

minations, no results being omitted. These show the reliability of the method :

54.63	54.44
54.48	54.49
54.61	54.44
54.40	54.44

With careful work the method presents no particular difficulty.

Of course it does not follow from the foregoing that the method is very generally applicable to nitro bodies. Investigations will be made to determine the limits of its utility.

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A MODIFIED METHOD OF FINE SILVER ASSAY.

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IN the government assay offices and in the laboratories of silver refineries the assay of fine silver is usually performed according to the method of Gay-Lussac. Two solutions are required, a standard solution of sodium chloride, 100 cc. of which will very nearly precipitate one gram of pure silver, and a second solution, the exact decimal of the former, by means of which the titration is carried to an end. The quantity of fine silver weighed for assay is so adjusted that it will contain one or two milligrams over one gram of pure silver, a preliminary fine assay being made, if necessary, in order to determine the exact quantity to be taken. It is dissolved in nitric acid, 100 cc. of the standard solution of salt are added, and by vigorous shaking the precipitate is caused to collect. In the clear solution the excess of silver is precipitated by means of the decimal solution, added one cc. at a time, and shaken before each addition, in order to observe the cloudiness produced. Fractions of one cc. are estimated by the depth of cloudiness on the last addition of decimal solution causing a perceptible precipitation.

This tentative method, though accurate, is apt to be tedious, much time being consumed if the fineness of the silver is not known within 0.002 to 0.003. About three minutes shaking is required in order to obtain a perfectly clear solution, which is very irksome if there is no mechanical agitator at the operator's disposal.

I have for some time used a modification of this method, largely obviating the shaking, and have found it both speedy and accurate. Instead of making the final titration with the decimal solution of sodium chloride, I prefer to titrate out with potassium thiocyanate according to the method of Volhard, using a ferric salt as an indicator. The standard solution employed is the same as in the original method, variations due to temperature and evaporation being eliminated by running a proof of pure silver with each daily set of assays. The solution of potassium thiocyanate is not an exact decimal of the first, but is standardized against pure silver so that one cc. will precipitate exactly one milligram of silver. A correction for this solution is not required, since in this dilution possible variations would fall beyond the limit of accuracy, which I place at 0.2 to 0.3 milligram. Results are stated in milligrams of silver per thousand.

In performing the assay exactly one gram of the sample is weighed into a well annealed bottle (eight ounce) fitted with an accurately ground stopper; nitric acid, diluted with about two volumes of water free from chlorine, is added, and solution hastened by placing on a hot iron plate. Heating should be continued until the last traces of nitrous acid have been expelled, which would otherwise interfere with the accuracy of the method. Two proofs of pure silver are weighed and dissolved in the same manner; it is not necessary to weigh an exact gram, but the actual weight taken should be accurately ascertained.

When the nitrous fumes have disappeared, enough water is added to prevent crystallizing of the silver nitrate, and 100 cc. of standard salt solution, delivered with great accuracy from an automatic pipette, is run into each assay. The stopper is inserted and the solution shaken until the silver has collected, when it is filtered, five cc. of a solution of ferric ammoniac alum added, and the thiocyanate solution run in from a burette until the characteristic color of ferric thiocyanate no longer disappears. This titration should be performed in the cold.

Suppose, for instance, that 1001.3 milligrams of pure silver had been taken for a proof and eight and four-tenths cc. of thio-

cyanate (equal to eight and four-tenths milligrams silver) had been required, then the titer of the salt solution is

$$1001.3 - 8.4 = 992.9.$$

The standard of the salt solution having thus been obtained from the average of two proofs, the fineness of the assays is found by adding the number of cubic centimeters of thiocyanate solution required to the standard found.

Copper and other impurities liable to be found in fine silver do not interfere with the accuracy of this method. It is necessary to separate the silver chloride by filtration because it slowly decomposes silver thiocyanate, and the wash-water must be free from chlorine.

I have repeatedly tested this method and found it accurate, as shown by the following data taken at random from my note book :

	Milligrams taken.	Thiocy- anate. cc.	Standard.	Thiocy- anate. cc.	Milligrams found.	Differ- ence.
Proof	1000.0	- 8.5	= 991.5			
	1000.0	- 8.5	= 991.5			
			Average, 991.5			
Fine silver taken.	996.7		991.5	+ 5.3	= 996.8	+ 0.1
	996.9		991.5	+ 5.2	= 996.7	- 0.2
	998.9		991.5	+ 7.5	= 999.0	+ 0.1
Proof	1000.0	- 7.0	= 993.0			
	1000.4	- 7.5	= 992.9			
			Average, 993.0			
Fine silver taken.	994.0		993.0	+ 1.0	= 994.0	..
	997.0		993.0	+ 4.2	= 997.2	+ 0.2
	999.0		993.0	+ 6.3	= 999.3	+ 0.3
Proof	1000.0	- 8.2	= 991.8			
	1000.0	- 8.0	= 992.0			
			Average, 991.9			
Fine silver taken.	998.0		991.9	+ 5.9	= 997.8	- 0.2
	1001.8		991.9	+ 9.8	= 1001.7	- 0.1