# STUDIES ON THE METHOD OF QUANTITATIVE DETERMINATION OF THE SOIL COLLOIDS

THESIS FOR DEGREE OF M. S.

MITCHAEL IVANOVITCH WOLKOFF

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## DEFINITION.

According to the present conception, the colloid is defined (1) as matter so finely divided that the surface energy becomes a predominant factor. Since von Weimarn (2) advanced the crystalloidal theory, which he has supported with data of his numerous experiments, colloids are almost universally considered as being midway between the suspensions on one side and the true solutions on the other. The accompanying diagram adopted from Ostwald (3) is suggestive of the relation of colloids to the suspensions and the true solutions.

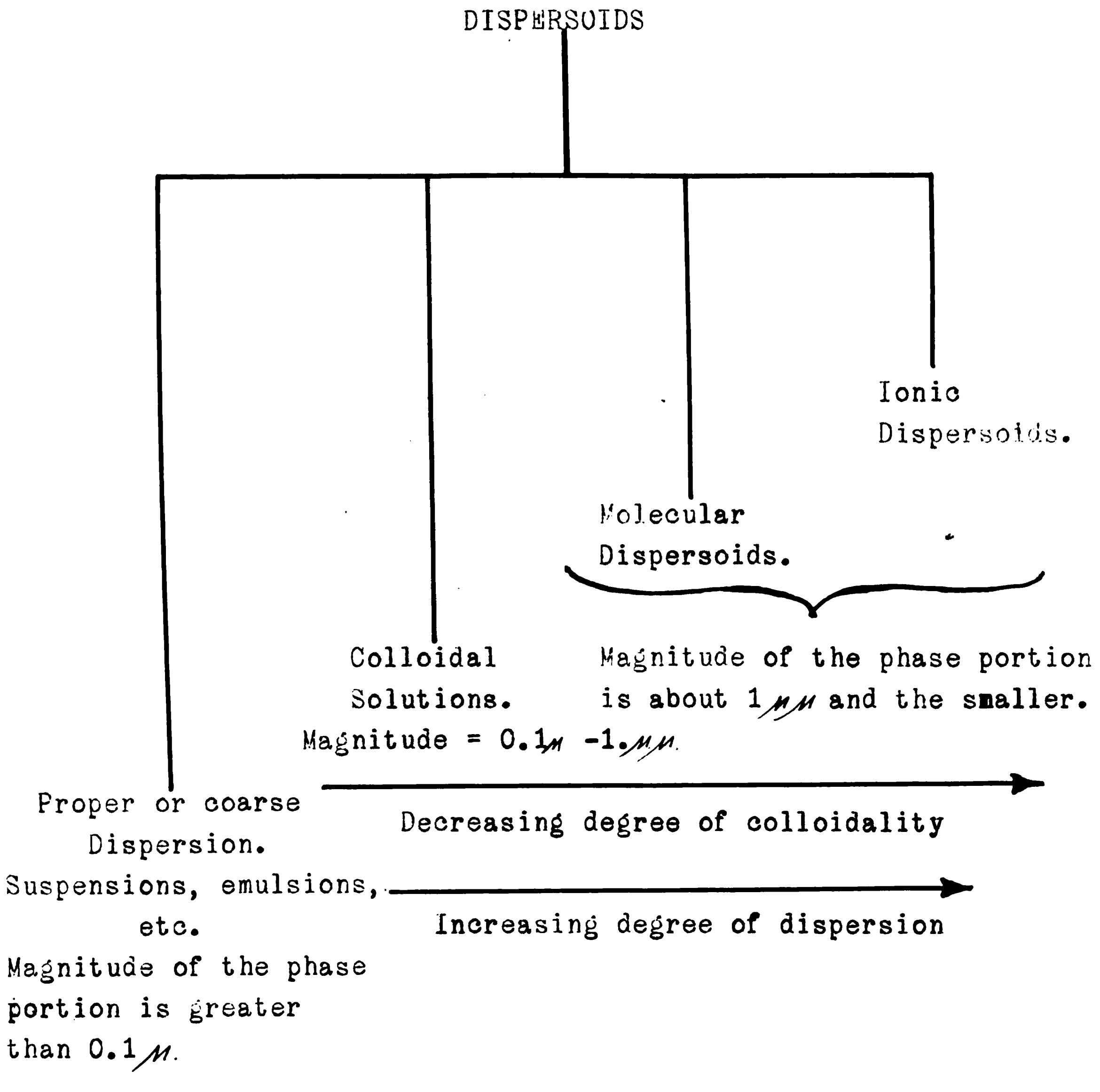
## GENERAL REVIEW OF LITERATURE.

### HISTORICAL.

Although Graham(4) is considered to be the father of colloidal chemistry, a number of investigators during the last half of the 18th and first part of the 19th centuries studied and described certain substances which we now call colloidal. Thus, Bergman (5) in 1779 described the colloidity of alkali silicates in excess of acids. Ruhland (6) in 1812 suggested that certain sols of metals are the metals in "a very fine state of division". Later a similar view was advanced by Poggendorf (1848) (7). Berzelius (8) in 1848 observed the suspensions of arsenius sulphide. Wackenroder wrote (9) in 1846 on the floccula-

Figure 1.

CLASSIFICATION OF DISPERSOIDS.
After Wo. Ostwald.



ting action of frost in the case of suspended sulphur. Sobreso and Selmi (10) (1850) studied the coagulation of sulphur suspensions by salts. Schmidt (11) discovered that gum could be purified through the animal membrane. Finally Graham in (4) 1861 published the results of his classical experiments, dividing matter into colloidal and crystalloidal, and proposing a method of separation of the colloids from the substances in the true solutions. Since that time the colloids have attracted the attention of many investigators and writers. Among the most prominent ones could be mentioned Ostwald, von Bemmelen, Hardy, Schulze, von Weimarn, Bancroft, Rohland, etc. Notwithstanding this fact, the chemistry of colloids, especially the chemistry of soil colloids, is rightly regarded as being more or less in a state of infancy, promising to yield gratifying results to the investigator.

## THE FORMS OF COLLOIDS IN SOILS.

Because of the enormous specific surface of a colloidal particle the most important property of colloids is its surface energy, and due to this surface energy they are considered of so great importance in the soil management.

Perhaps there is not a single chemical, physical, or biological process takes place in the soil which is not influenced by the presence of its colloidal portion. In this connection we must mention, however, that we do not agree with Sjollema (12) who thinks that practically all soil constituents, except quartz grains and the undecomposed mineral fragments, are colloidal, for the simple reason that they adsorb the organic dyes.

Soil colloids can be classified after Taylor (13) as follows:

1. Humus and decayed organisms.
2. Hydroxides of iron, aluminum, etc.
3. Amorphous silicates, resulting from weathering of the crystalline silicates.
4. Bacteria.

The humus as a whole can not be classified with the colloids because some humus particles are very coarse Besides, it is doubtful altogether, as pointed out by Sohngen (14) that there was ever prepared a colloidal solution of carbon. Muravlinski (15), on the other hand, working with the alkali extracts of the Russian chernosem soils found that an alkali extract, when tested with a defractometer gave a more pronounced cone and a greater number of sub-microns in the ultramicroscope than the water extracts. Since the mineral constituents have been found to be predominant in the water extracts and mostly organic in the alkali extracts, he concluded that the soil colloids generally belong to organic matter.

It is very probably that not the hydrates of iron and alumina are present in the soil, but mostly oxides, as regarded by Russel (16) and Cameron and Bell (17) for aluminum hydrate is of rare occurance in the ordinary soils. This was found by Liebrich (18) and also by Cameron and Bell (loc.cit.).

Kahlenberg and Lincoln (19) have shown that the hydrolysis is practically complete if the silicate is pre-

sent in a dilute solution. In such a case the silica must be present as colloidal silicate and not as silicic acid.

Most of the colloids in a soil, being mixed with a large body of solids and only a small portion of water, necessarily come in contact with the solid coarse soil constituents and become adsorbed forming a coating around them (Russel - loc. cit.).

Gans (20) thought that there is a constant ratio between $Al_2O_3$ and $SiO_2$ in clay soils but this was later disproved by Stremme (21).

## ORIGIN.

The origin of the inorganic soil solloids lies in the mother rock. The weathering is considered by Cornu (22) as a process of a gel-forming from the rocks by means of the atmospheric agencies in combination with the gradually formed humic acids. If humic acids are lacking, the minerals may hydrolize (Luz (23)) forming calcium, magnesium, and sodium silicates, clay silicates and colloidal ferric hydroxide. Clay silicates may further decompose into hydrated colloidal clay and colloidal silicic acid. In the case of orthoclase, for instance, the following steps are suggested by Lyon, Fippin and Buckman (24):-

$$KAlSi_3O_8 + H_2O = HAlSi_3O_8 + KOH$$

$$KOH + CO_2 = K_2CO_3 + H_2O$$

$HAlSi_3O_8 = HAlSiO_4 + 2SiO_2$, which is either quartz or colloidal silica, or changes into a complex hydrated silicate.

The colloids resulting from the weathering of rocks are mostly in the gel forms and it is hardly possible, as Taylor (25) thinks that some of them, being formed as sols of different electric charges, precipitate one another. There is hardly any evidence showing the soil colloids to be positively charged, which is in accord with Coehn's (26) theoretical consideration that all soil colloids should be negatively charged, since they are solids and their dialectric constant is necessarily less than that of water.

The humic colloids, of course, are resulted from the plant and animal life. Besides, there are some minor factors influencing the available amount of colloids present in the soil at a given time. Fertilizers may increase or decrease the colloidal formation; urine which is a part of the applied manure, contains colloids (27). Climate also may modify the colloidal content of a given soil, as shown by Lipman and Waynick (28) in a recently published article.

During the last few years a considerable interest has been taken in the question of soil colloids. A great deal has been written on the subject, especially in other countries. The contributions of Rohland (29), Ramann (30), and Niklas (31) have very good discussions on the soil colloids. The possible functions of colloids in the soils are liberally discussed, many hypothesis are advanced, and experimental data are gradually being accumulated Therefore, it seems advisable to present at this time a short review of the subject, limiting it, however, mainly to the experimental phases.

The most important role of colloids in the soil is, perhaps, that of adsorption and naturally this question has been studied more than any other one. The studies, however, deal mostly with pure colloids and applied to soils only from analogy.

Ostwald (32) demonstrated that colloidal ferric hydroxide adsorbs electrolytes. Cornu and Lazarevic (33) showed that hydrogels either simple or mixtures resulting from the mutually precipitated colloids, adsorb crystalloids. Sohngen (34) found that colloids adsorb nitrogen and oxygen, thus providing a better condition for the growth of bacteria. In the culture media containing starch, inorganic salts and water, colloidal silicic acid and humus favored, while ferric hydroxide and aluminum hydroxide retarded the cleavage of starch by B. ocraceus, although they had no influence upon the growth of the organism. The cleavage in urea by bacteria is favored by the presence of colloids. Sokolovski (35) found that the adsorption in the soil is the greatest at the surface and showed that it is dependent upon the specific surface of the soil. Assuming that most of the colloids are formed at the surface and thereby increase the effective surface of the soil, a specific relation was pointed out to exist between the adsorption and the soil colloids. Besides the specific surface, the adsorption depends upon the mass of the soil. The adsorbing property of a soil changes with the change of its hygroscopic property. It diminishes with the heating of the soil. Parker (36) noticed that the smaller the soil particles the greater the selective

adsorption of potassium from potassium chloride in solution. Rakovsky (37) noted that the adsorption by starch of sodium hydroxide increased in the presence of salts of potassium and sodium, the increase of 0.1% of salt causing often the increase in adsorption as much as 10 - 12%. Similar influence was noticed upon barium hydroxide. Findley (38) found that the solubility of carbon dioxide in colloidal solution of ferric hydroxide was greater than in pure water. The different soils possess a different adsorbing property; thus, Rohland (39) admits that, in the opposition to regularity of the rate of adsorption by clay or clay colloids no such regularity is noticed in the case of muck or marshy soils. From results of determining the freezing point of soils at different moisture contents, Bouyoucos (40) forwarded the hypothesis that a part of the soil moisture either adsorbed by the colloidal portion of the soil or held by it in the chemical combination. From theoretical consideration Anon (41) sees an analogy between the clay suspensions and the negatively charged colloidal solutions in their power of adsorption.

Closely relating to the question of adsorption in the soil is its acidity, and this is one of the most important questions with respect to soil management. Baumann and Gully (42) attribute the acid reaction of peat moss not to the free acid, since such an acid does not exist, but to the adsorption of bases by the colloids, which leave the acid radicle or free mineral acid behind. This view is supported by Czapeck (43), Wieler (44), Harris (45), et. al. Some investigators oppose this ex-

planation. Tacke and Suchting (46) think that the evidences are strong for the existence of free humic acids in the soils they have studied. Tacke, Deutsch and Arnd (47), Rindel, Oden, and Ehrinburg and Barr (48) for different reasons support their views. Thayer (49) prepared humic acids from different soils and considered these acids to be colloidal in their nature. In fact, no one seems to deny that the humic acids are colloidal. Thus, it appears that the colloids of the muck soils, no matter in what form they exist, are attributed to be largely responsible for the acidity of those soils.

Yariloff (50) suggests that the "ripening" of the soil in the spring, i.e. the condition when the soil is the most suitable for the spring cultivation, is brought about by the bacterial action, resulting in the increase of the formation of gases, and to the increase of the colloidal content. Vernadsky (51) considers the colloids to be the seat of action of soil gases in reduction, oxidation, and hydration processes that take place in the soil. Findley and Williams (52) and later Findley and Howell (53) have found that the solubility of $CO_2$ and $N_2O$ in colloidal solution of ferric hydroxide is higher than in pure water, and increases with the concentration of the colloid. Lynde and Dupre (54) as a result of their studies on osmosis in soils, hold that the colloidal portion of the soil acts as a semipermiable membrane. If this is the case, the colloids in the soil should modify the rate of capillary movement of water in a soil and, finally, to affect its evaporation. This later process was, in fact, suggested by Keen (55) as being modified by the presence of colloids. He has found that water evaporates slower from the soil than from sand, but ignited soil behaves like sand. That this characteristic of a soil is not due to the humus content was shown by the fact that when humus was removed by 2% solution of caustic soda, the soil acted as before. His conclusion was that the colloids are responsible for this property of the soils.

Impermeability of a soil is sometimes associated with the occurance of the colloidal silica (56), or with aluminum silicate (57), although the influence of the latter compound is doubted by Cameron and Bell (58). Bouyoucos (59) has observed that on increase of the temperature of some soils the percolation of water in those soils had decreased, after attaining the maximum point at some 30 or 40°C. The diminished rate of percolation of water he attributed to the swelling of the present colloidal gels.

Rohland (loc. cit.) contends that the soil containing humus and the peat soils are rich in colloids. Such soils have a much greater water holding capacity, and the greater power to absorb the water vapor. So Attenberg (60) thinks that in the analysis of a soil there should be made a test of the physical properties, such as hygroscopicity, pore space, capillarity, water holding capacity, relation to the root hair, flocculation, Brownian movement, etc. of different grades. Indeed, König, Hasenbaumer and Krönig (61) by the use of

four mixtures of $CHBr_3$ and $C_6H_6$ of different densities and with the aid of the centrifuge separated the soil particles and found the lightest portion to contain the most of the available plant food. Takadora (62) examined some soils for their property to swell on wetting and found the order of the degree of swelling for different soils to be:- Mineral acid soil $>$ humus soil $>$ clay soil $>$ sandy soil. They have tested several other properties, but the results were variable. Sharp (63) in a preliminary paper announced that by the application of sodium salts to the soil and then by leaching them out the soil becomes impervious to water. The leachings from so treated soils contain a larger amount of suspended material than those of the untreated soils.

There have been several attempts made to determine the more direct influence of colloids upon the crop production. Thus, Voelcker (64) found that aluminum silicate caused a large increase in crop of tares and mustard. The increase due to the application of sodium silicate was somewhat smaller, while kaolin did not affect the crop yield at all. The increase in the crop production was attributed to the improvement of the physical condition of the soil resulting in the larger retention of moisture. Lyon, Fippin and Buckman (65) state it was found that the roots of the growing plants, leaving an acid residue, coagulate some colloids, causing the salts adsorbed by the colloids to diffuse out and be available for the use by the root hairs. This, they think, accounts for the fact that the plant is able to obtain more nutrient material from the soil than is possible to dissolve with the solvents ordinarily present in it. Giles and Carrero (66) have met with entirely different success. They grew rice in water cultures and found that the presence of colloidal iron decreased its growth. Gregoire (67) reported some results on growing the barley in solution cultures with some colloids.

Gedroitz (68) after determining the amounts of colloids in a large number of soils, using the dialyser as a method of separation, came to the conclusion that the colloidal sol is not important in the soil at all since there is not an appreciable amount of it in any given soil. The gel, according to this investigator, is the important portion of the soil for all the physical changes in the soil which are brought about by liming, heat and frost are due to their presence.

There remains another question involving the soil colloids, which was studied quite extensively. The question is that of flocculation of the soil colloidal solutions or soil suspensions.

In 1866, or only a few years after the publication of Graham's classical investigations on colloidal substances, Schulze (69) recorded some of his results on the calcium and magnesium salt requirements for flocculation of clay suspensions. Later Schloessing (70) worked along the same line. Durham (71) made an interesting discovery that although it requires a very small amount of sulphuric acid to flocculate the suspension of white clay (kaolin?), on further additions of sulphuric acid he reached the point when suspension did not clearify for a long time. Now, if to this mixture of clay suspension and sulphuric acid he added either more acid or some water the suspension clearified quickly. Evidently, there is an equilibrium between the ions of true solution and the solid particles of clay. The flocculating action of sodium carbonate, on the other hand, continued to increase with the increase in concentration. While working on the method of mechanical analysis, Hilgard (72) noticed that clay suspension coagulated on passing through the narrow glass tube and flocculation is approximately inversely proportional to the size of the particles. A moderate increase in temperature decreased the flocculation in his case. He (73) also studied the effect of lime on the texture of clays.

Brewer (74) found the different clay suspensions to be of different stability. In fact, some suspensions settle within a few days, while others remain turbid at the end of seven years, when kept at nearly the same temperature and in a quiet place. The acids he found to flocculate more quickly than the salts. Barus (75) in 1888 observed that non-electrolytes retard the clearing of suspensions. Later (76) he tested the hypothesis that the hydration of clay or kaolin particles is responsible for keeping their particles in suspension, and came to the conclusion that such is not the case. He determined the densities of tripoli and bole in both water and ether and found them to be the same in both liquids. Since tripoli has practically the same density as quartz, and bole approaches that of kaolin, he justified his conclusion on these grounds. Spring (77) noticed that the clearing power of salt depends upon the valence of the salt and the cation of the electrolyte, confirming in part the quantitative formula of Schulze (78) that the coagulating power of trivalent cation: divalent: monovalent as 350:20:1.

Bodländer (79) also measured the power of different salts for clearing the kaolin suspensions. Quincke (80) from his studies on pure colloids and kaolin suspensions advanced a theory on coagulation which in short implies the change in surface tension between the liquid and the oily substances. He claims to have observed oily films around the solid particles. Hall and Morison (81) while studying the efficiency of electrolytes in flocculating the kaolin suspensions found that the order of efficiency of acids to be $HCl > HNO_3 > H_2SO_4$. In the case of cations of the salts it is $Al > Ca > K > Na$. Acids are better coagulants than their salts. Exception~~s~~ is ~~are~~ $Al_2(SO_4)_3$ which is equal to $H_2SO_4$, but does not exceed it.

Maschhaupt (82) found that NaOH stabilizes soil suspensions at low concentrations, while if present above .015 N, it causes flocculation. Similar results were obtained with $Na_2CO_3$ in which case the coagulation begins above 0.16 N. Oden (83) in rather extensive studies with peat colloidal solutions used NaCl for the flocculation. He had to saturate his colloidal solution with the above salt and allow it to stand for 24 hours in order to bring about flocculation. McGeorge (84) working with suspensions of Hawaiian clays obtained results similar to those of

Hall and Morison with the exceptions that he found $Al_2(SO_4)_3$ to be the best flocculant among both salts and acids and the order of efficiency of strong acids was $HNO_3 > HCl > H_2SO_4$.

This brief and not at all an exhaustive review of the literature on the soil colloids reveals a fact that, notwithstanding the large amount of energy that has been spent on the question of the soil colloids, our knowledge regarding this very important and interesting branch of science is yet very fragmentary. The results of the singular experiments indicate that this field of the investigation is able to yield very good results. But until now the most fundamental problem in the soil colloids is not solved. There is no adequate method for determining the quantity of colloids in soil, while this knowledge is of prime importance in order to understand certain of the phenomena in the soil which are influenced by colloids in their process. The necessity of the method for estimation of colloids in the soil was recognized a long time ago and a great many attempts have been made to solve this problem. The following is a brief review of the proposed methods of estimating the soil colloids with a few remarks on their applicability.

## REVIEW OF THE METHODS OF ESTIMATING THE SOIL COLLOIDS.

As early as 1856 Schmidt (85) has discovered that the gum could be rarefied through the animal membrane. This was the beginning of colloidal chemistry and at the same time an unconscious method of separation of colloids from crystalloids. But Thomas Graham is considered as the

father of colloidal chemistry. Among the series of classical experiments performed by Graham we find the first method of determining the colloids in the sol forms.

Following are some of his experiments on dialyzing:-

1. 10 gms. NaCl and 2 gm. Japanese gelatin was dissolved in hot water and diluted to 100 c.c., cooled to become a firm jelly. Then 100 c.c. of solution of 2% gelatin was poured on the top of it. Left for 8 days and analyzed for NaCl at different depths.

The following amounts of NaCl found at the end of 8 days in different layers, beginning from the top,

| No. of stratum | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| NaCl gms. | .015 | .015 | .026 | .035 | .082 | .130 | 212 | .35 | 486 |

| No. of stratum | 10 | 11 | 12 | 13 | 14 | 15 & 16 |
|---|---|---|---|---|---|---|
| NaCl gms. | 630 | 996 | 1.172 | 1.19 | 1.2 | 3.45 |

Total 9.992 gm. of 10 gm.

In another instance NaCl was let to dialyze through the parchment paper and the results obtained are given below -

100 c.c. of sol + 2 gm. of NaCl - NaCl diffused out 86%
50 c.c. " " + 2 " " " " " " 92
25 c.c. " " + 2 " " " " " " 96

The dialyzing continued for 24 hours at 10° - 12°C.

The natural conclusion was that the salts in solution have the power to pass through the colloidal layer whether it is in the form of jelly or as parchment paper.

Graham worked with an astonishingly large number of substances and classified them according to their property to dialyze through either animal or vegetable parchment paper. In order to give an idea of such power in

different substances the following table may be cited:

100 c.c. 10% solution was used in each case at 10 - 15°C for 24 hours employing the loop dialyzer.

| Substance used. | Gms. passed. | Relative diffusion |
|---|---|---|
| Gum Arabic | 0.029 | .004 |
| Starch sugar | 2.00 | .266 |
| Cane " | 1.607 | .214 |
| Milk " | 1.387 | .185 |
| Mannite | 2.621 | .349 |
| Glycerine | 3.300 | .440 |
| Alcohol | 3.57 | .476 |
| NaCl | 7.50 | 1.000 |

The substances whose dialyzing power is similar to that of gum arabic are considered colloidal, and according to Graham they could be separated from the non-colloids by dialyzing.

Gedroitz (86) proposed to use this method for determining the amount of colloids present in the soil. He separated the colloidal solution from the soil mechanically by shaking in water for three minutes and dialyzing the solution for some 3 - 4 months. Such method has, it seems, very little value for either practical work or for the theoretical investigations.

In the first place it is impossible to thoroughly separate colloids from cyrstalloids by dialysis, as shown by Graham's work. Crystalloids do not diffuse after a certain dilution is obtained. Also, the small amount of colloids does diffuse and is lost. Oden (87), for instance, has found the dialyzing to be not an efficient method of purification of colloidal solution obtained from humus, because some of the colloid material goes through the membrane. Kahlenberg (88) points out that it is even possible in some cases to have colloidal particles to pass out leaving some crystalloidal substances behind. König (89)

has shown that oxidation may take place during the dialyzing. Leaving the solution for a considerable period of time, which is required for the dialyzing, some colloidal material will go into solution and pass through the dialyzing membrane.

If we consider now the difficulty of controlling the bacterial action during the process we may rightly conclude that the dialyzing in its present form is not applicable for determining the colloids in soils even if we are able to separate the colloidal solution from the soil proper. The time required is another prohibitive factor for application of the method for practical purposes.

Up to the present time the dialysis, with some modifications from the original Graham apparatus, is used very extensively, especially by biologists. Only very recently the principle discovered by Graham is being developed and the time required for dialyzing is shortened. Martin (90) has discovered that colloidal particles cannot be forced through the colloidal or gelatinous membrane. With this fact as a basis he put a layer of gelatin or of gelatinous silicic acid upon the Chamberland's filter and forced the solution containing colloids through it. With this device he was able (by applying high pressure - 30 - 100 atmos.) to obtain a clear solution of salts, but free from proteins.

Bechhold (1906) (91) discovered that the concentration of gelatin plays an important role in passing through the membrane. Using collodium, eising, gelatinous formaldehyde, or other similar substance, upon some support he forced the solution through the filter. The most important of his results are summarized in the following table:--

| Dispersoid used. | Concentration of membrane which holds back the colloid sol. | Remarks. |
|---|---|---|
| Sol of Platinum | 2% | Size of particle =44 $\mu\mu$ |
| Cell $Fe(OH)_3$ | 2 | |
| Casein (Milk) | 2.5 | |
| Colloidal gold | 3. | Size 40 $\mu\mu$ |
| 1% Haemcglolain sol | 4 | |
| 1% Gelatin sol | 4 | |
| Serum Albumen | 4 - 4.5 | Mol wt. 15,000 - 3,000 |
| Silicic acid (coll) | 4.5 | |
| Neuter Albumosen A | 8 | Mol. wt. 2,400 |
| " " B & C | 10 | Traces passed |
| Dextrin | 10 | Passed little - Mol. wt. 965 |
| All crystalloids | -- | Passed all |

Later, Schoep (92) constructed an apparatus, with which he could use very high pressure without breaking the membrane. The objection to this form of separation is the absorption of a disperse phase by a material through which a solution passes.

The adsorption in the soil is varied roughly with the fineness of the soil grains and this property was used by several soil investigators for estimating the soil colloids. Thus, ~~when~~ Mitscherlich (93) opened the subject by proposing the method of estimating the hygroscopicity of soils. But since hygroscopicity is the property especially pronounced in colloids this was a step toward the estimation of colloids in soils.

The method consists of further drying the air-dry soil in a thin layer over phosphorus pentoxide. Then it was placed in a desiccator over 10% solution of sulfuric acid for 24 hours, where the condensation of water in the soil takes place. The process may be hastened by providing the partial vacuum in the desiccator. Then the percentage of the water adsorbed is determined.

Since there is a danger of coagulation of some colloids by drying and thereby reducing its power of adsorption, Ehrenberg (94) suggested to reverse the process, i.e. first adsorption and then drying. Lipman and Sharp (95) found that for the best results the layer of soil should be about 1 m.m. thick. They also found that the absorption of water is increased with the increase in temperature and vice versa.

Sjollema (1905) (96) first to my knowledge proposed to use the dyeing material for adsorption by soil, and he struck the right cord, if his success in popularizing the method can be judged by the number of his followers.

His method consisted in treating the small quantity of soil with a dye solution. Since not all the soil particles adsorb a certain one dye he used several of them. Then the water was decanted and the soil was analyzed under microscope, comparing different soils.

Endel (1902) (97) went further and advanced the following method: A portion of soil is mounted in Canada balsam, colored in the cold solution of fuchsin, and the picture is taken, magnifying the examined sample 280 times. The colored portions of a picture are cut out and their weight relative to the total weight of the picture gives the percentage of the colloids in a soil.

Aschley (98) (1909) made a thorough study of clays and proposed to use malachite green for comparative estimation of colloidal material in clays.

This method is also based upon the adsorptive power of colloidal particles and consists of treating 20 gms. of clay with 400 c.c. of water containing from 1 to 3 gm. of dye. This was vigorously agitated for an hour, and permitted to settle over night. The sample of the solution is taken out with the pipette and compared with the standard solution of the same dye.

Two very striking features are brought forth by Aschley's proposal:- (1) Ease of manipulation, and (2) the inadequacy of the method itself. Since that time a considerable number of men either proposed a new method or modified a given one, suggesting some new detail for improvement of existing method.

Thus, König (99) and his associates (1911) advocated Methyl violet.

Gorski (1912) (100) proposed crystal violet and Pelet-Jolivet (101) suggested the methylin blue.

The described methods, based on adsorption of dyes by colloids, even at their best are open to serious criticism. Van der Leeden and Schneider (102) compared three methods; von Bemmelen's, which will be given later, Mitscherlich's and Pelet-Jolivet, and came to the conclusion that in order to rely upon these methods one should keep in mind the following points - (1) Many silicates (wholly non-colloidal) adsorb dyes; (2) The mixture of gels, containing an abundance of $Al_2O_3$ and $Fe_2O_3$ in comparison with $SiO_2$ are not colored with methyline blue; (3) The presence of the capillary water influences the adsorption of dye; (4) The presence of the electrolytes modifies the adsorption of dye also. This point was very strongly brought out by Gedroitz (103) in his experiments. The same soil adsorbs different amounts of dye according to the treatment with one salt or another. The dyes used by Gedroitz were methyl violet and crystal violet; and (5) Uncertainty, whether clay does not adsorb the dye.

Another class of men tried to determine the colloidal portion of a soil by purely chemical means - chemical analyses. The first representative of this school was von Bemmelen (104), who was one of the first to introduce the colloidal chemistry to the soils. Von Bemmelen suggested that the soil, besides the insoluble particles, contains (A) amorphous colloid silicates, and (B) kaoline silicates. Treating the soil first with HCl and then with $H_2SO_4$ one can approximately separate these two groups from each other and from the soil.

Method:- Treat the soil with boiling HCl (sp. grav. 1.19) and silicate (A) will be dissolved. Al, Fe, etc. bases go in solution. Remaining silica goes down as ppt. and can be extracted with an alkali. A free colloidal ferric oxide and the bases bound with the humic substances go into solution also. Colloidal $SiO_2$ could also be obtained if treated at this stage with the strong alkali. The remaining soil is then treated with the concentrated $H_2SO_4$ and the bases go in solution, while silica goes down as a precipitate.

Von Bemmelen did not add anything new by advancing this method. It was known long before his time and used by geologists for determining the so-called "Zeolites" in

soils.

The method per se can hardly stand criticism. Concentrated $H_2SO_4$ or HCl are capable of dissolving a great many substances in addition to the hydrated silicates.

FRAPS (105) (1914) proposed a method of determining the amounts of the ammonia soluble inorganic soil colloids. His method is as follows :- Digest 100 gms. of soil with 2000 c.c. of N/5 HCl at room temperature for 24 hours. Filter and wash thoroughly. Wash back into the bottle with 2000 c.c. of 4% $NH_3$ and let digest at room temperature for 24 hours, shaking every half hour for 4 hours. Filter on a large folded filter getting as much of the soil as possible on the filter and continue to pour back the filtrate until it comes through clear. Discard the residue. Take 1500 c.c. of the filtrate, coagulate with ammonium carbonate (and heat, if necessary), let settle, collect on the ash free filter, ignite and weigh.

Fuse the precipitate with sodium and potassium carbonate, dissolve in HCl and evaporate to render silica insoluble. Filter off and weigh silica, if pure; if contaminated with iron, purify. Precipitate iron and alumina in the filtrate with ammonia, ignite and weigh the precipitate. Fuse with potassium acid sulfate and dissolve, reduce iron with zinc, and filtrate with permanganate.

The author confesses, however, that the outlined method is intended only for soils low in lime; in the case with soils of high lime content several extractions should be made and much stronger HCl should be used.

The method is not supposed to estimate the total colloidal constituents of the soil.

Pence (106) suggests a possible method for determining the hydrated silicic acid in clay consisting of the following:- To 5 gms. of clay in a casserole add 120 c.c., 5% $Na_2CO_3$. Boil 10 minutes over the free Bunsen flame with the rotaty motion to prevent burning. Let settle. Decant through a hardened filter paper. Repeat twice. Transfer the clay to filter paper and wash with hot diluted $Na_2CO_3$. Determine $SiO_2$ in the filtrate. The method is not very delicate, not being able to detect as much as .2% of the colloidal silica, and depends on a "compensation of errors".

Hilgard (107) has simplified the problem considerably, proposing the method of separating the colloids from soils by first loosening them by either prolonged, gentle kneading of the wet clay, by prolonged digestion in hot water, or by the boiling for a short time. Then the colloids are thrown down by some electrolyte, such as NaCl, which can be washed out of the coagulated colloids.

Dupont (108) went somewhat further, when he advanced a new method of mechanical analysis, the part of which was a separation of colloids. If this portion be taken out of the entire method, the determinations of colloids in soils would consist in breaking the soil aggregates by means of oxalic acid and boiling for 30 minutes on water bath. Filter and separate from clay by centrifuging for 12 minutes at 800 or even better at 1000 - 1200 revolutions per minute. The resulting colloidal solution is treated with ammonium carbonate, which

will coagulate the mineral colloids. The coagulated material is collected, evaporated and burned; weighed before and after the burning.

After a careful study of the literature bearing on different methods the only rational and the most promising method appeared to be the one proposed by Hilgard and modified by Dupont, i.e. one based upon the mechanical forces for the separation of the colloidal portion of the soil from the soil proper. The metHod, however, is not free from objections. The employing of oxalic acid and the boiling are the features open to serious criticism, since some of the colloidal material, thus treated, will go into solution and be lost, introducing an error in the colloidal determinations. Again, is it possible to get all the particles from the soil which are capable to stay in suspension? What is the bases for the centrifuging for that length of time and at a given speed? What is the stability of the resultant solution? Is ammonium carbonate the best and the most convenient coagulant possible of employment? How much of a given electrolyte to add for the best results? Can not the dialysis answer the same purpose as an electrolyte? These and other questions may be properly raised. It seemed advisable, therefore, to study this method experimentally and, if possible, to suggest a desirable improvement.

## THE THEORETICAL BASIS FOR THE METHOD.

This method of separation of the colloidal portion of the soil proper is based upon the undisputable fact that the attraction between the solid soil particle for

water is greater than that of a solid particle for another solid particle. Since this is true, it is possible to gradually loosen the individual soil particles and finally separate them one from another. The process of separation is hastened if the mechanical force of agitation of the soil mass in water is applied to it. It is true there will be an unavoidable error due to the increase of solubility of the soil material during the agitation, but this error is very small in comparison with other factors involved. The similar error, of course, is repeated in every other proposed method.

## EXPERIMENTAL.

The experimental work was naturally divided into two parts; namely; (1) the separation of the colloidal portion of the soil from the soil mass, and (II) the separation of the colloids from the crystalloids.

### I. The Separation of the Colloids from the Solid Mass.

In the first place it was decided to ascertain how much of the separated material from a given soil by shaking and centrifuging could be separated again from the quartz sand after it had been added to it and dried.

Experiment 1. Separation of colloidal clay and colloidal muck solutions from quartz sand to which they were previously added and dried.

To a given portion of acid washed quartz was added a colloidal clay or muck material, either in the form of sol or as a precipitate. The colloidal solutions were obtained by shaking a brick yard clay and a muck soil with about 10 times their weight of distilled water for 4 hours and cen-

trifuging at the rate of 2000 revolutions per minute for 15 minutes. The resultant solutions could be kept for several weeks without an appreciable sedimentation on the bottom of the vessel. The precipitates were obtained either by adding a small quantity of HCl N/5 or by passing the solution through a Chamberland's filter and collecting the residue. After the precipitated material was added to the quartz the whole mass was well mixed and allowed to dry. If the solution was added, it was permitted to evaporate, stirring the contents occasionally. Before the mixture became dry it was thoroughly mixed. In each case an adequate portion was taken, water was added as in mechanical analysis shaken for 4 hours and centrifuged at the rate of 2000 revolutions per minute for 15 minutes. The upper liquid was decanted, to the sediment more distilled water was added, thoroughly stirred and centrifuged as before. This process was repeated until the solution became clear. Then the 200 c.c. portion of the obtained solution was evaporated and the total dry material was calculated. A sample of the untreated quartz was run as a check and the dry weight of it was substracted from the total weight of the treated samples. The results are given below.

| No. | Wt. of quartz taken. | Nature of colloid, | In what form added. | Wt. of colloid added. | Wt. of colloid obtained. | % of colloid recovered |
|---|---|---|---|---|---|---|
| 1 | 25 gms. | clay | ppt. HCl. | .1484 | .1416 | 95.41 |
| 2 | 25 " | " | " " | .3195 | .2827 | 88.48 |
| 3 | 25 " | " | " " | .3079 | .2537 | 82.41 |
| 4 | 25 " | " | " Cham. | .9957 | .7209 | 72.40 |
| 5 | 25 " | " | " " | .9409 | .7482 | 79.53 |
| 6 | 25 " | " | " " | .4169 | .3212 | 77.94 |
| 7 | 25 " | " | solution | .1250 | .1126 | 90.00 |
| 8 | 25 " | muck | " | .1250 | .1033 | 82.64 |
| 9 | 25 " | " | " | .1250 | .1000 | 80.00 |

The results presented in this table show that it was impossible to recover all the fine material from the quartz after drying, no matter in what form the colloidal material was added. The results also indicate that the gel obtained by means of hydrochloric acid is just as reversible (or even more) as that obtained by a Chamberland's filter or by drying.

The attempt was made to repeat the experiment with the artificially prepared colloid added to the quartz sand. For this purpose a solution of the colloidal ferric hydroxide was prepared by Graham's method (91), the dialyzing being continued with the daily change of water for 14 days. The colloidal solution contained .701 gms. of dry matter per 100 c.c. of solution. 100 and 200 c.c. portions of this solution were added to 100 gms. of quartz and evaporated to dryness. But when 25 gms. samples were taken, shaken with water for 4 hours and centrifuged in the usual manner, the resultant solution was found to be perfectly clear, practically none of the iron hydroxide being able to stay in suspension. Evidently, the drying of the colloidal material with quartz was detrimental to its stability. Briggs, Martin and Pearce (109) found that the oven-drying even reduced the percentage of clay obtained in the mechanical analysis of soils. In order to ascertain to what extent the similar drying affects the amount of dry material which is possible to obtain from a field soil the following experiment was performed -

Experiment 2. Effect of Drying upon the Quantity of the Colloidal Material Obtained.

A quantity of fresh silt loam was sifted through a two millimeter mesh and divided into two portions. One half was allowed to dry at the room temperature, while the other one was kept in the atmosphere saturated with the water vapor. After 10 days the samples from each portion were taken, shaken with water, and the separation of the colloidal solution was brought about by means of the centrifuge. The percentage of moisture of each portion was determined and the per cent of the fine material obtained was calculated, basing on the weight of the oven-dry soil.

TABLE II.

| Sample. | % $H_2O$. | Time of shaking. | Amn't Taken. | Amn't obtained. | % obtained. | Aver. % obtained. |
|---|---|---|---|---|---|---|
| 1.Dried | 1.81 | 4 hours. | 4.9111 | .2268 | 4.62 | 4.70 |
| 2. " | 1.81 | 4 " | 4.9111 | .2350 | 4.78 | |
| 3.Fresh | 22.93 | 4 " | 5.694 | .6235 | 10.94 | 10.59 |
| 4. " | 22.93 | 4 " | 5.694 | .5832 | 10.24 | |
| 5.Dried | 1.81 | 15 " | 4.9111 | .3943 | 8.03 | 7.82 |
| 6. " | 1.81 | 15 " | 4.9111 | .3734 | 7.60 | |
| 7.Fresh | 22.93 | 15 " | 5.694 | .6542 | 11.49 | 11.46 |
| 8. " | 22.93 | 15 " | 5.694 | .6500 | 11.42 | |

| | Sample | Relation between them. |
|---|---|---|
| 1. | Dried | 44.4 |
| 2. | " | |
| 3. | Fresh | 100.00 |
| 4. | " | |
| 5. | Dried | 68.2 |
| 6. | " | |
| 7. | Fresh | 100.00 |
| 8. | " | |

It is an undisputable fact, as revealed by the results presented in this table, that the drying of the soil makes a large portion of the colloidal material highly irreversible. In the case with the 4-hour shaking more than twice as much of the material was obtained from the fresh soil than from the dried sample of the same soil. When the shaking continued for 15 hours, the direction of the magnitude of the obtained material was the same, but the ratio between them was not as wide as in the samples of 4-hour shaking. Evidently, the amount of agitation to which a given soil is subjected has a considerable influence on the amount of the colloidal matter. This point was tried and the results are presented in the table of the next experiment.

Experiment III. Effect of length of shaking of the soil in water upon the quantity of colloidal material obtained in the mechanical separation.

In this experiment the samples of the air-dry brickyard clay and muck were taken and shaken in water from 3 minutes to 36 hours. The rest of the procedure remained the same, i.e. the solutions were centrifuged at the rate of 2000 rev. per minute for 15 minutes. The results follow.

TABLE III. CLAY SOIL.

| Ave. of No. of trials. | Time of shaking. | Amount of clay taken. | Dry. Wt. of colloids obtained. | % of colloids obtained. |
|---|---|---|---|---|
| 1 | 3 min. | 20 gms. | 4.2341 gms. | 21.17 |
| 3 | 1 hour | 20 " | 4.5110 " | 22.56 |
| 3 | 4 " s | 20 " | 4.7154 " | 23.58 |
| 2 | 16 " | 5 " | 1.2582 " | 25.16 |
| 2 | 26 " | 5 " | 1.2513 " | 25.03 |
| 2 | 36 " | 5 " | 1.2669 " | 25.34 |

TABLE III a. MUCK SOIL.

| | | | | |
|---|---|---|---|---|
| 2 | 4 hours | 5 gms. | .0553 gms. | 1.11 |
| 2 | 16 " | 5 " | .0739 " | 1.48 |
| 2 | 26 " | 5 " | .0853 " | 1.71 |
| 2 | 36 " | 5 " | .0900 " | 1.80 |

It is evident that the length of shaking has a considerable influence upon the total colloid material which is possible to bring in a disperse state. These results are in accord with those obtained by Briggs, Martin and Pearce (110) for the finest clays, and show that the greater the period of time of agitation to which the sample was subjected the more solid material was brought in suspension until it reached the practically constant value in the case with clay. In muck the constant was not reached, but the increase due to 10 hours agitation between 26 and 36 was not as great as between 16 and 26 hours, showing this value is being approaching the constant. The accompanied chart illustrates this point.

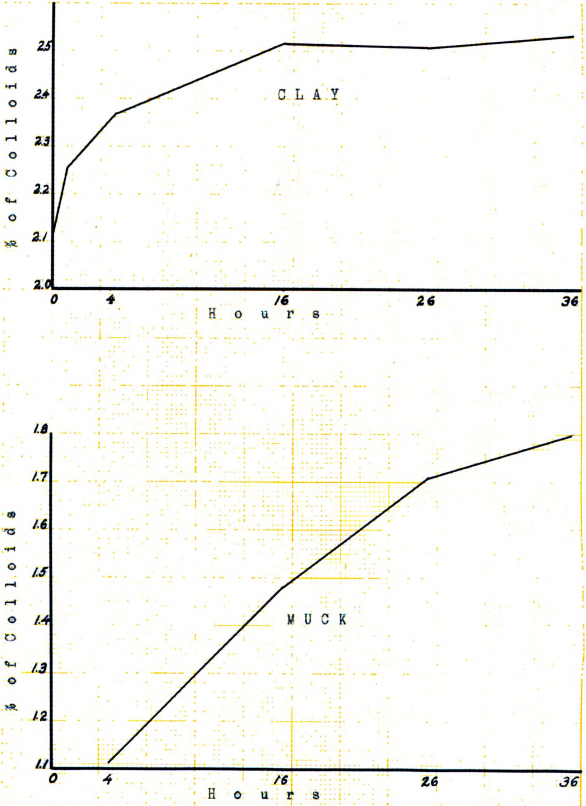
The next factor influencing the amount of the colloidal material as well as the quality of the same is the speed of the centrifuging. In order to throw some light upon the question the following experiment was performed.

Experiment 4. Effect of speed of the centrifuging on the amount of the colloidal material obtained and on the stability of the resultant hydrosol.

10 gm. portions of clay were brought in suspension by agitating in water for 4 hours. Then, two samples were subjected to 15 minutes centrifuging of 1000 revolutions per minute; other two samples were centrifuged at the rate of 2000 revol. per min., and the remaining two were let to run at 2800 revol. per min. The centrifuging was repeated until the resultant solution in each case was nearly clear. The 400 c.c. portions were set aside for 10 days in bottles in which the column of the solution reached 13 inches. At

Figure 2.

Showing the Relation between the Length of Shaking and the Amount of Colloids Obtained.



the end of the 10 day period the upper 12 inches of the solution was carefully s~~y~~iphoned off and the dry weight of the material in both the upper 12 inches and the lowest inch was determined. The results are summarized in the next table.

TABLE IV.

| Speed of centrifuging. | No. of trials. | Amn't taken. | Average Dry Wt. obtained. | % obtained. | % settled in 10 days. aver. of 2 trials. |
|---|---|---|---|---|---|
| 1000 | 4 | 10 gms. | 3.1023 | 31.02 | 53.25 |
| 2000 | 4 | 10 " | 2.3620 | 23.62 | 27.90 |
| 2800 | 4 | 10 " | 2.1201 | 21.20 | 20.34 |

As one should expect, both the amount of the solid material and the stability of the obtained solution vary with the variation of the speed employed. The greater the force developed in a given length of time the more of the solid material will settle, the easiest sedimentation being that of the coarsest particles, as one notices in the figure of the right hand column. More than half of the solid matter settled in 10 days in the samples subjected to the lowest speed and nearly 80% remained in suspension in the case when the highest speed was employed. Possibly, besides the size of the particles the stability of different solutions was affected by the mass action, since the solutions resulted from the lowest speed of the centrifuging were more concentrated than those resulted from the higher speeds.

There is still another factor remains which influences both the quantity and the quality of the suspension. Time has undoubtedly the same influence as the speed of the centrifuging and it seemed advisable to determine just to what extent it modifies the suspension.

Experiment 5. Effect of time of the centrifuging on the amount of the colloidal material obtained and on the stability of the resultant solution.

In this experiment the usual procedure was followed with the exception of the time, which was varied, and the speed of 2000 revolutions per minute remained the same throughout the experiment. As in the preceding experiment, 400 c.c. of the solutions was set aside for 10 days without disturbing, and the percentage of the settled material was determined.

TABLE V.

| Time of centrifuging. | Trial. | Total solid material obtained. | Dry material in upper 12" after 10 days. | Dry material in lowest 1" after 10 days. | % in lowest inch after 10 days. |
|---|---|---|---|---|---|
| 10 minutes | 1 | 1.2928 gms. | .0800gms. | .1120gms. | 58.33 |
| | 2 | 1.2424 " | .0790 " | .1000 " | 55.87 |
| | Ave. | 1.2676 " | . | | 57.10 |
| 15 " | 1 | 1.0563 " | .1125 | .0525 | 31.82 |
| | 2 | .9677 | .1077 | .0470 | 30.38 |
| | Ave. | 1.0165 | | | 31.10 |
| 20 " | 1 | | .1100 | .0388 | 26.07 |
| | 2 | | .1120 | .0385 | 25.57 |
| | Ave. | | | | 25.82 |
| 30 " | 1 | .9102 | .1178 | .0210 | 15.13 |
| | 2 | .8434 | .1126 | .0385 | 15.07 |
| | Ave. | .8768 | | | 15.10 |
| 45 " | 1 | .5775 | .1225 | .0233 | 15.91 |
| | 2 | .5570 | .1168 | .0125 | 11.72 |
| | Ave. | .5673 | | | 13.82 |
| 60 " | 1 | .4995 | .1030 | .0105 | 9.25 |
| | 2 | .5087 | .1045 | .0120 | 10.30 |
| | Ave. | .5041 | | | 9.78 |

The percent of the solid material in the lowest inch of the solution varies from 58 to a little over 9. If there were no sedimentation at all and the particles were uniformly distributed throughout the liquid, the percent of the solid material in the lowest inch of the solution would be some 7.7. Since such a solution does not remain on standing of uniform concentration in all its depths, one will notice that the solution resulted from the centrifuging for 60 minutes has settled very little indeed. The stability gradually decreased with the decrease of time of the centrifuging. In connection with the above experiments it should be mentioned that when the artificially prepared colloidal ferric hydroxide was centrifuged at the speed of 2800 revolutions per minute for 45 minutes, there was no sediment left on the bottom of the tube.

As a summary of the results of the first part of the problem the following points should be mentioned:-

1. The soil colloids on drying even at the room temperature become highly irreversible. The examination of the soil for the colloidal content, therefore, should be made before the soil is dried out after it is taken from the field.

2. The length of shaking of the soil with water has an influence upon the quantity of the suspended material obtained. Care should be taken to thoroughly agitate the soil in order to break all the aggregations and to wash the colloidal particles off the coarse soil fragments.

3. The speed of the centrifuging effects both the quantity and the quality of the colloidal solution. If but a low speed is applied only a very coarse suspension of low stability is obtained, though the amount of the solid material is comparatively great. Thus, a considerable speed should be employed in order to obtain the solution that would nearest approach the hydrosols of the artificially prepared colloids.

4. Time has similar effect on the resultant solu-

tion: the longer the solution is centrifuged the less the material stays in suspension and the better the stability becomes, and vice versa. Therefore, a reasonable time should be allowed for the centrifuging. Time, as it seems from our experiments, may take place of the speed, i.e. the longer the solution is centrifuged the less speed it requires for bringing its stability to a desirable degree.

## II. SEPARATION OF THE COLLOIDS FROM THE TRUE SOLUTION

After an extensive review of the literature the most practical methods of the separation of colloids from the true solution appeared to be (a) coagulation or flocculation by means of an electrolyte and (b) dialyzing, as described by Graham (loc. cit.).

In the first question, namely, the coagulation of the colloidal particles by means of the electrolytes, it was decided to undertake several additional experiments in selecting the most convenient electrolytes for the purpose.

For the next few experiments on flocculation the soil colloidal solutions were prepared by adding to a bulk of fresh soil about 10 times its weight of distilled water, shaken well, and allowed to stand over night. Then, the upper portion was siphoned off and centrifuged at the rate of 2000 revolutions per minute for 15 minutes. The resultant solution would stand for several weeks without appreciable sedimentation. In most of the experiments recorded the same solutions were employed. The exceptions will be mentioned later on.

### NATURE OF SUSPENSIONS USED.

| N. soil used. | Reaction of soil to litmus paper. | Dry matter per 100 c.c. of suspension. | Freezing point depression of solution. |
|---|---|---|---|
| 1. Brickyard Clay (subsoil) | neutral | .3633 | .003 |
| 2. Miami Silt Loam | " | .0700 | .002 |
| 3. Clyde Silt " | " | .0913 | .003 |
| 4. Muck | " | .0274 | .002 |
| 5. Brickyard Clay (soil) | " | .8098 | |
| 6. Peaty Muck | " | .0338 | |
| 7. Kaolin | | .0247 | |

The bacterial action in the colloidal solutions during the experiment ~~were~~ was not controlled.

The acid, salt and alkali solutions were N/5 in strength and were the same throughout the experiments.

Experiment 6. Qualitative Test of Electrolytes for Flocculation of Colloidal Solutions.

In this experiment to 5 c.c. of suspension was added 5 c.c. of N/5 electrolyte, shaken vigorously for a short time and let stand over night. The best flocculated solution was recorded with five positive signs (xxxxx). Next in apparent efficiency was marked four and so on until a negative sign was used, if no precipitate appeared at the bottom of the test tube in 24 hours. Duplicate determinations were made in all of the experiments.

### TABLE VI.

### EFFICIENCY OF ELECTROLYTES IN FLOCCULATING SOIL COLLOIDAL SOLUTIONS.

| 5 c.c. of Electrolyte N/5. | 1 Clay (subsoil) | 2 Miami Silt Loam. | 3 Clyde Silt Loam | 4 Muck. |
|---|---|---|---|---|
| 1. HCl | xxxxx | xxxxx | xxxxx | xxxxx |
| 2. NaCl | xxxxx | - | - | - |
| 3. KCl | xxxxx | xxxx | xxxx | - |
| 4. $NH_4Cl$ | xxxxx | xxx | xxx | - |
| 5. $BaCl_2$ | xxxxx | xxxxx | xxxxx | xxxxx |

Table Vl. (continued)

| 5 c.c. of Electrolyte N/5 | 1 Clay (subsoil) | 2 Miami Silt Loam. | 3 Clyde Silt Loam. | 4 Muck. |
|---|---|---|---|---|
| 6. $CaCl_2$ | xxxxx | xxxxx | xxxxx | xxxx |
| 7. $HgCl_2$ | xxxxx | - | - | - |
| 8. $MgCl_2$ | xxxxx | xxxxx | xxxxx | x |
| 9. $SnCl_4$ | xxxxx | xxx | xxx | xxxx |
| 10. $HNO_3$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 11. $NaNO_3$ | xxxxx | - | - | - |
| 12. $KNO_3$ | xxxx | xxx | xxx | - |
| 13. $NH_4NO_3$ | xxxxx | xxx | xxx | - |
| 14. $Ca(NO_3)_2$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 15. $Hg_2(NO_3)_2$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 16. $AgNO_3$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 17. $Pb(NO_3)_2$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 18. $H_2SO_4$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 19. $KHSO_4$ | xxxxx | xxxxx | xxxx | xxx |
| 20. $(NH_4)_2SO_4$ | xxxx | - | - | - |
| 21. $K_2SO_4$ | xxxxx | xxxxx | xxx | - |
| 22. $K_2S_2O_7$ | xxxxx | xxxxx | xxxxx | xxx |
| 23. $MnSO_4$ | xxxxx | xxxxx | xxxx | xx |
| 24. $CuSO_4$ | xxxxx | xxxx | xxxxx | xxx |
| 25. $FeSO_4$ | xxxxx | xxxxx | xxxxx | xxxx |
| 26. $Fe_2(SO_4)_3$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 27. $K_2S$ | xxxx | xxx | xxx | - |
| 28. $NaSO_3$ | xxxx | - | - | - |
| 29. $NaHSO_3$ | xxxx | - | - | - |
| 30. $Na_2S_2O_3$ | xxxx | - | - | - |
| 31. $AlK(SO_4)_2$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 32. $Fe(NH_4)_2(SO_4)_2$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 33. $FeS$ | - | - | - | - |
| 34. $ZnS$ | - | - | - | - |
| 35. $NaOH$ | xxxxx | xxxx | xxx | x |
| 36. $KOH$ | xxxxx | xxxxx | xxxxx | - |
| 37. $Ba(OH)_2$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 38. $MgO$ | xxxx | - | - | - |
| 39. $CaO$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 40. $H_3PO_4$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 41. $NaHPO_4$ | xxxxx | - | - | - |
| 42. $CaH_4(PO_4)_2$ | xx | - | - | - |
| 43. $Ca_3(PO_4)_2$ | - | - | - | - |
| 44. $KH_2PO_4$ | xxxx | x | x | - |
| 45. $K_2HPO_4$ | xxxx | x | xx | - |
| 46. $K_2CO_3$ | xxxxx | xxx | xxx | - |
| 47. $Na_2CO_3$ | xxx | - | - | - |
| 48. $NaHCO_3$ | xxxx | - | - | - |
| 49. $CaCO_3$ | - | - | - | - |
| 50. $3MgCO_3Mg(OH)_2$ | xxxx | - | - | - |
| 51. $FeCO_3$ | - | - | - | - |
| 52. $(NH_4)_2CO_3$ | xxxx | - | - | - |
| 53. $CH_3COOH$ | xxxxx | xxxx | xxx | - |
| 54. $NaC_2H_3O_2$ | xxxxx | - | - | - |

Table VI. (continued)

| 5 c.c. of Electrolyte N/5 | 1 Clay (subsoil) | 2 Miami Silt Loam | 3 Clyde Silt Loam | 4 Muck. |
|---|---|---|---|---|
| 55. | | | | |
| 56. $Ca(C_2H_3O_2)$ | xxxxx | xxxxx | xxxxx | xxxx |
| 57. $Pb(C_2H_3O_2)_2$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 58. $C_2H_2O_4$ | xxxxx | xxx | xxxx | xxxx |
| 59. $C_6H_8O_7$ | xxxxx | xxxxx | xxxxx | xxxxx |
| 60. Oleinic $C_{17}H_{33}COOH$ | - | - | - | - |
| 61. $As_2O_3$ | - | - | - | - |
| 62. $(NH_4)_2C_2O_4$ | xxxxx | xxxxx | xxxxx | - |
| 63. $NaKC_4H_4O_6$ | xxxxx | - | xxx | - |
| 64. KBr | xxxxx | xxxxx | xxxxx | - |
| 65. KI | xxxxx | xxxxx | xxxxx | - |
| 66. KSCN | xxxxx | xxxxx | xxxxx | - |
| 67. $PbO_2$ | - | - | - | - |
| 68. $K_2Cr_2O_7$ | xxxxx | xxx | xxx | x |

| | 5 Clay (soil) | 6 Peaty Muck | 7 Kaolin |
|---|---|---|---|
| 1. HCl | xxxxx | xxxxx | xxxxx |
| 2. NaCl | xxxxx | - | xxxxx |
| 3. KCl | xxxxx | - | xxxx |
| 4. $NH_4Cl$ | xxxxx | - | xxxxx |
| 5. $BaCl_2$ | xxxxx | xxxxx | xxxxx |
| 6. $CaCl_2$ | xxxxx | xxxx | xxxxx |
| 7. $HgCl_2$ | xxxx | - | - |
| 8. $MgCl_2$ | xxxxx | x | xxxxx |
| 9. $SnCl_4$ | xxxxx | xxxx | xxxxx |
| 10. $HNO_3$ | xxxxx | xxxxx | xxxxx |
| 11. $NaNO_3$ | xxxxx | - | xxxxx |
| 12. $KNO_3$ | xxxx | - | xxxxx |
| 13. $NH_4NO_3$ | xxxxx | - | xxxxx |
| 14. $Ca(NO_3)_2$ | xxxxx | xxxxx | xxxxx |
| 15. $Hg_2(NO_3)_2$ | xxxxx | xxxxx | xxxxx |
| 16. $AgNO_3$ | xxxxx | xxxxx | xxxxx |
| 17. $Pb(NO_3)_2$ | xxxxx | xxxxx | xxxxx |
| 18. $H_2SO_4$ | xxxxx | xxxxx | xxxxx |
| 19. $KHSO_4$ | xxxxx | xxx | xxxxx |
| 20. $(NH_4)_2SO_4$ | xxxxx | - | xxxxx |
| 21. $K_2SO_4$ | xxxxx | - | xxxxx |
| 22. $K_2S_2O_7$ | xxxxx | xxx | xxxxx |
| 23. $MnSO_4$ | xxxxx | xx | xxxxx |
| 24. $CuSO_4$ | xxxxx | xxx | xxxxx |
| 25. $FeSO_4$ | xxxxx | xxxx | xxxxx |
| 26. $Fe_2(SO_4)_3$ | xxxxx | xxxxx | xxxxx |
| 27. $K_2S$ | xxxxx | - | - |
| 28. $NaSO_3$ | xxxxx | - | x |
| 29. $NaHSO_3$ | xxxxx | - | - |
| 30. $Na_2S_2O_3$ | xxxx | - | - |
| 31. $AlK(SO_4)_2$ | xxxxx | xxxxx | xxxxx |
| 32. $Fe(NH_4)_2(SO_4)_2$ | xxxxx | xxxxx | xxxxx |
| 33. FeS | - | - | xxxxx |

Table VI (continued)

| 5 c.c. of n/5 Electrolyte | 5 Clay (soil) | 6 Peaty Muck | 7 Kaolin |
|---|---|---|---|
| 34. ZnS | - | - | - |
| 35. NaOH | xxxxx | - | xxxxx |
| 36. KOH | xxxxx | - | xxxxx |
| 37. $Ba(OH)_2$ | xxxxx | xxxxx | xxxxx |
| 38. MgO | xxxxx | - | xxxx |
| 39. CaO | xxxxx | xxxxx | xxxxx |
| 40. $H_3PO_4$ | xxxxx | xxxxx | xxxxx |
| 41. $NaHPO_4$ | xxxxx | - | xxx |
| 42. $CaH_4(PO_4)_2$ | x | - | - |
| 43. $Ca_3(PO_4)_2$ | - | - | - |
| 44. $KH_2PO_4$ | xxxxx | - | - |
| 45. $K_2HPO_4$ | xxxxx | - | - |
| 46. $K_2CO_3$ | xxxxx | - | - |
| 47. $Na_2CO_3$ | xxxx | - | - |
| 48. $NaHCO_3$ | xxxx | - | - |
| 49. $CaCO_3$ | - | - | - |
| 50. $3MgCO_3Mg(OH)_2$ | xxxxx | - | xxx |
| 51. $FeCO_3$ | - | - | - |
| 52. $(NH_4)_2CO_3$ | xxxxx | - | |
| 53. $CH_3COOH$ | xxxxx | - | - |
| 54. $NaC_2H_3O_2$ | xxxxx | - | xxxxx |
| 55. | | | |
| 56. $Ca(C_2H_3O_2)_2$ | xxxxx | xxxx | xxxxx |
| 57. $Pb(C_2H_3O_2)_2$ | xxxxx | xxxxx | xxxxx |
| 58. $C_2H_2O_4$ | xxxxx | xxxx | xxxxx |
| 59. $C_6H_8O_7$ | xxxxx | xxxxx | xxxxx |
| 60. Oleinic $C_{17}H_{33}COOH$ | - | - | - |
| 61. $As_2C_3$ | - | - | - |
| 62. $(NH_4)_2C_2O_4$ | xxxxx | - | x |
| 63. $NaKC_4H_4O_6$ | xxxxx | - | xx |
| 64. KBr | xxxxx | - | xxxxx |
| 65. KI | xxxxx | - | xxxxx |
| 66. KSCN | xxxxx | - | xxxxx |
| 67. $PbO_2$ | - | - | - |
| 68. $K_2Cr_2O_7$ | xxxxx | - | xxxx |

The results presented in the above table show that besides the familiar difference in efficiency of different electrolytes with the same colloidal solution, the same electrolyte does not act alike with different suspensions, the easiest solutions to flocculate being those of clay and kaolin, followed by loams and, finally, mucks. This question is almost entirely overlooked by many soil investi-

gators. As far as we were able to determine, no studies of any importance have been recorded in soil literature on the flocculation of other suspensions but those of different clays and kaolin. As a result, the conclusions regarding this (as well as perhaps others) process have been based upon the results obtained from studies with a limited number of soils. But such conclusions, judging from the results presented in the above table, may be erroneous, due undoubtedly to the fact that soils differ one from another in many respects, namely - chemically, physically, and biologically. The soils in our experiment have different origin and different history with respect to their management. Being from the same locality, they have only one factor in common, namely, the climate. Very probably, a given type of soil, if exposed to different climatic conditions, would behave differently with the same electrolyte.

Strong acids are very good coagulants but they are not always better than some of their salts. This point is especially well brought up by the next experiment. The salts of heavy metals seem to have a much stronger flocculating power than those of lighter ones. The trivalent cation is more efficient than divalent one and this latter is better than a monovalent cation. Yet, the tetravalent stannic chloride does not seem to do as efficient work as the divalent barium chloride or calcium chloride. Contrary to the prevalent opinion, bases flocculate when used in this concentration. Only muck resists monovalent bases and yields fairly easily to divalent both barium hydroxide and calcium hydroxide.

Experiment 7. A Minimum Amount of Electrolyte in Solution Required for Flocculation of a Given Amount of Soil Colloidal Solution.

For this experiment all solutions were brought to as nearly the same concentration, as was possible. All stock colloidal solutions were so diluted that they contained .02735 gms. of dry material when 100 c.c. of solution was evaporated. To determine the minimum electrolyte requirement the procedure adapted was as follows:- 10 c.c. of colloidal solution was placed in each of a series of from 8 to 16 25-c.c. graduated tubes. Then, to the tube No.1 was added 0.1 c.c. of N/5 salt solution, to No. 2, .2 c.c., to No. 3, .3 c.c. etc. increasing gradually the amount of salt added. The solutions were vigorously shaken and allowed to stand over night. Now, if solutions in tubes NNo. 1, 2, and 3 have not settled, while the rest of the solutions clearified, then .4 c.c. of that salt or acid was the requirement recorded. Often all solutions in a series were found to be flocculated; in such case another series was prepared with 15, 20, 25, or even 50 c.c. to which the small quantities of a flocculant were added. The recorded results, however, for convenience were all calculated to indicate the requirement per 10 c.c. of colloidal solution.

TABLE VII.

MINIMUM ELECTROLYTE REQUIREMENT FOR COAGULATION OF 10 c.c OF SOIL COLLOIDAL SOLUTIONS OF EQUAL CONCENTRATIONS.

Table VII (continued)

| Electrolyte N/5 | 1 Clay (subsoil) c.c. | 2 Miami Silt Loam. c.c. | 3 Clyde Silt Loam. c.c. | 4 Muck. c.c. |
|---|---|---|---|---|
| HCl | .033 | .10 | .10 | .20 |
| $BaCl_2$ | .05 | .10 | .15 | .30 |
| $CaCl_2$ | .1 | .2 | .2 | 1.0 |
| $MgCl_2$ | .1 | .5 | .5 | Negative with 10 c.c |
| $SnCl_4$ | .05 | .1 | .1 | .2 |
| $HNO_3$ | .05 | .1 | .1 | .2 |
| $Ca(NO_3)_2$ | .1 | .2 | .2 | 2.0 |
| $Hg_2(NO_3)_2$ | .033 | .033 | .05 | .05 |
| $AgNO_3$ | .5 | 1.0 | 1.0 | 1.0 |
| $Pb(NO_3)_2$ | .02 | .033 | .05 | .033 |
| $H_2SO_4$ | .05 | .10 | .15 | .2 |
| $KHSO_4$ | .1 | .15 | .2 | .3 |
| $K_2S_2O_7$ | .1 | .15 | .3 | .5 |
| $MnSO_4$ | .033 | .15 | .15 | 1.5 |
| $CuSO_4$ | .025 | .05 | .1 | .1 |
| $FeSO_4$ | .025 | .15 | .1 | .3 |
| $Fe_2(SO_4)_3$ | .025 | .025 | .05 | .1 |
| $AlK(SO_4)_2$ | .02 | .02 | .05 | .1 |
| $Fe(NH_4)_2(SO_4)_3$ | .025 | .2 | .15 | 1.5 |
| NaOH | 1.5 | 5.0 | Negative with 10 c.c. | Negative with 12c.c |
| $Ba(OH)_2$ | .1 | .15 | .2 | 2.0 |
| $Ca(OH)_2$ | .2 | .3 | 1.0 | 2.0 |
| $H_3PO_4$ | .1 | .2 | .3 | 1.0 |
| $Ca(C_2H_3O_2)_2$ | .05 | .15 | .15 | 2.0 |
| $Pb(C_2H_3O_2)_2$ | .02 | .025 | .05 | .035 |
| $C_2H_2O_4$ | 2.0 | - | - | .5 |
| $C_6H_8O_7$ | .15 | 1.5 | 2.0 | 1.0 |
| $(NH_4)_2CO_3$ | 3.0 | Negative with 10 c.c. | | |

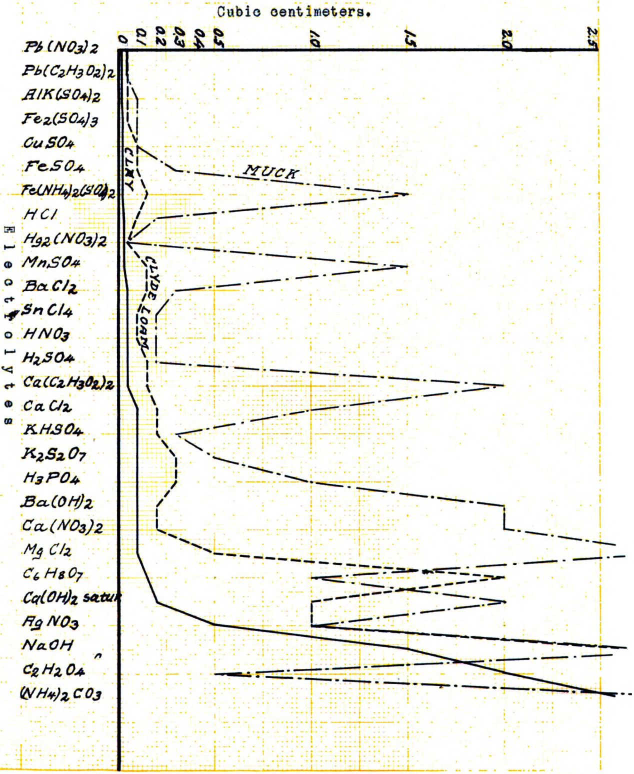
| | 5 Clay (soil) c.c. | 6 Peaty Muck. c.c. |
|---|---|---|
| HCl | .033 | .20 |
| $BaCl_2$ | .05 | .4 |
| $CaCl_2$ | .1 | 1.5 |
| $MgCl_2$ | .1 | Negative with 10 c.c. |
| $SnCl_4$ | .05 | .15 |
| $HNO_3$ | .05 | .2 - .3 |
| $Ca(NO_3)_2$ | .05 - .1 | 2.0 - 3.0 |
| $Hg_2(NO_3)_2$ | .02 | .1 |
| $AgNO_3$ | .3 | -- |
| $Pb(NO_3)_2$ | .02 | .1 |
| $H_2SO_4$ | .05 | .25 |
| $KHSO_4$ | .1 | .4 |
| $K_2S_2O_7$ | - | .6 |

The results presented in this table and the illustration by the accompanied chart show the difference of efficiency of different electrolytes with different soils much better than the qualitative results in the preceding table. The trivalent ferric sulphate and aluminum potassium sulphate are not the leading ones; the salts of lead, being only divalent, both nitrate and acetate act better especially in the case with muck solutions. There is not the slightest indication of following the formula of Schulze (111).

As the chart shows, the silt is more resistant to the action of electrolytes than clay, and muck is the most resistant of the three selected classes. There is one striking fact brought out by this chart. With the best coagulants the minimum electrolyte requirement of all solutions is nearly the same, as one notices in the cases of $Pc(NO_3)_2$, $PCl(C_2H_3O_2)_2$, $Hg_2(NO_3)_2$ and to some extent $Fe_2(SO_4)_3$ and $AlK(SO_4)_2$, but with others the variations are great and often very irregular, evidently being dependent not only upon the cation, but the anion, the chemical composition of the colloidal particles and the salts present in the original solutions. Undoubtedly, a great role is played by the so-called humic substances of the soil whose protective action was suggested by Fickendey and later by Kepzeler and Spangenberg (112), and perhaps the similar observations mislead Lyon, Fippin and Buckman (113) to make the statement that "the gelatinous colloids of the soil, such as some of the humic materials, are not agglutinated by the addition of electrolytes."

# Figure 3.

Showing the Minimum Electrolyte Requirement for the Solutions from Different Types of Soils.



In order to ascertain to what extent this difference in resistance of colloidal solutions to the flocculating action of electrolytes could be ascribed to the protective influence of humic material, an experiment was undertaken and the following obtained results may typify the case.

Experiment 8. Effect of Muck Colloidal Solution on the Stability of Clay Colloidal Solution.

The clay colloidal solution was mixed with muck colloidal solution in proportions from 100% to 0% of clay. The minimum electrolyte requirement of these resultant solutions was determined in the usual way. Both clay and muck suspensions were freshly prepared, and the dry matter in both of them , as well as the mixtures, was determined.

TABLE VIII.

| | | | Electrolyte Requirement. | |
|---|---|---|---|---|
| % of clay solution. | % of Muck solution. | Dry weight per 100 c.c. of solution. | Ca(OH) saturation at 20°C. per 10 c.c. of solution. | $HNO_3$ N/5 per 10 c.c. solution. |
| 100 | 0 | .0730 | .3 c.c. | .05 c.c. |
| 75 | 25 | .0578 | .4 c.c. | .10 " |
| 50 | 50 | .0411 | .6 | .15 " |
| 25 | 75 | .0261 | 1.4 | .20 " |
| 0 | 100 | .0105 | 2.8 | .25 " |

The figures in the table leave no doubt regarding the influence of organic material upon the stability of the solution. That the difference in stability of the colloidal solutions in the foregoing experiment was not due to the difference in their solid material content but rather in spite of it, is absolutely proved by the next experiment.

Experiment 9. Effect of Solid Material Present on the Stability of Soil Colloidal Solution.

The original stock solution of clay from Expt. VI. was diluted 2, 8 and 32 times and the minimum coagulant re-

quirement of each solution was determined.

TABLE IX.

| Concentration per 100 c.c. of sol. | | $CaCl_2$ N/25 | $Ca(NO_3)_2$ N/25 | $Ca(OH)_2$ saturated. | $CaSO_4$ saturated. | $H_2SO_4$ N/25 |
|---|---|---|---|---|---|---|
| Relation. | Gms. | | | | | |
| 1 | .18165 | .3-.4 | .3-.4 | .3-.4 | .3-.4 | .5 |
| ¼ | .04541 | .3 | .3 | .2 | .3 | .3 |
| 1/16 | .01135 | .2 | .2 | .2 | .2 | .3 |

| | | $AlK(SO_4)_2$ N/25 | $KHSO_4$ N/5 | $K_2SO_4$ N/5 | $FeSO_4$ N/25 | $HNO_3$ N/25 |
|---|---|---|---|---|---|---|
| 1 | .18165 | .4 | .2 | .9 | .4 | .4 $^{1}$ |
| ¼ | .04541 | .2 | .1 | .6 | .15 | .2 -.3 |
| 1/16 | .01135 | . | .1 | .4 | .1 | 2 |

Muck colloidal solution was freshly prepared, a portion of which was diluted to 1/3 of its original concentration and the electrolyte requirement per 10 c.c. of each solution follows:-

TABLE IV a.

| Electrolyte N/5 | Original | 1/3 of Original |
|---|---|---|
| $AlK(SO_4)_2$ | 0.1 c.c. | 0.05 c.c. |
| $Fe_2(SO_4)_2$ | 0.1 c.c. | 0.05 " |
| $Pb(NO_3)_2$ | 0.05 " | 0.038 " |

The results indicate very plainly, first, that with the decrease of concentration of colloidal solution the minimum electrolyte requirement for flocculation of that solution decreases also. For the solutions used this is true without exceptions. Second, that the decrease in the minimum coagulant requirement is not proportional to the decrease in concentration of colloidal solution. This unproportionality is probably due to the mechanical difficul-

ties of bringing the particles together to form an aggregate large enough for stopping the Brownian movement, since there are less chances for particles to strike a certain number of particles in a dilute solution than in a concentrated one.

There is a great deal of discussion regarding the nature of coagulation. Some authors describe it as a purely physical phenomenon, while others seem to favor the application of chemical laws to the same effect observed. A few examples will illustrate the point.

Whitney (114) explains the flocculation by means of surface tension. Using his own words; - "If the potential of the surface particle of water is less than of a particle in the interior of the mass of liquid there will be surface tension and the two grains will not come together, because they would enlarge the surface area and increase the number of surface particles of the liquid. If, on the other hand, the potential of the particle on the surface of the liquid is greater than the potential of a particle in the interior of the liquid mass, the surface will tend to enlarge and the grains of clay may come close together and be held there with some force, as their close contact increases the number of surface particles in the liquid around them. This probably explains the phenomenon of flocculation."

Quincke (115) later proposed a similar theory employing the change in surface tension between liquid and the oily substances around the solid particles. Bary (116) thought that liquid penetrates the solid particles and the

attraction between the two balances itself against the elasticity of the solid and the surface tension. Upon the addition of an electrolyte the osmotic pressure is changed, causing the withdrawal of water from the colloidal particles and coagulation results. Bancroft (117) in his recently published articles, summarizing the most important investigations on the subject, comes to the conclusion that in coagulation the adsorption is taking place only at the surfaces of the solid particles.

Duclaux (118), on the other hand, considers the colloids as electrolytes with the power of ionization and, although, the stability of colloidal solution is based on the equilibrium between the intermicellar liquid and the colloidal particles proper, yet the disturbance of this equilibrium implies the chemical change. Jordis (119) also attributes the coagulation to the chemical action. The similar view is held by Ashley (120). Anhenius (121) noticed a close analogy between agglutination and the precipitation and concluded their nature to be the same, i.e. the chemical The recent work of Beans and Eastlack (122) on the electrical synthesis of colloids gives an additional point of proof that the ions are not so loosely connected with the colloid particles to regard them in physical combination and consequently, the coagulation must be accompanied by a chemical change.

The following experiment, which suggested itself by an accident, it seems throws some light upon the phenomenon of flocculation.

Experiment 10. Effect of Concentration of Colloidal Solution on the Time Required for Coagulation, the Amount of

Electrolyte Added Remaining the Same.

In this experiment the clay and muck colloidal solutions were diluted to $\frac{1}{2}$, $\frac{1}{4}$, 1/8, etc., their original concentrations. To 5 c.c. of each of the resultant solutions was added 5 c.c. of electrolyte N/5, vigorously shaken for a few seconds and set aside. The time in minutes when the first floccules could be observed was recorded in the table that follows:-

### TABLE X a.

### CLAY COLLOIDAL SOLUTION.

| Electrolyte used. | Concentration of colloid solution per 100 c.c. Temp C. | .3633 | | .18165 | |
|---|---|---|---|---|---|
| | | Observed Min. | Calculated. | Obs. min. | Calc. |
| $HCl$ N/5 | 21.9 | .5 | 3.5 | 4.5 | 7 |
| $H_2SO_4$ " | 25. | .5 | 1.9 | 3.5 | 3.75 |
| $HNO_3$ | 21.1 | .5 | 5.6 | 4. | 11.2 |
| $H_3PO_4$ | 21.6 | 1.0 | 3.75 | 6. | 7.5 |
| $CH_3COOH$ | 22. | 1.0 | 3.5 | 7 | 7. |
| $C_2H_2O_4$ | 21 | 2.5 | 8.8 | 7 | 17.5 |
| $C_6H_8O_7$ | 21 | 0.5 | 3.1 | 1.5 | 6.3 |
| $CaCL_2$ | 23.7 | 0.5 | 2 | 4. | 4 |
| $Ca(NO_3)_2$ | 19.2 | 1.0 | 2.8 | 5. | 5.6 |
| $FeSO_4$ | 20.8 | 3. | 3.12 | 6.5 | 6.25 |
| $KOH$ | 20.8 | 3 | 4. | 9. | 8. |

| Electrolyte used. | Concentration of colloid solution per 100 c.c. Temp C. | .090825 | | .0454 | |
|---|---|---|---|---|---|
| | | Obs. Min. | Calc. | Obs. Min. | Calc. |
| $HCl$ N/5 | 21.9 | 14. | 14. | 31. | 27.5 |
| $H_2SO_4$ " | 25. | 9. | 7.5 | 17 | 15 |
| $HNO_3$ | 21.1 | 11. | 12.5 | 28. | 25 |
| $H_3PO_4$ | 21.6 | 13. | 15 | 30. | 30 |
| $CH_3COOH$ | 22. | 17 | 14.- | 30 | 27.5 |
| $C_2H_2O_4$ | 21 | 26 | 35 | 52 | 70 |
| $C_6H_8O_7$ | 21 | 11 | 12.5 | 21 | 25 |
| $CaCl_2$ | 23.7 | 11 | 8 | 26 | 16 |
| $Ca(NO_3)_2$ | 19.2 | 13 | 11.1 | 29 | 22.2 |
| $FeSO_4$ | 20.8 | 13. | 12.5 | 24 | 25 |
| $KOH$ | 20.8 | 21. | 16.1 | 39 | 32.2 |

Table X a (continued)

| Electrolyte used. | Concentration of colloid solution per 100 c.c. Temp C. | .02227 | | .01135 | |
|---|---|---|---|---|---|
| | | Obs. min. | Calc. | Obs. min. | Calc. |
| HCl N/5 | 21.9 | 66 | 55 | 109 | 109 |
| $H_2SO_4$ " | 25. | 32. | 30 | 60 | 60 |
| $HNO_3$ | 21.1 | 55 | 50 | 100 | 100 |
| $H_3PO_4$ | 21.6 | 64 | 60 | 120 | 120 |
| $CH_3COOH$ | 22. | 60 | 55 | 110 | 110 |
| $C_2H_2O_4$ | 21 | 140 | 140 | - | |
| $C_6H_8O_7$ | 21 | 50 | 50 | 100 | 100 |
| $CaCl_2$ | 23.7 | 38 | 32 | 64 | 64 |
| $Ca(NO_3)_2$ | 19.2 | 45 | 44.5 | 89 | 89 |
| $FeSO_4$ | 20.8 | 54 | 50 | 100 | 100 |
| KOH | 20.8 | 57 | 64.5 | 129 | 129 |

TABLE X b MUCK COLLOIDAL SOLUTION.

| | | Original. | | ½ orig. | | ¼ orig. | |
|---|---|---|---|---|---|---|---|
| $AlK(SO_4)_2$ | 20.2 | 8 | 13 | 24 | 26 | 53 | 51.5 |
| $Fe_2(SO_4)_3$ | 21.0 | 3 | 11.- | 11 | 21.5 | 23 | 43 |
| $Pb(NO_3)_2$ | 21.4 | 1½ | 2½ | 4 | 5 | 10 | 10.5 |

| | | 1/8 orig. | |
|---|---|---|---|
| $AlK(SO_4)_2$ | 20.2 | 103 | 103 |
| $Fe_2(SO_4)_3$ | 21.0 | 86 | 86 |
| $Pb(NO_3)_2$ | 21.4 | 21 | 21 |

The results reveal a striking regularity of time requirement by differently diluted colloidal solutions. With the exceptions of the most concentrated solutions and the minor discrepancies in a few cases the time necessary for flocculation is nearly inversely proportional to the concentration of that colloidal solution, or it is a demonstration of mass action law stating that "the velocity of a chemical reaction is proportional to the quantities present in condition to react." In our case the amount of electrolyte added was the same in all cases and always present in abundance, while another component, the colloid solution, varied and, being a limiting factor, altered the velocity of re-

action.

The figures on the right side of the column are calculated, taking the result of the most dilute solution for a basis. The close agreement between the results observed and the theoretical values is still better demonstrated by the charts 4 and 5.

Taking into consideration the reactions were allowed to take place at room temperature, which necessarily fluctuated in the course of time needed for the completeness of experiment with each electrolyte studied, one notices the close coincidence of the two lines, which seem to indicate that there is a close relation between the chemical reactions and the reaction between the electrolyte and the colloidal particles or, rather, the ions associated with those particles However, whether a flocculation is a chemical reaction, or a reaction that only obeys the chemical law is more than we can say from the results thus far at our disposal.

The natural conclusion from the foregoing experiments on the flocculation of the soil colloidal particles is that only few salts and acids could be profitably employed with the different soils. In the case with some salts, such as $(NH_4)_2CO_3$, which is used by Fraps and Dupont, it takes a large amount even for the clay suspension. The amount necessary to flocculate other soils with a considerable percent of the organic matter would be so great that it would make the results very unreliable for the quantitative work.

Using few of the most efficient salts, such as aluminum potassium sulphate, ferric sulphate and lead acetate; hydrochloric acid, a representative of the strong acids, and calcium hydroxide, which is so much used in practice, it was

Figure 4.

Showing the Relation between the Law of Mass Action and the Flocculation of Clay Colloidal Solution.

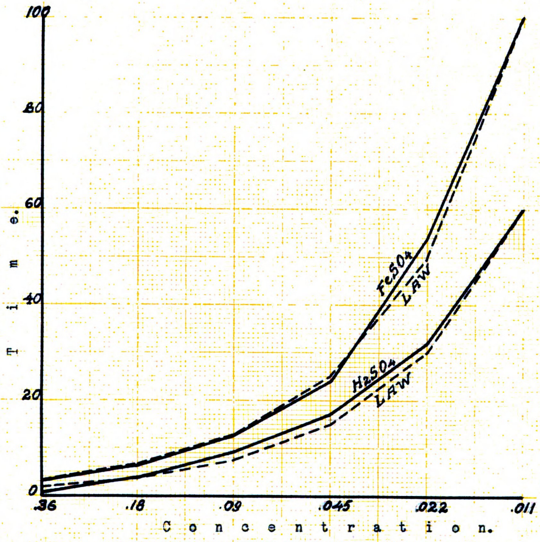
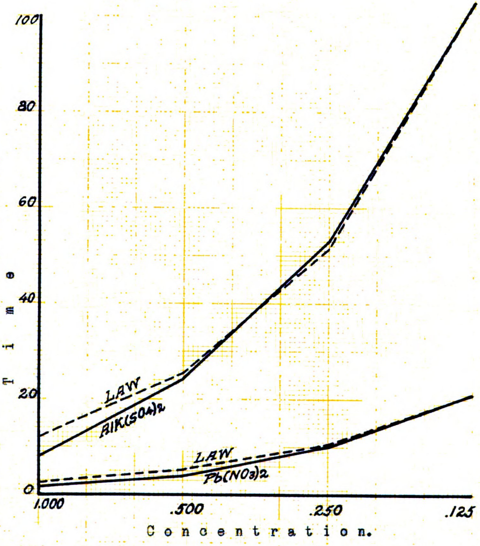


Figure 5.

Showing the Relation between the Law of Mass Action and the Flocculation of Muck Colloidal Solution.



decided to test their efficiency more closely in order to find out how much of each substance would be adsorbed by the flocculated material.

### Experiment XI. Adsorption of Ions by the Flocculatd Soil Colloids as Determined by the Electric Conductivity Method.

To 200 c.c. portions of the soil colloidal solutions were added different amounts of the electrolytes so that on the smallest addition of the electrolyte the coagulation would not be complete, while in the case of the largest amount of electrolyte added, there would be an excess of it present. The solutions were thoroughly shaken in bottles and allowed to stand over night. On the following morning the solutions were transferred to washed tubes and centrifuged in order to have all the particles settled. The liquid from the tubes was decanted off and the gel was well drained Then the sediment, which is firmly held on the bottom of the tube, was washed out with distilled water and finally diluted to 200 c.c., i.e. to the original volume. This solution was shaken in order to break the aggregates as much as possible, and the electric conductivity of the solution was determined. All the conductivity determinations were made at 25°C. In some cases the electrical resistance of the clear solution after centrifuging was also determined, but since the nature of the magnitude of their resistance was always the same, the determinations in several cases were omitted and the readings are recorded only in few instances.

## TABLE XI a

| Amount of N/5 electrol. | $AlK(SO_4)_2$ Precipit. | $AlK(SO_4)_2$ Solution. | $Fe_2(SO_4)_3$ Precipit. | $Fe_2(SO_4)_3$ Solution. |
|---|---|---|---|---|
| 0.1 c.c. | 49,800 | 9,419 | 51,755 | 9,883 |
| 0.2 " | 52,210 | 8,718 | 52,700 | 8,655 |
| 0.3 " | 53,555 | 7,678 | 60,105 | 7,868 |
| 0.5 " | 62,485 | 6,183 | 72,725 | 6,861 |
| 1.0 " | 73,175* | 4,559 | 72,450* | 5,595 |
| 2.0 " | 56,010 | 2,866 | 45,785 | 3,394 |
| 4.0 " | 40,115 | 1,749 | 27,785 | 2,025 |
| 8.0 " | 28,150 | 1,072 | 18,363 | 1,026 |
| Dist $H_2O$ | 54,220 | | 55,630 | |

| Amount of N/5 electrol. | $Pb(NO_3)_2$ Precipit. | HCl Precipit. | Ca(OH)2 Saturated Precipitate. |
|---|---|---|---|
| 0.1 c.c. | 54,140 | 52,064 | |
| 0.2 " | 54, 130 | 56,165 | |
| 0.3 " | 53,127 | 58,805 | |
| 0.5 " | 51,570 | 70,415 | 60,580 |
| 1.0 " | 56,270* | 101,230* | 59,835 |
| 2.0 " | 60,790 | 88,420 | 52,855 |
| 4.0 " | 51,100 | 62,980 | 40,390 |
| 8.0 " | 40,785 | 24,870 | 31,570* |
| Dist $H_2O$ | 54,220 | 54,210 | |
| 12 c.c. | | | 29,855 |
| 16 c.c. | | | 27,770 |
| 20 c.c. | | | 25,472 |
| $H_2O$ | | | 60,101 |

## TABLE XI b. MUCK COLLOIDAL SOLUTION.

| Amount of N/5 Electrolyte. | $AlK(SO_4)_2$ Precipitate. | $Fe_2(SO_4)_3$ Precipitate. | $Pb(NO_3)_2$ Precipitate. |
|---|---|---|---|
| 1 c.c. | 94,640 | 104,430 | 71,500 |
| 2 " | 90,850 | 113,800* | 65,000* |
| 4 " | 52,030 | 43,770 | 50,450 |
| 8 " | 31,830 | 21,740 | 38,590 |
| Distilled water | 184,250 | 187,750 | 135,630 |

The above figures show that the adsorption of a coagulant during the process of coagulation increases with the increase of the coagulant present. This is natural and it is in accord with the results obtained by Parker (loc.cit.) working with soils. Further, the results of the clay suspensions with aluminum potassium sulphate, ferric sulphate, hydrochloric acid, and to some extent with lead nitrate give adnormally high resistances around the point of the minimum electrolyte requirement. (The sign (*) indicates the point of the first complete precipitation.) In fact, the resistance at that point is much higher than that of distilled water used. It is true, that the distilled water was not of the highest quality, but it would be absurd to suppose the solutions to be of higher purity than the distilled water. The duplicates and in several instances the triplicates of the determinations were made with the similar results for each particular electrolyte. It seemed, therefore, that there was some change in the structure of the colloidal gel resulting in the diminishing of its conductivity. In order to determine whether such is the case, the suspension of clay with 1.0 c.c. of aluminum potassium sulphate, whose resistance on centrifuging, decanting and diluting to the original solution was 72,450 ohms (see the above table), was centrifuged once more for 15 minutes. The solution, which was perfectly clear to the naked eye, was decanted off and its resistance determined. It read 55,940 ohms. as against 72,450 with the solid particles in it, or against 55,630 ohms of the distilled water. To verify this point the following short experiment was undertaken 200 c.c. of clay colloidal solution was flocculated with 10 c.c. of alum. The gel was separated from water by centrifuging and decantation. Then it was washed out of the tube, diluted to 200 c.c. and the electrical resistance determined. After this, it was centrifuged again, separated from the clear solution and the resistance of both the clear

Figure 6.

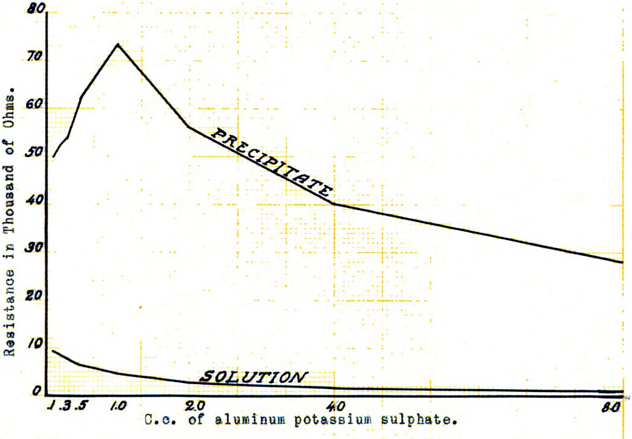
Showing the Resistance of the Colloidal Gel and the Solution on Addition of Different Amounts of N/5 Hydrochloric Acid.

CLAY COLLOIDAL SOLUTION.

Figure 7.

Showing the Resistance of Colloidal Gel and Solution on Addition of Different Amounts of N/5 Aluminum Potassium Sulphate.

CLAY COLLOIDAL SOLUTION.



solution and the resultant diluted precipitate was taken. This operation was repeated four times, using the same distilled water, whose resistance was likewise determined. the results follow -

TABLE XI c.

| Dist. Water. | First precipit. | | Second precipit. | | Third precipit. | | Fourth precipit. | |
|---|---|---|---|---|---|---|---|---|
| | Clear solution. | dilut. gel. | Clear sol. | dilut. gel. | clear sol. | dilut. gel. | clear sol. | diluted gel. |
| 49,668 | 634 | 10,054 | 9,842 | 37,085 | 33,349 | 42,437 | 38,180 | 54,293 ohms. |

It will be seen by examining the figures in the above table that the resistance of the diluted gel is always greater than that of the next clear solution, which is obtained by the centrifuging of the suspension and by decantation.

Consequently, the assumption regarding the interference of the solid particles in the gel form with the conductivity of the solution was correct. Besides, it seems that the purity of the solution at this point, so far as salts in solution are concerned, is gradually approaching that of the distilled water used.

The next logical step was to find out whether the increase in the adsorption of the salts due to the excessive application of these salts in the flocculation would be noticed in the total weight of the gel obtained.

Experiment XII. Effect of the Amount of Salt on the Dry Weight of the Gel Obtained.

In a series of four cylinders, each containing 200 c.c. of the colloidal solution of either clay or muck were added different amounts of N/5 electrolyte. The least amount was just enough for the complete coagulation. After standing for 24 hours the solution was centrifuged for 15 minutes at the rate of 2000 revol. per minute, and clear solution was carefully decanted. The remaining gel was transferred to the evaporating dish and the dry weight of the evaporated material was determined.

TABLE XII a CLAY SUSPENSION.

| C.C. of the electrolyte N/5 added. | HCl | | $AlK(SO_4)_2$ | | $Fe_2(SO_4)_3$ | |
|---|---|---|---|---|---|---|
| | 1 gms. | 2 gms. | 1 gms. | 2 gms. | 1 gms. | 2 gms. |
| 1 | .0923 | .0923 | .0930 | .0925 | .0966 | .0980 |
| 2 | .0925 | .0920 | .0922 | .0912 | .1027 | .1043 |
| 4 | .0925 | .0925 | .0940 | .0970 | .1093 | .1112 |
| 8 | .1043 | .1042 | .0958 | .0975 | .1192 | . 1165 |

| | $Pb(NO_3)_2$ | | $Ca(OH)_2$ (Saturated) | |
|---|---|---|---|---|
| | 1 gms. | 2 gms. | 1 gms. | 2 gms. |
| 1 | .0955 | .0950 | | |
| 2 | .0967 | .0958 | | |
| 4 | .0978 | .0980 | | |
| 8 | .1030 | .0992 | .0820 | .0950 |
| 16 | | | .1028 | .0983 |
| 24 | | | .1112 | .0983 |
| 32 | | | .1138 | .0997 |

200 c.c. of original solution evaporated = .1015 gms.

TABLE XII b. MUCK SUSPENSION.

| C.C. of electrolyte N/5 added. | $AlK(SO_4)_2$ | | $Fe_2(SO_4)_3$. | | $Pb(NO_3)_2$ | |
|---|---|---|---|---|---|---|
| | 1 gms. | 2 gms. | 1 gms. | 2 gms. | 1 gms. | 2 |
| 2 | .0821 | .0802 | .0800 | .0807 | .1045 | |
| 4 | .0845 | .0813 | .0885 | .0912 | .1089 | |
| 6 | | | | | .1096 | |
| 8 | .0855 | .0815 | .1004 | .1080 | .1123 | |
| 12 | .0876 | .0819 | .1023 | .1056 | | |

The results presented in the table (XII) leave no doubt regarding the influence of the amount of electrolyte added. The adsorption of the salt sometimes becomes so great that the dry weight is larger than that of the original solution. Similar to the results of the preceding table, they show that the best results are obtained when only enough of the electrolyte is added to cause a complete coagulation of the suspended material. If any excess of the salt, or acid, or base is added the adsorption of that salt, or acid, or base may cause the error, which would be larger than if the dry matter of the original solution was determined by the evaporation. The washing of the excess of salt would remove some of the reversible colloids that would pass through the filter paper.

The general conclusion from the results obtained in the last two experiments is as follows:- The flocculation of the soil colloidal solution with N/5 hydrochloric acid, aluminum potassium sulphate, ferric sulphate and, perhaps, lead nitrate and calcium hydroxide can be employed as a means of separation of the colloidal material from the substances in the true solution, providing that only enough of the electrolyte is added to cause a complete flocculation. At this point the amount of the electrolyte adsorbed is very small and can be disregarded in the determination of the gel. Although only two soils were studied for this purpose, yet these soils may be considered as representatives of two extreme cases. The clay soil is a splendid type of the mineral soil, while the muck soil similarly represents the organic type. Considering that most of the common soils lie between these two extremes, it is believed, that the general conclusion presented above is justified on these grounds.

## Dialysis.

It seemed advisable to compare the dialyzing with the flocculation of the soil colloidal solution as a means of their purification from the crystalloids.

Experiment XIII. Efficiency of Dialyzing in Purification of the Soil Colloidal Solutions.

A series of dialyzers were prepared with a vegetable parchment paper for the membrane. The clay, muck and ferric hydroxide colloidal solutions were dialyzed, changing the distilled water daily. The purity of the colloidal solutions was determined by means of measuring its electrical resistance. Since there was no apparent chemical change in the colloidal solution during the dialyzing and, therefore, no marked change in the structure of the particles occurred, it is supposed that the influence of the solid particles on the electric resistance was practically the same throughout the experiment. All readings were made at 25°C. After reading the colloidal solution was returned to the dialyzers, thus leaving the volume of the dialyzed solution the same. The readings of both the colloidal solution and the outside distilled water was made in order to determine the difference in their resistance after 24 hours, and in few of the latest determinations after several days of standing.

TABLE XIII.

ELECTRICAL RESISTANCE AT 25°C. WITH THE SAME ELECTRODES.

Table XIII (continued)

| Days of Dialyzing. | Clay colloidal sol. | | Ferric hydroxide. | |
|---|---|---|---|---|
| | Colloidal solution. ohms. | $H_2O$ outside ohms. | Colloidal solution ohms. | $H_2O$ outside ohms. |
| 0 | 2,228 | - | 2,587 | |
| 1 | 3,145 | 3,917 | 3,623 | 6,500 |
| 2 | 5,085 | 6,139 | 4,168 | 8,405 |
| 3 | 8,151 | 13,054 | 4,674 | 11,203 |
| 4 | 12,629 | 23,655 | 5,004 | 13,383 |
| 6 | 17,220 | 27,620 | 5,514 | 16,655 |
| 8 | 23,765 | 54,625 | 6,219 | 27,425 |
| 13 | 37,850 | 74,655 | 7,155 | 33,390 |
| 15 | 44,725 | 101,915 | 7,754 | 47,650 |
| 17 | 47,900 | 107,910 | 8,534 | 50,455 |
| 20 | 52,825 | 114,565 | 9,184 | 56,410 |
| 28 | 58,225 | 106,100 | 11,685 | 93,775 |
| 35 | 67,845 | 150,315 | 17,540 | 134,300 |
| 45 | 71,080 | | 24,710 | |
| 55 | 88,420 | 153,410 | gelatinized | |

TABLE XIV.

ELECTRICAL RESISTANCE AT 25°C. WITH THE SAME ELECTRODES.

| Days of dialyzing. | Muck colloidal solution. | |
|---|---|---|
| | Colloidal solution. ohms. | $H_2O$ outside ohms. |
| 0 | 6,820 | |
| 1 | 14,080 | 28,275 |
| 2 | 21,180 | 56,640 |
| 3 | 24,765 | 79,325 |
| 5 | 29,825 | 89,170 |
| 7 | 33,140 | 133,215 |
| 13 | 40,090 | 113,880 |
| 17 | 41,660 | 165,750 |
| 23 | 42,535 | 115,320 |
| 33 | 39,820 | 115,790 |

The distilled water used in these three dialyzers had the electrical resistance between 173,760 and 186,100 ohms.

It will be seen from the figures presented in the above tables and the illustration by the charts that the dialysing is an extremely slow process of purification of the colloidal solution. Yet, the dialyzing of clay and muck

Figure 8.

Showing the Resistance of the Dialysed Clay Colloidal Solution and the Water Outside of the Dialyser.

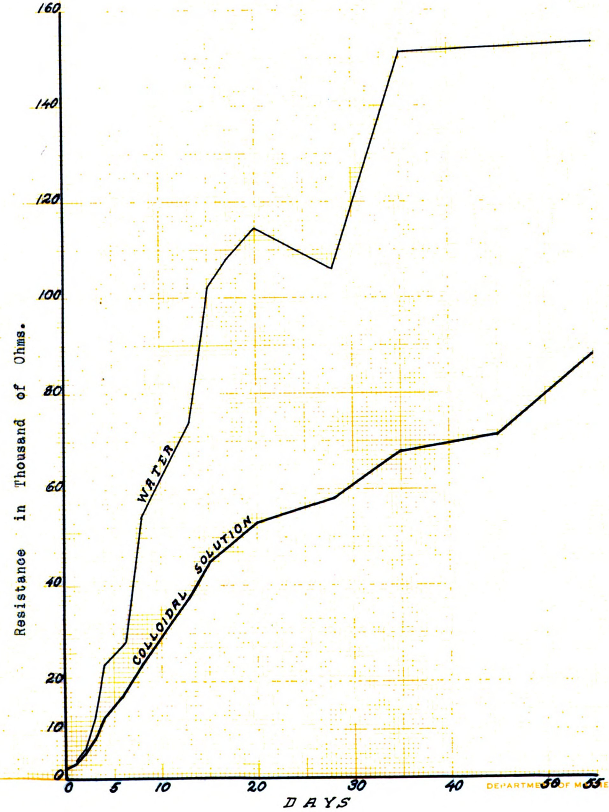
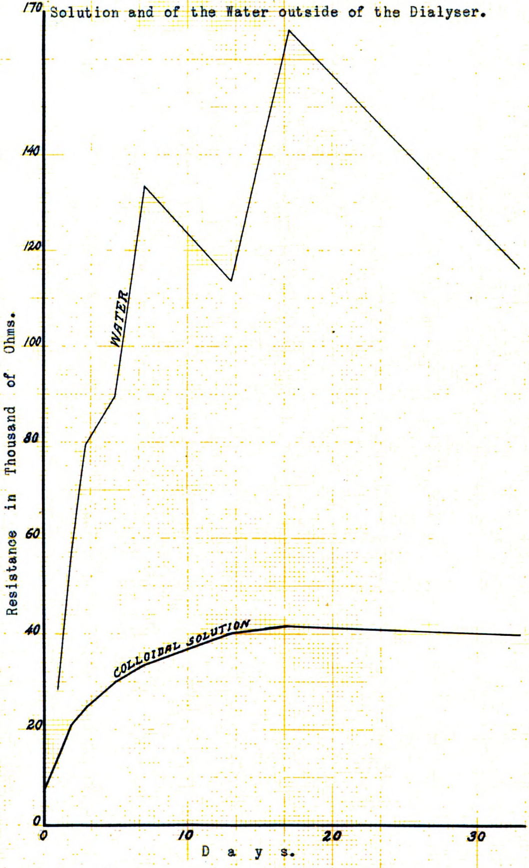


Figure 9.

Showing the Resistance of Dialysed Muck Colloidal Solution and of the Water outside of the Dialyser.



suspensions is much faster than that of the prepared ferric hydroxide. Since it is probable that some of the colloidal particles go through the parchment paper, taking the factor of time into an account, and considering the fact that some of the solid particles stick to the membrance and dry out on it, making it almost impossible of removing, the dialyzing in its present form can hardly be used advantageously for the quantitative determination of the soil colloids.

## DISCUSSION.

From the foregoing experiments the following points outstand as having an important bearing on the method of mechanical determination of the soil colloids: -

1. The results of experiments 1 and 2 emphasize the importance of having the samples to be analyzed in the fresh state, since the drying makes the largest portion of colloids either irreversible or, if reversible, very slowly so.

2. The shaking of the sample should be continued for a considerable length of time. 15 hours is an appropriate period to be set for a minimum.

3. The centrifuging should be both fast and prolonged. The length of the centrifuging takes place of its speed and vice versa. In order to obtain the soil colloidal solution of the high stability the centrifuging should be done at the rate of at least 2000 revolutions per minute for 30 minutes.

4. In the quantitative determination of the colloidal portion of the soil the centrifuging should be repeated until the solution after centrifuging is fairly clear. From 8 to 15 repetitions is usually sufficient, depending

upon the nature of the soil and the weight of the sample taken for the analysis. It should be mentioned that it is almost impossible to reach the point when the solution after centrifuging is perfectly clear, especially in the case of very heavy soils. But as a matter of fact the amount of solid material present in such a semi-turbid solution is very small in comparison with the solutions obtained by the first few centrifugings. An experiment was performed, though not recorded in this paper, in which 14 repetitions of the centrifuging was made and the dry weight of each portion was determined. It does not seem necessary to record the entire experiment here, but it will suffice to say that by the first centrifuging 22% of the total weight of dry matter was obtained, and only 1% by the 14th. By the first seven centrifugings over 75% of the total was obtained. Thus, one notices that the existing error, is not large and should not diminish the value of the method.

5. In separation of colloids from the substances in the true solution one of several electrolytes can be employed. Among the best ones are aluminum potassium sulphate, ferric sulphate, hydrochloric acid, and, to some extent, lead nitrate and calcium hydroxide.

6. The minimum amount of the electrolyte employed to cause a complete flocculation should be added. If the electrolyte is added in excess, the increase in the adsorbed coagulating ions may give erroneous results.

## Directions for the Method.

From the study of the method proposed by Dupont, the following modification is offered which, it is believed, has several advantages over the former one by being based

upon the experimental evidences:-

A sample of soil taken directly from the field is sifted through a two millimeter mesh, mixed well and the weighed portions are taken for both the colloidal and the moisture content determinations.

10 grams, or any other appropriate amount, of the fresh soil is placed in the shaking bottle which is used in mechanical analysis, filled with distilled water up to 5½ oz. mark, few drops of ammonia added and shaken for 15 hours or more in the shaking machine. When the particles are disintegrated, transfer the contents of the bottle into the centrifuge tubes dividing the solid portion equally between two or four tubes. Add enough water to fill the tubes and centrifuge for 30 minutes at the rate of 2000 revolutions per minute.

Decant the liquid off, transfer the settled gel into the evaporating dish, evaporate, cool and weigh. Knowing the total volume of the solution obtained, the volume taken for the flocculation, and the weight of the oven-dry soil, calculate the percentage of the colloidal material. The duplicates should easily check within 0.5%.

## SUMMARY.

1. The drying of the soil even at the room temperature decreases the amount of the colloids present in solution. It makes the colloidal particles either irreversible or, if reversible, very slowly so.

2. Shaking of the sample of soil in water influences the amount of colloidal material to be brought in suspension

3. The time and the speed of the centrifuging modifies both the quantity of the colloids in suspension and the

stability of the resultant hydrosol. The stability of the solution increases with the speed and the time of centrifuging, while the amount of the solution decreases with it.

4. Besides the fact that the flocculating efficiency of different electrolytes with the same colloidal solution is different, the results show that the efficiency of the same electrolyte with the solutions from different soils varies considerably depending largely upon the chemical composition of the soil.

5. Schulze's valency law does not hold true with the soil colloidal solutions studied.

6. Humus material hinders the coagulating power of the electrolytes.

7. It takes a greater amount of an electrolyte for the flocculation of the more concentrated soil colloidal solution than that for the less concentrated one.

8.,In the flocculation of the soil colloidal solutions by the electrolytes the reaction obeys, within the experimental error, the law of mass action.

9. The adsorption of the flocculating substance is increased with the increase of the amount of the substance present in solution at the time of flocculation.

10. The solid particles of the gel resulting from the soil colloidal solutions studied hinder the electrical conductivity of these solutions.

11. The dialyzing is not an adequate method for the quantitative determination of colloids in the crystalloidal solution.

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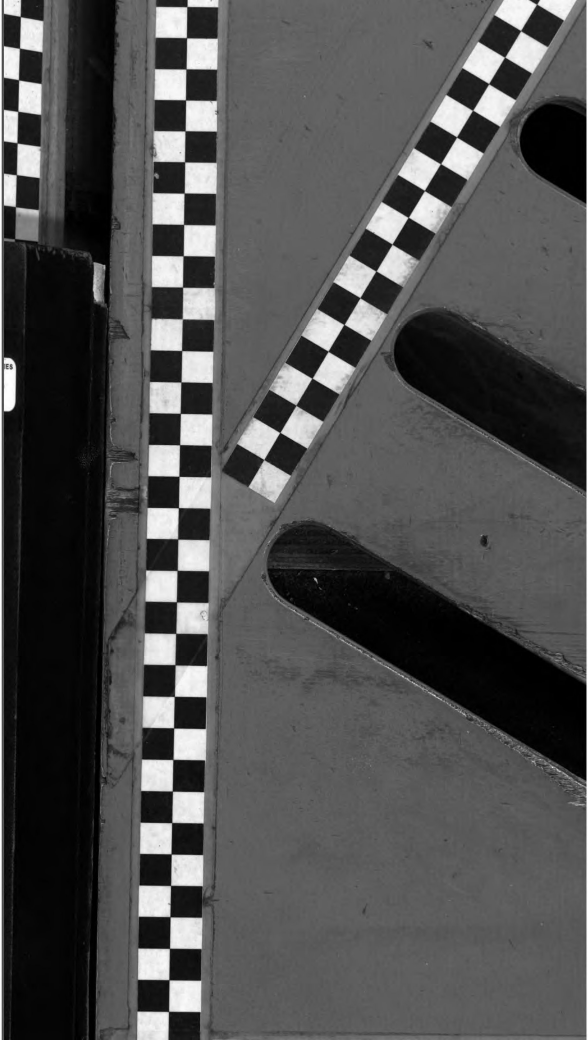
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