CHEMISTRY

1958

SovietRxiv

Fig. 1. Heating curves of thallium dichromate: a —unwashed; b —washed with acetone (the same curve is obtained after washing with ethyl alcohol); c — washed with water and then with acetone

Figure 1: Fig. 1. Heating curves of thallium dichromate: a —unwashed; b —washed with acetone (the same curve is obtained after washing with ethyl alcohol); c —washed with water and then with acetone

Abstract

Full Text

CHEMISTRY

N. I. BASHILOVA

STUDY OF THALLIUM DICHROMATE AND ITS APPLICATION IN QUANTITATIVE ANALYSIS

(Presented by Academician I. I. Chernyaev on 13 VIII 1957)

The literature data on thallium dichromate are very limited and relate mainly to the last century ([1]-[5]).

As early as 1867, Karstanjan ([5]) expressed the opinion that sparingly soluble thallium compounds—its mono- and dichromate—could be used for the quantitative determination of this metal. Indeed, the best method for the gravimetric determination of thallium, according to a number of authors ([6]-[8]), is its determination in the form of the monochromate ([9]).

Thallium has never been determined quantitatively in the form of the dichromate. Moreover, this compound was considered ([10]) unsuitable for the gravimetric determination of thallium. Its precipitation from hydrochloric acid solution under strictly limited conditions was used in analysis ([10]) only for separating Tl(I) from Tl(III) and Fe. However, the determination of thallium in the form of the dichromate when it is precipitated from acid solutions is of unquestionable interest, since in this case it appears possible to carry out the determination of thallium with simultaneous separation from the principal elements accompanying it. This advantage of the method is especially valuable for thallium—a metal belonging to the group of dispersed elements.

Fig. 1. Heating curves of thallium dichromate: *a* —unwashed; *b* —washed with acetone (the same curve is obtained after washing with ethyl alcohol); *c* — washed with water and then with acetone.

In the study of water-salt systems formed by thallium monochromate and chromic anhydride, as well as by thallium sulfate and chromic anhydride, we established, in particular, that thallium dichromate is an incongruently soluble compound, completely precipitated from solutions by an excess of chromic anhydride. This served as the theoretical basis for developing a method for the quantitative determination of thallium in the form of the dichromate.

To use thallium dichromate in gravimetric analysis as the weighed compound, it was necessary to find the conditions for its quantitative separation from the mother liquor while preserving its composition.

It was established that thallium dichromate is insoluble, in particular, in acetone and ethyl alcohol.

For the study of thallium dichromate after washing it with the named solvents, phase differential thermal analysis was used, in particular. The heating curves obtained on Kurnakov' s pyrometer—

are presented in Fig. 1. The first two of them (Fig. 1 *a*, *b*), corresponding respectively to thallium dichromate well separated from the mother liquor by filters and to thallium dichromate washed with acetone (or ethyl alcohol), are analogous. They are characterized by two endothermic effects. Visual observations of these effects showed that the first of them corresponds to the appearance of a liquid phase, while the second corresponds to complete melting of the salt. The temperatures of the thermal effects in the thermograms differ somewhat. They are, naturally, lower on the heating curve of unwashed thallium dichromate, which therefore contains a certain amount of dry residue from the mother liquor.

The identical character of these thermograms indicates that thallium dichromate does not change its composition when washed with acetone or ethyl alcohol.

The heating curve of thallium dichromate washed with water and only then with acetone (Fig. 1 *c*) is characterized by a small additional endothermic effect, which occurs in the solid state and corresponds to the polymorphic transformation of thallium monochromate, recorded thermographically upon heating. The presence of this effect indicates decomposition of thallium dichromate and, consequently, confirms the incongruent character of its dissolution.

Table 1

Determination of thallium as dichromate

No.	Tl_2SO_4, g per 100 ml, taken for precipitation	CrO_3, g per 100 ml, taken for precipitation	H_2SO_4, g per 100 ml, taken for precipitation	Found* Tl_2SO_4, g	Error, mg
1	0.1000	0.25	–	0.0998	–0.2
2	0.1000	0.75	1	0.0998	–0.2

No.	Tl_2SO_4, g per 100 ml, taken for precipitation	CrO_3, g per 100 ml, taken for precipitation	H_2SO_4, g per 100 ml, taken for precipitation	Found* Tl_2SO_4, g	Error, mg
3	0.1000	0.75	10	0.0992	−0.8
3**	0.1000	0.75	10	0.0999	−0.1
4	0.1000	1.5	–	0.0999	−0.1
5	0.1000	1.5	10	0.0998	−0.2
5**	0.1000	1.5	10	0.1000	0.0
6	0.1000	2.25	18	0.0988	−1.2
6**	0.1000	2.25	18	0.0997	−0.3
7	0.1000	8.0	–	0.0998	−0.2

* Mean values from several determinations.
** The precipitate of thallium dichromate was kept with the mother liquor, whose volume did not exceed 100 ml, for 2–4 hours while cooling to 1-3°. In the remaining determinations—18-20 hours at room temperature.

It is characteristic that decomposition of thallium dichromate under the action of water into monochromate and chromic anhydride proceeds very slowly. This is of independent interest and is probably explained by the fact that both thallium dichromate and thallium monochromate are sparingly soluble compounds.

To find the conditions for the quantitative determination of thallium as dichromate, we carried out a systematic study of its precipitation from neutral and acidic (sulfuric-acid and nitric-acid) solutions with chromic anhydride, as well as with the dichromates of sodium, potassium, and ammonium.

The results for the determination of thallium as dichromate, some of which are presented in Table 1, prove the possibility of quantitative determination of thallium by this method and thereby refute the contrary assertions found in the literature ([10]).

The results obtained made it possible to find the dependence of the mean error in the determination of thallium, when precipitating it from sulfuric-acid solutions with chromic anhydride, on the different ratio of these components in the solution. This dependence made it possible to determine the maximum permissible concentrations of the named components for the quantitative precipitation of thallium and to establish the optimal conditions for the determination of thallium.

Comparison of the results of analyses carried out with cooling of the solution with the precipitate of thallium dichromate and at room temperature shows (Table 1) that, in the former case, quantitative results of the determination are obtained even in those cases where, without cooling, they do not occur.

Determination of thallium as dichromate makes it possible to vary widely both the acid concentration in the solution and the concentration of the precipitating

chromate. The experimental material obtained makes it possible, for each particular case, to determine the concentration of chromic anhydride necessary for the quantitative precipitation of thallium, depending on the concentration of acid in the solution.

In the general case, for its quantitative determination it is expedient to precipitate thallium in the form of the bichromate from solutions containing up to 10 g of H_2SO_4 (or HNO_3) in 100 ml of solution, with chromic anhydride (or sodium bichromate), the concentration of which averages 1 g per 100 ml of the liquid phase.

When thallium is precipitated with potassium or ammonium bichromate, the results of thallium determinations are too high and are satisfactory only in some cases.

Determination of thallium in the form of the bichromate, as we have established, can be carried out not only by the gravimetric method but also by an indirect volumetric method, according to the amount of precipitant that has reacted.

One variant of the method may also be the radiometric determination of thallium in the form of the bichromate, using the radioactive isotope Tl^{204}.

Table 2

Determination of thallium in the form of the bichromate in the presence of other metals

No.	Taken Tl_2SO_4, g	Present	Found Tl_2SO_4, g	Error, mg
1**	0.1000	**Sulfate salts***:Zn, Cd, Al, Fe(III),Cu(II) 1 g eachNi, Co 0.5 g eachIn, Ga, Ge 0.1 g each	0.09990.1000	−0.10.0
2**	0.1000	**Nitrate salts**:Ag, Bi, Hg(II) 0.01 g each	0.09970.1000	−0.30.0

No.	Taken Tl_2SO_4, g	Present	Found Tl_2SO_4, g	Error, mg
3***	0.1000	**Nitrate salts**:Pb, Bi 0.02 g eachAg, Hg(II) 0.01 g eachBa 0.1 g	0.09990.1002	−0.1+0.2
4**	0.1000	All salts indicated for Nos. 1 and 2, in the same amounts	0.09970.0999	−0.3−0.1

* The amounts of sulfate salts are given without water of crystallization.
** Precipitation was carried out from sulfate solutions.
*** Precipitation was carried out from nitrate solutions.

The proposed new method for the quantitative determination of thallium has a number of advantages compared with the known methods for its determination. The principal advantage of the method, among others, is the possibility of direct determination of thallium without preliminary separation of the principal accompanying elements. This possibility is confirmed by the results of the determination of thallium in the form of the bichromate from acidic solutions containing other metals. Some of these data are presented in Table 2.

The results obtained show that direct determination of thallium in the form of the bichromate is possible in the presence of metals that, under the conditions of the analysis, do not form insoluble compounds (Table 2, No. 1), irrespective of their concentrations. In addition to the metals indicated in Table 2, satisfactory results for the determination of thallium are also obtained

in the presence of Tl (III), Fe (II), Cr (III), Sb (III). Naturally, the number of such metals can be considerably increased.

The determination of thallium in the form of the dichromate is also possible in the presence of small amounts of metals precipitated as chromates (Table 2, Nos. 2, 3). For this group of metals, their maximum permissible concentrations have been established.

Thus, it has been shown that the quantitative determination of thallium in the form of the dichromate is at the same time a method for its quantitative separation from accompanying elements; moreover, this difficult problem is solved by simple and readily accessible means.

The determination of thallium in the form of the dichromate can be widely applied in the analysis of various intermediate products of industrial production and all other materials containing thallium. The possibilities for the quantitative separation of thallium from accompanying elements during its quantitative precipitation in the form of the dichromate, in addition to analytical application, have considerably broader prospects for use.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov
Academy of Sciences of the USSR

Received
31 VII 1957

CITED LITERATURE

1. W. Crookes, Chem. News, **8**, 255 (1863).
2. W. Crookes, J. Chem. Soc., **17**, 142 (1864).
3. M. Helberling, Ann. Chem. Pharm., **134**, 19, 19 (1865).
4. E. Willm, Ann. Chem. Phys., **4**, 5, 59 (1865).
5. Dr. Carstanjen, J. Prakt. Chem., **102**, 135 (1867).
6. L. Moser, A. Brukl, Monatsh., **47**, 709 (1926).
7. J. R. A. Andersen, Anal. Chem., **25**, 111 (1953).
8. S. A. Songina, *Rare Metals*, 1955, p. 292.
9. N. I. Bashilova, *Chemistry of Rare Elements*, issue 3, 105 (1957).
10. O. L. Forchheimer, R. P. Epple, Anal. Chem., **23**, 10, 1445 (1951).

Note: Figure translations are in progress. See original paper for figures.