ART. V. — *The Titration of Mercury by Sodium Thiosulphate;* by JOHN T. NORTON, JR.

[Contributions from the Kent Chemical Laboratory of Yale University—XCV.]

ACCORDING to J. J. Scherer* mercurous nitrate, mercuric nitrate and mercuric chloride may be estimated by direct titration with sodium thiosulphate, Hg_2S, $2HgS.Hg(NO_3)_2$, and $2HgS.HgCl_2$ being the precipitates obtained in each case. I have been unable to obtain access to Scherer's original publication, but Sutton† gives the following very general directions for this process:

(*a*) "*Mercurous salts.*—The solution containing the metal as a protosalt only is diluted, gently heated and the thiosulphate delivered in from the burette at intervals, meanwhile well shaking until the last drop produces no brown color. The sulphide settles freely and allows the end of the reaction to be easily seen. One cm³ of the $\frac{1}{20}$ normal solution of thiosulphate = 0·02 grams Hg or 0·0208 HgO.

(*b*) *Mercuric nitrate.*—The solution is considerably diluted, put into a stoppered flask, nitric acid added and the thiosulphate cautiously added from the burette, vigorously shaken meanwhile, until the last drop produces no further precipitate. Scherer recommends that when the greater part of the metal is precipitated the mixture should be diluted to a definite volume, the precipitate allowed to settle and a measured quantity of the clear liquid taken for titration; the analysis may then be checked by a second titration of the clear liquid if needful. One cm³ of $\frac{1}{20}$ normal thiosulphate = ·015 of Hg. or ·0162 of HgO.

(*c*) *Mercuric chloride.*—With mercuric chloride the end of the process is not so easily seen. The very dilute solution is acidified with hydrochloric acid, heated nearly to boiling, and the thiosulphate cautiously added so long as a white precipitate is seen to form; any great excess of the precipitant produces a dirty-looking color. Filtration is necessary to distinguish the exact ending of the reaction. One cm³ of $\frac{1}{20}$th normal thiosulphate = ·015 Hg or ·0162 HgO."

Fresenius‡ gives practically the same directions, but omits all mention of that portion of the process dealing with mercurous nitrate.

In view, therefore, of the scant information available on the subject and of the apparent difficulty of working the process accurately according to the directions given, an attempt was

* His Lehrbuch der Chemie, i, 513.

† Volumetric Analysis, p. 220.

‡ Quantitative Analysis.

made to ascertain whether the careful regulation of temperature, dilution and amount of acid present might not produce beneficial results.

That portion of the process dealing with mercuric chloride was first taken up. The mercuric chloride used was pulverized, dried at 100° and its purity proved by several determinations as mercuric sulphide. The sodium thiosulphate was made up of approximately $\frac{1}{20}$th normal strength and standardized on decinormal iodine, which in turn was titrated against decinormal arsenious acid made from pure resublimed arsenious oxide.

For the action of sodium thiosulphate upon the mercuric chloride Scherer gives the equation,

$$3HgCl_2 + 2Na_2S_2O_3 + 3H_2O = 2HgS.HgCl_2 + 2Na_2SO_4 + 4HCl.$$

According to my experience, the action results in the formation of a dense white precipitate which refuses to settle either by shaking or standing, thus making it impossible to fix the end reaction by reading the first drop of thiosulphate which produces no further white precipitate in the solution containing the mercuric chloride. Recourse must be had therefore to filtering. By far the quickest and neatest method is to use the asbestos filter deposited on a large perforated platinum cone.* This cone is set in a glass funnel by means of a rubber connector and the funnel is passed through the stopper of a large side-necked Erlenmeyer connected with an exhaust pump. A little asbestos fiber shaken in the liquid to be filtered was found to be very beneficial in preventing the precipitate from running through the filter. In all the following experiments the thiosulphate was run into the solution containing the mercuric chloride in excess, the whole shaken up with asbestos fiber, filtered and the excess of thiosulphate determined by $\frac{1}{20}$th normal iodine. This method of procedure seems to be far preferable to attempting to catch the end of the reaction by running in the thiosulphate until the last drop produces no precipitate. In the experiments shown in Table I no attention was paid to the temperature of the solution and the thiosulphate was run in until the liquid turned brown. In every case the solution was allowed to stand until there was no further visible change of color.

A glance at the table shows that the results are most irregular. In Table II is seen the result of regulating the temperature and the length of standing after the addition of the sodium thiosulphate.

* Amer. Chem. Jour., i, 321.

TABLE I.

	$HgCl_2$ taken calc'd as Hg. grams.	$Na_2S_2O_3$ in excess. cm^3.	Volume at beginning. cm^3.	$HgCl_2$ found calc'd as Hg. grams.	Error. grams.
1.	0·0446	46·28	200	0·0343	0·0103—
2.	0·0354	46·28	400	0·0326	0·0028—
3.	0·0356	44·97	400	0·0225	0·0131—
4.	0·0345	44·5	100	0·0308	0·0037—
5.	0·0354	44·43	50	0·0326	0·0028—
6.	0·0382	22·59	50	0·0354	0·0028—
7.	0·0375	8·58	50	0·0385	0·0010+
8.	0·0371	1·84	50	0·0304	0·0067—
9.	0·0731	2·28	50	0·0774	0·0043+
10.	0·1486	9·34	50	0·1489	0·0003+

TABLE II.

	$HgCl_2$ taken as Hg. grams.	Volume at beginning. cm^3.	Temperature. C.	Standing minutes.	$Na_2S_2O_3$ in excess. cm^3.	$HgCl_2$ as Hg. found.	Error. grams.
1.	0·0738	50	36°	40	16·68	0·0494	0·0244—
2.	0·0741	50	70	15	15·42	0·0738	0·0003—
3.	0·0741	75	70	12	16·07	0·0733	0·0008—
4.	0·0744	50	70	10	14·6	0·0755	0·0011+
5.	0·0764	50	72	7	6·77	0·0771	0·0007+
6.	0·0762	50	75	10	8·54	0·0799	0·0037+
7.	0·0756	50	73	15	9·99	0·0815	0·0059+
8.	0·0774	50	68	15	10·84	0·0767	0·0007—
9.	0·0745	75	69	7	6·62	0·0805	0·0060+
10.	0·0736	50	68	5	15·82	0·0714	0·0022—

These results, although better than those of Table I, are still very uncertain. On the supposition that the change from white to black, which takes place in the solution after the addition of an excess of sodium thiosulphate more or less quickly according to the temperature, was due to an increased amount of HgS in the compound $2HgS.HgCl_2$, the next step was to ascertain whether this could be avoided by stopping the addition of the thiosulphate at the first indication of a change of color in the white precipitate, diluting the solution with a large amount of cold water and immediately throwing it on the filter. The following table (III) shows the result of the experiments.

In the case of quantities of mercuric chloride up to 0·1 gram the results shown in Table III are very satisfactory, but when larger amounts of mercuric chloride are used the errors again become prominent. In Table IV, the effect of lowering the temperature to 60° C. and of increasing the dilution to 100^{cm^3} is shown.

TABLE III.

	$HgCl_2$ taken as Hg. grams.	Volume at beginning. cm^3.	Temperature. C.	$Na_2S_2O_3$ in excess. cm^3.	$HgCl_2$ found as Hg. grams.	Error. grams.
1.	0·0749	50	70°	4·15	0·0751	0·0002 +
2.	0·0749	50	75	0·72	0·0728	0·0021 —
3.	0·0756	50	72	1·46	0·0759	0·0003 +
4.	0·0753	50	70	2·57	0·0750	0·0003 —
5.	0·0390	50	70	3·43	0·0395	0·0005 +
6.	0·0388	50	72	8·19	0·0390	0·0002 +
7.	0·0380	50	76	2·03	0·0393	0·0013 +
8.	0·1494	50	78	4·99	0·1498	0·0004 +
9.	0·1489	150	78	4·38	0·1512	0·0023 +
10.	0·1480	50	70	0·52	0·1438	0·0042 —
11.	0·1498	50	78	1·47	0·1540	0·0042 +
12.	0·1484	50	71	2·09	0·1517	0·0033 +
13.	0·1480	75	72	1·59	0·1509	0·0029 +

TABLE IV.

	$HgCl_2$ taken as Hg. grams.	Volume at beginning. cm^3.	Temperature. C.	$Na_2S_2O_3$ in excess.	$HgCl_2$ found as Hg. grams.	Error. grams.
1.	0·0759	100	60°	3·06	0·0766	0·0007 +
2.	0·0384	"	"	2·81	0·0387	0·0003 +
3.	0·1498	"	"	1·1	0·1500	0·0008 +
4.	0·1503	"	"	1·63	0·1506	0·0003 +
5.	0·1479	"	"	2·41	0·1480	0·0001 +
6.	0·1489	"	"	2·12	0·1503	0·0014 +
7.	0 2244	"	"	2·63	0·2259	0·0015 +
8.	0·1490	"	"	2·33	0·1484	0·0006 —
9.	0·0758	"	"	2·	0·0762	0·0004 +
10.	0·0383	"	"	2·58	0·0379	0·0004 —

From this table it is plain that Scherer's process for the estimation of mercury in the form of mercuric chloride is capable of yielding accurate results if carried out under certain fixed conditions. These conditions, which must be closely adhered to, are as follows: The solution containing the mercury in the form of mercuric chloride is placed in a liter flask, diluted to 100^{cm^3} and heated to a temperature of 60° C. The sodium thiosulphate in $\frac{1}{20}$th normal solution is run in from a burette until the white precipitate formed begins to take on a brownish tinge. The solution is then diluted with cold water, some asbestos fiber added to coagulate the precipitate and the whole is quickly thrown on the filter. After careful washing of the precipitate, the filtrate is diluted to a definite volume, 3 grams of potassium iodide added and the excess thiosulphate

titrated with iodine and starch solution. The duration of the process need not exceed 15 minutes. It is worthy of note that there is no necessity of using any hydrochloric acid in addition to that formed in the reaction. This certainly eliminates one probable source of error—the interaction of hydrochloric acid and sodium thiosulphate.

In dealing with the estimation of mercury in the form of mercurous nitrate the same method of procedure was employed as in the case of mercuric chloride. A solution of mercurous nitrate was prepared by dissolving as much as possible of 20 grams of the salt in about 200$^{cm^3}$ of water, filtering off the clear liquid and diluting to a definite volume. The standard of the solution was determined by precipitation as metallic mercury by means of the electric current. Contrary to the statement made in Sutton, the brown precipitate of Hg_2S— formed as shown in the equation,

$$Hg_2(NO_3)_2 + Na_2S_2O_3 = Hg_2S + Na_2SO_4 + N_2O_5—$$

does not settle and leave a clear supernatant liquid, but the solution remains cloudy and it is impossible to see any end reaction. Although the conditions of dilution, temperature and amount of acid present were carefully considered, no arrangement or adjustment of these conditions was found under which satisfactory results could be obtained. Table V gives the result of experiments.

TABLE V.

	$Hg_2(NO_3)_2$ taken as Hg. grams.	HNO_3 1 : 3. cm^3.	Volume at beginning. cm^3.	Temperature. C.	$Na_2S_2O_3$ in excess. cm^3.	$Hg_2(NO_3)_2$ found as Hg. grams.	Error. grams.
1.	0·0148	none	50	50°	4·28	0·0129	0·0019—
2.	0·0148	"	75	60	4·45	0·0117	0·0031—
3.	0·2976	"	300	60	12·67	0·2760	0·0216—
4.	0·1488	"	100	40	2·19	0·1386	0·0102—
5.	0·1488	"	100	50	6·92	0·1378	0·0110—
6.	0·1488	"	200	50	0·78	0·1388	0·0100—
7.	0·0744	"	100	65	0·73	0·0636	0·0108—
8.	0·0744	1	100	55	0·49	0·0733	0·0011—
9.	0·0744	2	100	40	1·16	0·0660	0·0084—
10.	0·0744	1	100	55	1·35	0·0685	0·0059—
11.	0·0744	1	100	55	0·82	0·0686	0·0058—
12.	0·0744	$\frac{1}{2}$	200	55	1·71	0·0685	0·0059—
13.	0·0744	4	100	40	1·77	0·0649	0·0095—
14.	0·0744	$5\frac{1}{2}$	100	40	1·34	0·0645	0·0099—
15.	0·0744	1	100	45	1·71	0·0654	0·0090—
16.	0·0744	10	100	45	1·55	0·0669	0·0075—
17.	0·1488	1	100	40	0·73	0·1391	0·0097—

The errors in experiments 1, 3, 4, 5, 6, 10, 11, 12 and 17 are, proportionally to the amount of material handled, practically the same and this fact caused me to make a careful revision of all standards; but no mistake could be found. The reaction upon which the process depends requires the formation of Hg_2S, but this mercurous sulphide breaks down immediately into mercuric sulphide and mercury. The latter is probably acted upon by the free nitric acid present to form mercuric nitrate, which in turn is transformed into the compound $2HgS.Hg(NO_3)_2$ by the action of the thiosulphate. At any rate, with an error so large, whatever its source may be, the process is plainly impracticable.

The third step in Scherer's process deals with the action of sodium thiosulphate on mercuric nitrate. In the following experiments a solution of mercuric nitrate was prepared either by dissolving as far as possible 20 grams of mercuric nitrate in about 200^{cm^3} of cold water, filtering off the supernatant liquid and diluting to a definite volume (exps. 1–8), or by dissolving the salt in strong nitric acid and diluting (exps. 9–19). The standard of the solution was obtained by precipitation as metallic mercury by means of the electric current. The yellow precipitate, formed according to Scherer's reaction,

$$3Hg(NO_3)_2 + 2Na_2S_2O_3 = 2HgS.Hg(NO_3)_2 + 2Na_2SO_4 + 2N_2O_5,$$

on adding the sodium thiosulphate settles much better than in the case of either mercuric chloride or mercurous nitrate; but, as the supernatant liquid takes on a permanent yellow color towards the end of the reaction, it is impossible to see when the thiosulphate produces no further precipitation. On this account, therefore, the same method of procedure was adopted as in the case of the mercuric chloride and mercurous nitrate, i. e., filtration and titration of the excess of sodium thiosulphate with iodine and starch solution. The result of the experiments is shown in the following table.

These results seem to show the impossibility of obtaining accurate results according to Scherer's method for the determination of mercuric nitrate by direct titration with sodium thiosulphate. The constant plus error cannot be accounted for on the hypothesis that the nitric acid present decomposes the sodium thiosulphate, for in that case the error would lie in the other direction. It is more probable that the constitution of the compound $2HgS, Hg(NO_3)_2$ is not definite enough to make it the basis for an analytical process.

TABLE VI.

	$Hg(NO_3)_2$ taken as Hg. grams.	Volume at beginning. cm^3.	HNO_3 1 : 3 cm^3.	Temperature. C.	$Na_2S_2O_3$ in excess. cm^3.	$Hg(NO_3)_2$ found as Hg. grams.	Error. grams.
1.	0·1167	200	none	60°	0·46	0·1384	0·0217 +
2.	0·1167	100	1	60	3·63	0·1348	0·0181 +
3.	0·1167	100	2	60	0·23	0·1375	0·0208 +
4.	0·1167	100	none	60	0·17	0·1360	0·0193 +
5.	0·1167	300	"	21	0·12	0·1232	0·0065 +
6.	0·1167	300	"	21	0·15	0·1375	0·0208 +
7.	0·1167	200	"	21	11·8	0·1461	0·0294 +
8.	0·1167	200	20	21	15·97	0·1403	0·0236 +
9.	0·1278	200	none	21	5·23	0·1647	0·0369 +
10.	0·1278	200	"	"	1·35	0·1653	0·0375 +
11.	0·1278	100	"	"	1·43	0·1662	0·0384 +
12.	0·0752	200	"	"	2·09	0·0996	0·0244 +
13.	0·0255	100	"	"	2·01	0·0280	0·0025 +
14.	0·0255	200	5	"	3·44	0·0264	0·0009 +
15.	0·0255	200	10	"	0·85	0·0334	0·0079 +
16.	0·0255	300	none	"	1·96	0·0264	0·0009 +
17.	0·0255	200	"	"	1·9	0·0287	0·0032 +
18.	0·0255	200	"	"	1·76	0·0290	0·0035 +
19.	0·0639	200	"	60	1·53	0·0831	0·0192 +

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