slope	bush	unfertilized



LEACHING STUDIES

Leachates of 200 cc.; timing 4 hrs.; pH 5  
(Begun November 21, 1933)

Number of Leachate	Material											
	Alumi- num Phos- phate :10 mg.	Ferric Phos- phate :10 mg.	Ti- tanium Phos- phate :10 mg.	Sassa- fras S. L. 10 gms.	Key- port L. 10 gms.	Sassa- fras S. 5 gms.	Elk- ton Si. L. 10 gms.	Hagers- town Si. L. 10 gms.				
1	70	22	100	20.5	20.5	9	9	29	29	7	8	16
2	55	11	61	15	15	10	10	31	31	4	5	16
3	49	11	72	13	13	9	9	20	21	5	5	7
4	49	8	29	10.5	10.5	9	9	23	23	5	6	5
5	56	8.5	29	7	8	7	8	19	19	5.5	5.5	5
6	40	9.5	29	8	7	9	9	18	17.5	5.5	5.5	2.5
7	40	10	18	5	5.5	8	8	19	19	5	5	3
8	39	9	18	5.5	5	7	6	15.5	15	5.5	5.5	2
9	40	9	11	5.5	5.5	7	7	13.5	13.5	5.5	5.5	2.5
10	34	10	24	5	5	8	8	16	17	6	6	2
11	33	8	10.5	6	6	7	7	14	14	6	6	3
12	27	7.5	12	6	5.5	7	7	17	15	6	6	3
13	30.5	7.5	11.5	5	5	8	7.5	12	12	6	6	2
14	34	8	9	5	5	6.5	7	14	14	6	6	2
15	33	7	6	5	5	7.5	7.5	14	14	5.5	6.5	2
16	34	7	8	4	4	7	7	12.5	12	6	6.5	2
17	31	7	14	4.5	5	6.5	6	13.5	13.5	5.5	5.5	1.5
18	33.5	6.5	"	4.5	4	7	7	13	13	5.5	5.5	2
19	30.5	8	"	5	4.5	6.5	6.5	14	13.5	5.5	5.5	2
20	25	7	"	3.5	3.5	6.5	6.5	13	13	6.5	6	2

(Cont'd.)

Number of Leachate	Material										
	Alumi- num :Phos- phate :10 mg.	Ferric :Phos- phate :10 mg.	Ti- tanium :Phos- phate :10 mg.	Sassa- fras S. L. 10 gms.	Key- port L. 10 gms.	Sassa- fras S. 5 gms.	Elk- ton Si. L. 10 gms.	Hagers- town Si. L. 10 gms.			
21	32	8	9.5	4 : 4	5.5 : 5.5	10 : 10	6 : 6	2			
22	28	8.5	"	2.5 : 3	5 : 5	9.5 : 9	5.5 : 5.5	1.5			
23	26.5	8.5	"	2.5 : 2.5	5.5 : 5.5	8 : 7.5	6 : 5	2			
24	26	7.5	"	3.25 : 3.25	5.5 : 5.5	9.5 : 10.5	5.5 : 5	1.5			
25	27	7	9.5	" : "	" : "	" : "	" : "	"			
26	19	8	"	" : "	" : "	" : "	" : "	"			
27	21	6	9.5	" : "	" : "	" : "	" : "	"			
28	15	8	"	2.5 : 2.5	4.5 : 4.5	8.5 : 8.5	5 : 4.5	1.5			
29	19	6	"	" : "	" : "	" : "	" : "	"			
30	21	7	"	" : "	" : "	" : "	" : "	"			
31	19	6.5	9.5	" : "	" : "	" : "	" : "	"			
32	18.5	6	"	3 : 3	5 : 5	9 : 9	4.5 : 4.5	1.5			
33	18.5	6.5	"	" : "	" : "	" : "	" : "	"			
34	18.5	"	"	3 : 3	5 : 5	9 : 9	4.25 : 4.5	1.5			
35	18.5	"	20.5	" : "	" : "	" : "	" : "	"			
36	18.5	"	"	" : "	" : "	" : "	" : "	"			
37	18.5	6.5	"	" : "	" : "	" : "	" : "	"			
38	"	"	"	2.5 : 2.5	5 : 5	8.5 : 8.5	3.5 : 3.5	1			
39	"	"	9.5	" : "	" : "	" : "	" : "	"			
40	"	"	"	" : "	" : "	" : "	" : "	"			
41	15.5	8	"	" : "	" : "	" : "	" : "	"			
42	15.5	8	"	3 : 3	5 : 5.5	8.5 : 8.5	4 : 3.5	1.5			



(Cont'd.)

Number: of Leach- ate	Material											
	Alumi- num :Phos- phate :10 mg.	Ferric :Phos- phate :10 mg.	Ti- tanium :Phos- phate :10 mg.	Sassa- fras S. L. 10 gms.	Key- port L. 10 gms.	Sassa- fras S. 5 gms.	Elk- ton Si. L. 10 gms.	Hagers town Si. L. 10 gms.				
65	"	"	"	"	"	"	"	"	"	"		
66	"	"	"	1	1	2.5	2.5	3	3	1.5	1.5	.25
67	.5	6	10	"	"	"	"	"	"	"	"	"
68	"	"	"	"	"	"	"	"	"	"	"	"
69	"	"	"	"	"	"	"	"	"	"	"	"
70	"	"	"	1	1	2	2	2.5	2.5	1.5	1.25	.25
71	0	5.5	6.5	"	"	"	"	"	"	"	"	"
72	"	"	"	"	"	"	"	"	"	"	"	"
73	"	"	"	"	"	"	"	"	"	"	"	"
74	"	"	"	.75	.75	2	2.25	3	3	1.5	1.75	.25
75	0	5.5	7	"	"	"	"	"	"	"	"	"
76	"	"	"	"	"	"	"	"	"	"	"	"
77	"	"	"	"	"	"	"	"	"	"	"	"
78	"	"	"	1	1	2	2	2.5	2.5	1.75	1	
79	0	4.75	8	"	"	"	"	"	"	"	"	"
80	"	"	"	"	"	"	"	"	"	"	"	"
81	"	"	"	"	"	"	"	"	"	"	"	"
82	"	"	"	1	1	1.5	1.5	3	3	1.5	1.5	
83	"	4.75	8	"	"	"	"	"	"	"	"	"
84	"	"	"	"	"	"	"	"	"	"	"	"
85	"	"	"	"	"	"	"	"	"	"	"	"
86	"	"	"	.5	.75	1	1	2.5	2.5	1.5	1	

(Cont'd.)

Number: of Leach- ate	Material							
	Alumi- num :Phos- phate :10 mg.	Ferric :Phos- phate :10 mg.	Ti- tanium: :Phos- phate :10 mg.	Sassa- fras : S. L. : 10 gms.	Key- port : L. : 10 gms.	Sassa- fras : S. : 5 gms.	Elk- ton : Si. L. : 10 gms.	Hager- town : Si. L. : 10gms.
87	5.5	9	" : "	" : "	" : "	" : "	" : "	" : "
88	"	"	" : "	" : "	" : "	" : "	" : "	" : "
89	"	"	" : "	" : "	" : "	" : "	" : "	" : "
90	"	"	.25: .5	.75: .75	3 : 3	1.75:1.50		
91	5.5	8	" : "	" : "	" : "	" : "	" : "	" : "
92	"	"	" : "	" : "	" : "	" : "	" : "	" : "
93	"	"	" : "	" : "	" : "	" : "	" : "	" : "
94	"	"	0 : 0	1 : 1	3 : 3	1.5 : 1.5		
95	5.5	7.5	" : "	" : "	" : "	" : "	" : "	" : "
96	"	"	" : "	" : "	" : "	" : "	" : "	" : "
97	"	"	" : "	" : "	" : "	" : "	" : "	" : "
98	"	"	:	.25: .5	1 : 0	0 : 0		
99	4.75	7	:	" : "	" : "	" : "	" : "	" : "
100	"	"	:	" : "	" : "	" : "	" : "	" : "
101	"	"	:	" : "	" : "	" : "	" : "	" : "
102	"	"	:	:	:	:	:	:
103	4	7.5	:	:	:	:	:	:
104	"	"	:	:	:	:	:	:
105	"	"	:	:	:	:	:	:
106	"	"	:	:	:	:	:	:
107	4	9.5	:	:	:	:	:	:
108	"	"	:	:	:	:	:	:

(Cont'd.)

Number: of Leach- ate	Material							
	Alumi- num :Phos- phate :10 mg.	Ferric :Phos- phate :10 mg.	Ti- tanium :Phos- phate :10 mg.	Sassa- fras S. L. 10 gms.	Key- port L. 10 gms.	Sassa- fras S. 5 gms.	Elk- ton Si. L.	Hagers town Si.L. 10 gms
109	"	"	:	:	:	:	:	:
110	"	"	:	:	:	:	:	:
111	4		:	:	:	:	:	:
112	"		:	:	:	:	:	:
113	"		:	:	:	:	:	:
114	"		:	:	:	:	:	:
115	5		:	:	:	:	:	:
116	"		:	:	:	:	:	:
117	"		:	:	:	:	:	:
118	"		:	:	:	:	:	:
119	5.5		:	:	:	:	:	: