to be 52.074 and 107.941 respectively. However interesting these results may be, they have little real significance, since an error of five-thousandths of a per cent. in either ratio causes an error of over one-tenth of a unit in the atomic weights of both silver and chromium.

The most important results of this research are as follows:

1. Pure silver dichromate was prepared.

2. It is shown that silver dichromate cannot be completely dried without decomposition.

3. It is shown that silver dichromate when crystallized from nitric acid retains traces of the nitric acid.

4. The proportion of moisture and nitric acid in silver dichromate treated in definite fashions was determined.

5. The specific gravity of silver dichromate is found to be 4.770 at 25° referred to water at 4°.

6. The per cent. of silver in silver dichromate is found to be 49.9692.

7. With several assumed values for the atomic weight of silver referred to oxygen 16.000, the atomic weight of chromium is found to have the following values:

If Ag = 107.93	Cr = 52.06
If Ag = 107.88	Cr = 52.01
If Ag = 107.85	Cr = 51.98

8. If these results are averaged with those previously found by Baxter, Mueller, and Hines, the atomic weight of chromium is found to be as follows:

If Ag = 107.93	Cr = 52.06
If Ag = 107.88	Cr = 52.01
If Ag = 107.85	Cr = 51.98

We are greatly indebted to the Carnegie Institution at Washington for generous pecuniary assistance in pursuing this investigation; also to the Cyrus M. Warren Fund for Research in Harvard University for many pieces of platinum apparatus.

CAMBRIDGE, MASS., December 10, 1908.

THE CENTRIFUGE IN QUANTITATIVE ANALYSIS.

BY H. G. PARKER.

Received March 5, 1909.

The centrifuge has proved so successful an adjunct to qualitative analysis as to suggest the possibility of using this sort of separation for quantitative determinations, as ordinarily made in the usual gravimetric analysis. For this purpose various forms of apparatus were constructed and put to the test of the ordinary requirements of the quantitative laboratory. The method developed in a very unexpected manner. It was thought at the outset, that determinations in a few favorable cases might be affected, but it soon became evident that the field was a very wide one indeed; in fact, it appeared that the method was applicable to all substances that could be separated from a solution by means of the centrifuge, which includes the great bulk of precipitates used in quantitative chemical analysis in the gravimetric way.

As it seemed desirable to work with fair quantities of solution, a centrifuge of substantial design was constructed and attached to the spindle of a foot-power machine, which was abstracted from the work-shop of the physical laboratory for the purpose. Afterwards, the centrifuge was driven by a small electric motor.

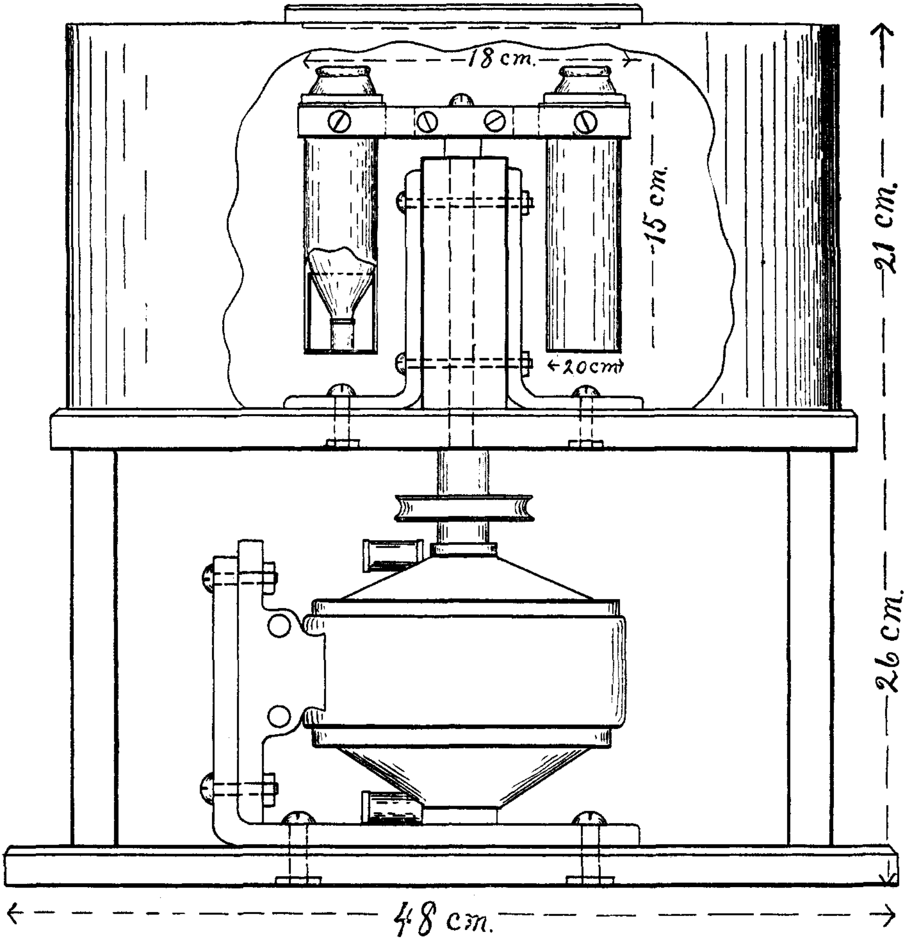

Fig. 1.

The centrifuge consisted of the usual steel spindle, coupled directly to the shaft of the motor. At the top of the spindle was a cast iron head, to which were attached two steel arms, 3 mm. thick and 20 mm. wide. The usual ring for supporting the jacket was attached to these arms by stout screws. The jacket, for containing the separating flask, was of brass tubing and the bottom of the jacket and the flange at the top were secured to the tube with a silver solder. Ordinary soft solder was of no use in this connection, as the centrifugal force would shear off the flange when the motor was started, unless very firmly secured. The radius of rotation was about 20 centimeters, measuring from the spindle to the outer extremity of the jacket. The speed was varied from approximately 1500 to 1800 revolutions per minute and the rotation was continued from two to three minutes.

Various precipitating or separating flasks were used, but for most purposes a flask 14 cm. long with a diameter at the widest part of 3.5 cm. was most commonly used. A flask of this size would contain about 75 cc.

The neck of the separating flask fits into a platinum crucible in a firm, water-tight joint, made by means of a short section of pure gum tubing, which is held between the outside of the neck and the inside of the crucible, as shown in Fig. 2.

The proper way to make this connection is to place the section of rubber tubing, about 1 cm. long, partly over the neck of the separating flask, which has been wetted a moment previous. The neck of the flask is then inserted in the crucible and twisted firmly into place. The operation is both simple and familiar, but must be performed exactly as stated. The rubber slips on the glass and not on the platinum and spreads out into a bushing which renders the joint perfectly secure.

The flask and crucible, as a composite vessel, are placed within a metal container, or jacket, as usual with centrifuges. The jacket has a flange at the upper end which rests in the ring attached to the revolving spindle. The separating flask is supported on a short section of metal tubing, while the crucible rests squarely upon the bottom of the jacket, as shown in Fig. 2.

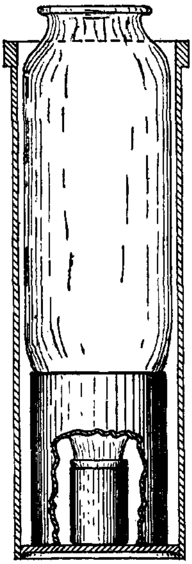

Fig. 2.

The space between the flask and jacket is filled with water from the wash-bottle, so that the hydrostatic pressure is the same inside and outside. This arrangement eliminates any tendency to leak when the spindle is rotated.

At the beginning of a determination the crucible is weighed and fastened to the flask, as above stated. The solution is placed in the separating flask, which is conveniently supported in an arm clamp. The reagent is added, and, if necessary, the solution is boiled. This may be done without danger to the rubber bushing on the neck of the flask, by placing a ring of asbestos paper around the crucible below the rubber. The platinum is cooled by the solution and the bushing is preserved perfectly. Care must be observed, however, not to allow the flame to come in contact with the platinum immediately over the rubber. The heating of the solution in the separating flask is more conveniently accomplished by means of a small plate of copper or brass, provided with a hole or socket, into which the crucible rests. The plate is covered with asbestos board and there is no danger to the rubber. The heat is transferred to the crucible by conduction and the solution may be boiled very quickly. By lowering the heating plate slightly the contact with the crucible may be varied and the boiling regulated with great exactness. The arrangement is shown in Fig. III.

When precipitation is complete, the flask and crucible are placed in the metal jacket and rotated in the centrifuge until the precipitate is thrown down into the crucible and the solution left perfectly clear. Ordinarily, this takes about two or three minutes. The flask is then removed and the solution drawn off by means of an ordinary siphon bottle. The last portions of the solution are best removed by tilting the separating flask slowly sidewise and allowing the solution to run into the flask by gravity, from whence it may be withdrawn by the siphon. The precipitate is washed by means of a stream of water from the wash-bottle and the process repeated. As all but a very small per cent. of the solution is drawn off each time, the washing is thorough with a very small amount of water. Three repetitions are usually an abundance. The solution should be agitated thoroughly with a stream from the wash bottle each time. When permissible, boiling the solution, by heating the crucible, breaks up the precipitate very thoroughly. After the final

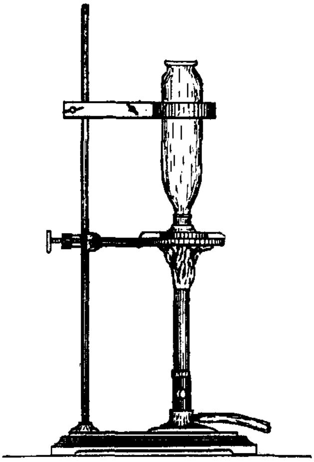
Fig. 3.

washing, the crucible is removed from the flask and dried, or ignited, as the case may demand. After cooling, it is weighed in the ordinary manner. As there is no filter paper to be burned, the crucible needs only to be large enough to accommodate the actual precipitate and the cooling is quickly accomplished; also there is less chance of error in weighing, due to variations in the condition of the platinum surface.

It is, of course, necessary that the two arms of the centrifuge shall be equally loaded and it is convenient to run duplicate determinations at the same time, filling both flasks to the same level. If the amount of solution to be used in the determination exceeds the capacity of the separating flask, the precipitation may be performed in an ordinary beaker and the precipitate and solution transferred in portions, to the separating flask. The precipitate is allowed to remain each time the solution is drawn off, so that, at the end of the operation, the crucible contains the entire amount. The only disadvantage of the method is that it requires the washing of an extra beaker and takes a little more time. The washing of the sides of the separating flask is best performed by means of a slightly bent stirring rod, tipped with rubber. It is convenient, at the last washing, to fill the flask only partly with wash water and to rub down briskly the inside of the glass walls of the flask with the tip of the stirring rod, while the flask remains in its place in the centrifuge. Certain precipitates which tend to "creep" are carried down readily by this method.

Two sizes of crucibles were found convenient, one of a diameter of 10 mm. and a length of 20 mm.; the other 15 mm. in diameter and 27 mm. long. The sides were nearly parallel and were fairly stout, especially at the upper edge.

Sometimes, in the case of the larger crucible, the stopping of the centrifuge would cause a slight whirling motion of the solution in the flask, which would tend to carry light particles from the surface of the precipitate upward into the flask. This was prevented by hanging over the edge of the flask during centrifugalization, a stirring rod with a slight pear-shaped enlargement at the lower end. The bulb was arranged to hang centrally over the opening and formed a sort of loose stopper, which did not obstruct the downward passage of the precipitate but effectually prevented any agitation of the contents of the crucible. See Fig. IV.

It is hardly necessary, perhaps, to state that the centrifugal separation may be made as complete as desired; it is important, however, to determine whether the method of manipulation as above described will leave any weighable amount of precipitate in the wash-water. Various precipitates were investigated, including all of the well-known types met with in chemical analysis, but as the results were uniformly negative, it is scarcely necessary to record them. Some precipitates, such as free sulphur, or light particles of organic matter, do not separate readily by the centrifugal method, but these are not of very frequent occurrence in quantitative determinations. The completeness of the separation may be judged by a close inspection of the solution, just as in the case of filtration. It does no injury to run the centrifuge longer than necessary.

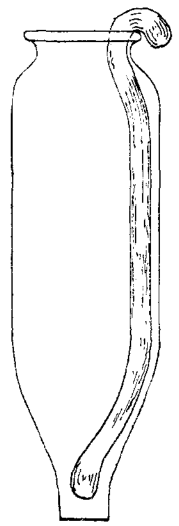

Fig. 4.

The centrifugal method, as described, has some decided advantages over the usual process of filtration. In the first place, it is very much quicker. This is due partly to the avoidance of the frequently tedious filtration and partly because there is no filter to burn. Further, the cooling of the crucible is much quicker than usual, on account of its smallness. The saving in time varies according to the nature of the precipitate. A complete sulphuric acid determination, for example, may be made within an hour, including the weighings and the necessary wait for the final cooling of the crucible. There is sometimes a slight delay in evaporating off the last few drops of wash-water in the crucible after it is removed from the separating flask. The amount of liquid remaining is very small and may be disposed of by heating the upper part of the crucible gently, by means of a small Bunsen flame. This part of the operation generally requires from one to five minutes.

Another advantage of the method is the large reduction of the personal and accidental error. The amount of washing may be definitely prescribed with entire assurance that all parts of the precipitate will be treated exactly alike. The control of the conditions of washing is very complete and duplicate determinations check each other in a very satisfactory manner. The chance of loss by splashing, or spattering is practically eliminated.

Precipitates easily decomposed by heat, which have heretofore required the tared filter, are easily handled, as well as substances easily oxidized. The exposure to the atmosphere is reduced to a minimum. If necessary to exclude the air entirely, the separating flask may be filled with an inert gas before the precipitate is agitated by means of the stream from the wash-bottle. As there is no filter to complicate the conditions, the treatment may be exactly that demanded by the precipitate itself.

Calcium carbonate may be prepared with no danger of having part of it converted into the oxide during the burning of the filter.

In conclusion, it is evident that the method is capable of wide application. The errors of solubility and occlusion with certain precipitates still remain. It is undoubtedly true that the empirical rules of procedure in quantitative analysis give results closely approximating the correct percentages because of balancing opposing errors. The writer has called attention to this in a former article upon the occlusion of barium chloride by barium sulphate. The error due to occlusion was almost exactly equal to the error due to the solubility of the sulphate, when the precipitation and washing were performed as described in the standard manuals. The apparent accuracy of the method resulted from the balancing of opposing errors. The most uncertain accidental factor in a gravimetric determination is the washing. Drying and igniting may be prescribed with some certainty that the conditions wished for may be reproduced with a fair degree of accuracy In washing, we must always face the two difficulties, under-washing making results heavy, over-washing making results light.

The present paper is to be regarded as preliminary. The method makes desirable some revision of the generally accepted rules of quantitative analysis. As a small amount of liquid is a convenience, it may become desirable to work with much more concentrated solutions. It will be necessary to examine the exact solvent effect of the wash-water under the new conditions, which is as closely quantitative as any other part of the method.

The question as to the value of the method rests upon two considerations, first, as to whether the centrifugal separation is complete; second, whether or not there is any manipulation in the method that involves a mechanical loss of a portion of the precipitate or permits the addition thereto of foreign matter. As to the first, the centrifuge is too well established to need an elaborate defense. Numerous experiments were made to check this point with uniformly negative results. Gelatinous precipitates, such as aluminum hydroxide, separate easily, the only difficulty being that a somewhat larger crucible is desirable on account of the bulkiness of such substances. As to the second question, it seems that a reasonable amount of care should prevent accidental errors entirely. It is desirable that a sharp distinction should be made between the errors due to the centrifugal method and the inherent chemical errors involved in precipitation, washing, etc. The present paper is concerned particularly with the method. It will be followed as rapidly as circumstances will permit with the particular details of individual precipitates and the numerical results obtained.

The question of using the centrifuge as an adjunct to quantitative chemistry has been a matter of thought from time to time for some years, but the matter took definite shape in its present form in the autumn of 1907.

WILLIAM JEWELL COLLEGE, LIBERTY, MO.

NOTE.

The Determination of Ammonia without a Condenser.—Often it is desired to determine the nitrogen content of a substance without distillation and it was with the idea of devising a suitable general method that this work was undertaken. Kober[1] describes a method for the determination of nitrogen in urine without using a condenser. The same method is used under various circumstances where heat is not desired. Kober's method is to make a solution of urine by digestion similar to the regular Kjeldahl and after the solution is complete to slightly dilute it. Sodium hydroxide solution is added by drawing it over from another vessel by means of suction. After the solution is alkaline, air is drawn through at as rapid rate as possible without drawing over some of the solution. The ammonia carried over with the air is absorbed by standard acid. A specially strong suction pump is needed.

Cottonseed meal was selected for the experiments here described because of its variable nitrogen content and its difficulty of digestion. At first the method as carried out by Kober gave very discordant results. This was due to two difficulties: (1) Some of the ammonia was not absorbed by the acid, and (2) all the ammonia was not carried over.

Various forms of absorption tubes were tried until finally the one giving best results was a Folin tube supplemented by a tube filled with glass beads wetted with acid, as shown in Fig. 1.

The second difficulty seemed to arise from the facts that the solution, which was just brought to boiling by the heat of neutralization, cooled too rapidly; and that the stream of air drawn by the ordinary glass pump was not strong enough to carry over the ammonia by the time the solution cooled.

If the flask (Kjeldahl) containing the solution were placed in an asbestos box, the solution kept warm for an hour and a half. To the solution was added scrap aluminium which reacts rapidly with the alkali, setting free hydrogen. With these modifications the results checked with results obtained by the ordinary Kjeldahl.

It was also found that the digestion could be made with sulphuric acid and aluminium, and the results check with digestion using salicylic acid and mercury. The air must be drawn through at least an hour, but it generally requires somewhat longer to remove all ammonia.

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[1] *Jour. Amer. Chem. Soc.*, 30, 1131.