

point at any time by taking the reading of the position of the interference bands from the fixed mirror. As a reference point, it was found to be almost as convenient to use the interference bands reflected from the surface of the plate glass covering the gage. However, they were less intense than those reflected from the silvered mirror. If the gage cannot be mounted rigidly in a fixed position, two mirrors may be attached to opposite sides of the diaphragm so that they rotate in opposite directions. If the mirrors are so attached that the line joining the centers of the mirrors is perpendicular to the line joining the points of attachment to the diaphragm, then one optical system will do for both mirrors. The pressure, then, may be measured in terms of the distance between the two sets of interference bands.

Summary and Conclusions

A very simple optical system was constructed, by means of which it was possible to measure deflections of a three-meter optical lever with an average error of about 0.003 mm. An all-glass optical lever pressure gage was constructed. It had an average observational error of 0.006 mm. pressure and withstood an atmosphere pressure in either direction. A much more delicate gage had an average observational error of 0.0002 mm. pressure.

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THE PREPARATION OF NEPHELOMETRIC TEST SOLUTIONS

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The nephelometer, devised by Richards¹ and now employed in many atomic weight determinations, serves to compare the light reflected by two silver halide suspensions. These suspensions are formed in measured samples of the supernatant analytical solution, which is saturated with respect to the silver halide, by the addition of a known excess of silver ion in one case and an equivalent amount of the halide ion in the other. That the chief source of error in these nephelometric measurements resides in the preparation of the suspensions was fully recognized by Richards,² who laid great stress on the necessity of precipitating the two suspensions under conditions as nearly identical as possible.

No systematic study³ has been made of the effect on the reproducibility

¹ Richards, *Proc. Am. Acad. Arts Sci.*, 30, 385 (1894); Richards and Wells, *Am. Chem. J.*, 31, 235 (1904); THIS JOURNAL, 27, 502 (1905).

² Richards, *Am. Chem. J.*, 35, 511 (1906).

³ See P. V. Wells, "The Present Status of Turbidity Measurements," *Chem. Reviews*, 3, 331 (1927).

of these suspensions of the many factors involved in their preparation. However, since the rate of addition of the precipitant and the manner of mixing it with the saturated solution would influence the number of particles formed in the suspension, it is conceivable that many of the irregularities met with in nephelometric observations are due to slight variations in one or both of these conditions.⁴ A number of experiments which bear out this viewpoint will be described briefly in this note.

A saturated solution of pure silver chloride was prepared as follows. A dilute solution of pure silver nitrate was added slowly to a dilute solution of pure hydrochloric acid. After the resulting precipitate had been washed repeatedly with twice distilled water to remove the excess chloride, it was allowed to stand in a solution of 0.5 *M* nitric acid. Frequent shakings over a period of time were considered sufficient to saturate the acid solution. The above operations and all subsequent ones involving this solution were carried out in a dark room illuminated only by red light.

For precipitating the suspensions standard solutions were made up in the usual way. The silver solution contained 1.00 mg. of silver per ml. and the chloride solution contained an equivalent amount of chloride ion.

Nephelometric test solutions were prepared by mixing 20 ml. of the saturated solution and 2 ml. of the precipitant. Unless otherwise specified, samples of the first solution were always measured by means of a transfer pipet and those of the second from a buret. The precipitation of the suspensions in these test solutions was performed by three different methods which will be designated as pouring, stirring and instantaneous, and which are described briefly below.

Pouring (P).—The two solutions were measured out into separate nephelometer test-tubes. The saturated solution was then poured directly into the precipitant and the resulting solution was decanted back and forth between the two tubes to insure thorough mixing. This process apparently was first described by Stas.⁴

Stirring (S).—In this case the precipitant was added directly to the sample of the saturated solution and the two solutions were then mixed by stirring with a glass rod provided with a small glass ring at the lower end. This method was used by Richards, who considered it superior to that of Stas because it afforded more efficient mixing and also because it lessened the danger of contamination.

Instantaneous (I).—This third, new method was tried because it appeared to offer a means of obtaining a more uniform addition of the

⁴ Richards evidently considered this question, for he states [*Am. Chem. J.*, 31, 239 (1904)]: "This procedure obviates any possible inconsistency arising from unequal speed of precipitation—a matter to be discussed in a subsequent paper." This paper, so far as the author can ascertain, was not published.

precipitant and also more rapid mixing of the two solutions. The device used is shown in Fig. 1. The outer tube was approximately 160 mm. \times 28 mm.; the inner tube was 80 mm. \times 10 mm. and was sealed together about 35 mm. from the top to form a small cup. Into the outer tube the sample of the saturated solution was delivered from a pipet. The cup, the top edge of which was above the surface of this solution, was filled with the precipitant, which was measured directly from a long-tipped buret. The drop of solution which adhered to the tip of the buret was readily removed on the bottom of the stopper. Then, with the ground-in glass stopper held firmly in place, the tube was quickly inverted and violently shaken for a short time. For comparison in the nephelometer the solution with the suspension was transferred, by pouring, to the usual nephelometer tube.

After a number of preliminary experiments involving the comparison of the suspensions prepared by the three different methods against suspensions of kieselguhr and barium sulfate as standards, the following procedure was adopted as the most satisfactory for our purpose. At one time three suspensions precipitated by one precipitant were prepared by each of the three methods. At fixed time intervals the three similar suspensions were compared with each other in the nephelometer and also one of them was compared with one suspension prepared by each of the other two methods. This procedure minimized the possibility of a serious error in the preparation of the sensitive suspensions and also eliminated any disturbing effects arising from a variation in temperature.

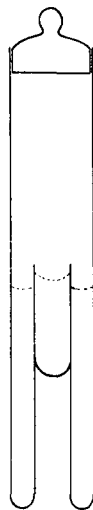


Fig. 1.

The turbidities of the suspensions prepared by the three methods, using silver or chloride ion as the precipitant, were consistently different. The general order of magnitude of the variations found is given below, the (I) turbidity being taken as a standard of reference:

(I)	(P)	(S)
1.0	1.4	1.6

These values represent the relative turbidities after the suspensions had been standing almost two hours. As a rule the turbidity of a suspension underwent very little change after the first hour.

The extreme variations in the turbidities of the different types of suspensions originate apparently in the speed with which the precipitant is added to the saturated solution rather than in the rate of mixing of the two solutions, for the latter factor is very much the same in the (I) and (P) methods. Indeed, the relative turbidities reflect roughly the relative speeds of adding the precipitant to the other solution, the more rapid rate resulting in the weaker turbidity. This conclusion would indicate

that the rate of mixing is a subordinate factor in determining the turbidity of a suspension.⁵

Originally it was hoped that the procedure adopted would furnish some information regarding the reproducibility of the turbidities obtainable by the different methods. Unfortunately, the data available are insufficient for a decisive answer to this question. In general, however, the order of decreasing reproducibility was, for both precipitants (P)—(S)—(I). This result is understandable in terms of our previous conclusion because in the (I) method a slight variation in technique would result in a relatively large change in the rate of adding the precipitant and thus would cause a large percentage change in the turbidity of the suspensions. The intermediate position of the (S) method is also understandable on the same ground when it is noted that, although considerable care was taken to insure uniform stirring, no particular attention was paid to the rate of delivery of the precipitant from the buret. At the conclusion of the investigation, to see whether the rate of addition in the case of the (S) method could affect the turbidity of the resulting suspension, the following experiments were tried. Three suspensions were prepared at one time by adding the precipitant from a pipet (A) as rapidly as possible, (B) dropwise with moderate rapidity, and (C) dropwise, very slowly. In each case the solution was promptly stirred after all the precipitant was added. The relative turbidities, using that of (A) as a basis, were:

Precipitant	(A)	(B)	(C)
Chloride	1.0	1.2	1.2
Silver	1.0	1.4	1.4

From these data it is quite obvious that a serious variation in the turbidity of a suspension can be induced by too rapid addition of the precipitant. On the other hand, when the rate of addition is fairly slow, there is a wide range in the speed of adding the precipitant, which results in the same turbidity.

Since the (S) method is the one commonly used in atomic weight investigations, the above results suggest the origin of many of the unaccountable inconsistencies which are found in making comparisons of the turbidities of the two suspensions, for the manner of adding the precipitant appears to be more significant than the stirring operation. Consequently, it is possible that a pipet would be superior to the customary buret because the rate of delivery of the standard solution can be controlled more readily.

⁵ Kleinmann, *Biochem. Z.*, **99**, 149 (1919), studied the formation of silver chloride suspensions on the addition of sodium chloride solutions to a solution containing a slight excess of silver nitrate. Controlling the rate of addition of the precipitant and also the speed of stirring, he found the first factor was by far the more important in determining the turbidity of the resulting suspension. He likewise found that the more rapid addition of the precipitant resulted in a weaker turbidity.

Otherwise, according to the present evidence the (P) method is to be preferred.

The foregoing tests were made with a saturated solution of silver chloride which differed in one essential respect from the solutions examined in atomic weight investigations. In the latter case the saturated solution always contains, in addition to nitric acid, an extra ion introduced by the hydrolysis of the halide sample being analyzed. To determine whether this extra ion would modify in any way the results obtained with the acid solution, a new series of experiments was carried out with a saturated solution of silver chloride which was 0.5 *M* with respect to cadmium nitrate and also 0.1 *M* with respect to nitric acid. Only one divergence in the general results was noticed. When the precipitant was the chloride ion, the sequence of decreasing reproducibility of turbidities by the various methods was clearly (I)—(S)—(P).

This reversal in sequence is so marked as to be noteworthy. As a possible basis for its explanation it is allowable to suggest the phenomenon of adsorption. In the first place the apparent abnormality occurred only in the case of the negatively charged sol which can adsorb the positive cadmium ion. In the second place it is known³ that adsorbed material can inhibit or "poison" the growth of precipitated nuclei. Indeed, some evidence of this effect has already been noted in atomic weight investigations. Thus, Hönigschmid and Birkenbach⁶ in their analysis of bismuth trichloride found that the suspension precipitated with silver developed much more rapidly than that precipitated by chloride. Again in the study of the Ag:Br ratio Hönigschmid and Zintl⁷ observed a decided difference in the rate of precipitation of the two suspensions. In this case the solution tested contained both arsenious and arsenic acids.

If adsorption is involved, as we have supposed, in the formation of a suspension and therefore in its ultimate turbidity, one consequence can be pointed out. Since the effect of adsorption can influence only one suspension, it may act under certain conditions to accentuate irregularities in the rate of adding the precipitant, especially if the nephelometric comparison is made after an arbitrary period of time. The effect in question would depend primarily on the specific nature of the extra ion. In this phenomenon of adsorption we have, therefore, another factor which contributes to the well-known sensitiveness of nephelometric suspensions to the conditions attending their preparation. In conclusion it may be suggested that in some cases one of the three methods of adding the precipitant may be decidedly superior. Each case, however, would have to be examined individually.

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⁶ Hönigschmid and Birkenbach, *Ber.*, **54B**, 1873 (1921).

⁷ Hönigschmid and Zintl, *Ann.*, **433**, 224 (1923).