

The results are in percentages of stannous chloride. The theoretical percentage is 50.49.

The method has the advantage of being less interfered with by the presence of other substances, than is the usual method of titrating with ferric chloride and permanganate. The titrations may be made in the presence of iodides and bromides and in the presence of iron salts, these cases conflicting with the permanganate method.

Although definite data have not yet been obtained, it is believed that the method may be applied in the presence of many organic bodies also.

STANFORD UNIVERSITY,
July 15, 1897.

THE VOLUMETRIC DETERMINATION OF THE NITRO GROUP IN ORGANIC COMPOUNDS.

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Received July 31, 1897.

AS was pointed out in the previous paper, "The Titration of Stannous Salts with Iodine," it is possible to accurately determine the amount of stannous tin in a solution by means of standard iodine. This suggested the possibility of determining certain oxidizing agents by utilizing the reducing power of stannous chloride. The following results show that the process is applicable to the determination of the nitro group, at least in dinitrobenzene.

There are requisite for the method :

(1) A standard solution of iodine whose value is accurately known.

(2) A dilute solution of stannous chloride, preferably of such strength that one cc. of it is equivalent to about three cc. of the iodine. The object of using so strong a solution is to avoid the necessity of using too large a volume of it.

The process of determination was as follows :

Weighed samples of pure dinitrobenzene, which had been recrystallized from alcohol, were placed in Erlenmeyer flasks, holding about 500 cc. Ten to fifteen cc. of alcohol were added in order to bring the samples into solution. The relationship between the iodine and stannous chloride solutions was now accurately determined. The flasks were then all connected, in

series, with a Kipp generator for carbon dioxide, and when filled with the gas, the stopper of each was removed, and so much of the stannous chloride solution added as was estimated to be sufficient to reduce the dinitrobenzene and leave a small excess (ten to twenty cc. excess is sufficient). Connection with the gas generator was again established, and a slow stream of the gas was kept passing through the apparatus throughout the process of reduction. The flasks are heated on the water-bath to hasten the process. Under these conditions one and one-half to two hours was found sufficient time to complete the reduction. The addition of twenty to twenty-five cc. of strong hydrochloric acid appeared to hasten the process somewhat.

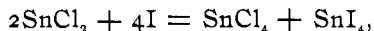
Upon completion of reduction the flasks are removed and the excess of stannous chloride titrated with standard iodine solution, and the net volume of stannous chloride calculated.

The most likely reaction between the nitro group and stannous chloride is as follows :



The results obtained confirm this.

The reaction between iodine and stannous chloride being



it follows that a factor can be found which will be the nitro equivalent of the iodine solution. Then knowing the relationship between the iodine and stannous chloride, we can calculate the volume of iodine equivalent to the volume of stannous chloride used, then from the nitro equivalent of the iodine we can easily calculate the percentage of nitro group in the body. The nitro factor of the stannous chloride might, of course, be determined, but would not be so satisfactory as that of the iodine, on account of the rapidity with which the stannous chloride changes.

Following are eight selected results of the determinations upon dinitrobenzene :

54.68	54.83
54.51	54.64
54.76	54.66
54.94	54.92

The theoretical percentage is 54.76.

Following are eight results obtained from *one series* of deter-

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.

STANFORD UNIVERSITY,
July 20, 1897.

A MODIFIED METHOD OF FINE SILVER ASSAY.

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Received August 23, 1897.

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.