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PAPERS FROM THE CHEMICAL LABORATORIES

No. 75; THE VOLUMETRIC ESTIMATION OF SILVER,
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University of Toronto Studies

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CII.—*The Volumetric Estimation of Silver.*

By William Robert Lang and John Obins Woodhouse.

In this journal (Lang and Allen, Trans., 1907, **91**, 1370) there was described an apparatus for the estimation of sulphates and salts of barium based on the rapid clearing of turbid solutions in narrow tubes. The same apparatus was used to determine silver by standard sodium chloride with a view to improving on the well-known Gay-Lussac method, but great difficulty was experienced in determining the end-point, the silver solutions not clearing sufficiently rapidly. The

apparatus was therefore modified considerably, with the result that estimations of silver were done in half an hour with an average error of less than a-tenth of one per cent.

The principal differences from the former apparatus were the use of fine sand to retain the silver chloride precipitate, the replacement of the funnel by a short piece of thin-walled glass tubing, which enables the slightest opalescence to be easily observed, and the permanent attachment to an exhaust for washing the precipitate and solution down the tube.

A rubber cork, pierced with two holes, is inserted in a flask, A, of about 600 c.c. capacity. Through it passes a tube, C, of about 60 mm. diameter, fitted with a stopcock, D, and to its upper end is sealed about 4 cm. of a thin test-tube, E, of 1—1·5 cm. diameter. About 8 cm. from the lower end of the tube C, a plug of glass-wool is inserted and the remainder filled with sand, previously washed free

from impurities. The sand is held in its place by a second plug of glass-wool, and the curved piece of tubing, B, filled with glass-wool and attached to C by a small piece of rubber tubing. The curved portion may, of course, be sealed on, but in these circumstances is not so readily filled. This prevents the back suction from displacing the sand. Through the second hole in the cork a small piece of tubing passes, connected by a length of rubber tubing, $F.M$, to a three-way tap, H. J is a small hand aspirator to force a portion of the contents of A up the tube C for titration in E, whilst K leads to the exhaust pump. It is advisable to have a space between the tap H and the water pump, as this ensures there always being a ready vacuum available the moment the connexion is made through H to the flask.

The first set of experiments was made with quantities of a solution of silver nitrate of known strength, using $N/10$ sodium chloride in excess as precipitant, and titrating back with $N/10$ silver nitrate. A portion of the silver solution, equivalent to 0·5 gram of silver, is

placed in the flask A and diluted to about 100 c.c. with distilled water, 50 c.c. of the $N/10$ sodium chloride solution is then run into the flask directly, and the whole heated to boiling to coagulate the precipitated silver chloride.

$N/10$ Silver nitrate is then run in directly to the solution and precipitate up to within a few c.c. of the calculated amount necessary. The rubber cork with its attachment is replaced and the three-way tap, H, opened, and air drawn through the solution for a few minutes. This materially assists the settling of the precipitate. The tap is adjusted, and by means of the aspirator, J, some of the liquid and precipitate forced through the layer of sand and glass-wool * into E, which it reaches in a perfectly clear condition, the silver chloride being completely retained by the sand. A drop of $N/10$ silver nitrate is added, when a precipitate is formed, varying in intensity with the excess of salt still present. The liquid and precipitate are then sucked and washed down into A, and, if the thickness of the precipitate justifies it, about 1 c.c. of the silver solution is added *directly* to the contents of the flask. The stopper is again inserted, and the operation of forcing the mixture up into E, titrating, and washing down again, continued until no change is visible in the clear liquid, when a drop of the silver solution is added. The thin walls of E render the faintest opalescence readily observable, more particularly if a corresponding glass tube containing distilled water be used for comparison. The results of the first set of experiments are as follows :

In each case, 50 c.c. of silver nitrate solution were employed ($= 0.5$ gram Ag) and 50 c.c. of a solution of sodium chloride added, each c.c. of which is equivalent to 0.01081 gram Ag. This corresponds with 50.0463 c.c. $N/10$ sodium chloride. On titrating back and calculating the amount of silver equivalent to the nett sodium chloride used by the sample, the errors varied from zero to $+0.54$ per cent. Each titration required twenty minutes.

In order to reduce this error, if possible, samples containing 1 gram of silver were taken, 100 c.c. of sodium chloride added (1 c.c. = 0.01081 gram Ag), and the excess titrated back with $N/100$ silver nitrate solution (table I).

As in analyses of silver alloys by Gay-Lussac's method, the precipitation is effected in the presence of free nitric acid, a series of experiments was carried out to ascertain the effect of varying proportions of acid. The volume of the solution containing 1 gram of silver was 100 c.c. ; the amount of acid varied from 10 c.c. to 50 c.c., and the resulting errors from $+0.094$ to -0.216 per cent., the mean error being -0.0634 per cent., the presence of the nitric acid thus tending to make the precipitation more complete.

* Glass-wool and asbestos were found to be incapable of retaining the precipitate.

TABLE I.

Grams Ag employed.	N/100-AgNO₃ used to titrate back, in c.c.	Nett N/10-NaCl used, in c.c.	Equiv. to grams Ag.	Diff. in Ag found, in grams.	Error per cent.
1·0	72·00	92·8926	1·0032	0·0032	+ 0·32
1·0	76·20	92·4726	0·9987	0·0013	− 0·13
1·0	75·05	92·5876	0·99994	0·00006	− 0·006
1·0	73·20	92·7726	1·0019	0·0019	+ 0·19
1·0	72·30	92·8626	1·0029	0·0029	+ 0·29

Average error = + 0·266 per cent. and 0·068 per cent.   Mean error = 0·198 per cent.
Average time taken = 27 minutes.

To test the usefulness of this apparatus as applied to the practical estimation of silver in bullion, the usual conditions under which this is done by the Gay-Lussac method were adhered to, namely, 1 gram of pure silver dissolved in about 15 c.c. of nitric acid, 100 c.c. of $N/10$ sodium chloride added, and the excess titrated with $N/100$ silver nitrate. (When necessary, any excess of silver solution added was titrated with $N/100$ sodium chloride.)

The following table contains the results of these experiments, and the time taken:

TABLE II.

Grams Ag employed.	N/100-AgNO₃ used to titrate back, in c.c.	Nett N/10-NaCl used, in c.c.	Equiv. to grams Ag.	Diff. in Ag found, in grams.	Error per cent.
1·004	72·00	92·8926	1·0032	0·0008	− 0·08
1·000	73·30	92·7626	1·0018	0·0018	+ 0·18
0·9994	74·75	92·6176	1·00027	0·00087	+ 0·087
1·0018	73·80	92·7126	1·00129	0·0005	− 0·05
1·0034	73·00	92·7926	1·0021	0·0013	− 0·13
1·0030	72·30	92·8626	1·0029	0·0001	− 0·01
1·0035	72·30	92·8626	1·0029	0·0006	− 0·06

Average error = − 0·066 per cent. and + 0·133 per cent.
Mean error = − 0·067 per cent.   Average time taken = 30 minutes.

It may be added that no excessive shaking up of the mixture is required other than sufficient to ensure proper mixing after each addition of the reagent.

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