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A CENTRIFUGAL METHOD FOR PREPARING COLLOIDAL FERRIC HYDROXIDE, ALUMINUM HYDROXIDE AND SILICIC ACID

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The two methods which have been most used for the preparation of electrolyte-free colloidal ferric hydroxide and aluminum hydroxide are in many respects unsatisfactory. The first, in which the hydroxide is formed by the hydrolysis of the acetate and the acetic acid removed by vigorous boiling was first proposed by Crum[1] in 1853 for preparing colloidal aluminum hydroxide. Crum failed to prepare colloidal ferric hydroxide by this method but Péan de Saint-Gilles[2] succeeded in doing so in 1855. The second method is based upon the peptization of the freshly precipitated hydroxides by their respective chlorides. The excess of electrolytes in this case is removed by dialysis. This method was first used by Graham[3] in 1862.

The disadvantages offered by each of these methods are numerous. Either prolonged boiling or prolonged dialysis is necessary to remove the excess of electrolyte. The removal of electrolyte is always far from complete. Graham was never able to remove the last 1.5% of hydrochloric acid from his sol by dialysis, though Nicolardot[4] succeeded in reducing the content to 0.16%. Neidle and Barab[5] by hot dialysis obtained sols of ferric hydroxide containing 38.7 gram equivalents of ferric iron to 1 gram equivalent of chlorine. Péan de Saint-Gilles was unable to remove all of the acetic acid from his sol for he found that if the boiling were carried too far precipitation would result. The degree of dispersion obtained varies widely. That of the Graham colloid changes on standing. It is almost impossible to make up successive sols with duplicated properties. This is shown by the widely different properties attributed to each by different investigators. Both require low concentrations for stable sols. Crum recommended a concentration of not over 0.1% for aluminum oxide.

Weiser[6] improved the method of Crum and Péan de Saint-Gilles by adding only enough acetic acid to the thoroughly washed, freshly precipitated hydroxides, to peptize them. The amount of acetic acid required was

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[1] Crum, *Ann.*, **89,** 168 (1853).

[2] Saint Gilles, *Compt. rend.*, **40,** 568 (1855).

[3] Graham, *J. Chem. Soc.*, **15,** 250 (1862).

[4] Nicolardot, "Recherches sur les sesquioxide de fer." *Thesis*, Paris, **1905.**

[5] Neidle and Barab, THIS JOURNAL, **39,** 80 (1917).

[6] Weiser, *J. Phys. Chem.*, **24,** 30, 277 (1920).

considerably less than that necessary to form the normal acetates and he found that vigorous boiling for from 25 to 40 hours was sufficient to remove the excess of acid.

In both the Graham method and the method of Weiser the freshly precipitated hydroxides are used as a basis for the sol, peptization being effected in the first case by the hydrochloric acid formed in the hydrolysis of the chloride, and in the second case by the addition of small amounts of acetic acid. It is well known that both ferric and aluminum hydroxides may be peptized to a certain extent merely by the removal of the precipitating agent by thorough washing with distilled water. The washing of these precipitates through the filter, which frequently happens in quantitative analyses, is an example of this. Weiser made a comparative test of the peptizing power of the various acids and of water on aluminum hydroxide. He found that 0.508 g. out of 0.750 g. or about 68% was peptized by 5 cc. of 0.2 N acetic acid while 0.477 g. out of 0.750 g. or about 63% was peptized merely by repeated washings with distilled water.

Principle Underlying the Present Investigation.—The above data indicate that thorough washing is about as effective a peptizing agent as dilute acids. If complete peptization could be effected by thorough washing it would appear to have two distinct advantages over the peptization by means of acids: (1) the removal of the electrolyte set free in the precipitation of the hydroxides (NH_4Cl) would be more complete, for Weiser and Graham were obliged to discontinue the washing as soon as peptization started; (2) the addition of a peptizing agent and its consequent imperfect removal by prolonged dialysis or boiling would be unnecessary.

Several investigators have demonstrated the possibility of throwing colloidal particles out of solution by means of a high centrifugal force.

> Franklin and Freudenberger[7] separated the colloidal particles of platinum and prussian blue from their respective sols by prolonged application (6–7 hours) of a centrifugal force of 1520 times gravity.
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> Friedenthal[8] in 1909 succeeded in separating the casein from cows' milk by centrifugal force. Perrin,[9] by fractional centrifuging, prepared sols of gamboge having particles of fairly uniform size. He failed, however, to fractionate colloidal ferric hydroxide by this means.

These results indicate the possibility of removing additional amounts of electrolyte from a solution by washing even after it has become colloidal.

A Sharples Laboratory Supercentrifuge, operated by an electric motor at 32,500 revolutions per minute, has been used in this laboratory for the past year for the separation of a highly hydrated emulsoid complex from

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[7] Franklin and Freudenberger, *Trans. Am. Electrochem. Soc.*, **8**, 29 (1905).

[8] Friedenthal, *Kolloid Z.*, **15**, 75 (1914).

[9] Perrin, "Les Atomes," Libraire Felix Alean, **1914**, 135.

suspensions of a heavy clay subsoil. It was considered probable that by means of this machine washing could be continued until enough of the precipitating agent was removed to make possible the existence of the hydroxides in a stable colloidal condition, comparatively free from electrolytes and of a relatively high concentration.

Experimental

Removal of Deposit from the Centrifuge Bowl.—In the earlier work with the centrifuge the material deposited in the bowl was removed by scraping with a long spatula. On account of the small diameter of the bowl (5 cm.) this method was found very unsatisfactory when one wished to remove the total content very carefully and in the exact order in which it was deposited. This difficulty was overcome by means of a device made as follows. The inside diameter of the bowl was carefully measured, its circumference calculated, and a rectangular piece of celluloid prepared which was of the same length as the inside depth of the bowl and the same width as its circumference. This was rolled up and slipped into the bowl. Its natural resilience held it firmly against the walls, forming a uniform celluloid lining or sleeve. After making a run, the bowl bottom was removed, a long, narrow (6 mm.), sharply pointed spatula slipped between the sleeve and the bowl and worked around the entire circumference. This loosened the sleeve so that it could be removed by seizing the two edges at the seam with a small pair of pliers and exerting a steady pull. By unrolling the sleeve the entire contents of the bowl become visible. Division of the deposit could be made at any point at which its appearance indicated advisable and the entire deposit removed almost quantitatively by means of a spatula.

1. Preparation of the Iron Hydroxide

In preparing the colloidal ferric hydroxide, ammonium hydroxide was added to a concentrated solution of ferric chloride (slowly as the neutral point was being approached) with constant stirring until minute floccules of ferric hydroxide were barely visible. The more granular precipitate formed by adding an excess of ammonium hydroxide was found to be more slowly reversible than that obtained by the above procedure. The precipitate was allowed to settle and was washed by decantation until it commenced to become colloidal. This solution was then passed through the centrifuge at the rate of about 3 liters per hour. At the end of the run the sleeve was found to be coated with an extremely finely divided layer of reddish-brown ferric hydroxide. This material was removed, placed in a mortar with a little water, then mixed to a uniform paste with the pestle. This procedure facilitated the uniform dispersion of the oxide when it was poured into a large bulk of water for the next washing. After being thoroughly washed on the mechanical shaker with 1 to 2 liters of water the suspension was passed through the centrifuge a second time at a somewhat slower rate than at first. After this process had been repeated four times, the contents of the bowl could be divided into two distinct parts, (1) a yellowish-brown, fairly stiff deposit on the lowest 5 cm. of the sleeve which graded slowly into (2) a dark red, highly hydrated, semifluid deposit which was barely stiff enough to adhere to the sleeve when it was removed with considerable care. The deposit of the dark red oxide was fairly uniform over the upper three-fourths of the sleeve.

The material was divided into two fractions: Sol A, which included all the yellowish-brown oxide from the bottom of the bowl up to the point where the dark red material was apparently homogeneous, and Sol B, the dark red material. Sufficient water was added to each of these separates to bring them to such a consistency that they could be readily removed and measured by means of a pipet. The strength of the sols was then determined by evaporating 10 cc. to dryness on a water-bath, drying at 105° and weighing. After being standardized, these were used as stock solutions for making up sols of any desired concentration. The liquid which was discharged on the fourth and subsequent washings (Sol C) was a beautiful cherry-red sol which gave no reaction for ionic iron with thiocyanate or ferrocyanide and only a very slight opalescence when dissolved in nitric acid and tested for chlorides with silver nitrate.

Purity and Solubility.—Sol B when dissolved in nitric acid likewise gave only a barely perceptible opalescence with silver nitrate. Its color was not changed by the addition of a few drops of potassium thiocyanate. A dirty brown precipitate was formed by potassium ferrocyanide which assumed a greenish tinge on standing. The addition of one drop of *N* hydrochloric acid produced the intense blue color characteristic of the ferric iron. When poured into concentrated acid in the cold, the colloid flocculates, but on heating, the coagulum readily dissolves.

Another sample was washed seven times by means of the centrifuge and analyzed for chlorides. One gram equivalent of chlorine was found to every 396 gram equivalents of ferric iron. The amount of chlorine could doubtless be still further reduced by additional washings.

Stability.—All three sols are stable on standing. If the first 2 cm. of material in the bottom of the bowl is discarded none of the material in Sol A, which contains the largest particles, is thrown down by 20 minutes' centrifuging in a centrifuge of the ordinary tube type making 2,000 revolutions per minute.

By boiling on the water-bath the sols may be reduced to an almost syrupy consistency but may be restored to their original concentration by the addition of water. A large part of the material may be rather easily brought back into colloidal condition even after evaporation to dryness.

Color of Sols.—The color of the sols is influenced by at least three factors: concentration, size of particle, and depth of the liquid examined. In the concentrated stock solutions Sol A is yellowish-brown, B is reddish-brown, and C slightly more reddish than B. On dilution to the proper extent all may be brought to a red color, on still further dilution all appear yellow. This holds, of course, for the Graham and Péan de Saint-Gilles colloids as well. All three sols are turbid in reflected light when fairly concentrated. Sols B and C are clear in concentrated solutions when examined through transmitted light; Sol A is distinctly turbid in concentrated solutions and slightly so even in fairly dilute solutions.

Color of Coagulum.—Because of the influence of concentration on the color of the sols it was found that the color of the coagulum was a better indication of the relative colors of the particles in the sols. Five cc. each of Graham's, and Péan de Saint-Gilles' colloids and of Sols A, B, and C were placed in test-tubes and flocculated by means of aluminum sulfate. There was a remarkably uniform gradation in color from the brownish red of the Graham colloid through the lesser red of the Péan de Saint-Gilles colloid to the yellowish brown of Sol A. From the fact that Sol A was made up of that fraction of the oxide which was deposited first in the bowl of the centrifuge, we should assume that it was made up of the largest and least hydrous particles. Sol B which was made up of that fraction deposited in the top of the bowl would be naturally made up of somewhat smaller particles than A. Sol C whose particles were not thrown down by the centrifugal force used to throw out the others would be expected to be the most highly dispersed of the three. On the other hand, we should expect that the Graham colloid, which in this case was prepared by pouring a solution of ferric chloride into boiling water, conditions favoring extremely rapid hydrolysis, would be the most highly dispersed of the lot. Sols A, B, and C would be expected to be less highly dispersed since they were formed by peptizing the almost visible floccules by the removal of the flocculating ion. These results bear out the work of Weiser and others that the color of hydrous iron oxide may vary from red to yellow depending upon the size of the particles.

II. Preparation of the Aluminum Hydroxide Colloid

Sols of aluminum hydroxide have been prepared in a way similar to that used for ferric hydroxide by the thorough washing of the hydroxide precipitated from aluminum chloride by ammonium hydroxide. Since there is less tendency for aluminum hydroxide to come down in the granular, more slowly reversible form, it is not necessary to control so carefully the amount of the precipitating agent. The addition of ammonium hydroxide to a slight excess will give good results.

The color of the concentrated stock solutions ranges from white in the case of Sol A to bluish-white in the case of Sols B and C. A is turbid in transmitted light, B and C are clear.

The reactions of the aluminum sols to heat and acids are similar to those described for iron.

Sensitiveness to Polyvalent Ions.—The early work on the preparation of colloidal aluminum hydroxide is full of references to its extreme sensitiveness to polyvalent electrolytes.[1] Previous investigations[10] have indi-

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[10] Rose, *Kolloid Z.*, **15**, 1(1914). Weiser, *J. Phys. Chem.*, **24**, 277(1920).

cated that the precipitation of colloidal aluminum hydroxide by sulfates is distinctly different from the precipitation by chlorides or nitrates, in that repeated washings fail to remove enough of the precipitating agent to allow the precipitate to assume colloidal condition. This stimulated a desire to find out whether the more thorough washing used in this investigation would bring back the precipitate from the sulfate into a stable colloidal condition.

A concentrated solution of aluminum sulfate was precipitated with a slight excess of ammonium hydroxide and allowed to stand for one week. The supernatant liquid was poured off, distilled water added to replace it and the precipitate thoroughly broken up by stirring and by shaking in a mechanical shaker for 15 minutes. The suspension was then passed through the centrifuge as rapidly as possible (1 liter per minute). All the oxide was found in the lower fourth of the bowl. This was removed and mixed to a pasty consistency in a mortar with a little water. This paste was then poured into a bottle containing 2 liters of water, shaken as above described and centrifuged. This time the aluminum hydroxide was found deposited higher up in the bowl, indicating that a longer application of centrifugal force had been necessary to throw it down. After the second washing it was found necessary to cut down the rate of flow through the centrifuge to 4 liters per hour in order to throw out the bulk of the aluminum hydroxide. With the fourth washing the rate was reduced to 2 liters per hour; and some aluminum hydroxide was so finely dispersed that even this application was insufficient to throw it out of suspension.

When the celluloid sleeve was removed after the fourth washing, the upper two-thirds of it was found to be coated to a depth of 2 mm. with a transparent, gelatinous, deposit of aluminum hydroxide which appeared bluish-white when removed with a spatula. This material was found to be readily miscible with water in all proportions, forming a beautiful bluish-white sol which seemed as stable as that formed, from the chloride. All of the sulfate ion was not removed, for when a little of the concentrated sol is dissolved in hot nitric acid and barium chloride solution added, on standing a few crystals of barium sulfate are formed. Whether any more sulfate can be removed by further washing is yet to be determined; but the results seem to show conclusively that the sulfate ion is not so strongly adsorbed by the precipitated aluminum hydroxide but that it may be sufficiently removed by washing to allow the aluminum hydroxide to go into a stable colloidal condition. It also indicates that the previously termed "irreversibility" is due to the adsorption of sulfate rather than to the formation of a definite chemical compound, which is in accord with the views of Bancroft and of Weiser.[11]

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[11] Weiser, *J. Phys. Chem.*, **24**, 277 (1920).

III. The Preparation of Colloidal Silicic Acid

Silicic acid sols are generally prepared by pouring a solution of sodium silicate into an excess of dil. hydrochloric acid.[12] The sodium chloride formed and the excess of acid are removed as far as possible by dialysis. Dialysis is usually considered complete when the wash water yields no test for chlorides with silver nitrate. Such sols have a strong tendency to gelatinize and gelation is so difficult to revert that it has commonly been considered irreversible. Several other methods of preparation also have been used.[13]

The preparation of a sol of aluminum hydroxide from the "irreversible" precipitation of the hydroxide in an excess of sulfate ions by the washing out of the precipitating agent indicated the possibility that the irreversibility of silicic acid gels might be of the same character. Silicic acid was precipitated by slowly adding dilute hydrochloric acid (1:3) to dilute (1:3) commercial sodium silicate. Precipitation occurred before neutralization so the solution was still slightly alkaline. The precipitate was washed by decantation until most of the chloride was removed, then all lumps were carefully broken up and the mixture was passed through the centrifuge at the rate of one liter per minute. The washing of the precipitate was continued until practically all of it had been converted into the colloidal condition. This occurred after 15 washings. Table I gives detailed data on these washings. The first column shows the number of washings, the second the rate at which the suspension was passed through the centrifuge, the third the approximate amount of silicic acid thrown down, the fourth the total volume of wash water used, the fifth column shows the degree of alkalinity of the wash water expressed in terms of the number of cubic centimeters of 0.2 *M* hydrochloric acid necessary to neutralize 100 cc. of the wash water up to the sixth washing. Thereafter the alkalinity is expressed in terms of hydrogen-ion concentration determined colorimetrically by the method of Gillespie using thymol blue as indicator.

It was necessary to cut down the rate of addition from 1000 cc. per minute to 350 cc. per minute after the first washing in order to throw down the more highly dispersed material. After the third washing a sol of fair concentration was obtained. After four washings the rate of feed was cut to $^1/_{10}$ the original value and still a considerable amount of the silicic acid was left in suspension. Practically all chlorides were removed after the sixth washing, but the wash water was still alkaline (P_{H} 9.7). After 15 washings the wash water was still alkaline and the hydrogen-ion concentration did not seem to decrease further as long as

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[12] Graham, *Phil. Trans.*, **151,** 183 (1861).

[13] Berzelius "Lehrbuch," 3rd ed., vol. 4, II, pp. 5, 122 (1883).
G. Crimaux, *Compt. rend.*, **98,** 105 (1884).
Desch, "The Chemistry and Testing of Cement," **1911, 58.**

TABLE I

WASHING THE SILICIC ACID PRECIPITATE

Washing	Rate	Precipitate	Total volume of water	Alkalinity of wash water	Nature of wash water discharged
	Cc. per min.	Bowls full	Cc.	Cc.	
1	1000	7	5500	5.2	Fairly clear
2	350	6	4000	5.0	Slightly opalescent
3	200	5	4000	5.8	Very opalescent
4	200	4.5	4000	5.6	Considerable silicic acid in colloidal condition
5	100	4	4000	4.4	
6	100	3	3000	1.7	Practically free from chlorides
				P_H	
7	100	3	2000	9.7	Clear bluish-white sol.
8	100	2.5	2000	9.5	
9	100	2	2000	9.4	
10	100	1.7	1500	9.3	
11	100	1.5	1500	9.1	
12	100	1	1000	8.8	
13	100	1	1000	9.0	
14	100	0.75	1000	8.8	
15	100	0.5	1000	8.8	

washings were continued on the coarser non-colloidal material. The last four washings showed a hydrogen-ion concentration equivalent to P_H 8.8.

The sols discharged on the tenth and subsequent washings were poured together yielding a mixture with a Sörensen value of 9.0. One liter of this mixture was acidified by adding 7 cc. of 0.2 *M* hydrochloric acid. It was found possible to throw down the bulk of this colloidal silicic acid by prolonging sufficiently the application of the centrifugal force. This was accomplished by cutting down the rate of addition to 25 cc. per minute. As the capacity of the bowl was approximately 300 cc. each part of the sol was subjected to a centrifugal force 30,000 times gravity for 12 minutes. The silicic acid thrown down was resuspended in a liter of distilled water and washed again. The effect of the repeated washings on the hydrogen-ion concentration of the wash water is shown in Table II.

TABLE II

WASHING THE ACIDIFIED SOL OF SILICIC ACID

Rate, 25 cc. per minute

Washing	P_H	Washing	P_H	Washing	P_H
1	4.0	4	6.4	6	6.5
2	5.8	5	6.5	7	6.5
3	6.0				

The Sörensen value was readily reduced to 6.5 but seemed to be constant at that point.

Another fraction of the alkaline sol was washed using the same rate of feed as in Table II, but no acid was added. The results of this experiment are presented in Table III.

TABLE III

WASHING THE DISCHARGED SOL P_H 9.0

Rate, 25 cc. per minute

Washing	P_H	Washing	P_H	Washing	P_H
1	9.0	3	7.1	5	6.5
2	8.4	4	6.5	6	6.5

When this highly dispersed silicic acid was thrown down and repeatedly washed the hydrogen-ion concentration was readily reduced to the Sörensen value 6.5 which is identical with the value obtained when approached from the acid side. Since 6.5 seems to be the final constant value obtained whether approached from the acid or the alkaline side, it seems quite probable that this represents approximately the true Sörensen value of the colloidal silicic acid.

Physical Properties.—When the celluloid sleeve was removed after the deposition of the highly dispersed silicic acid it was found to be covered at the bottom with a rather stiff greasy white deposit which became clear and transparent and semifluid at the upper end of the bowl. In the middle of the bowl the deposit was transparent and very sticky. This material was divided into two fractions, one consisting of the white material (Sol A) and the other the more fluid transparent material (Sol B). Both were readily dispersed in distilled water forming bluish-white, very stable sols. By heating on the water-bath the sol can be concentrated to an almost syrupy consistency which can be brought back to the original sol condition by the restoration of the original water content. If the boiling is carried too far minute needle-like crystals of silicic acid separate. The sols show no tendency whatsoever to gel even in the highest concentrations. Mixtures of equal volumes of 0.2 M hydrochloric acid and of 0.2 M sodium hydroxide solution and 0.2% silicic acid are perfectly stable. Some of the silicic acid apparently goes into true solution in the alkali on long standing.

Purity of the Sol.—As noted above the sol appeared free from chlorides after 6 washings. This test was made by precipitating the silicic acid with aluminum sulfate and then treating the clear supernatant liquid with silver nitrate. This test is open to the objection that there may have been present minute traces of chlorides which were carried down by the precipitated silicic acid. A further test was made on the sol having a Sörensen value of 6.5 by adding a little sodium carbonate to 100 cc. of the sol to neutralize any free hydrochloric acid, then evaporating to dryness on the water-bath. The silicic acid was still further dehydrated by heating for 2 hours in the oven at 105°. It was then digested with nitric acid, diluted and the supernatant liquid tested with silver nitrate. The test was negative. Similar tests on standard sodium chloride solutions show that under the conditions of the test the presence of 1 part of chlorine in 4,000,000 of sol could have been detected. This result was to have been expected from the effects of the repeated washings on the reaction of the sol. The hydroxyl ion is considered highly adsorbed by silicic acid and the fact that it was so completely removed as to enable the sol to yield a slightly acid reaction is additional evidence of the thoroughness of the removal of impurities by repeated washings.

While thus far the method outlined has been used only for the preparation of colloidal ferric and aluminum hydroxides and silicic acid it would appear that with perhaps slight alterations in procedure a large number of sols of similar substances might be prepared.

The writer is indebted to Professors M. F. Miller and W. A. Albrecht for suggestions and criticisms.

Summary

1. A method is described for preparing colloidal ferric hydroxide, aluminum hydroxide and silicic acid from the fresh precipitates of these substances by the removal of the excess of precipitating agent by thorough washing by means of a supercentrifuge.

2. This method appears to have certain advantages over the older methods: (a) the removal of the electrolytes formed on precipitation is more complete; (b) the addition of a peptizing agent and its consequent incomplete removal by either prolonged dialysis or boiling is unnecessary; (c) sols of a more uniform degree of dispersion can be prepared, since particles of similar size and of similar degrees of hydration are deposited in the same zone in the centrifuge bowl; (d) sols of any desired concentration from a semi-gel to the merest trace can be prepared by the addition of water to the more concentrated form, and all concentrations are very stable; (e) while the method thus far has been used for the preparation of colloidal iron and aluminum hydroxides and silicic acid only, it would appear that with perhaps slight alterations in the procedure a large number of sols of similar substances might be prepared.

3. Aluminum hydroxide precipitated by ammonium hydroxide in the presence of an excess of sulfate ion is not irreversible.

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