XXII.—*Note on Volhard's Method for the Assay of Silver Bullion.*

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THE method of estimating silver by means of ammonium thiocyanate described by Volhard (*Chem. News*, 1878, 37, 77) gives results with pure silver which are said by van Riemsdijk to be accurate to 0.25 part per 1000 (*Algemeen Verslag. Munt-Collegie*, 1878; Appendix, 38).

The general practice appears to be, after adding the normal solution, to make successive additions of decinormal solution, each sufficient to precipitate 0.25 milligram of silver, the reason assigned by van Riemsdijk being that an appreciable colour cannot be obtained without an excess of about that amount of the thiocyanate solution.

A limit of accuracy of less than 0.1 per 1000 of silver can, however, be obtained in testing the purity of fine silver by taking the following precautions.

One gram of silver is dissolved in a slight excess of dilute nitric acid in a bottle fitted with a stopper and subjected to prolonged heating to expel all traces of nitrous acid. 100 c.c. of normal solution of ammonium thiocyanate are added from a burette found by repeated trials to deliver a constant quantity of solution, the variation in the amount being less than 0.0025 c.c. The strength of the normal solution is adjusted so that from 0.5 to 1.0 milligram of silver remains in solution. The bottle is then well shaken and its contents immediately filtered. The precipitate needs very little washing, as the loss of even 2 or 3 c.c. of the liquid would not affect the result. Five c.c. of a saturated solution of iron alum decolorised by nitric acid, or better still of ferric nitrate, are then added, and the decinormal solution of thiocyanate run in drop by drop. When all the silver is precipitated, the addition of one drop (0.05 c.c. equivalent to 0.05 milligram of silver) of the decinormal solution converts the colourless silver solution to one of a pale straw colour. An additional weight of 0.1 milligram in the silver originally taken is readily recognised in the final reading. No time is saved by omitting to filter off the main bulk of the precipitate, as it must then be allowed to settle after each addition of decinormal solution, and the end reaction is not observed so easily, although quite distinct when 0.25 c.c. is added at a time.

Similar results can be obtained for alloys containing less than 50 parts of copper per 1000 of silver. The colour of the copper nitrate, however, masks the result if more than this amount is present. In that event, the light straw colour is not reached until the real limit is passed, and it is necessary to use checks of pure silver with the addition

of about the same amount of copper as in the alloys to be assayed. With this precaution, fairly good approximate assays can be obtained with alloys as low as 300 fine as indicated by Volhard.

This method is less liable to error, although far less rapid, than the Gay Lussac method as ordinarily practised in Mints, the limit of accuracy of which is 0.2 to 0.3 per 1000. It has been used at the Royal Mint in comparing the Silver Trial Plates now in course of preparation with those made in 1873.

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