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THE INFLUENCE OF THE AGE OF FERRIC ARSENATE ON ITS PEPTIZATION.

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Precipitates to be peptized into colloidal suspension are often made up in large quantities and used at different intervals. It is obvious that with increasing age of the precipitate more peptizing agent may be required. Furthermore the rate of change may not be uniform. Any quantitative study of peptization must begin with experiments similar to those described in this paper. These experiments dealt with the age factor in the peptization of ferric arsenate by ferric chloride.

I. Methods of Work.

All the samples of ferric arsenate were made by adding 3 cc. of 5 *N* ferric chloride from a buret to 17.6 cc. of 0.5 molal disodium arsenate contained in a 125 cc. bottle. This bottle was tall and narrow, of the type used for oil samples, and well adapted for use in a shaking machine. The actual amount of ferric arsenate precipitate in this mixture was 1.32 g. It is evident that this method of precipitation secured greater uniformity than if an attempt were made to weigh out equal portions from a wet precipitate.

The shaking machine devised held 6 bottles and was run by an electric motor to give 180 shakes per minute. As soon as the precipitates were made they were shaken 3 minutes as timed by the stopwatch. After this thorough mixing they were peptized immediately by further addition of ferric chloride or set aside to age before peptization. This addition of extra ferric chloride as peptizing agent did not, in all cases, clear up the precipitate in the 6 minutes of shaking. Precipitates one hour old or less yielded to this treatment, but older precipitates sometimes stood several hours after the attempt to peptize before the ferric chloride had sufficiently diffused into the mass. Experience taught us to wait 24 hours before deciding whether peptization was complete. In all these experiments the bottles were tightly corked to prevent evaporation.

II. Amount of Ferric Chloride Required to Peptize a Fresh Precipitate.

To determine the exact amount of ferric chloride needed to peptize a fresh precipitate we added 5 *N* ferric chloride in varying volumes to separate bottles, each containing 17.6 cc. of 0.5 molal disodium arsenate. The bottles were then shaken 6 minutes which allowed 3 minutes for the usual mixing and 3 more for further peptization. For example, we added 4.4 cc., 4.5 cc., etc., up to 4.9 cc. of ferric chloride. Since we considered 3 cc. of ferric chloride the amount necessary to form the precipitate of ferric arsenate, this volume (3 cc.) was subtracted from the total volume added to indicate the amount needed for peptization.

The product obtained by the addition of a total volume of 4.7 cc. of ferric chloride was a beautiful red colloid of splendid, fiery "bloom" in transmitted light but of a dull, muddy appearance in reflected light. When less than 4.7 cc. was used partial peptization resulted, the mixture becoming gelatinous in a few hours, but with more than 4.7 cc. the colloid was clear with no bloom and with depth of color increasing in direct proportion to the excess of ferric chloride. Repeated attempts to secure exact peptization by using a very small amount more or less than 4.7 cc. of ferric chloride failed; hence we concluded that 1.7 cc. of excess ferric chloride (4.7 cc. total volume less 3 cc. to form the precipitate) was just enough to peptize 1.32 g. freshly precipitated ferric arsenate. Practically the same results were obtained by first adding 3 cc. to form the precipitate, shaking 3 minutes, and then adding the excess ferric chloride for peptization.

III. Amount of Ferric Chloride Required to Peptize Older Precipitates.

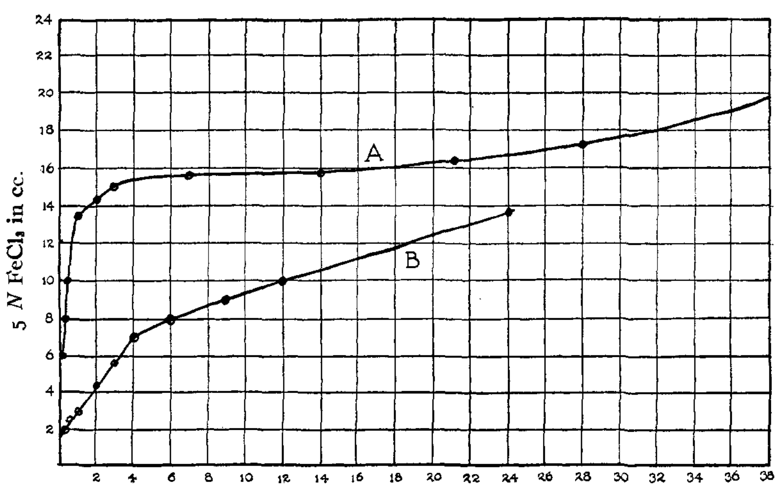
In order to determine the amount of 5 *N* ferric chloride required to peptize a precipitate a day old, for example, a series of trials was always made, so that while some samples were not completely peptized, others contained more than enough of the peptizing agent. By this tedious process all the results in Table I and Fig. 1 were obtained.

TABLE I.

Relative volumes of $5N$ $FeCl_3$ required to peptize equal amounts of ferric arsenate of different ages.

Age of Precipitate.	Volume of 5 N $FeCl_3$. Cc.
Fresh	1.7
15 minutes	2.0
30 minutes	2.5
1 hour	2.8
2 hours	4.5
3 hours	5.7
4 hours	7.0
6 hours	8.0
9 hours	9.0
12 hours	10.0
24 hours	13–14
2 days	14.5
3 days	15.0
7 days	15–16
14 days	15–16
21 days	16–17
28 days	17–18
56 days	23–25

The values corresponding to ages of fifteen minutes to two hours may be in error to the extent of about 0.3 cc. of the peptizing agent and the error may be as great as one or two cc. when the age of the precipitate varied from two days to two months. Fig. 1 shows the same results graphically. Curve A is plotted in days and Curve B in hours.



Days for Curve A, Hours for Curve B.

Fig. 1.

Volumes of 5 N ferric chloride required to peptize equal amounts of ferric arsenate of different ages.

The increase in the amount of peptizing agent is regular and rapid up to the age of 4 hours when there is a slowing up of the rate of increase. When measured in days as in Curve A it is to be noted that the effect of age of the precipitate is greatest during the first 24 hours and after that age is very much less. Curve A flattens rather suddenly after it reaches the two-day point. For example, reference to Table I shows that while 14 cc. of ferric chloride were required to peptize the one-day old precipitate only 18 cc. was required to peptize an equal weight of a one-month old precipitate. This is exactly the change (18 cc. less 14 cc.) produced by aging from fresh to three hours (5.7 cc. less 1.7 cc.) yet a whole month was required to produce it.

Discussion.

It is evident that any attempt to compare peptizing effects must be made with fresh precipitates or, if that is not convenient, after they have aged two or three days.

Highly hydrated precipitates such as ferric arsenate change phase on standing, becoming less hydrated and therefore making diffusion of peptizing agents more difficult. In the case of ferric arsenate this change of phase is evidently most rapid in the first day or two. After that there is a comparatively slow further change, not great in extent. Furthermore the smaller particles unite to form larger aggregates which, of course, expose less surface to the action of peptizing agents, consequently slowing up the rate of peptization.

It was suggested to us that after a precipitate aged two days or more it should be possible to peptize it with 1.7 cc. of ferric chloride (the amount needed by a fresh precipitate of ferric arsenate) if this solution were added slowly enough and given plenty of time for diffusion. Not only was this not true but when 9 cc. of 5 N ferric chloride was added in 0.5 cc. portions during 6 days the precipitate was far from peptized after two weeks' standing. To one precipitate aged 12 hours there were added in small portions 5 cc. of 5 N ferric chloride. It was shaken at intervals and after 5 weeks was not completely peptized. To another sample which had stood 4 weeks we added 50 cc. of 5 N ferric chloride. It was shaken 6 minutes and after 5 hours was not peptized satisfactorily—very different from the action of 1.7 cc. on a fresh precipitate. In all cases of standing to age the bottles were tightly corked to prevent evaporation.

Since ferric phosphate is very similar to ferric arsenate in its colloidal relations as shown by Holmes, Rindfusz and Arnold[1] it seemed advisable to compare the two in this series of experiments. While 3.2 cc. of 5 N ferric chloride was required for peptization of a given weight of fresh ferric phosphate only 5 cc. was required to peptize a precipitate that had stood 4 weeks. When ferric arsenate had aged 4 weeks, 8 times as much

[1] THIS JOURNAL, 38, 1970 (1916); 40, 1014 (1918).

ferric chloride was needed for peptization as by a fresh sample. The explanation of this difference is that the change of phase of ferric phosphate to a less hydrated condition and its agglutination is far slower than that with ferric arsenate. Hence there is only a slow change in the amount of surface exposed and in resistance to diffusion. When samples of the two precipitates are allowed to stand a long time ferric arsenate becomes very compact and is difficult to shake loose from the walls of the bottle while ferric phosphate remains more "mushy" and does not become compact in an equal time.

Ferric arsenate can be peptized by ammonium hydroxide or sodium hydroxide as well as by ferric chloride. A limited number of age experiments were tried using these two peptizing agents. The results in general were very similar to those obtained with ferric chloride.

Summary.

The amount of ferric chloride required to peptize a given weight of ferric arsenate rapidly increases if the precipitate is allowed to age before peptization—up to an age of one or two days. After this there is only a very small increase in the amount of ferric chloride needed even if the precipitate is allowed to stand a month before peptization.

The explanation is found in a decrease in hydration of such a precipitate as ferric arsenate—rapid during the first day and slow afterwards; also in the formation of larger aggregates with a consequent decrease in external surface of the particles. Both influences retard diffusion of a solution of a peptizing agent and greatly check the rate of peptization.

Similar results were obtained using ammonium hydroxide and sodium hydroxide as peptizing agents instead of ferric chloride.

Ferric phosphate, changing its degree of hydration more slowly than ferric arsenate and also forming larger aggregates more slowly, exhibits a different peptization curve. The increase in the amount of ferric chloride required to peptize such a precipitate is much slower from the first.

In general, quantitative peptization studies with hydrated precipitates must be made with fresh precipitates or, if that is not convenient, must be preceeded by experiments similar to those above described in order to learn for each substance when the change in its resistance to peptization becomes negligible.

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