

and the solution allowed to slowly crystallize. *b* gives the spectrum of the mother-liquor from the resulting crystals, showing increase in intensity of the neodidymium and samarium bands; *c* is the spectrum of the solution of the crystals, showing marked weakening of the neodidymium bands, and strengthening of the praseodidymium.

These changes in the absorption bands cannot be due merely to the presence of lanthanum in the solutions, since the effect of such addition was repeatedly tried on different solutions and no changes in the character of the absorption bands could be detected other than a uniform weakening due to dilution. As soon, however, as crystallization began, the crystals and mother-liquor showed differences from the original solution.

In fractioning by this method, it was noticed that the heavy band in the orange was not resolved into the component bands described by Welsbach, even when the remainder of the lines had undergone marked changes, this observation confirming the statement of Crookes that "probably didymium will be found to split up in more than one direction, according to the method adopted."¹ In certain fractions the relative intensities of the bands bore out the observations of previous investigators as to the compound nature of both neodidymium and praseodidymium. Thus in one portion the neodidymium band λ -428 was intense, while the other didymium bands were comparatively faint. We also obtained fractions which showed the band λ -443 much more strongly than any other bands.²

CORNELL UNIVERSITY, August, 1897.

THE TITRATION OF STANNOUS SALTS WITH IODINE.

By S. W. YOUNG.

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FRESENIUS³ describes very briefly a method by Lenssen, for titrating stannous chloride with iodine in neutral or faintly alkaline solution. As was pointed out in a previous paper,⁴ it was evident that the action of iodine on stannous chloride was a quantitative one also in acid solution. Further study has con-

¹ *Chem. News*, 54, 27.

² See also Crookes: *J. Chem. Soc.*, 56, 260.

³ *Syst. Quant. Chem. Anal.*, 1st Am. Ed., p. 342.

⁴ *This Journal*, 19, 517.

firmed this point, and it has been found perfectly possible to titrate stannous salts with great accuracy in acid solution, provided, of course, there are neither oxidizing or reducing substances also in the solution.

The method of operation is very simple, and consists simply in bringing the stannous salt into solution, preferably with dilute hydrochloric acid, adding starch paste and then standard iodine solution until a blue color is produced. The essential precautions are :

(1) Care to prevent oxidation of the stannous salt solution by undue exposure to air. The solution should be prepared rapidly and titrated immediately.

(2) Since the titration is carried on in acid solution, it is essential that the potassium iodide used in the preparation of the standard iodine solution should be particularly free from iodate, since if this latter were present, it would be decomposed rapidly by the acid in the solution titrated and considerable iodine would be set free from the action of the iodic acid on the potassium iodide. This would, of course, make the results of the titration too low.

As thiosulphate cannot be satisfactorily used in acid solution to titrate against iodine, it will be found very convenient to use a dilute solution of stannous chloride for that purpose. This solution may most conveniently be kept under coal oil, and since its strength changes rapidly even then, its relationship to the iodine solution should be very frequently determined—at least once a day.

The most convenient method for preparing the stannous chloride solution is to treat metallic tin with concentrated hydrochloric acid until the action becomes rather slow. Then filter rapidly through cotton wool, preserving this solution under oil for future use. To prepare from this the dilute solution for titration, the standard of the strong solution is roughly determined, and a portion is then diluted to the desired strength and the standard of this is accurately determined.

In this work the iodine has been first standardized by the usual method with thiosulphate.

Following are the results of determinations made with the method, of the percentage of stannous chloride in the salt

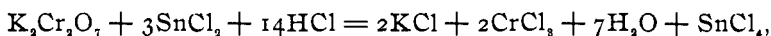
$K_2SnCl_6 \cdot 2H_2O$, described by Richardson.¹ The agreement of the results is very good. Compared with the theoretical the values run a trifle high (three-tenths to four-tenths per cent.).

The cause of this, it was thought, might lie in the fact that the standardizing of the iodine solution took place under entirely different conditions from those existing in the actual determination, *i. e.*, in neutral instead of acid solution.

In general the standard of iodine by thiosulphate is likely to be a trifle high.

The following method for standardizing was then tried: A fresh solution of stannous chloride was prepared of such strength as to be approximately equivalent to the iodine solution. Portions of C. P. potassium bichromate were weighed out (about two-tenths gram). These were titrated with the stannous chloride solution until the bichromate had been completely reduced and then titrated back with iodine solution until the starch iodine blue was produced. The green color of the chromium chloride does not interfere.

The reaction between potassium bichromate and stannous chloride being



and the relationship between the iodine and the stannous chloride solutions being accurately determined, the stannous chloride equivalent of the iodine solution may be calculated. By this method the stannous chloride equivalent was found to be 0.004150 gram per cubic centimeter.

By the thiosulphate method the standard of the same solution had previously been found to be 0.004178 gram per cubic centimeter.

Following are the results of the titration by the thiosulphate standard upon the salt $K_2SnCl_6 \cdot 2H_2O$.

50.95	50.85	51.05
51.17	50.70	50.88
50.87	50.88

Following are the same results calculated by the bichromate standard:

50.60	50.51	50.72
50.82	50.36	50.53
50.52	50.53

¹ *Am. Chem. J.*, 14, 91.

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.

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THE VOLUMETRIC DETERMINATION OF THE NITRO GROUP IN ORGANIC COMPOUNDS.

BY S. W. YOUNG AND R. E. SWAIN.

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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