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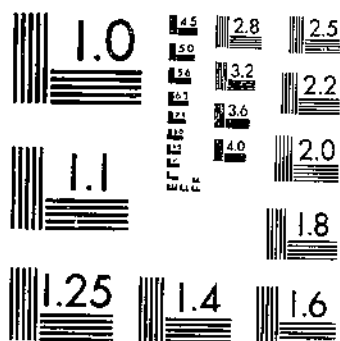
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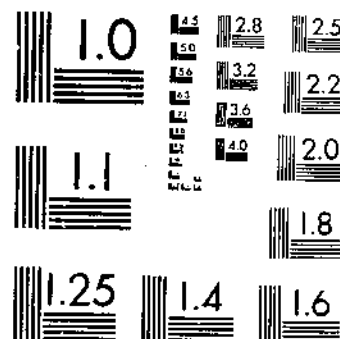
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1 OF 1

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NATIONAL BUREAU OF STANDARDS-1963-A

UNITED STATES DEPARTMENT OF AGRICULTURE  
WASHINGTON, D. C.

# MECHANICAL ANALYSIS OF FINELY DIVIDED NATURAL PHOSPHATES

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## CONTENTS

	Page		Page
Introduction	1	Experimental determination of settling velocities	14
Methods of mechanical analysis	2	Particle-shape factor for natural phosphates	17
Types of natural phosphates used in the investigation	3	Comparison of large-scale separations with analyses by the pipette method	18
Separation of large samples without the use of dispersing agents	4	Outline of pipette method for mechanical analysis of natural phosphates	20
Method of large-scale separation	5	Preparation and dispersion of sample	21
Results of large-scale separations	7	Separation into size classes	21
Specific gravity of natural phosphates	9	Summary	22
Development of mechanical analysis method	11	Literature cited	23
Dispersing agents	11		
Effect of temperature	12		

## INTRODUCTION

It is usually the custom to express the mechanical composition of finely divided natural phosphates in terms of the percentages of material passing through or retained by sieves of various mesh size. This method of mechanical analysis has a serious disadvantage in that it does not give any information on the size distribution of the material passing through the sieve of smallest mesh used in the test. The sieves now available for practical use are limited to a fineness not exceeding 325 mesh, corresponding to a mesh opening of about 0.044 millimeter, or  $44\mu$ .

In experiments with finely divided natural phosphates, accurate information on their mechanical composition is often of primary importance, particularly as regards the distribution of particle size in the material passing, for example, a 300-mesh or 325-mesh sieve. When commercial phosphate rock is ground by a uniform procedure so that a certain percentage will pass through a sieve of a given mesh, the size distribution of the material passing through the sieve

<sup>1</sup> The authors express their appreciation to W. H. Fry for assistance in the microscopical examination of the mechanical separates, to H. E. Middleton for assistance in the experimental determination of the settling velocities of phosphate particles, and to Hubert Lakin and Mrs. Dorothea M. Darnell, of the soil physics laboratory, for assistance in the analytical work.

will vary considerably with the grade and type of rock and also when the rock is of the same grade and type with different grinding methods. The various types of hard phosphate rock frequently occur in deposits which also contain considerable naturally very finely divided phosphate which has physical properties similar to those of the soil clays and usually contains considerable colloidal phosphate (4).<sup>2</sup> Sieve tests on this type of phosphate are of no significance, inasmuch as frequently less than 5 per cent by weight of the material is retained on a 300-mesh sieve and as much as 90 per cent is composed of particles  $5\mu$  and less in diameter.

### METHODS OF MECHANICAL ANALYSIS

It is evident that it is desirable to have a method of analysis which will give reliable information on the distribution of particle size in the subsieve fractions of finely divided natural phosphates. A search of the literature revealed a total lack of information in regard to accurate methods for the mechanical analysis of these materials. Considerable work has been done, however, on methods of determining the distribution of particle size in the subsieve fractions of a wide variety of other materials. These methods may be grouped into two general classes, namely, those in which the separations are made in a gaseous medium, usually by air currents, and those in which the separations are made in a liquid medium, usually water.

Air-separation methods have not been generally used except on materials that react with or are appreciably soluble in water. So many difficulties in the matter of the quantitative separation and recovery of the fine fractions arise in these methods that they can not be considered desirable for accurate work. Finely ground phosphatic materials tend to form small, rather closely cohering aggregates which are not readily broken up into the individual particles by agitation with air. It is also obvious that air-separation methods fail entirely with ground materials that have been allowed to become wet, and also with materials, such as the claylike phosphates, which in their natural state are composed of comparatively soft aggregates of very fine individual particles.

Methods in which the separations are made in a liquid medium, usually water, have been used for many years in the mechanical analysis of soils and similar materials. These methods, of which there are several types, are all based on the well-known fact that the smaller particles in liquid suspension fall more slowly than the larger ones. Olmstead, Alexander, and Middleton (9) have recently pointed out the difficulties encountered in some of the water-suspension methods and have outlined a pipette method for the mechanical analysis of soils, based on an improved dispersion procedure, using 0.005 N sodium oxalate as the dispersing agent. In the pipette method of mechanical soil analysis, a 10-gram sample is treated with hydrogen peroxide to remove organic matter, washed to remove soluble substances, and shaken in a sodium oxalate solution to break down soil aggregates and maintain their dispersion.

The particles of silt and clay, after separation from the sands, are suspended in 1 liter of dilute sodium oxalate solution. After a

<sup>2</sup> Italic numbers in parentheses refer to Literature Cited, p. 23.

definite time a portion of the suspension is pipetted off at a certain depth, evaporated to dryness, and weighed. This sample contains an exact aliquot of the material in the sample below a certain size. Stokes's equation of the fall of solid spheres in a viscous medium gives a relation between the settling velocity of particles, the density and viscosity of the fluid medium, the density of the solid particle, and a shape factor.

In order to apply this pipette method of mechanical analysis to the natural phosphates it becomes necessary (1) to determine the dispersion produced by chemical deflocculents, (2) to determine the density of the material and the shape factor as required in Stokes's formula, and (3) to consider the effect of the density and viscosity of the fluid medium as influenced by temperature changes. In the pipette method actual separations of fine material of silt and clay sizes are not made. Separations of large samples of natural phosphates were, therefore, very carefully made in order to provide a basis of comparison of the determinations by the pipette method. These determinations and an outline of the method of mechanical analysis based thereon were the subject of this investigation.

#### TYPES OF NATURAL PHOSPHATES USED IN THE INVESTIGATION

It is important that any method for the mechanical analysis of finely divided natural phosphates shall be applicable to all types of these materials, particularly those of economic importance. Consequently, the present investigation was extended to include all the commercial types of natural phosphate produced in the United States at the present time.

In the order of their present commercial importance, the domestic types of natural phosphates are as follows: Florida land pebble (7, 15); Tennessee brown rock (15); Florida hard rock (7, 15); Tennessee blue rock (15); the phosphates of Idaho, Montana, Utah, and Wyoming (6, 15); the soft and "waste-pond" phosphates of Florida (4, 7); and South Carolina phosphate (14, 15). The general characteristics of the phosphates and the nature and extent of the deposits are discussed in the publications cited.

The South Carolina deposits were formerly an important source of phosphate rock in the United States. Exploitation of these deposits ceased, however, several years ago, owing to the low grade of the rock and the cost of mining in competition with Florida land-pebble phosphate. This type of phosphate was not included in the present investigation because large samples representative of the commercial product were not available.

As the name implies, Florida soft phosphate is a soft, claylike material. It is commonly closely associated with both the Florida land-pebble and hard-rock phosphates, but it occurs to a greater extent in the hard-rock than in the land-pebble deposits. Individual deposits of variable size are in both districts. During the process of preparing Florida hard-rock phosphate for the market, the soft phosphate present in the matrix is washed into waste ponds, where it settles out with the clay and other impurities, the finer particles concentrating at points farthest from the entrance to the ponds. The abandoned waste ponds in the Florida hard-rock phosphate district

contain a considerable tonnage of this material, which is used to some extent as a fertilizer. The waste ponds in the Florida land-pebble district contain a much smaller percentage of finely divided phosphates than those in the hard-rock district. For the purpose of this bulletin, the fine phosphatic material settling out in the Florida hard-rock phosphate waste ponds will be referred to as waste-pond phosphate. This material and the soft phosphate from which it is derived are usually composed of very fine particles, a large percentage of which are colloidal in size (4).

Samples representing shipments of commercial grades of Florida land-pebble, hard-rock, and waste-pond phosphates; Tennessee brown-rock and blue-rock phosphates; and Idaho and Wyoming phosphates were used in this investigation. The Florida soft phosphate (No. 728) was not a commercial material, the sample being obtained directly from an individual deposit.

The Florida soft and waste-pond phosphates were obtained in the form of comparatively soft lumps, which, for use in the experiments, were crushed to pass a 10-mesh sieve. Grinding during the crushing operation was avoided as much as possible, in order not to break up hard particles that might otherwise fail to disintegrate under the action of water and dispersing agents alone.

The other types of phosphate were obtained in the form of hard pebbles, lumps, or massive pieces, depending on the type of rock. They were first crushed to about 10-mesh size and then ground to pass a 100-mesh sieve having openings of 0.147 millimeter square. In the grinding, which was done as uniformly as possible in a rotary-disk power mill, the entire sample was run through the mill and the 100-mesh material sieved out, the operation being repeated until the sample was completely reduced to the desired fineness. The method of grinding was duplicated as closely as possible on all the samples of hard phosphate, in order to determine whether the distribution of particle size in the material finer than  $50\mu$  varies considerably with the type and grade of rock.

#### SEPARATIONS ON LARGE SAMPLES WITHOUT THE USE OF DISPERSING AGENTS

As in other types of analytical procedures, accurate standards are of primary importance in the development of methods of mechanical analysis. Such standards are, however, usually very hard to prepare, owing to the difficulty of accurately determining the distribution of particle size independently of mechanical-analysis methods themselves. Because of the wide variations in the physical and chemical characteristics of different types of finely divided materials it is essential, also, that the standards should be prepared from the same type of material as that upon which the method is to be used. Most methods of mechanical analysis have been designed to give reproducible and comparative values rather than absolute values, as shown by the widely varying results often obtained on the same samples by different methods.

Preliminary experiments<sup>a</sup> indicated that it might be possible to

<sup>a</sup> Prior to the present investigation, L. B. Olmstead of the soil physics laboratory of this bureau had made several large-scale separations of finely divided natural phosphates, using ammonium hydroxide as a dispersing agent.

separate finely divided natural phosphates quantitatively into the desired groups of particle sizes by means of water sedimentation without the use of dispersing agents, the progress and accuracy of the separation being determined by means of the microscope. The results obtained by such a procedure would be independent of many of the variable factors encountered in the indirect methods of determining particle sizes and would serve as standards in the development of analytical methods.

For the purpose of the present investigation it was thought best to effect the separations into fractions having the same range of particle size as customarily used in the mechanical analysis of soils in the United States; namely, (1) particles greater than  $50\mu$  in diameter; (2) particles from  $50\mu$  to  $5\mu$ ; and (3) less than  $5\mu$ . Following the terminology used in soil analysis, the material comprising these classes will be designated as (1) "sand," (2) "silt," and (3) "clay." It should be noted, however, that these terms are used in this bulletin only for the sake of convenience, and in order to avoid any implication that the chemical composition of the material is similar to that of the soil they will always be inclosed in quotation marks. In soil analysis, the sand fraction includes particles ranging from  $2,000\mu$  to  $50\mu$  in diameter and is customarily divided into five size classes by means of sieves. In this bulletin all particles coarser than  $50\mu$  in diameter are designated as "sand," no further separation of this fraction into size classes being made.

#### METHOD OF LARGE-SCALE SEPARATION

In order to obtain sufficient material for specific-gravity determinations and for future chemical and physical studies, separations were attempted on 800-gram samples of each type of the natural phosphates. The procedure used is described in detail, as follows:

Eight hundred grams of the phosphate was weighed into a 2.5-liter bottle, a small sample also being weighed out for moisture determination at  $105^{\circ}\text{C}$ . The bottle, to which 2 liters of distilled water was added, was vigorously agitated for one hour in a mechanical shaker. The larger particles were then allowed to settle and the upper portion of the suspension was decanted through a 300-mesh sieve into 2-liter cylinders, the process being repeated until the suspension in the bottle settled clear after standing for 10 minutes. The object of this treatment was to separate discrete particles coarser than 300 mesh from the finer discrete particles and aggregates. During the first stages of this separation sufficient time was allowed prior to decantation to prevent the sieve from becoming clogged. After removal of the greater portion of the fine material, the time of standing was shortened so that some of the particles larger than  $50\mu$  were decanted and caught on the sieve. The material collected on the sieve was washed back into the shaker bottle after each decantation so that the sieve was always clean at the beginning of the pouring. This routine was continued until a microscopical examination showed that the material remaining in the shaker bottle contained no particles finer than  $5\mu$  and only a comparatively small quantity of

\*The 300-mesh sieve used in this investigation was fitted with Tyler phosphor bronze twilled wire cloth, which passes material finer than  $50\mu$  equivalent diameter.



material finer than  $50\mu$ . This material was then dried at  $105^{\circ}\text{C}$ . and dry sieved on a 300-mesh screen until only a negligible quantity of fine material was obtained by further sieving. The coarser fraction was composed of particles having at least two dimensions larger than  $50\mu$ , and the particles passing the sieve represented a portion of the material between  $50\mu$  and  $5\mu$  in diameter.

With several of the samples the suspended material decanted into the 2-liter cylinders flocculated quite rapidly, giving comparatively clear supernatant liquids. In such cases the liquid was filtered off by means of Pasteur-Chamberland tubes (grade F) in order to remove the soluble salts causing flocculation, and the residue was thoroughly agitated with the suspension subsequently obtained by shaking the material remaining in the shaker bottle with a fresh portion of water. This operation was repeated until the material in the cylinders remained in suspension for 8 to 10 hours. The filter tubes were then removed and the adhering material was washed back into the cylinders. With some of the phosphates the very fine particles decanted into the cylinders remained in suspension for the desired length of time from the beginning of the separation. In such cases filtering and washing were unnecessary. The suspensions obtained in this way were composed of particles smaller than  $50\mu$  in diameter.

After the separation at  $50\mu$  was complete the following procedure was used to separate the material into particles  $50\mu$  to  $5\mu$  in diameter and particles smaller than  $5\mu$  in diameter, respectively. The suspended material was thoroughly agitated by churning with a rod equipped with a perforated brass plate having holes 1 millimeter in diameter. The suspension was allowed to stand until a microscopic examination of the material remaining in suspension showed that all particles larger than  $5\mu$  had settled to the bottom of the cylinder. Eight hours was sufficient for this purpose. A siphon was then lowered into the cylinder to a distance of at least 5 centimeters above the top of the layer of settled material, the total height of the column of liquid having been previously regulated so that siphoning was done at a depth of about 20 to 25 centimeters. The process of agitating with water and settling for eight hours was repeated until the liquid siphoned off was comparatively free from suspended material. The material remaining in the cylinder contained, however, an appreciable percentage of particles smaller than  $5\mu$  in diameter.

In order to effect a final and practically complete separation of the  $5\mu$  material the time allowed for settling was progressively shortened. At each change in the settling time the material siphoned off was carefully examined under the microscope in order to make sure that no particles larger than  $5\mu$  were carried over. This process was continued very carefully until the weight of particles smaller than  $5\mu$  in diameter remaining in the cylinders was insignificant in comparison with the total weight of material left behind, as determined by microscopical examination. The material remaining in the cylinders constituted the greater portion of the "silt" fraction of the original sample. It was evaporated on a steam bath and dried in an oven at  $105^{\circ}\text{C}$ . The dry product was then combined with the "silt" material separated from the "sand" fraction by dry sieving, as previously described.

The material siphoned from the cylinders constituted the "clay" fraction. It was concentrated either by means of Pasteur-Chamberland filters or by evaporation on a steam bath, with final drying in an oven at 105° C.

As a final check on the efficiency of the separation the three fractions of dry material were carefully examined under the microscope. In no case did the "silt" fraction contain more than an insignificant quantity of "clay" particles. Examination of the "clay" fraction for "silt" particles was difficult because of the state of aggregation of the particles after drying. Owing to the possible inclusion of "silt" particles the values obtained for "clay" may be somewhat too large, but it is believed that, because of the care taken in making the separations, the error on this account was very small. An exact separation at  $5\mu$  can not be hoped for (or expected) even if all the particles near  $5\mu$  had the same hydraulic value. It must be assumed that the small amount of "silt" carried over in the "clay" fraction is compensated by a corresponding quantity of coarse "clay" left in the "silt" fraction. The "sand" and "silt" fractions were free of aggregates except those composed of particles originally cemented together by material insoluble in water.

The time required to make a quantitative separation on 800 grams of material by the method just described depends upon the ease with which dispersion of the very fine particles is obtained. With the facilities and apparatus available in the average mechanical-analysis laboratory, it will usually require from 10 to 14 days to make a complete separation of the more easily dispersed types of phosphate by this method. Even with prolonged washing, some samples of phosphate will not remain suspended in pure water long enough to allow separation into the mechanical fractions, and in such cases it is necessary to use a dispersing agent. Lithium oxalate serves very well for this purpose, since, so far as is known to the writers, appreciable quantities of lithium do not ordinarily occur in the natural phosphates, and consequently the use of this salt does not interfere with the chemical analysis of the separates. In the case of samples requiring a dispersing agent, a concentration of lithium oxalate equivalent to approximately 0.005 N was maintained in the cylinders during the process of separating the "clay" from the "silt." Soluble calcium salts prevent the deflocculation of finely divided materials, and, in the present investigation, the samples failing to disperse in pure water were known to contain appreciable quantities of calcium sulphate and calcium carbonate as such. Many of the natural calcium phosphates occurring in the United States contain calcium sulphate and calcium carbonate, but it seems that in most cases these compounds are combined with the calcium phosphate, forming a complex molecule which is very insoluble in water.

#### RESULTS OF LARGE-SCALE SEPARATIONS

The results obtained on 11 samples, representing eight types of natural phosphates, are given in Table 1. These samples and the results obtained on them by the large-scale separations were used as standards in developing the method of mechanical analysis described later.

TABLE 1.—Mechanical analysis of 800-gram samples of phosphates

Sample No.	Type or source of phosphate	Location of deposit	"Sand" >50 $\mu$	"Silt" 50 $\mu$ to 5 $\mu$	"Clay" <5 $\mu$	Solution and mechanical losses
910	Florida land pebble.....	Mulberry.....	Per cent 41.7	Per cent 43.3	Per cent 11.8	Per cent 12.2
912	do.....	do.....	35.1	45.4	19.2	3
947	do.....	Brewster.....	43.2	42.0	9.6	.2
952	Florida hard rock.....	Dunnellon.....	33.7	43.8	22.3	.2
728	Florida soft.....	Jallette.....	30.4	20.9	48.7	.0
727	Florida waste pond.....	Dunnellon.....	.2	12.9	85.3	1.6
915	do.....	do.....	5.1	19.5	75.1	.2
906	Tennessee brown rock.....	Wales.....	45.2	38.8	14.0	1.0
908	do.....	Mount Pleasant.....	37.6	46.8	13.8	1.7
948	Wyoming.....	Cokeville.....	49.8	43.6	6.6	.0
973	Idaho.....	Conda.....	25.0	55.5	27.9	.6

<sup>1</sup> A small portion of the "silt" and "clay" was accidentally spilled in this separation.

<sup>2</sup> These samples would not deflocculate in pure water. Lithium oxalate was used as a dispersing agent.

As previously mentioned, the samples of hard phosphate were ground by a uniform procedure to pass a 100-mesh sieve. The results show, however, a considerable variation in the distribution of particle size with the different types of rock, particularly in the "sand" and "clay" fractions. This is due not only to variations in the physical nature of the phosphates themselves but also to the presence of variable quantities of impurities, such as quartz and silicates. Some of the points noted in connection with the separations are summarized briefly in the following paragraphs.

The Florida land-pebble and hard-rock phosphates, except Florida land pebble No. 910, dispersed easily and completely in pure water after a few preliminary washings. Florida land pebble No. 910, and also Tennessee brown-rock phosphate No. 906 required considerable preliminary washing before deflocculation was obtained. Each sample required about 50 liters of wash water, after which a stable suspension was readily obtained. The Florida soft and waste-pond phosphates swelled considerably upon addition of water. Stable suspensions were easily obtained, but a comparatively large number of pourings was required to complete the separations because of the slow disintegration of the aggregates of very fine particles. The "sand" fraction of the waste-pond phosphate consisted almost entirely of small roots and other forms of vegetable matter. A stable suspension of the Idaho phosphate was easily obtained in pure water, but small quantities of fine material continued to go into suspension with repeated washing and decantation, and a considerable number of decantations was required to effect a complete separation.

Even with prolonged washing it was not possible to obtain sufficiently stable suspensions of the Tennessee brown rock No. 908 and Wyoming phosphate to permit of making the separations in pure water. These samples were dispersed with lithium oxalate. The number of decantations required to complete a separation at 5 $\mu$  ranged from about 20 for the samples easiest dispersed to 75 for the hardest. Large-scale separations were attempted on Tennessee blue-rock phosphate (No. 930), but satisfactory results were not obtained even when lithium oxalate was used as a dispersing agent.

## SPECIFIC GRAVITY OF NATURAL PHOSPHATES

The pipette method of mechanical analysis depends on the relation of settling velocity to particle size. This relation is usually expressed by Stokes's formula for the fall of a solid sphere in a viscous fluid,

$$V = \frac{2}{9} r^2 \frac{(d - d')}{\eta} g$$

where  $V$  is the settling velocity of a sphere of radius  $r$  and density  $d$  in a medium of density  $d'$  and viscosity  $\eta$ , under a gravitational acceleration,  $g$ . From this formula it is evident that the velocity with which a spherical solid particle of a given size falls in a medium of given density and viscosity is directly dependent on the difference in the densities of the particle and the fluid medium through which it falls.

Dana (1) states that the specific gravity of crystalline fluorapatite ranges from 3.17 to 3.23, and that of South Carolina phosphate ranges from 2.2 to 2.5. According to Schucht (12), the specific gravity of Florida phosphate ranges from 2.2 to 3.2, and Penrose (10) reports that phosphatic nodules occurring near Wilmington, N. C., have gravities ranging from 2.6 to 2.7. As reported by Mansfield and Girty (6), the specific gravity of Idaho, Utah, and Wyoming phosphates ranges from 2.86 to 2.93. Hayes (3) gives 2.83 to 3.07 as the specific gravities of the matrix of Tennessee white-rock phosphate, but data on the gravities of Tennessee brown-rock and blue-rock phosphate do not seem to be available in the literature. Schaller (11) gives the following values for the gravities of several calcium phosphate minerals, which have compositions approximating that of phosphate rock. These are dahllite 2.97 to 3.053, francolite 3.09 to 3.128, colophonite 2.10 to 2.82, and quercyite 2.83 to 2.87.

Because of the wide variations in the figures reported in the literature and the complete lack of data on certain types of the domestic phosphates, specific gravity determinations were made on 22 samples of phosphate from various deposits in the United States in order to determine whether the variations were sufficient to preclude the use of an average value for all the samples. The natural phosphates are mixtures of calcium phosphate with varying quantities of impurities, such as quartz, silicates, iron, and aluminum compounds, and, as pointed out by Jacob, Hill, and Holmes (4) the chemical composition of the fine material separated from the ground rock and also from the claylike phosphates may be very different from that of the original sample and the coarse material separated therefrom. In mechanical analysis by the pipette method it is important to know whether the specific gravity of the original sample differs materially from that of the particular size particle for which it is desired to calculate the settling velocity. Consequently, specific gravity determinations were also made on the "sand," "silt," and "clay" fractions obtained from several samples by the method previously described.

The samples for the specific gravity determinations were prepared in the same manner as those used for the large-scale separations, as

described on page 4. The determinations were made in water at 25° C. by the pycnometer method with an accuracy of  $\pm 0.02$ . The results, given in Table 2, show that with these particular samples the specific gravity of the original material varied from 2.89 to 3.15, the average being 3.02. The gravities of the waste-pond phosphates, which contained 19.4 to 25.3 per cent of phosphoric acid ( $P_2O_5$ ), varied from 2.89 to 2.98, with an average of 2.93, and those of the other phosphates, which contained 30 per cent or more of phosphoric acid, varied from 2.95 to 3.15, with an average of 3.06. In general it seems that a particular type of phosphate is characterized by an approximately constant specific gravity which is slightly different from those of the other types. For the purpose of mechanical analysis, the results do not indicate sufficiently wide variations in the specific gravities to preclude the use of an average value of 3 for the domestic types and grades of natural phosphates.

TABLE 2.—*Specific gravities of natural phosphates*

Sam- ple No.	Type or source of phosphate	Location of deposit	Specific gravity
790	Florida land pebble.....	Unknown.....	3.00
910	do.....	Mulberry.....	3.02
912	do.....	do.....	3.09
947	do.....	Browser.....	3.06
771	Florida hard rock.....	Unknown.....	2.96
932	do.....	Dunnellon.....	3.09
728	Florida soft.....	Juliette.....	3.09
725	Florida waste pond.....	do.....	2.89
915	do.....	do.....	2.97
727	do.....	Dunnellon.....	2.93
824	do.....	do.....	2.93
825	do.....	do.....	2.91
827	do.....	do.....	2.98
828	do.....	Felicia.....	2.94
726	do.....	do.....	2.89
762	Tennessee brown rock.....	Mount Pleasant.....	3.15
908	do.....	do.....	3.12
496	do.....	Wales.....	3.12
772	Tennessee blue rock.....	Glover.....	3.10
930	do.....	Gordonsburg.....	3.14
773	Idaho.....	Conda.....	2.98
948	Wyoming.....	Cokeville.....	2.95

The results given in Table 3 indicate that the specific gravities of the mechanical fractions do not vary in any constant manner from that of the original sample, and consequently there is no definite relation between the gravity of the original sample and the gravity of particles of any particular size present therein. The differences are not, however, great enough to cause serious error when the average specific gravity value, 3, of the original material is also used as the average gravity of the different mechanical fractions. No explanation is offered for the discrepancies in some of the results given in Table 3, but it should be noted that during the process of separation the mechanical fractions were subjected to repeated washing with water, thereby removing the more readily soluble salts.

TABLE 3.—Specific gravities of "sand," "silt," and "clay" fractions of natural phosphates

Sample No.	Type of phosphate	Specific gravities			
		Original material	"Sand," > 50 $\mu$	"Silt," 50 $\mu$ to 5 $\mu$	"Clay," < 5 $\mu$
910	Florida land pebble.....	3.02	3.04	3.04	3.12
912	do.....	3.09	3.06	3.12	3.16
947	do.....	3.06	3.04	3.07	3.06
932	Florida hard rock.....	3.09	3.13	3.13	3.13
727	Florida waste pond.....	2.93	(1)	3.06	2.95
906	Tennessee brown rock.....	3.12	3.22	3.14	3.11

(1) Sufficient material not available for the determination.

### DEVELOPMENT OF MECHANICAL-ANALYSIS METHOD

The method of large-scale separation just outlined is useful for the preparation of mechanical-analysis standards and also for the study of the composition and properties of the different fractions, but when only the distribution of particle size in a sample is desired a less difficult and more rapid method is needed. The pipette method of mechanical soil analysis, as developed by Olmstead, Alexander, and Middleton (9) is essentially the same in principle as the method used in the large-scale separations, except that a dispersing agent is used and an actual separation of the particles finer than 5 $\mu$  is not made. The following pages are concerned with the application of the pipette method to the mechanical analysis of finely divided natural phosphates.

#### DISPERSING AGENTS

It seems that an efficient dispersion of a freshly ground phosphate rock should be easily obtained because of the absence of aggregates of fine particles. As soon as the material is wet with water, however, aggregation does occur, apparently owing in many cases to the presence of soluble calcium salts. Also, in the case of the natural soft phosphates and waste-pond phosphates, the fine particles are already in an aggregated state. The results obtained in the large-scale separations showed that complete dispersion of the aggregates could be obtained in most cases by prolonged agitation and washing with pure water alone. Such a procedure is, however, impractical from the standpoint of routine analysis and even fails entirely in the case of some samples of phosphate, which will not disperse in pure water. Consequently, it is necessary to use a chemical dispersing agent.

Sodium carbonate, sodium oxalate, and ammonia are probably the most widely used dispersing agents in the mechanical analysis of soils. In order to determine the relative effectiveness of these compounds as agents for the dispersion of finely divided natural phosphates, analyses were made on three types of phosphate by the pipette method as outlined by Olmstead, Alexander, and Middleton (9), except that treatment of the samples with hydrogen peroxide was omitted. The depth and time at which to pipette the samples

were calculated from Stokes's formula, using the customary particle-shape factor ( $\frac{2}{3}$ ), and taking 3 as the average density of the phosphates.

The data given in Table 4 show that, with one exception, slightly higher results are obtained with sodium oxalate, indicating that this compound is a more efficient dispersing agent than sodium carbonate, which in turn is decidedly better than ammonium hydroxide. These results are directly in line with those previously obtained on soils (9). Although the results obtained with sodium oxalate and sodium carbonate agree closely, sodium oxalate is preferable as a dispersing agent because the solubility of the oxalates of calcium and magnesium is much lower than that of the corresponding carbonates, which accounts, in part at least, for the somewhat higher results obtained with the oxalate.

TABLE 4.—Yield of "clay" obtained from natural phosphates with various dispersing agents<sup>1</sup>

Sample No.	Type of phosphate	"Clay" obtained from treatment with—					
		Ammonia <sup>2</sup>		Sodium carbonate <sup>3</sup>		Sodium oxalate <sup>3</sup>	
		5 $\mu$	2 $\mu$	5 $\mu$	2 $\mu$	5 $\mu$	2 $\mu$
		<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>	<i>Per cent</i>
727	Florida waste pond.....	89.6	74.4	90.9	80.2	91.3	81.2
906	Tennessee brown rock.....	17.1	11.8	18.7	14.8	18.9	13.9
910	Florida land pebble.....	12.7	7.9	12.9	8.4	14.1	9.2

<sup>1</sup> Results obtained by the use of settling velocities calculated from Stokes's formula using the particle-shape factor ( $\frac{2}{3}$ ) and an average density of 3 for the natural phosphates.

<sup>2</sup> 0.01 N.

<sup>3</sup> 0.005 N.

#### EFFECT OF TEMPERATURE

From a consideration of Stokes's formula, it is evident that the settling velocity of fine particles is theoretically dependent on the temperature of the suspension medium, in so far as this affects the density and viscosity of the medium. From the standpoint of convenience in laboratory operations, it is desirable to know whether variations in temperature can be neglected without introducing errors larger than those obtained with duplicate pipettings on the same sample. In order to obtain information on this point, determinations of the percentages of 5 $\mu$  "clay" in seven samples of phosphate were made at 10°, 20°, and 30° C. The samples were pipetted at a constant depth (10 centimeters) after settling for a constant period of time (73 minutes).

As calculated from Stokes's formula, the time required for 5 $\mu$  particles to fall 10 centimeters in water at 25° C. is 55 minutes, using the customary particle-shape factor ( $\frac{2}{3}$ ), and taking 3 as the density of the phosphates. The results given in Table 4 show, however, that much higher values were obtained for "clay" when the samples were pipetted after 55 minutes at a depth of 10 centimeters than were obtained by the large-scale separations. (Table 1.) After several trials, it was found that when the samples were

pipetted after 73 minutes at a depth of 10 centimeters, the temperature being approximately 25° C., the values obtained for 5 $\mu$  "clay" approximated closely those obtained by the large-scale separations. Consequently a falling time of 73 minutes was arbitrarily chosen for the experiments at different temperatures.

In carrying out these experiments weighed samples of the phosphates were dispersed in a definite volume of 0.005 N sodium oxalate, and the cylinders containing the suspensions were placed in a large water thermostat, the temperature of which was controlled to  $\pm 0.02^\circ$  C. When the temperature became constant, the suspensions were stirred in place with a mechanical stirrer, and samples were pipetted after allowing the suspensions to stand for the desired length of time (73 minutes).

When a pipette full of suspension is removed from a sedimentation cylinder it should contain an exact aliquot of all material smaller than the largest particle present in the suspension at the depth of the pipette tip. As many duplicates as desired may be withdrawn from the cylinder. But once an aliquot of material has been withdrawn no portion containing coarser material will be a true aliquot. It will contain an excess of the larger particles. On the other hand, subsequent pipettings made at longer settling times, shallower depths, or higher temperatures, which contain only finer material, should be exact aliquots of the original sample. In these experiments the samples were all taken from the same suspensions, pipetting being done first at the lower temperatures. Inasmuch as these experiments were concerned only with the apparent percentages of 5 $\mu$  "clay" obtained at different temperatures, the results obtained by pipetting at the higher temperatures were not affected in any way by the previous pipettings at lower temperatures, which is not true when pipetting is done in the reverse order.

The results given in Table 5 show variations of 0.0 to 0.9 per cent in duplicate pipettings at a given temperature, whereas the average difference in 20 sets of duplicate pipettings is only 0.26 per cent. On the other hand, the differences obtained when the same samples were pipetted at 10° and 20° C., respectively, ranged from 0.7 to 1.4 per cent, and these differences agree rather closely with those, 0.8 to 1.3 per cent, found when pipettings were made at 20° and 30° C., respectively. The average results on all the samples are 1 per cent higher for pipettings made at 10° than for those made at 20° C., and the latter in turn are 1 per cent higher than those at 30° C. These differences can not be attributed to experimental error alone. Consequently, for accurate work the settling velocity must be calculated on the basis of the temperature and viscosity of the suspension medium during the time of settling.

The permanency of phosphate suspensions dispersed with 0.005 N sodium oxalate is indicated by the fact that no tendency to flocculate was observed, although it required more than a week to complete a series of experiments at the three temperatures.



TABLE 5.—Yield of  $5\mu$  "clay" obtained from natural phosphate at various temperatures from samples pipetted at a depth of 10 centimeters after settling for 73 minutes

Sample No.	Type or source of phosphate	Percentage of "clay" obtained at a temperature of—		
		10° C.	20° C.	30° C.
727	Florida waste pond.....	92.3 92.0	91.1 91.1	89.7 89.8
	Average <sup>1</sup> .....	92.5	91.1	89.8
910	Florida land pebble.....	13.6 13.9	12.6 12.7	11.9 11.5
	Average <sup>1</sup> .....	13.8	12.7	11.7
912	Florida land pebble.....	20.2 20.6	19.5 19.5	18.3 18.4
	Average <sup>1</sup> .....	20.4	19.5	18.4
947	Florida land pebble.....	11.0 11.1	9.8 10.2	8.9 9.4
	Average <sup>1</sup> .....	11.1	10.0	9.2
932	Florida hard rock.....	23.7 24.1	23.0 23.1	22.1 22.1
	Average <sup>1</sup> .....	23.9	23.1	22.1
906	Tennessee brown rock.....	16.8 16.9	16.0 15.7	----- -----
	Average <sup>1</sup> .....	16.9	15.9	(?)
973	Idaho.....	26.5 27.2	25.7 26.6	25.1 25.1
	Average <sup>1</sup> .....	26.9	26.2	25.1

<sup>1</sup> Average of duplicate determination made on the same suspension.<sup>2</sup> Sample lost due to breakage of cylinder.

## EXPERIMENTAL DETERMINATION OF SETTLING VELOCITIES

As calculated from Stokes's formula  $5\mu$  phosphate particles, when suspended in water at 25° C., should settle a distance of 10 centimeters in 55 minutes. Rough determinations showed, however, that the time actually required for the particles to settle this distance is more than 70 minutes. Consequently a careful study was made of the rate of fall of finely divided natural phosphates at different temperatures in order to determine the time required for  $5\mu$  particles to settle a distance of 10 centimeters.

In carrying out these experiments, samples of the phosphates were dispersed in cylinders with 0.005 N sodium oxalate. The cylinders were placed in a thermostat and after reaching a constant temperature the suspensions were stirred with a mechanical stirrer. After standing for the desired length of time, a small pipette, closed at the top by means of a rubber tube and pinchcock, was lowered into the suspension until the tip was exactly 10 centimeters below the surface, and a fraction of a cubic centimeter of the liquid was drawn into the pipette by opening the pinchcock. Kohn (6) has shown that a pipette removes not a layer of liquid but a sphere whose center is at the tip of the pipette. Consequently, in order to obtain

material only very near the tip of the pipette, it is necessary to reduce to a minimum the volume of liquid removed.

The material pipetted from the suspension was examined under the microscope, and the diameters of the largest particles were determined by means of an eyepiece micrometer. The first pipetting was made after the suspension had settled for a time sufficiently long to insure the absence of  $5\mu$  particles in the liquid withdrawn at a depth of 10 centimeters. In making subsequent pipettings the suspension was always stirred again and the time of settling was progressively reduced by 5-minute intervals until  $5\mu$  particles were found to be present at a depth of 10 centimeters. The settling time was then varied by 1-minute intervals until a time was found at which an insignificant number of  $5\mu$  particles was present, but upon decreasing the time of settling by 1 minute an appreciable increase in the number of  $5\mu$  particles appeared in the sample. Aggregates having a porous structure and very thin plates of mineral material were not regarded as "normal"  $5\mu$  particles, but these were present in comparatively unimportant quantities, and their inclusion in the "clay" fraction did not introduce serious error.

In this way the time required for normal  $5\mu$  phosphate particles to fall 10 centimeters at  $20^\circ$ ,  $25^\circ$ , and  $30^\circ$  C. was determined. The results, which are given in Table 6, show that at all temperatures the experimentally determined settling times are much greater than those calculated for corresponding temperatures from Stokes's formula. In calculating the theoretical settling time, the following values were used for the terms in Stokes's formula:  $g = 980$  dynes/centimeter/second;  $d = 3$ ;  $d' = 1^5$ ;  $\eta^a = 0.01008$ ,  $0.00894$ , and  $0.00800$  centimeter-gram-second units for pure water at  $20^\circ$ ,  $25^\circ$ , and  $30^\circ$  C., respectively.

TABLE 6.—Experimental settling velocities of  $5\mu$  phosphate particles compared with theoretical velocities calculated from Stokes's formula

Temperature	Time required for $5\mu$ particles to settle for a distance of 10 centimeters	
	Experimental values	Calculated values
$^\circ$ C.	Minutes	Minutes
20	89	82
25	79	55
30	71	49

The particle-shape factor ( $\frac{2}{3}$ ), as customarily used in Stokes's formula, applies only for spherical particles. Microscopical examination shows, however, that the "silt" fractions of finely divided

<sup>a</sup> This is not the actual density of the suspension medium (0.005 N sodium oxalate), but it is not necessary to use the correct value since the variations in the density of the natural phosphates are greater than the error introduced by the use of this value for the density of the suspension medium.

<sup>b</sup> These are the values given in the international critical tables (8) for the viscosities of pure water at  $20^\circ$ ,  $25^\circ$ , and  $30^\circ$  C. The international critical tables give 1.022 (referred to water=1) as the viscosity of 0.1 N sodium oxalate solutions at  $25^\circ$  C., but no figures are available on the viscosities of 0.005 N solutions. Rough determinations by the authors indicated, however, that the viscosity of a 0.005 N sodium oxalate solution is very close to that of pure water.

natural phosphates are composed of particles which are not spherical but irregular in shape. Consequently, it is to be expected that such particles will fall at a slower rate than spherical particles. Since it is known that the "silt" particles of natural phosphates are not spherical in shape, it seems reasonable to conclude that within certain limits the finer particles are also nonspherical. It is recognized, however, that this assumption may not hold in the case of particles much finer than  $5\mu$  in diameter.

If the experimental settling times given in Table 6 accurately represent the relation between settling velocity and temperature, mechanical analyses made on the same sample at different temperatures should agree closely when the sample is pipetted at a depth of 10 centimeters after settling for the proper time at that temperature. The results given in Table 7 show that this is the case, the values obtained at the different temperatures agreeing within the limits of the experimental error of the method itself, not only on the natural phosphates but also on ground limestone and marl.

TABLE 7.—Yield of  $5\mu$  "clay" obtained from samples pipetted at a depth of 10 centimeters after settling for the experimentally determined lengths of time at various temperatures

Sample No.	Type of material	Percentages of "clay" obtained at—		
		20° C. <sup>1</sup>	25° C. <sup>2</sup>	30° C. <sup>3</sup>
910	Florida land-pebble phosphate	12.5	12.6	12.2
947	do	9.6	9.6	9.1
932	Florida hard-rock phosphate	22.9	22.6	22.8
727	Florida waste-pond phosphate	89.4	89.2	88.6
906	Tennessee brown-rock phosphate	15.7	15.7	15.8
973	Idaho phosphate	24.5	24.3	24.3
977	Ground limestone	1.2	.9	1.0
978	Marl	45.8	46.0	46.7
Average		27.7	27.6	27.0

<sup>1</sup> Samples pipetted at 10 centimeters after settling for 60 minutes.

<sup>2</sup> Samples pipetted at 10 centimeters after settling for 79 minutes.

<sup>3</sup> Samples pipetted at 10 centimeters after settling for 71 minutes.

In making the analyses, 25 cubic centimeters of the suspension was pipetted out. According to Kohn (5), the pipette removes a sphere of liquid whose center is at the tip of the pipette. Consequently, it is assumed that the lower half of the sphere thus removed contains enough particles larger than the given size to counter-balance the deficiency in these particles in the upper half of the sphere, giving a final result that is approximately the same as would be obtained by the removal of a layer of liquid at the tip of the pipette.

In making the experimental determinations of the settling velocities of the  $5\mu$  phosphate material, it was assumed that the particles were of average density as well as normal in shape. It is realized, however that those particles observed under the microscope may have had a lower specific gravity than the average for all the  $5\mu$  material, inasmuch as the heavier particles would have fallen to a lower level. The experimental evidence indicates, however, that the particles were

of average density. In the first place, the percentages of  $5\mu$  material obtained by using the experimentally determined settling velocities check very well with the results obtained by the large-scale separations. In the large-scale separations the uncertainty occasioned by the possible lack of uniformity in the density of the individual particles was eliminated because of the almost complete absence of particles smaller than  $5\mu$  in the "silt" fractions. Microscopical examination of the "clay" fractions prior to drying also showed that they contained an insignificant number of particles larger than  $5\mu$ .

#### PARTICLE-SHAPE FACTOR FOR NATURAL PHOSPHATES

By using the experimental settling times given in Table 6 and the values for the various terms in Stokes's formula which were used in calculating the theoretical settling times of  $5\mu$  particles (Table 6), the particle-shape factor ( $K$ ) for the natural phosphates is calculated as follows:

Substituting in Stokes's equation,  $V = K r^2 \frac{(d-d')}{\eta} g$ , where  $K$  is the shape factor, the experimental values determined at  $20^\circ$ ,  $25^\circ$ , and  $30^\circ$  C. and solving, the result is:

AT  $20^\circ$  C.

$$\frac{10}{89 \times 60} = K_{20} \frac{(0.00025)^2 (3.0 - 1.0) 980}{0.01008}, \quad K_{20} = 0.1541$$

AT  $25^\circ$  C.

$$\frac{10}{79 \times 60} = K_{25} \frac{(0.00025)^2 (3.0 - 1.0) 980}{0.00894}, \quad K_{25} = 0.1540$$

AT  $30^\circ$  C.

$$\frac{10}{71 \times 60} = K_{30} \frac{(0.00025)^2 (3.0 - 1.0) 980}{0.00800}, \quad K_{30} = 0.1533$$

These calculations give the values 0.1541, 0.1540, and 0.1533 based upon the experimentally determined periods of time required for  $5\mu$  phosphate particles to settle a distance of 10 centimeters when the temperature of the suspension medium is  $20^\circ$ ,  $25^\circ$ , and  $30^\circ$  C., respectively. An average value of 0.154 is taken as the particle-shape factor for the natural phosphates. Since this value is based upon experimental data it also accounts for any other deviations that may result from the application of the theoretical form of Stokes's formula.

As applied to the natural phosphates Stokes's formula becomes

$$V = 0.154 \frac{r^2 (3 - 1) 980}{\eta}$$

or finally

$$V = \frac{301.84 r^2}{\eta}$$

If it is assumed that  $2\mu$  phosphate particles have the same shape as the  $5\mu$  particles, the above formula may be used to calculate the

time and depth at which to pipette the sample in order to determine the percentage of particles  $2\mu$  and smaller in diameter. In determining the percentages of  $2\mu$  particles, it is more convenient to allow the suspension to settle for a constant time of 6 hours and to vary the depth of pipetting, rather than to use a constant depth and variable time as is done in the determination of  $5\mu$  particles.

The sedimentation-velocity graphs used in pipetting  $5\mu$  and  $2\mu$  phosphate particles are shown in Figure 1.

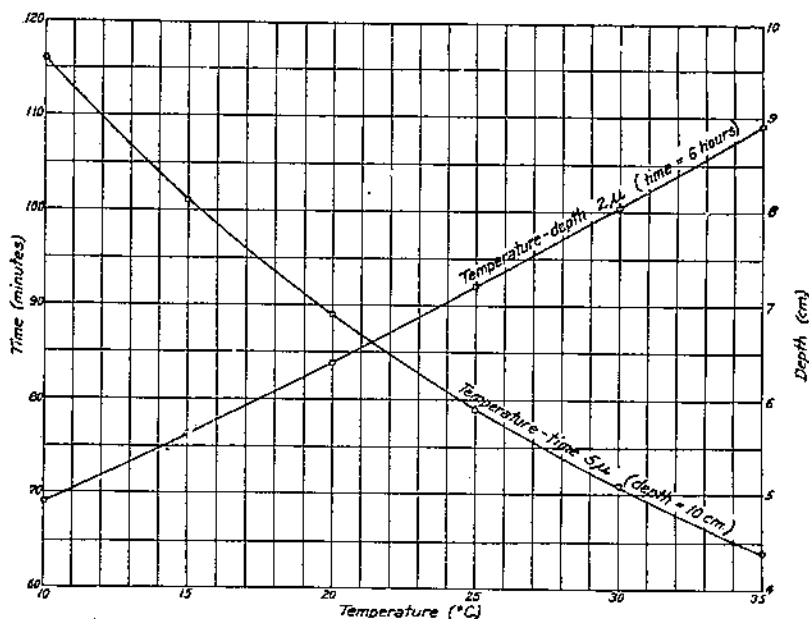


FIGURE 1.—Sedimentation-velocity graphs used in pipetting 2-micron and 5-micron particles

#### COMPARISON OF LARGE-SCALE SEPARATIONS WITH ANALYSES BY THE PIPETTE METHOD

The samples of phosphate, upon which large-scale separations had been made, were also analyzed by the pipette method using the procedure outlined later. In general, the results shown in Table 8 obtained by the two methods agree very closely. Duplicate determinations by the pipette method do not give results that will check more closely than those obtained on the Florida land-pebble and hard-rock phosphates by the large-scale separations and by the pipette method, respectively. These particular samples dispersed readily in pure water, and the large-scale separations were completed in a comparatively short time.

TABLE 8.—Comparison of results obtained by large-scale separations with those obtained by the pipette method

Sample No.	Type or source of phosphate	"Sand," >50 $\mu$ by—		"Silt," 50 $\mu$ to 5 $\mu$ by—		"Clay," <5 $\mu$ by—		Solution and me- chanical losses by—		"Clay," <2 $\mu$ by—	
		Large-scale separation	Pipette method	Large-scale separation	Pipette method	Large-scale separation	Pipette method	Large-scale separation	Pipette method	Large-scale separation	Pipette method
910	Florida land pebble.....	P. cl. 41.7	P. cl. 42.1	P. cl. 43.3	P. cl. 45.5	P. cl. 11.8	P. cl. 12.4	P. cl. 13.2	P. cl. 0.0	P. cl. 8.2	P. cl. 8.2
912	do.....	35.1	35.4	45.4	45.5	19.2	19.0	.3	.1	13.6	13.6
947	do.....	48.2	47.7	42.0	42.8	9.6	9.4	.2	.1	6.2	6.2
932	Florida hard rock.....	33.7	33.2	43.8	43.9	22.3	22.8	.2	.1	17.7	17.7
727	Florida waste pond.....	.2	.5	12.9	10.1	85.3	89.1	1.6	.3	78.9	78.9
915	do.....	5.1	1.7	19.5	13.9	75.1	84.0	.2	.4	71.9	71.9
728	Florida soft.....	30.4	32.5	20.9	15.7	48.7	51.3	.0	.5	40.3	40.3
906	Tennessee brown rock.....	46.2	47.0	38.8	37.2	14.0	15.7	1.0	.1	11.4	11.4
908	do.....	37.6	36.7	46.8	46.4	13.9	16.4	1.7	.5	11.4	11.4
930	Tennessee blue rock.....		35.7		54.1		9.2		1.0	1.6	1.6
948	Wyoming.....	49.8	50.1	43.6	40.6	6.6	8.9	.0	.4	5.3	5.3
973	Idaho.....	26.0	25.6	45.5	49.8	27.9	24.4	.6	.2	17.7	17.7

<sup>1</sup> A small portion of the "silt" and "clay" was accidentally spilled in this separation.

<sup>2</sup> Lithium oxalate used as a dispersing agent in the large-scale separations.

<sup>3</sup> A large-scale separation was not made on this sample.

In making the large-scale separations on samples Nos. 908 and 948, it was necessary to use lithium oxalate as a dispersing agent. Considerable time was required to complete the separations on the Florida waste-pond and soft phosphates because of the large quantities of "clay" particles present. The Idaho phosphate dispersed readily in pure water but continued to give up "clay" particles upon further washing with pure water, so that considerable time was required to complete the separation. In view of the fact, however, that the large-scale separations were based solely upon microscopical examination of the material separated from suspension, the results obtained on these samples agree satisfactorily with those obtained by the pipette method.

Graphs obtained by plotting the percentages of material finer than a given size against the logarithm of the diameters of the particles in millimeters are shown in Figure 2. The data used in plotting these graphs were obtained from analyses by the pipette method. The curves for ground phosphate rocks have the same general slope, differing principally in the percentages of fine material present in the samples. Since these samples were originally ground to pass a 100-mesh sieve, the upper ends of the curves all terminate at a particle diameter of 0.147 millimeter, corresponding to the mesh opening of the 100-mesh sieve.

The curves for the soft and waste-pond phosphates also have the same general slope in the region of the finer particles but this slope is quite different from that of the ground phosphate rocks. The curve for marl is somewhat similar to those for the soft and waste-pond phosphates. A further study of the mechanical composition of different types of finely divided natural phosphates would undoubtedly reveal some interesting facts in regard to the distribution of particle size in the material finer than 2 $\mu$ .

Results obtained on marl and ground limestone indicate that the pipette method is also applicable to the mechanical analysis of these materials, although the data secured to date do not warrant an absolute statement. The ground limestone examined contained little or

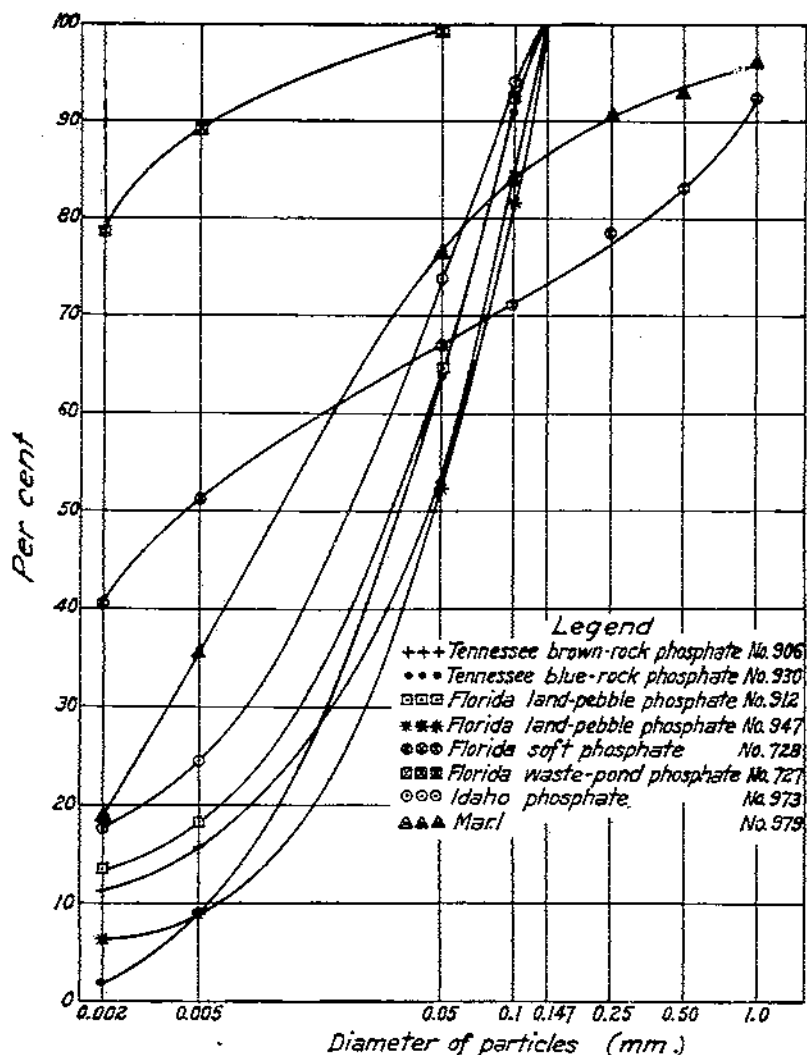


FIGURE 2.—Particle-size distribution curves obtained by plotting percentages of material finer than a given size against the logarithm of the diameters of the particles

no "clay." It is possible also that a different particle-shape factor is required for marls.

#### OUTLINE OF PIPETTE METHOD FOR MECHANICAL ANALYSIS OF NATURAL PHOSPHATES

The method as finally adopted is essentially the same as that outlined by Olmstead, Alexander, and Middleton (9) for the mechanical

analysis of soils, except that (1) removal of organic matter from the sample by means of hydrogen peroxide, prior to the analysis, is omitted, (2) recommendations for the separation of the "sand" fraction into different grades are not made because this is entirely a matter of sieving and consequently the number and range of the grades may be varied to meet the requirements of the individual laboratory, and (3) the settling velocities used for the natural phosphates are different from those used for soils. In the following pages the method is briefly described.

#### PREPARATION AND DISPERSION OF SAMPLE

Two samples of the phosphate are weighed out at the same time, a 10-gram sample for analysis and a 5-gram sample for moisture determination. The latter is dried to constant weight at 105° C. The 10-gram sample is placed in a 250 cubic centimeter glass electrolytic beaker and boiled with 100 cubic centimeters of distilled water.

The sample is now ready for washing. This is done by removing as completely as possible the solution from the sample in a beaker with a short Pasteur-Chamberland filter tube (grade F). The lower 12 centimeters of the tube is sawed off and fitted with a removable rubber stopper for this purpose. By means of a rubber bulb, back pressure is applied to the filter in order to remove the adhering material. The sample is well stirred with 125 cubic centimeters of distilled water, and the solution is again removed by filtration. This operation is repeated until the greater part of the soluble material is removed, six washings usually being sufficient.

After cleaning and removing the suction filter, the sample is evaporated to dryness on the steam bath and then dried to constant weight at 105° C. The sample is weighed as rapidly as possible in order to reduce to a minimum the adsorption of moisture from the air. The sample is then soaked for a few minutes with about 25 cubic centimeters of water, stirred with a rubber policeman, and transferred to a 250 cubic centimeter bottle (the ordinary narrow-mouth nursing bottle is well suited for this purpose). The beaker is again dried and weighed, the difference in weight being the portion of the sample left after removal of soluble material. To the bottle is added 10 cubic centimeters of 0.5 N sodium oxalate and the volume is made up to 150 cubic centimeters. The bottle is shaken for at least 2 hours on a reciprocating shaker having a horizontal movement of 10 centimeters and making 120 complete oscillations per minute. A shaker of this type is described in Bureau of Soils Bulletin 84 (2).

#### SEPARATION INTO SIZE CLASSES

A sieve fitted with Tyler 300-mesh wire screen cloth is clamped above a 1-liter graduated glass sedimentation cylinder on foot, and the "clay" and finer "silt" are decanted from the shaking bottle, through the sieve, into the sedimentation cylinder. After a few pourings the "clay" is completely removed from the bottle. The "sand" and the remaining "silt" are then transferred to the sieve by means of a stream of distilled water. The cylinder is filled to the 1-liter mark and set aside for sedimentation. Economical use



of water is necessary in decantation and washing on the sieve, because the total volume of the "silt" and "clay" suspension is limited to 1 liter.

The material remaining on the sieve is washed into a dish, preferably platinum, and, after evaporation, is dried for 2 hours at 105° C. Complete separation of the "sand" from the "silt" is then effected by shaking the dry sample on a 300-mesh sieve in a mechanical shaker. The material finally remaining on the sieve is weighed as the "sand" fraction. If desired, the "sand" fraction may be separated into different grades by using the proper sieves.

The material in the sedimentation cylinder is thoroughly stirred and the cylinder is allowed to stand on a support which is practically free from vibration for a period of time sufficient to allow particles  $5\mu$  in diameter to settle for a distance of 10 centimeters, as determined by reference to the graph given in Figure 1. A dry 25 cubic centimeter Lowy automatic pipette, which is clamped to a vertical support, is then carefully lowered into the suspension by means of a rack and pinion device (9) until the tip is exactly 10 centimeters below the surface, as indicated by a pointer moving over a fixed scale. The stopcock is then opened and the pipette is filled by suction in 20 to 40 seconds. A uniform suction is necessary and may be conveniently obtained by inserting a capillary tube between the pipette and the source of vacuum. The stopcock is then closed, and the pipette is raised and removed from the vertical support.

The contents of the pipette are drained into a tared weighing dish, and the washings from the pipette are added, since the pipette is calibrated for content rather than delivery. The liquid is evaporated on the steam bath and the dish is finally dried to constant weight at 105° C. The weight thus obtained is multiplied by 40 and the result, less the weight of solid material present in 10 cubic centimeters of the 0.5 N sodium oxalate solution, represents the total weight of "clay" in the original sample.

In order to determine the  $2\mu$  "clay" the suspension remaining in the cylinder is again thoroughly stirred and allowed to settle for 6 hours. A sample is then pipetted at the depth indicated by reference to the graph in Figure 1. The determination is completed in the same manner as described for  $5\mu$  "clay."

The weight of "silt" in the original sample is calculated by adding the weights of "sand,"  $5\mu$  "clay," and material lost by solution, and subtracting this total from the oven-dry weight of the original sample.

### SUMMARY

A method of separating 800-gram samples of natural phosphate samples into "sand," "silt," and "clay" sizes is developed and successfully applied to all commercial types of natural phosphates except Tennessee blue rock. In this method the fractions are separated by sedimentation in water without the use of any theoretical assumption, the progress and efficiency of the separation being checked solely by microscopical examination of the fractions.

The specific gravities of the original samples and of the fractions of the various types of phosphate rock produced in the United States do not range sufficiently to preclude the use of an average specific

gravity of 3 in calculating the settling velocities of phosphate particles by means of Stokes's formula.

The pipette method, as developed for the mechanical analysis of soils in the soil-physics laboratory of the Bureau of Chemistry and Soils, was successfully applied to the analysis of finely divided natural phosphates. The magnitude of the error involved when samples of natural phosphates are pipetted at a constant time and depth without regard to temperature was determined. An experimental study of the settling velocities of  $5\mu$  phosphate particles at various temperatures showed that the rate of fall is considerably slower than the theoretical rate calculated by means of the customary form of Stokes's formula. This discrepancy is apparently due to the irregular shape of the phosphate particles. As applied to natural phosphates, the particle-shape factor in Stokes's formula is 0.154, as determined experimentally, instead of the factor ( $\frac{1}{3}$ ), which is customarily used and which applies only to spherical particles.

A comparison of results obtained by the large-scale separation with those made by the pipette method shows very good agreement.

An outline of the pipette method for the mechanical analysis of finely divided natural phosphates is given in some detail. The essential differences from the same method applied to soils are: (1) The hydrogen peroxide treatment is omitted and (2) the settling velocities are calculated from a revised form of Stokes's formula.

The possibility of the utilization of the pipette method for the mechanical analysis of ground limestone and marls is pointed out.

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