CXVI.—*Studies with the Microbalance. Part III. The Filtration and Estimation of very small Amounts of Material.*

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QUANTITATIVE micro-analytical work involving precipitation and filtration is beset with considerable difficulty because errors due to adsorption, mechanical loss of material, solubility of precipitates, and accumulation of dust are apt to assume serious proportions in spite of the greatest care on the part of the operator. Moreover, the difficulty of estimating the magnitudes of these errors makes subsequent attempts to correct the experimental results very uncertain. In view of its importance, some preliminary work on the general analytical technique for dealing with 1—2 mg. of material was carried out in this laboratory in 1910 by G. A. Ampt, using the Steele–Grant microbalance. For filtering operations, he employed asbestos in small perforated silica crucibles weighing about 1 g. and transferred the precipitate into them in various ways. The results of his work (unpublished) showed that asbestos was unsuitable as a filtering medium for small amounts of material owing to mechanical and chemical alterations in weight, and that serious losses of precipitate were inevitable in any method of transference from one vessel to another. The obvious remedy is to carry out precipitation in the crucible itself and to adopt reversed filtration through a tube packed with platinum sponge for removal of mother-liquor and washings. Emich ("Mikrochemisches Praktikum," 1924, p. 62) has described such a device for use with 5—10 mg. of material; asbestos is employed instead of platinum sponge and the precipitation vessel with its filtering tube (3—4 g.) is weighed on a Kuhlmann balance to the nearest 0·005 mg. A few examples of analyses are given in which the errors are quoted as usually below 1—2 parts per 1000. As far as the author is aware, however, no general methods for the accurate analysis of amounts of material weighing less than 1 mg. have hitherto been described. When, therefore, the need arose for estimating with precision the composition of very small quantities of mixtures of silver and silver iodide by a procedure involving filtration, the capabilities of the Steele–Grant microbalance were utilised in investigating the conditions for successful quantitative work. The original problem has not yet been solved satisfactorily owing to the great difficulty of separating completely silver iodide from silver, but the methods which have been developed are fairly general in application and may be of use to others who are constrained to work with very small amounts of material. The apparatus required consists of a sensitive microbalance (weighing to 10^{-4} mg.), a silica crucible and filtering tube, a dust-free enclosure for carrying out filtration, an evaporator and electric oven, sundry small appliances such as silica pipettes, tubes, etc., and specially prepared reagents.

The Microbalance.—Two Steele–Grant instruments were available, each carrying a load of 100 mg. and weighing accurately to 10^{-4} mg. It was impracticable to work with a crucible and filtering tube which weighed together less than 500 mg. and consequently one of the balances was modified to enable it to carry this load without material reduction in its absolute sensitiveness. In the usual form of the instrument, a constant weight fused to one end of the beam counterpoises a load hanging from a silica fibre attached to the other end. This load consists of a very light rack carrying the object to be weighed, certain small weights and a silica bulb by means of which the beam is equilibrated through alteration of air pressure in the balance case. The bulb constitutes the major portion of the load, since it must be stoutly blown in order to resist deformation with varying external pressure. By removing the bulb from the rack and fusing it to the other end of the beam as part of the constant weight, almost the whole of the load on the fibre is available for the object to be weighed. It is, of course, necessary to determine the displacement value of the bulb in its new position, since the ratio of the lengths of the balance arms now enters into each weighing, but this may easily be done by means of a small known weight, the value of which has been found against the bulb of an unmodified instrument in the usual manner. This procedure was followed with one of the two available balances, and weighings consistent to the nearest 10^{-4} mg. could then be made in a load of 500 mg., or 1 part in 5×10^6 parts. It is perhaps scarcely necessary to remark that, when material other than silica is weighed, certain corrections are required for the difference in density between silica and the material; but for quantities less than 1 mg., these may usually be neglected.

Filtering Apparatus.—The silica crucible in which the analytical operations are conducted is 5—6 mm. in diameter and about 16 mm. in depth (Fig. 1, E), with a capacity of 0·3 c.c. It is provided with two hooks for handling and suspension, the lower of which is shaped to act, in addition, as a support for the filtering tube during weighing so that the point of the tube does not rest on the bottom of the crucible. The tube (Fig. 1, F) is also made from vitreous silica, 30 mm. in total length and 0·3 mm. in bore. It is bent at a right angle in its upper portion and near the lower end is a constriction above a 3—4 mm. column of platinum sponge. This is made by igniting ammonium chloroplatinate and introduced by suction in water, followed by careful compacting with a platinum wire. The lower orifice of the tube is then somewhat constricted in the oxy-gas flame. A suitable rate of passage of water through the finished filter with strong suction is about 3 c.c. per hour and finely-divided precipitates are completely retained by it. Care must be taken, however, that the filter is never ignited above a low red heat, otherwise the platinum sponge tends to shrink and may leave channels which impair its filtering quality. Attempts were made to replace the platinum by finely-ground silica, firmly compacted and then sintered together, but shrinkage was so marked that the resulting filters were useless.

FIG. 1.

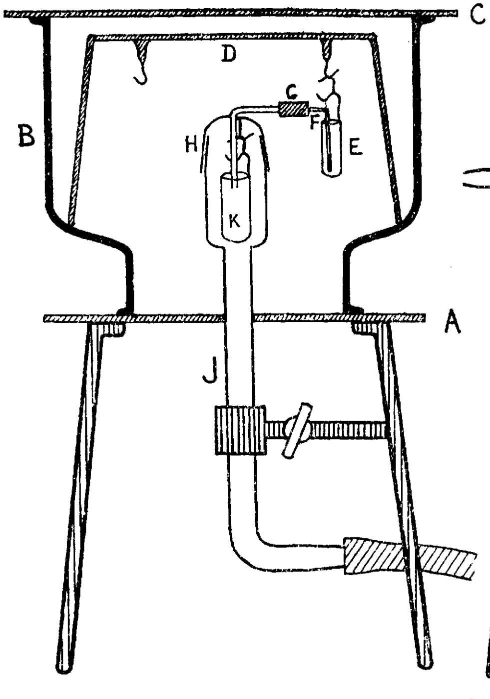
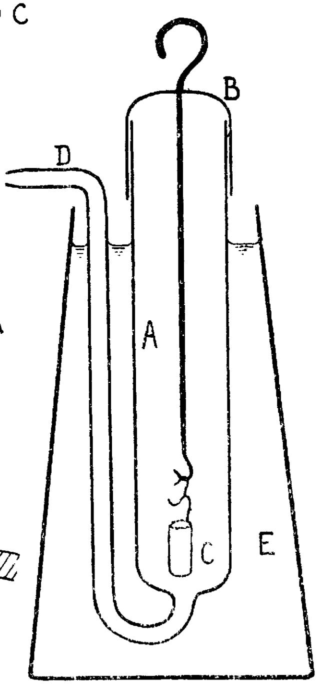


FIG. 2.



The dust-free enclosure in which filtration is carried out is shown in Fig. 1. A ground glass plate, A, with central perforation is cemented with pitch on top of an ordinary tripod with the ground surface upwards. On this rests a glass "dialysing jar" with ground ends, B, about 12 cm. in diameter and 10 cm. deep; this is closed above with the ground glass plate, C. On the ledge inside the jar stands a light glass framework, D, provided with suitable hooks from one of which the crucible, E, hangs. The filtering tube, F, is inserted in a short length of clean rubber tubing, G, on the end of the arm of the ground cap, H, of a vertically clamped glass tube, J, which passes snugly through the central perforation of the base plate of the chamber. The enlarged upper end of this tube encloses a silica crucible, K, of rather more than 1 c.c. capacity, which hangs from a hook cemented to the inside of the ground cap. By this device, the filtrate from E may be collected in K without contamination or loss. The lower end of the tube J is connected to an exhaust pump or an evacuated receiver during filtration. The crucible E is introduced by means of a bent silica rod after raising C, and the filtering tube is inserted by a pair of narrow-pointed forceps into the moistened end of G after raising B. The tips of these forceps require special preparation; if they are made of smooth metal or ivory, there is great risk of the silica tube slipping out, whilst if the metal is roughened, some of it is gradually transferred to the smooth silica tube where it is visible as greyish weighable stains. This trouble was obviated by arming the tips with good quality calendered writing paper, cemented on with a little varnish and subsequently trimmed to shape with a razor. After placing the filtering tube and crucible in position, they are easily and safely adjusted for filtration by raising or lowering J and sliding B on A. No lubricant is used on any of the ground surfaces except that of the cap H and, if care be taken that none is allowed to soil the interior of the enlarged end of the tube J, the crucible K may be readily introduced or removed without fear of contamination. By means of this apparatus, distilled water and pure concentrated nitric acid may be passed repeatedly from the crucible through the filtering tube without changes in weight greater than 0·0001 mg. Such constancy is not possible, however, if crucible and tube are made of glass, owing to the solubility and hygroscopic character of this substance. For these reasons also, it is advisable to prevent contamination of the filtrate where this is undesirable, by making the ground cap H and its arm from vitreous silica.

Evaporator and Electric Oven.—An evaporator is necessary in which liquids may be evaporated, or kept hot in order to coagulate precipitates, with complete protection from dust. A simple and efficient form is shown in Fig. 2; the wide glass tube, A, is 3·5 cm. in diameter and 18 cm. long and is closed above by a loosely fitting cap, B, carrying a vertical glass rod with a hook from which the crucible, C, hangs. The lower portion is immersed in a glycerol bath, E, regulated in temperature by hand, and a stream of pure dry filtered air is passed continuously through the tube D. In this way, exclusion of dust is assured and, if the glycerol be kept at 130—150°, aqueous solutions may be rapidly evaporated in a few minutes without loss by boiling or spraying. A small electric oven is used for ignitions up to a dull red heat; it consists of a vertical silica tube sealed at the lower end and surrounded with the usual heating coils and packing. The lid is a silica watch-glass, to the convex lower side of which is sealed a silica hook for suspending the objects to be heated. This cover is provided with a small silica handle and the upper part of the oven is covered with an inverted glass basin as a protection from dust.

Reagents.—Special purification of all reagents was found to be necessary, particularly as regards freedom from dust. Water was twice distilled in a silica apparatus in the usual way and preserved in a capped silica flask. The residue on evaporation corresponded to 1 mg. per litre, which included any dust contamination during the operation and was insignificant as a source of error. Acids, ammonia, and other liquids were distilled immediately before use by heating them in conical flasks and exposing to the vapours the outside of a clean silica test-tube full of water. The condensed drops were removed by an ignited silica pipette, fashioned like a medicine dropper, and either added at once to the crucible, or diluted to the required degree with water in small, covered silica tubes. Solid reagents were obtained by twice crystallising the best commercial analytical reagents in silica vessels, special care being taken to avoid contamination with fibres and dust.

The general technique for carrying out an analysis is as follows: The crucible and tube are cleaned by boiling concentrated nitric acid, washed repeatedly with water, dried over a small alcohol flame, and weighed together. During these operations, the crucible is handled on the end of a silica rod and, when clean, hangs from a silica hook mounted on a cork and protected from dust by a glass cover. After weighing, the filtering tube is removed from the crucible by forceps, the sample introduced, the tube replaced in its support so that the lower end does not come in contact with the sample, and the whole reweighed. The filtering tube is then put in place in the filtering apparatus, and the material in the crucible is dissolved by introduction of one or two drops of the appropriate solvent by a silica pipette, followed by heating, if necessary, in the evaporator. It has been found that even if effervescence takes place during solution, *e.g.*, calc-spar in acid, no loss by spraying occurs owing to the depth of the crucible and the very small amount of gas evolved. The precipitating agent is then added and the crucible is heated in the evaporator until clotting of the precipitate, or sufficient increase in grain size, has taken place. The crucible is then cooled in the filtering chamber, the liquid removed by the filtering tube, and the precipitate washed. The only satisfactory criterion of complete washing is the constancy in weight of the residue, but three or four applications of a few drops of the washing liquid are usually ample, since the filtering tube removes the liquid completely. Should the tube become choked, making filtration very slow, it may be freed by detaching the vertical tube, J (Fig. 1), from the exhaust pump and blowing into it for a few moments. When washing is finished, the filtering tube is detached from the rubber and placed in its support in the crucible, after its upper end has been rinsed with a drop or two of water. The whole is then dried in the evaporator, ignited, if necessary, and finally weighed. Analogous methods may also be applied to the filtrate in the crucible K (Fig. 1), should further analysis of this be desired.

In order to test the general accuracy attainable with this apparatus, certain standard analyses were performed after the various inherent sources of error in each case had been discovered and guarded against. The results are summarised in Table I, in which all weights are given in milligrams; they have not been specially selected and are therefore typical of the methods described. Carefully purified and tested salts were used, and the positive radicals were estimated in each case. Inspection of the figures shows that

TABLE I.

Estimation of positive radicals in pure salts.

Expt.	Salt.	Weight in mg.	Estimated as	Weight of ppt. in mg.	% of positive radical.	Pure salt requires
1	$AgNO_3$	0·6833	AgCl	0·5763	63·47	63·50
2	,,	0·3994	,,	0·3355	63·22	
3*	,,	0·1877	,,	0·1548	62·1	
4	KCl	0·8895	$KClO_4$	1·6455	52·20	52·44
5	,,	0·7829	,,	1·4529	52·37	
6	,,	0·0965	,,	0·1808	52·9	
7	$Pb(NO_3)_2$	0·9024	$PbSO_4$	0·8242	62·38	62·55
8*	,,	0·8245	,,	0·7498	62·11	
9	,,	0·1649	,,	0·1503	62·25	
10	$BaCl_2$	0·9288	$BaSO_4$	1·0309	65·33	65·94
11	,,	0·2856	,,	0·3173	65·40	
12	$CaCO_3$	0·4469	CaC_2O_4	0·5767	40·38	40·04
13	,,	0·3510	,,	0·4471	39·86	
14	,,	0·1482	$CaCO_3$	0·1474	39·8	
15	,,	0·0878	$CaSO_4$	0·1209	40·5	
16	,,	0·0844	,,	0·1161	40·5	

* Known source of error.

the analyses are reasonably accurate even for quantities of material as small as 0·1 mg., where the errors in the examples tried have not exceeded 1%, and for larger amounts the errors are usually much less proportionately.

There are several sources of error which, though easily controlled in ordinary routine, are apt to assume serious proportions in microanalytical work of this kind. The most variable of these is due to accumulation of dust, particularly when the crucible and tube are wet; however, a number of trials has shown that, by reducing to a minimum the time during which the apparatus and reagents are freely exposed, by avoiding agitation of liquid reagents, and by washing down the outside of the pipette with a few drops of water immediately before introducing any liquid into the crucible, errors due to dust are insignificant except when dealing with less than 0·1 mg. of material. Mechanical loss of precipitate is another source of error which has caused some trouble, especially when dealing with very finely-divided precipitates which cannot be made coarse-grained by the usual analytical methods. For example, it is practically impossible to precipitate at boiling temperature without loss in a small crucible with 2 or 3 drops of solution, and the only remedy is fairly prolonged heating after precipitation until the solid settles readily. Further, when washing such a precipitate as calcium oxalate, it is essential to allow the drops of washing liquid to fall into the crucible without forming a bridge between this and the point of the pipette, otherwise some of the solid will spread on the latter and be lost. Errors due to adsorption are also difficult to control and are generally much more serious than in ordinary analytical work, for a fraction of a drop may mean a large excess of reagent. For example, calcium oxalate precipitated with a considerable excess of ammonium oxalate may contain as much as 10% of its weight of the ammonium salt, which cannot be removed by washing; in this case, careful ignition of the precipitate to the carbonate at 400° removes the difficulty completely, but the general remedy is to use dilute solutions of reagents of known concentration. When adsorption cannot be prevented, it is sometimes possible to wash out the adsorbed material after ignition of the precipitate, as with barium chloride on barium sulphate (Pregl, "Organische Mikroanalyse," 1923, p. 147), or to estimate it by some means, as with silver nitrate or silver iodide by evaporation with a drop of dilute hydrochloric acid. The most serious of all sources of error is, however, the solubility of the precipitate, especially in the washing liquid. The reason is that the amount of liquid necessary is out of all proportion to the amount of precipitate, because it is mainly used in washing the interior of the crucible. It is rarely possible to employ less than 0·5 c.c., which, for 0·5 mg. of precipitate, corresponds to 1 litre per g. and involves a possible error of 1%, if the solubility of the precipitate is 10 mg. per litre. In Table I, Experiment 3 shows the effect of using too great an excess of hydrochloric acid in precipitating silver chloride, owing to increased solubility of the salt. Expt. 8 shows the effect of washing with dilute sulphuric acid, in which lead sulphate has the minimum solubility of 5 mg. per litre, instead of diminishing the solubility still further by addition of alcohol, as in Expts. 7 and 9. Some error due to solubility is inevitable, but it may be diminished by careful regulation of the conditions of precipitation, proper choice of the washing liquid, and strict economy in its use. It is, of course, possible to employ a saturated solution of the precipitate itself for washing, but great care is necessary to avoid introduction of solid particles. This procedure has not been adopted in obtaining the results given in Table I, nor have corrections for any possible sources of error been applied.

The technique described may easily be extended to a large number of micro-analytical problems, provided that these are not too complex. There is, of course, no point in using the microbalance for analysis when sufficient material for the usual laboratory procedure is available, although in some cases, the instrument offers a more accurate and much more expeditious method. For example, the composition of a mixture of sodium and potassium chlorides may be determined rapidly and accurately by evaporating less than 0·5 mg. with a single drop of nitric acid and weighing the mixed nitrates in the residue. Apart, however, from the fact that the chance of accidental error is always greater when dealing with very small quantities, the application of the Steele–Grant microbalance to analytical problems has certain limitations. Volatile liquids cannot be weighed without much trouble, although, when the composition of a liquid is in question, it may be measured with a small pipette. The simplest way to calibrate a pipette for use with the microbalance is to make up an aqueous solution of some stable anhydrous salt (*e.g.*, potassium chloride) of known concentration in the usual manner; a pipette-full of this solution is then evaporated to dryness and the residue weighed on the microbalance. Volatile solids and hydrated salts cannot usually be weighed without special contrivances, and also correct sampling of small amounts of heterogeneous material is extremely difficult. Further, some gelatinous precipitates are awkward to manipulate with the filtering tube owing to the tendency to become impacted in the end of it. Nevertheless, in spite of these limitations, the apparatus and micro-analytical methods here described have a considerable range of application with accuracy, and it is hoped that they may be of use to other investigators who find it necessary to work with very small amounts of material.

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