THE INDIRECT WEIGHING OF QUANTITATIVE PRECIPITATES. A RAPID AND ACCURATE METHOD FOR DETERMINING THE WEIGHT OF A PRECIPITATE WITHOUT SEPARATING IT FROM THE LIQUID FROM WHICH IT WAS PRECIPITATED.

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THANKS to the precision of the modern analytical balance, a gravimetric analysis, which consists essentially in the conversion of a weighed quantity of the substance to be assayed into an insoluble form, freeing it from impurities by washing, and drying and weighing it in the new form, is a process which is exact almost to the limit of perfection. But the difficulties in the way of properly preparing the material in a pure condition for subsequent weighing are many. The tendency of many precipitates to dissolve in the liquid used for washing out impurities, the mechanical adhesion of these impurities to the precipitated substance, and finally the difficulty of separation of the precipitate from the filtering medium, are too familiar to every analyst to need emphasis here. Many devices have been resorted to in order to obviate the errors arising from these causes, with the general result that an accurate gravimetric analysis is a process which requires considerable time for its completion and great care in its manipulation.

The disadvantages just alluded to have resulted in a very general attempt to devise volumetric methods which can be carried out with more ease and rapidity. Generally speaking, however, these volumetric methods, which are based upon the measurement of volumes of liquids which are known to contain definite proportions of the materials to be used, are open to serious criticism because of their inherent sources of error. Inaccuracies in calibration of the measuring apparatus, fluctuations in volume of solution due to changes in temperature, and changes in the composition of the dissolved material, give rise to serious errors, which are difficult to prevent and which greatly impair the value of this method of analysis.

It is obvious, therefore, that neither of these two classes of methods can be said to possess both of the requirements of an

ideal method of analysis, *viz.*, accuracy and rapidity. The desirability of some simple method by means of which the weight of a precipitated substance could be accurately determined without the necessity of first completely separating it from the liquid from which it was precipitated is apparent. Such a method would have the accuracy of a gravimetric process, without its attendant objectionable features, and would be more accurate than many of the volumetric methods. So far as I have been able to learn, no such method has been suggested up to the present time. That the operation is possible, however, is shown by the discussion below. That it is not only possible, but practicable and capable of wide application, is shown by the analytical data presented in a subsequent portion of this paper.

THE THEORETICAL DISCUSSION OF THE PROPOSED METHOD.

The formulas which are given below are based on facts which are so well known as to seem axiomatic; namely, that the weight of any substance is equal to its specific gravity times its volume ; and conversely, that the volume of any substance is equal to its weight divided by its specific gravity.

If now a certain definite volume (which may be represented by b) of a mixture of a liquid and a solid, or precipitate, be weighed, the weight thus obtained is obviously equal to the sum of the weights of the liquid and the precipitate. Or, if the weight found be represented by a and that of the precipitate and liquid by x and y respectively, then

$$a = x + y. \qquad (1)$$

Now the weight of the liquid v is, as was stated above, equal to its volume times its specific gravity. Its volume is obviously the total volume of the mixture minus that of the precipitate, and the volume of the precipitate is its weight divided by its specific gravity. Or, if we represent the volume of the precipitate by v, and that of the liquid by v', and their specific gravities by d and d' respectively, then

$$y = v'd', \qquad (2)$$
$$v' = b - v, \qquad (3)$$
$$v = \frac{x}{d}. \qquad (4)$$

Combining 2, 3, and 4, we have

$$y = \left(b - \frac{x}{d}\right) d'. \qquad (5)$$

Substituting this value for y in (1) the formula becomes

$$a = x + (b - \frac{x}{d})d', \qquad (6)$$

or

$$x = \frac{d(a - bd')}{d - d'}. \qquad (7)$$

In this formula a, the total weight, and b, the total volume, are known ; d, the specific gravity of the precipitate, is constant for precipitates of the same substance and can be determined once for all ; and d', the specific gravity of the liquid, can easily be determined. From these factors the value of x, the unknown weight of the precipitate, can be calculated.

From the above discussion it appears that in order to determine the weight of any precipitate without separating it from the liquid from which it was precipitated, it is only necessary to transfer the mixture to a vessel, the exact volume and weight of which is known ; weigh the whole; then draw off a portion of the liquid and determine its specific gravity. From this data and the known specific gravity of the precipitate, the weight of the latter can easily be calculated by means of the formula given above. This formula is a general one, and the process is, therefore, applicable to all precipitates of which the specific gravity is known or can be determined. The one condition by which its application is limited is, that the specific gravity of the precipitate must be constant, or, in other words, that the precipitate must always have the same composition. Most quantitative precipitates are of definite and invariable composition and hence meet this requirement. A few, however, vary in character with varying conditions of precipitation. This method of procedure could be used for determining the weights of such precipitates only when the conditions under which they were formed were so controlled as to insure uniformity in the composition of the precipitate.

Furthermore, the same formula, or modifications of it, will serve for other purposes. For example, if a known quantity of some substance is so treated as to produce a known weight of precipitate the specific gravity of the latter may be determined by a process identical with that described above. In this case x, the weight of the precipitate, will be known and d, its specific gravity, unknown. In order to simplify the calculation, the formula may be rearranged as follows :

$$d = \frac{d'x}{bd' + x - a}. \qquad (8)$$

Since no very satisfactory method for determining the specific gravity of solids in finely divided or amorphous condition has heretofore been proposed, the importance of this application of the formula is apparent. It is especially valuable in determining the specific gravity of those precipitates which decompose or change in composition during the washing and drying which is necessary in order to obtain them in a pure form.

Again, in case a substance can be readily obtained in pure condition, its specific gravity may be easily determined by placing a weighed quantity of it in the weighing-bottle and filling the latter with pure water, and weighing the whole. Since the specific gravity of the liquid in this case is known, no further data need be determined. The specific gravity of the solid can be computed from the formula (8), d' being a constant (i. e., the specific gravity of water at the temperature at which the weighing is made), and bd' likewise a constant for the same weighing-bottle.

Further, since this method of determining specific gravity can be carried out very rapidly, it may serve as a means of determining the rate of change in composition of certain variable precipitates, as, for example, the rate of dehydration of the hydrated oxides of aluminum or iron. Some data bearing on this application of the formula was accidentally accumulated during the investigations upon the accuracy of this method of obtaining weights of precipitates, and will be published at some later time.

METHODS OF OPERATION.

Briefly stated, the principle upon which this new method for determining the weight of quantitative precipitates is based, is that if the weight of a definite volume of a mixture of two substances, whose specific gravities are known, be determined, the proportion of each which is present in the mixture may be calculated. An indirect determination of the weight of a precipitate without previously separating it from the liquid from which it was precipitated, based upon this principle, consists of the following processes : first, a determination of the weight of a measured volume of the precipitate and mother-liquor ; second, the separation of a correct sample of the liquid from the precipitate ; third, a determination of the specific gravity of this liquid; and fourth, a calculation of the weight of the precipitate by means of the

formula described above. A previous knowledge, or determination, of the specific gravity of the precipitate is, of course, necessary. The details of these operations and precautions to be observed in each are described below.

Specific Gravity of the Precipitate.—It should be noted that the same accuracy in the determination of the specific gravity of the precipitate as in that of the liquid is not necessary. In practical work with such mixtures, the relative amount of precipitate present will always be small and any inaccuracy in the determination of its specific gravity will produce a correspondingly small error.

None of the methods which have been proposed for the determination of the specific gravity of a solid substance are very well adapted to work with finely divided or amorphous precipitates. Determinations based upon the loss of weight of the material when immersed in a liquid require the preparation of the substance in a perfectly pure and dry condition, which in itself is as difficult as the preparation of such precipitates for quantitative analysis, and the use of specially constructed apparatus. Methods based upon a measurement of the volume, or displacing power, of a weighed quantity of the substance are exceedingly unsatisfactory when applied to substances in powdered form, because of their tendency when dry to enclose air. It was found that methods based upon the use of the new formula as arranged for specific gravity (8) afforded by far the most satisfactory method for this purpose. As has been pointed out, this formula may be applied in two ways : first, by using a known amount of the material with pure water as the liquid for completing the desired volume, and second, by producing a known amount of the desired material by precipitation, weighing the mixture, and afterward determining the specific gravity of the liquid.

In all the following work a Geissler specific gravity bottle, or pycnometer, with a thermometer ground in as a stopper and a capillary overflow tube provided with a glass stopper, was used as the vessel in which a definite volume of liquid, or mixture of solid and liquid, was weighed. Such a pycnometer having been selected and its weight and volume once accurately determined, it can be used for a long series of determinations without the necessity of recalibration, since changes in its weight or volume are very slight, or practically none at all. Two of these pycnometers

were used, one having a capacity of approximately 100 cc. and the other of about 50 cc. These were calibrated as follows : The pycnometer was carefully cleansed and dried and its weight accurately determined. It was then filled with distilled water, which had been recently boiled and then cooled to a temperature slightly below that at which the bottle was to be calibrated. The thermometer was inserted and the temperature of the water allowed to rise slowly, the pycnometer being frequently shaken to insure uniform temperature throughout the whole. When the thermometer indicated 20° (that being adopted as the temperature most convenient for the working conditions of this laboratory), the overflow tube was closed, the outside of the pycnometer carefully dried, and the whole immediately weighed. The pycnometer was emptied, refilled, and reweighed several times until an exact knowledge of its water content at 20° was obtained. This weight was then divided by 0.998213 (the specific gravity of water at this temperature), and the result taken as the volume of the pycnometer. The weighings were all corrected for a slight difference in the length of the balance arms but were not reduced to the weight *in vacuo*, as this was not deemed necessary for the purpose of ordinary analytical work. In order to determine the specific gravity of any insoluble substance of which a quantity of pure material was available, it was only necessary, then, to introduce a weighed quantity of it into a pycnometer which had been calibrated as described above ; fill the latter with pure distilled water, properly cooled ; bring the mixture to the temperature adopted in calibration ; and complete the weighing as before. The specific gravity of the precipitate was then calculated from the formula. If the substance in question was in the form of a dry powder a little water was added to it after it had been weighed and the mixture stirred thoroughly to insure complete wetting of the material and exclusion of enclosed air bubbles. In case no supply of pure material of the substance whose specific gravity was to be determined was available, or could be prepared only with difficulty, the process was carried out exactly as will be described below for the indirect weighing of precipitates. In this case it was necessary to start with a known amount of some soluble material which was subsequently quantitatively precipitated in the desired form. The details of the method will appear in a subsequent paragraph.

Loevinsohn[1] has shown that the state of subdivision or mass of a substance has no effect upon its specific gravity, hence it is only necessary to insure that the composition of the precipitate shall be invariable in order that its specific gravity shall be constant, no matter what the conditions under which it was precipitated may be. The specific gravity of any invariable quantitative precipitate having been once accurately determined, this factor may be used for all subsequent indirect determinations of the weight of precipitates of this substance.

Weight of a Definite Volume of the Mixture.—Any apparatus, the exact volume of which is known, might serve as a weighing-bottle for the mixture, but since the volume and, conversely, the specific gravity of a liquid are affected by changes of temperature, a means of controlling or determining the latter is essential. A very small neck or opening which may be closed, in order to prevent evaporation of the liquid during weighing, is also very desirable for accurate work. The Geissler specific gravity bottle already mentioned is admirably suited to these needs.

The weighing-bottle having been prepared, the substance to be weighed was precipitated according to the method used in the ordinary analysis. After precipitation was complete, the mixture was cooled to a temperature slightly below that at which the pycnometer was calibrated. (The total volume of the mixture should not exceed two-thirds that of the pycnometer. If greater than this, the excess of liquid was removed by drawing it off through a filtering pipette.) A funnel with a short stem was placed in the neck of the pycnometer and the precipitate and mother-liquor were washed into it by means of a fine jet of cold water. After the precipitate was all washed in, the volume was completed with water which had been properly cooled, the water being allowed to flow down the sides of the pycnometer so as not to disturb the precipitate below and cause it to rise in the neck of the bottle. A very small amount of certain precipitates will rise to the surface by "creeping." In case this occurred, the material on the surface of the liquid was gently tapped with the bulb of the thermometer several times before inserting the latter. This generally sufficed to cause the floating particles to settle and thus prevent any loss of the precipitate. After the thermometer had been inserted, the capillary opening was closed with the

[1] Inaug. Diss., Berlin, 1883 ; abs. in *Ber. d. chem. Ges.*, **12**, 22.

finger, the bottle inverted, and its contents thoroughly mixed by shaking, so as to insure uniformity in the dilution of the liquid. This was repeated several times while the temperature of the liquid was rising to the desired point. When the thermometer indicated 20° the pycnometer was closed, dried, and immediately weighed. Except in very rare cases, no appreciable change in temperature occurred during the weighing, since the temperature of the balance case was usually but very slightly above that of the pycnometer. The weight thus obtained minus that of the pycnometer gave that of the volume of the mixture which the latter contained.

Separation of the Liquid from the Precipitate.—In order that the sample of liquid, which was withdrawn to be used in the determination of its specific gravity, should exactly represent the composition of the whole of the liquid, it was necessary that the process be rapid enough to prevent any concentration by evaporation, that the liquid should not be diluted by coming in contact with damp or wet apparatus, and that its separation from the precipitate should be complete. The ordinary method of filtration would generally result in a change in specific gravity through evaporation, and would be a return to one of the objectionable features of the usual methods of analysis. Two methods for accomplishing the desired result suggested themselves : first, the withdrawal of the desired sample by means of a filtering pipette, and second, a mechanical subsidence of the precipitate by means of a centrifugal and subsequent drawing off of a sample of the clear supernatant liquid. The use of a filtering pipette would afford a very convenient and rapid means of withdrawing a portion of clear liquid from the mixture, if the precipitate were in granular or crystalline form, but in the case of those precipitates which tend to clog up the filter or are so finely divided as to partially pass through the ordinary filtering media, the process is much less satisfactory. Moreover most of the forms of filtering pipette which have yet been suggested are more or less difficult to clean and dry rapidly.

Hence, in nearly every determination which was made in the present work the second method of separating the liquid from the precipitate was employed. The only centrifugal which was available was an old form of the Babcock milk tester. This was used with very satisfactory results. The separation was accomplished

as follows : The mixture in the pycnometer was shaken gently to insure uniform composition of the liquid and a portion of it poured into a large, clean, dry test-tube. The latter was placed in the centrifugal and whirled until the precipitate settled completely, leaving a clear, supernatant liquid. For most of the precipitates this required less than one minute. Barium sulphate and aluminum hydroxide required a little longer, but in no case was it necessary to spin the apparatus longer than three minutes. Evaporation of the liquid during this time was, of course, very slight and could be entirely prevented by closing the test-tube with a cork. As soon as the supernatant liquid was free from floating particles of the precipitate, a sufficient amount of it to fill the smaller pycnometer was drawn up into a dry pipette and its specific gravity determined. Duplicate samples drawn from various depths in the tube showed no appreciable variation in density.

Specific Gravity of the Liquid.—The determination of the specific gravity of the liquid component of the mixture is the most critical operation in the whole process. A single computation of the weight of a precipitate by means of the new formula will suffice to show that any very large error in the fifth decimal place of the factor for the specific gravity of the liquid will produce a small error in the fourth decimal place (or tenths of milligrams) of the weight obtained. It is therefore essential that the method to be adopted for determining the specific gravity of the liquid shall be capable of giving results with considerable accuracy to the fifth decimal place. This excludes the use of ordinary areometers, specific gravity balances, etc., and limits the operator to the use of specific gravity bottles of the best form. It has been shown by many analysts, however, that the Geissler pycnometer if carefully controlled will give results which are very accurate to the fifth decimal place. Extreme care, such as is used in the best of physical-chemical operations, will give results very closely approximating the truth in the sixth place, but such accuracy as this is not necessary for ordinary analytical work.

This method of determining the specific gravity of a liquid was therefore chosen as the one best adapted to the purposes of the present work. The process of such a determination is too familiar to all analysts to need detailed description. The pycnometer was filled with the liquid in question in exactly the same manner as it

was filled with water in calibration, and weighed under the same conditions. The weight of the liquid thus obtained, divided by the weight of the same volume of water, corrected for the specific gravity of water at the temperature of the weighing, gave the specific gravity of the liquid.

Calculation.—The calculation of the weight of the precipitate from the data obtained as described above was a comparatively simple process. The factor *b* in the formula, representing the volume of the large pycnometer, is a constant which in every calculation is to be multiplied by the specific gravity of the liquid. A table showing the product obtained by multiplying this factor by each of the digits, was prepared, which greatly facilitated the calculation.

Effect of Variations in Formula for Precipitate.—The exact composition of some of the common quantitative precipitates when in the moist condition is not known, since they may contain some chemically combined water which they lose on being dried for an analysis. Such a knowledge is not absolutely necessary for the purpose of this method of determining their weight, however. If a certain formula be assumed to represent the composition of such a precipitate and its specific gravity calculated on this basis, it is obvious that a weight calculated from the specific gravity thus obtained will be correct even though the formula which was adopted does not correctly represent the nature of the substance. The error in the determination of the specific gravity will be repeated in the opposite direction in the subsequent calculation and a correct result will thus be obtained.

It is, however, absolutely essential that the nature of the precipitate shall be the same under the conditions of the determination of its weight as under those which accompany the determination of its specific gravity. For those precipitates whose composition is likely to vary with the conditions under which they are produced, the determination of their specific gravity by the same process as is to be used later in weighing is the best method to pursue, since it will obviate any errors due to change in the nature of the precipitate. As has been shown, it is possible to do this by producing the precipitate in such a manner that its weight may be known, and its specific gravity calculated by the proper arrangement of the new formula.

EXPERIMENTAL WORK.

In order to test the accuracy of the new method of obtaining the weights of quantitative precipitates and also to compare this method with the older ones with regard to simplicity of manipulation, a large number of determinations of the weights of precipitates obtained from chemically pure material by the best methods of quantitative precipitation were made.   In general those precipitates which are of considerable technical importance and which are subject to peculiar disadvantages when weighed by the usual gravimetric methods, were selected for this experimental work.

Estimation of Chlorine as Silver Chloride.—Rodwell[1] states that the specific gravity of silver chloride is 5.505 at 0° C. and 4.919 at the melting-point.   Mohr[2] gives the figure 5.7 as the specific gravity of silver chloride but does not state the conditions under which the determination was made.   Loevinsohn[3] gives the following as the average results of several determinations of the specific gravity of silver chloride in different physical forms : freshly precipitated, 5.5667 ; dried, 5.5667 ; melted, 5.5549. Schröder,[4] in his work on the molecular volume of silver chloride, obtained results for its specific gravity which varied from 5.517 to 5.594 with an average of 5.553.

These results vary so widely as to make it impossible to determine from them what the true value for the specific gravity of silver chloride is.   It was therefore necessary to make a series of determinations, in order to obtain a correct factor to be used in the subsequent work of determining chlorine as silver chloride.

Since silver chloride decomposes quite rapidly when exposed to the light, several known quantities of pure silver chloride were produced immediately before beginning this work as follows : Measured portions of a standard hydrochloric acid solution (the exact chlorine content of which had been previously determined) were precipitated with silver nitrate according to the method usually adopted for that purpose.   The precipitate in each case was transferred to a large test-tube and whirled in the centrifugal. In this way the precipitate was quickly collected in a compact mass at the bottom of the tube and the supernatant liquid could

1 *Proc. Roy. Soc.*, **25**, 280.
2 Pogg. *Ann.*, **113**, 655.
3 Inaug. Diss., Berlin, 1883.
4 *Ann. Chem.* (Liebig), **192**, 295.

be almost entirely drawn off by means of a filtering pipette without disturbing the precipitate. The latter was washed with hot distilled water in this way until the washings gave no test for silver. The pure silver chloride thus obtained was perfectly white, the process being of so short duration as to prevent any decomposition.

The precipitate was immediately washed into a pycnometer, the latter filled with pure distilled water and weighed under the conditions outlined in the previous description of the method for determining specific gravity of precipitates. The following are the results of the determinations.

TABLE I.—SPECIFIC GRAVITY OF SILVER CHLORIDE.

	Hydrochloric acid taken. cc.	Silver chloride equivalent. Gram.	Calculated specific gravity.
1	30	0.4573	5.5591
2	40	0.6098	5.5561
3	35	0.5335	5.5455
4	45	0.6860	5.5680

Average, 5.5570

A sample of chemically pure sodium chloride was finely pulverized, dried in an air oven at 120° for an hour, and several samples of this powder weighed out for analysis. Each weighed sample was dissolved in distilled water, the solution heated to boiling, and the chlorine precipitated by silver nitrate solution, according to the usual method. The mixture was then cooled down to about 18°. It was then washed into the large pycnometer, brought to the proper temperature, and weighed. The precipitate settled so completely during the weighing that it was not necessary to whirl the mixture in the centrifugal in order to obtain a clear liquid for the specific gravity determination. After weighing, therefore, the mixture was cooled slightly, a portion of the clear supernatant liquid drawn off, transferred to the smaller pycnometer, weighed as soon as it reached the proper temperature, and the specific gravity calculated. From these data the weight of the silver chloride found was calculated. The following are the results which were obtained :

TABLE II.—DETERMINATIONS OF CHLORINE IN SODIUM CHLORIDE.

	Sodium chloride taken. Grams.	Silver chloride found. Grams.	Chlorine equivalent. Gram.	Chlorine found. Per cent.
1	0.8164	1.9998	0.4946	60.58
2	1.0205	2.5085	0.6202	60.76
3	1.0342	2.5320	0.6262	60.56
4	0.6186	1.5233	0.3757	60.73
5	0.4823	1.1851	0.2931	60.76
6	0.6877	1.6899	0.4179	60.75

The theoretical amount of chlorine in sodium chloride is 60.60 per cent. The results shown above are therefore within the limit of experimental error. They are no better than may be obtained by the ordinary methods of weighing, however. These determinations were the first that were made by the new process and it is probable that with more experience in manipulation better results would have been obtained. The process, however, does not offer any especial advantage over the usual gravimetric analysis in the case of a precipitate which is so easily prepared for weighing as is silver chloride. Should some substance which would render the washing of the precipitate tedious or difficult to complete be present in the solution, this new method might be of value.

Estimation of Sulphur as Barium Sulphate.—Several determinations of the specific gravity of barium sulphate by the older methods have been published. Mohr[1] gives 4.446 as the result obtained when the dried precipitate was used. Karsten[2] used ignited material and obtained 4.2003 as its specific gravity. Rose[3] made two determinations, using freshly precipitated salt with an average result of 4.5262. Schröder,[4] during his work on molecular volumes, made several determinations under different conditions and gives results varying from 4.022 to 4.512 with a mean value of 4.330. Wiedemann[5] made four determinations, using water at 14.9° as the standard of comparison. He obtained very concordant results, the average being 4.3962. None of these results being satisfactory for the present work, preliminary determinations of the specific gravity of barium sulphate were necessary. A quantity of pure barium sulphate was dried in the

[1] See Böttger's " Tabell. über dem Spez. Gew. Körpern."
[2] Schweigger's *Journal*, **65**, 394.
[3] Pogg. *Ann.*, **75**, 409.
[4] *Ibid.*, **106**, 226.
[5] *Ibid.*,[3]. **15**, 371.

oven at 140° and varying amounts of this material were weighed out for the determination of specific gravity. Each weighed portion was washed into the pycnometer and the latter filled with distilled water and the determination of specific gravity completed as usual. The following results were obtained:

TABLE III.—SPECIFIC GRAVITY OF BARIUM SULPHATE.

	Barium sulphate taken. Grams.	Calculated specific gravity.
1	3.7251	4.2982
2	1.6317	4.3330
3	2.0868	4.3225
4	1.2738	4.3293
5	3.0931	4.3000
6	2.8593	4.2791
7	1.7795	4.3062
		Average, 4.3098

The factor 4.31 was assumed as representing the correct value for the specific gravity of barium sulphate and was used in all subsequent determinations of the weight of precipitates of the latter.

A quantity of chemically pure potassium sulphate was finely pulverized, dried in the air-oven, and cooled in a weighing-bottle. Six samples were weighed out from this bottle into separate beakers. Each sample was dissolved in distilled water, 10 cc. of concentrated hydrochloric acid added, the solution heated nearly to boiling, a slight excess of barium chloride solution added, and the mixture boiled for a few minutes. After standing for a short time a part of the clear supernatant liquid was drawn off so as to reduce the total volume to about half that of the large pycnometer. The remainder of the mixture was then cooled, washed into the pycnometer, and the latter filled and weighed as usual. After this weighing the liquid in the pycnometer was thoroughly mixed by shaking, then poured into a large test-tube, the latter placed into the centrifugal and whirled until the precipitate had completely subsided. This required two or three minutes and the temperature of the liquid was raised several degrees. As soon as the supernatant liquid became clear, a portion of it was drawn off, cooled, transferred to the smaller pycnometer and its specific gravity determined. From the data thus obtained the weight of the barium sulphate precipitate was calculated. The following are the results obtained:

TABLE IV.—DETERMINATIONS OF SULPHUR IN POTASSIUM SULPHATE.

	Potassium sulphate taken. Grams.	Barium sulphate found. Grams.	Sulphur equivalent. Gram.	Sulphur found. Per cent.
1	2.4887	3.3581	0.4612	18.53
2	2.8379	3.8583	0.5299	18.67
3	2.2032	2.9823	0.4096	18.58
4	0.9574	1.2759	0.1753	18.32
5	0.6000	0.8063	0.1107	18.45
6	0.6459	0.8664	0.1190	18.42

The theoretical amount of sulphur in potassium sulphate is 18.40 per cent.

The determinations recorded above are all that were made by the new method and may therefore be regarded as showing what may be expected of this method in ordinary work. They show that if the amount of barium sulphate precipitated is not too large, very satisfactory results are obtained. Even with the very large amounts of precipitate obtained in Nos. 1, 2, and 3 above, the results compare very favorably with those which it is possible to obtain by the ordinary methods of weighing this precipitate. The whole process of determining the weight of barium sulphate precipitate by this method requires less than thirty minutes' time. The very difficult and tedious process of washing the barium sulphate free from impurities is unnecessary and all danger of loss of precipitate, because of its slight solubility in the water used for washing it, is avoided. This method as applied to the determination of the weight of a precipitate of barium sulphate may therefore be carried out with very much more rapidity and is much less susceptible to error than any of the methods now in use.

Estimation of Calcium as Calcium Oxalate.—The only results of determinations of the specific gravity of calcium oxalate are those published by Schröder.[1] He gives the following values for the precipitate at 4° : 2.181, 2.182, and 2.200. Previous work along this line being so meager, it was necessary to make a sufficient number of determinations to insure a very reliable average result. No pure calcium oxalate being available, a few perfect crystals of Iceland spar were selected as the starting-point for this work. These were ground to a fine powder in an agate mortar. The powder was then dried thoroughly and three portions of it weighed out into separate beakers. These were each dissolved in dilute

1 *Ber. d. chem. Ges.,* **12**, 561.

hydrochloric acid, the solution heated to boiling, ammonia and a slight excess of ammonium oxalate added, and the whole boiled gently for a few minutes. Souchay and Lenssen[1] have shown that under these conditions a stable precipitate having the composition $CaC_2O_4.H_2O$ is formed. These precipitates were washed by decantation, as described in the case of silver chloride, until free from chlorides, and their specific gravity determined by weighing with pure water. The results obtained are indicated by Nos. 1, 2, and 3 in the table below. From the same material a fourth portion of exactly 10 grams was weighed out, transferred to a liter flask, and dissolved in dilute hydrochloric acid. The volume was completed to the mark and four aliquot portions immediately drawn off before any appreciable change in volume due to rise in temperature had occurred. The calcium in these solutions was then precipitated as described above. The specific gravity of these precipitates was then determined by the usual method without separation from the mother-liquor. The results obtained are indicated by Nos. 4 to 7 inclusive in the table below.

TABLE V,—SPECIFIC GRAVITY OF CALCIUM OXALATE.

	Calcium carbonate taken. Grams.	Calcium oxalate equivalent. Grams.	Calculated specific gravity.
1	1.2594	1.8261	2.2524
2	1.5230	2.2083	2.2461
3	1.4184	2.0567	2.2418
4	1.0000	1.4500	2.2425
5	0.5000	0.7250	2.2528
6	1.0000	1.4500	2.2433
7	0.5000	0.7250	2.2470
		Average,	2.2465

Three aliquot portions of the solution of Iceland spar in hydrochloric acid described above were measured out, and two other samples of the finely ground material were weighed out and dissolved in dilute hydrochloric acid. The calcium was precipitated from the boiling solution by ammonia and ammonium oxalate and the precipitates allowed to stand until cool. The indirect weighing of these precipitates was then carried out as previously described, with the following results :

[1] *Ann. Chem. Pharm.*, 100, 322.

TABLE VI.--DETERMINATIONS OF CALCIUM IN ICELAND SPAR.

	Calcium carbonate taken. Grams.	Calcium oxalate found. Grams.	Calcium equivalent. Gram.	Calcium found. Per cent.
1	1.0000	1.4483	0.4000	40.00
2	0.5000	0.7266	0.2007	40.14
3	0.5000	0.7251	0.2002	40.04
4	1.0009	1.4542	0.4019	40.15
5	1.0785	1.5595	0.4207	39.97

The theoretical amount of calcium in calcium carbonate is 40.04 per cent. The results obtained are therefore well within the limits of experimental error. The weighing of the precipitate by this method does not require more than thirty minutes' time, so that a complete gravimetric determination of calcium by this method may be made in less than one hour and the results are as accurate as can be obtained by the best of the present methods. The washing of the precipitate and its subsequent conversion into carbonate or oxide by ignition are therefore unnecessary.

Estimation of Phosphoric Acid as Ammonium Phosphomolybdate. —The estimation of phosphoric acid is one of the most important as well as one of the most difficult problems which the technical analyst has to solve. Its precipitation as ammonium phospho-molybdate is now almost universally adopted, because this compound serves to effect the separation of phosphoric acid from other bodies and possesses the added advantage of being a readily subsiding precipitate. Earlier experimenters have considered that the composition of the compound is somewhat variable[1] and that its conversion into some more stable form prior to the final weighing is therefore necessary. More recently Hundeshagen,[2] in his analytical studies of this compound, has shown that its composition under all conditions, when free from molybdic acid and other impurities, is $12MoO_3.PO_4.3NH_4$. It is quite difficult to obtain the precipitate free from impurities, however, and nearly all the gravimetric methods now in use require the solution of the precipitate in ammonia and its subsequent precipitation as magnesium ammonium orthophosphate, the latter being ignited and weighed as magnesium pyrophosphate, or titrated volumetrically. There are numerous difficulties in this process. Bergami[3] is of the opinion that magnesium oxide is frequently thrown out along

[1] Fresenius' " Quantitative Analysis," p. 199.

[2] *Chem. News,* **60,** 168. 177, 188, 201. 215.

[3] Bull. 43, Division of Chemistry, U. S. Dept. Agr., p. 99.

with the phosphate precipitate, which produces too high results. Furthermore Gooch and Austin[1] found that if too much ammonium salts are present in the solution the precipitate is apt to be partially converted into a metaphosphate on ignition, which will likewise yield too high results when calculated back to phosphoric acid. These difficulties have led to numerous attempts to execute the final determination directly upon the yellow precipitate. Carnot[2] has shown that, with proper precautions, the yellow salt may be reprecipitated from its ammoniacal solution, washed dried at 100°, and weighed. This method has not come into very general use, however, since great care must be exercised to prevent loss of the precipitate during washing. Pemberton[3] has suggested a volumetric method for titrating the yellow precipitate, which has been modified by Kilgore[4] so as to yield fairly satisfactory results. It is open to the general objections of all volumetric methods of analysis, however. Kilgore's results show that within certain limits a precipitate of constant composition, free from molybdic acid, may be obtained. The new method is, therefore, applicable to this precipitate. Its desirability is apparent, since it will avoid the danger of loss of the material, because of its slight solubility in the wash-water, and at the same time afford a simple gravimetric method for determining the weight of the precipitate.

No determinations of the specific gravity of this yellow precipitate have yet been published. It was therefore necessary to accurately determine this factor before attempting to test the applicability of the new method to the weighing of this precipitate. Two methods of procedure were adopted. For the first a quantity of the yellow precipitate, which had been accumulated in previous work, was carefully purified by repeated washing and portions of it suspended in pure water properly cooled and weighed in the pycnometer at 20° as usual. After weighing, the contents of the pycnometer were rinsed into a white dish, dissolved in a measured excess of carefully standardized potassium hydroxide solution, and the excess of the latter titrated back with standard nitric acid according to Kilgore's method. From the amount of potassium hydroxide required, the weight of the ammonium phosphomolybdate

[1] *Am. J. Sci.,* 1899, pp. 187-198.
[2] *Bull. Soc. Chim.,* Paris, 1893, 343.
[3] This Journal, **15,** 382 ; **16,** 278.
[4] Bull. 43, Division of Chemistry, U. S. Dept. Agr., p. 91.

present in the mixture was calculated. This weight and the
weight of the mixture in the pycnometer afforded the data neces-
sary for the calculation of the specific gravity of the precipitate.
The results obtained are indicated by Nos. 1 to 4 inclusive in the
table below. For the second series of determinations a quantity
of pure disodium phosphate was obtained by recrystallization, and
dried between filter-paper. A weighed portion of this was dis-
solved in water, and aliquot portions of this solution precipitated
exactly as required by the Kilgore volumetric method, since this
has been shown to give a precipitate free from molybdic acid.
The specific gravity of these precipitates was determined by the
usual method without separating them from the mother-liquor.
Four determinations, using in each case 15 cc. of the solution
which contained 0.01119 gram of disodium phosphate per cubic
centimeter, were made, with the results indicated by Nos. 5 to 8
inclusive in the following table :

TABLE VII.—SPECIFIC GRAVITY OF AMMONIUM PHOSPHOMOLYBDATE.

	Ammonium phospho-molybdate equivalent. Grams.	Calculated specific gravity.
1	1.4600	4.011
2	1.4602	4.079
3	1.9405	4.050
4	2.9102	4.074
5	0.8793	4.040
6	0.8793	4.055
7	0.8793	4.086
8	0.8793	4.032

Average, 4.055

For the purpose of testing the accuracy of the new method of
weighing to the phosphoric acid precipitates, seven determina-
tions of the percentage of phosphoric acid in pure disodium phos-
phate were made. Two further aliquot portions were drawn from
the solution which was used in the specific gravity determination ;
a second solution was made up and three aliquot portions of this
were taken. Finally two small samples of the material were
weighed in two beakers and dissolved in water. The phosphoric
acid in each solution was precipitated as in Kilgore's method,
the mixture cooled, and the indirect weighing of the precipitate
completed as usual. The following are the results of the analyses,
stated in the same order as mentioned above.

TABLE VIII.—DETERMINATIONS OF PHOSPHORIC ACID IN DISODIUM
PHOSPHATE.

	Disodium phosphate taken. Gram.	Ammonium phospho-molybdate found. Grams.	Phosphorus pent-oxide equivalent. Gram.	Phosphorus pent-oxide found. Per cent.
1	0.1679	0.8796	0.03330	19.83
2	0.1679	0.8747	0.03309	19.71
3	0.3144	1.6554	0.06253	19.89
4	0.2695	1.4111	0.05339	19.81
5	0.3593	1.8962	0.07164	19.94
6	0.2328	1.2238	0.04630	19.84
7	0.2486	1.2974	0.04909	19.74

The theoretical percentage is 19.82

All calculations were based upon the formula $12MoO_3.PO_4.3NH_4$ for the yellow precipitate. Carnot stated that the precipitate when dried at $100°$ contains water of crystallization as represented by the formula $24MoO_3.P_2O_5.3(NH_4)_2O.3H_2O$. Whether or not this be correct, no error is produced by the assumption of the more commonly accepted formula since the latter was used in calculations of the specific gravity also. These determinations show that if proper care in manipulation is exercised, this simple method is capable of yielding very accurate results with this precipitate which has heretofore caused analysts so much trouble. The only extra precaution which is required in this application of the method is that the precipitate must always be thrown down under similar conditions, since otherwise it is apt to be contaminated by impurities.

Specific Gravity of Cuprous Oxide.—F. W. Clarke in his "Tables of Specific Gravity"[1] cites the following results of determinations of the specific gravity of this precipitate : 6.052 and 6.093 ;[2] 5.751 ;[3] 5.750 ;[4] 5.746 ;[5] 5.300, 5.342, and 5.375.[6]

The limitations of our library have prevented my verification of these figures, or study of the conditions under which the determinations were made.

The cuprous oxide which is precipitated from boiling Fehling's solution by reducing sugars is supposed to be more or less hydrated. The degree of this hydration probably varies with the concentration of the solution, etc. Moreover, cuprous oxide is

[1] Bull. of the U. S. Geological Survey, 1886.
[2] Herapath : *Phil. Mag.*, **64**, 321.
[3] Karsten : Schweigger's *Journal*, **65**, 394.
[4] Leroyer and Dumas : Böttger's " Tab. Unters. d. Spez. Gew,"
[5] Playfair and Joule : *Mem. Chem. Soc.*, **3**, 82.
[6] Peroz : *J. prakt. Chem.*, **47**, 84.

quite easily oxidized to the cupric condition.   These facts make
the preparation of a known quantity of pure cuprous oxide a some-
what difficult task.   It is probable, however, that within the ex-
tremely narrow limits to the conditions of carrying out the reduc-
tion as prescribed by the methods now adopted by the Official
Agricultural Chemists, the composition of the precipitate is prac-
tically invariable.   The amount of precipitate produced varies
with the time during which the sugar solution is boiled with the
Fehling solution.   Since it is almost impossible to keep this
time always exactly the same, the use of a known amount of a
reducing sugar in order to obtain a known amount of cuprous
oxide is not sufficiently accurate for the purposes of this work.
It was determined therefore to precipitate several quantities of the
cuprous oxide according to the official method, wash them thor-
oughly, use the pure material thus obtained for the specific gravity
determination, and afterwards dissolve the precipitate and deter-
mine the copper therein by some standard method.   Five such
precipitates were prepared and their specific gravity determined,
the amount of copper present in each case being determined by
titration with standard potassium cyanide solution.   The follow-
ing results were obtained :

TABLE IX.—SPECIFIC GRAVITY OF CUPROUS OXIDE.

	Potassium cyanide solution used. cc.	Cuprous oxide equivalent. Gram.	Calculated specific gravity.
1	85.6	0.5040	5.7000
2	76.3	0.4532	5.7336
3	81.7	0.4853	5.6788
4	77.3	0.4591	5.7058
5	84.6	0.4476	5.6852

Average, 5.7007

The factor 5.7 was therefore assumed as representing very
nearly the specific gravity of the cuprous oxide as precipitated
under the conditions required by Allihn's method.[1]   Since it is
not necessary that the exact nature of the precipitate be known,
or that the formula assumed to represent its composition be
exactly correct, it was not deemed essential that any allowance
for hydration of the precipitate be made.   In all this work, there-
fore, the precipitate was considered as being simply cuprous
oxide, and all calculations were made on this basis.

[1] Bull. 46, rev. ed., Division of Chemistry, U. S. Dept. of Agr., p. 35.

Determinations of Invert Sugar.—For the purpose of testing the accuracy of this method as applied to the weighing of cuprous oxide precipitated by invert sugar, a standard solution of the latter was made up, as follows : A quantity of pure sucrose (rock-candy) was pulverized and dried in the oven. 2.5 grams of this material were dissolved in 50 cc. of water and inverted according to the method of Clerget.[1] The solution was cooled, the excess of acid carefully neutralized with dilute sodium hydroxide solution, and the volume made up to 250 cc. One cc. of this solution contained, therefore, the equivalent of 0.01 gram sucrose or 0.010526 gram invert sugar. Several portions of this solution were measured out from a burette and boiled with Fehling's solution as prescribed by Allihn's method. It was found that if the mixture were allowed to stand in cold water until cool enough to weigh as usual, too high results were obtained because of a gradual deposition of cuprous oxide during the cooling. It was therefore decided to separate the precipitate from the mother-liquor as quickly as possible. After boiling for the prescribed two minutes, the mixture was poured into large test-tubes and the latter whirled in the centrifugal. The precipitate settled so quickly and so completely that the mother-liquor could be drawn off within thirty seconds from the completion of the boiling. The precipitates were then washed in the test-tubes with hot water, as described for the purification of the silver chloride precipitate. Two washings were always sufficient to leave no trace of alkali in the wash-water. The pure precipitate was then washed into the pycnometer with pure water, properly cooled, and the weight ascertained as usual. The following results were obtained :

TABLE X.—DETERMINATIONS OF INVERT SUGAR.

	Invert sugar taken. Gram.	Cuprous oxide found. Gram.	Invert sugar equivalent. Gram.	Error in milligrams.
1	0.2150	0.4026	0.2148	— 0.2
2	0.1889	0.3935	0.1891	+ 0.2
3	0.2311	0.4311	0.2311	..
4	0.1896	0.3581	0.1890	— 0.6
5	0.1595	0.3048	0.1592	— 0.3

Since in this case the liquid portion of the mixture is water at a constant temperature, the only variable in the formula for calculation is a, the weight of the mixture. Hence the calculation can

[1] Bull. 46, rev. ed., Division of Chemistry, U. S. Dept. Agr., p. 39.

be much simplified by rearrangement of the formula, so as to com-
bine all the constants of the operation into a single factor as fol-
lows :

Let c represent the weight of the pycnometer and contents.
Let c' represent the weight of the pycnometer.
Then

$$a = c - c'$$

and the formula

$$x = \frac{d(a - bd')}{d - d'}$$

becomes

$$x = \frac{d}{d - d'}(c - c' - bd') \text{ or } \frac{d}{d - d'}(c - (c' + bd')).$$

Now since Allihn's table for the dextrose equivalent of the
precipitate is expressed in terms of copper instead of cuprous
oxide, these results of the weighing must be divided by 1.1258,
the factor for conversion of cuprous oxide into its copper equiva-
lent. This is, of course, another constant in the calculation and
may be introduced in the formula, which would then become

$$x(\text{in terms of copper}) = \frac{d}{(d - d')1.1258}(c - (c' + bd')).$$

Now the only variable in this formula is c, the weight of the
pycnometer and contents. The whole expression may then be
simplified as shown in the following example : In the determina-
tions made above, the pycnometer weighed 41.7454 grams ; its
volume was 99.456 cc. The specific gravity of the precipitate
was taken as 5.7 and of water at 20° as 0.998213. The quantity
$(c' - bd')$ then became $(41.7454 + 99.456 \times 0.998213) = 141.0237$.
The fraction

$$\frac{d}{(d - d')1.1258}$$

became

$$\frac{5.7}{(5.7 - 0.998213)1.1258} = 1.077.$$

The calculated amount of copper in any particular case was
$(c - 141.0237)1.077$. For any other pycnometer, the value of c'
and b would be different, but, once determined, they are constant
and the corresponding factor may be easily calculated.

The whole process is, hence, extremely simple and may be
carried out with great rapidity. After sufficient practice to

become familiar with the details of the work, a determination was easily completed in twenty minutes. While it is probable that the results are not quite so accurate as those obtained by the electrolytic estimation of the copper, they are as good as are usually required of a satisfactory method, and are subject to less variations than may easily be produced by slight changes in the conditions under which the reduction of the Fehling solution is carried out, which would affect the amount of cuprous oxide precipitated by a definite amount of reducing sugar. The method is capable of yielding more accurate results than may be obtained by the common volumetric methods for the estimation of copper, as is shown below. It possesses the added advantage that the mother-liquor is very quickly separated from the precipitate, thus diminishing the probability of the deposition of additional copper, as may happen in the case of the slower process of filtration by the other methods.

Determinations of Reducing Sugars in Commercial Glucose.—For the purpose of comparing the results obtained by this method with those obtained by the volumetric estimation of the copper, the following process was adopted. 2.25 grams of commercial glucose were dissolved in water and the volume made up to 250 cc. Aliquot portions of this solution were measured from a burette and the cuprous oxide precipitated as required by Allihn's method. The weight of cuprous oxide obtained was determined by the new method as described above ; the contents of the pycnometer were then dissolved in dilute nitric acid, and the copper estimated by titration with standard potassium cyanide solution. The following results were obtained :

TABLE XI.—COMPARISON OF RESULTS OF NEW METHOD WITH CYANIDE METHOD.

Solution taken. cc.	By new method.			By potassium cyanide titration.		
	Cu_2O found. Gram.	Dextrose equivalent. Gram.	Dextrose per cc. Gram.	Cu_2O found. Gram.	Dextrose equivalent. Gram.	Dextrose per cc. Gram.
25.0	0.4078	0.2175	0.00870	0.4078	0.2175	0.00870
27.5	0.4476	0.2407	0.00875	0.4389	0.2357	0.00857
22.5	0.3723	0.1969	0.00875	0.3693	0.1953	0.00868
25.0	0.4089	0.2181	0.00872	0.4120	0.2199	0.00879

The potassium cyanide titration of copper has been in use in this laboratory for several years. The end reaction is somewhat difficult to detect, but with some experience in its use and proper

care in manipulation it has been found to give the most satisfactory results of any of the volumetric methods which have yet been tried. The determinations recorded above show that more concordant results may be obtained by the new method of weighing the precipitate than by the cyanide method of volumetric estimation.

Determination of Aluminum as Aluminum Hydroxide.—An attempt to apply this method of weighing to the aluminum hydroxide precipitate was made. The preliminary determinations of the specific gravity of the precipitate showed that the composition of the latter is not constant but varies with the time which elapses between the precipitation and the subsequent weighing of the precipitate. Considerable data bearing upon the rate of this change in composition has been accumulated and will be published at some later time. The work has proceeded far enough to show that it is probable that this method may be applied to the weighing of the aluminum hydroxide precipitate if proper conditions as to time, temperature, etc., are observed. Just what the most favorable conditions are, however, is not yet definitely determined.

CONCLUSIONS.

The work of investigating the applicability of this new method to the practices of technical analysis, is by no means complete. In fact, it is but just begun. Yet the results already obtained, which are embodied in this paper, seem sufficient to justify the belief that its application to the processes of gravimetric analysis will be a decided advance toward the much desired simplicity and ease of manipulation. They show that the use of this process greatly reduces the time required for a determination and at the same time yields very satisfactory results. A comparison of this method with the older ones when applied to the analysis of impure or mixed materials is yet to be made, but since many of the precipitates already experimented upon were weighed in the presence of solutions containing several other compounds, it is thought that the working conditions of these determinations very closely approximate those of ordinary analyses. The results already obtained, therefore, lead to the conclusion that the proposed method is a step toward the realization of the conditions of an ideal method of analysis, namely, accuracy and rapidity.

UNIVERSITY OF NEBRASKA, LINCOLN, NEBRASKA,
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