Notes

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Studies on Oxygen Determination by the Carrier Gas Method. IX.[1] Determination of Oxygen in Thallium and Thallium Compounds[2]

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Oxygen determination in thallium and thallium compounds was investigated by a modification of the Schütze-Unterzaucher method.

When oxygen in thallium compounds was determined by the conventional method for organic compounds, the oxygen content in almost all samples was 1—5% less than the calculated value.

A silica tube that was used for heat decomposition was subjected to erosion by thallium (I) oxide produced by the pyrolysis of thallium compounds and cracks were caused. In order to prevent this, the inside wall of the silica tube was coated with carbon which had been produced by the pyrolysis of naphthalene. Carbon powder was also added into the sample boat to reduce thallium oxides formed by the decomposition of thallium compounds.

All of the oxygen in thallium and thallium compounds was determined according to the proposed method, and quite favorable results could be obtained. About 40 min was required for one determination.

Thallium metal is liable to be oxidized, and coatings like thallium (I) oxide and thallium (III) oxide are formed when thallium is allowed in an exposure to air. Thallium compounds have long been used as rodenticide in the field of medicine. However, there have been only a few reports,[4] including ours,[2] on oxygen determination in thallium and thallium compounds. An attempt was made in this paper to determine oxygen in thallium and thallium compounds by the carrier gas method.

Experimental

Samples——In addition to thallium, some inorganic and organic compounds or complexes listed in Table I were employed as samples for the experiment. The composition and purity of these samples were confirmed by the carbon and hydrogen analysis.

Reagents and Apparatus——The reagents and apparatus used were the same as those previously reported.[5]

Procedures——The procedure employed was basically the same as that for the determination of oxygen in organic compounds,[5a] but the boat used was made of porcelain instead of platinum, because the latter material stands only single use, reacting with thallium. Carbon powder was uniformly sprinkled over the sample boat prior to the sample weighing and then the weighed sample was placed on the boat.

The inside wall of the silica tube, from the sample heater to the part packed with platinum-carbon, was coated with carbon, a pyrolysis product, after the assembly of the apparatus. The procedure of the carbon coating used in the present experiments was as follows: Nitrogen as a carrier gas was passed through the

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[1] Part VIII: T. Kuriki, K. Ohsawa, and K. Imaeda, *Bunseki Kagaku*, 24, 311 (1975).

[2] Preliminary accounts of this work has been presented: The 20th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1967.

[3] Location: *a*) *Ebara, Shinagawa-ku, Tokyo*; *b*) *Minamidai, Kawagoe-shi, Saitama.*

[4] W. Merz, *Anal. Chim. Acta*, **50**, 305 (1970); A.V. Andreev and I.M. Pronman, Nauch.-Issled. Proektn. Inst. Redkomet. Prom., No. 29, 146 (1970) [*C.A.*, **75**, 83876 (1971)].

[5] *a*) K. Imaeda, K. Ohsawa, and T. Kuriki, *Bunseki Kagaku*, **22**, 1456 (1973); *b*) K. Imaeda and T. Kuriki, *Bunseki Kagaku*, **23**, 47 (1974).

silica tube which was heated at about 900° by the sample heater and the cumbustion furnace, while about 50 mg naphthalene was placed upstream nearby the sample heater and was subjected to evaporation and pyrolysis.

Results and Discussion

Determination of Oxygen with Conventional Method

Oxygen determination in thallium compounds was carried out according to the method whereby oxygen in organic compounds is usually determined. With the method, however, the oxygen content in most of the samples tested was 1—5% less than the calculated value. When thallium (III) oxide and thallium carbonate were analyzed, there occurred devitrification

Table I. Analytical Results of Oxygen in Thallium Compounds by Carrier Gas Method with a Solid Reagent using a Silica Tube whose Inside Wall was coated with Carbon [Solid Reagent: Carbon Powder *ca.* 5 mg (in Sample Boat)]

Sample	Sample taken (mg)	CO_2 (mg)	O-found (%)	O-calcd. (%)	Δ%
Thallium (III) oxide	3.590	1.038	10.51	10.51	0.00
Tl_2O_3	3.524	1.047	10.80		+0.29
	3.561	1.041	10.63		+0.12
Thallium acetate	3.835	1.306	12.38	12.15	+0.23
CH_3COOTl	3.924	1.310	12.14		−0.01
	4.181	1.405	12.22		+0.07
Thallium carbonate	3.044	0.840	10.03	10.24	−0.21
Tl_2CO_3	3.350	0.932	10.12		−0.12
	3.862	1.081	10.18		−0.06
Thallium chlorate	4.541	2.062	16.51	16.68	−0.17
$TlClO_3$	4.295	1.983	16.79		+0.11
	3.445	1.565	16.52		−0.16
Thallium formate	3.753	1.325	12.84	12.83	+0.01
$HCOOTl$	4.389	1.534	12.71		−0.12
	3.614	1.287	12.95		+0.12
Thallium nitrate	3.599	1.791	18.09	18.02	+0.06
$TlNO_3$	3.869	1.894	17.80		−0.22
	4.270	2.086	17.76		−0.26
Thallium nitrite	4.948	1.698	12.48	12.78	−0.30
$TlNO_2$	4.256	1.482	12.66		−0.22
	3.645	1.283	12.80		+0.02
Thallium oxalate	3.756	1.323	12.81	12.88	−0.07
$Tl_2C_2O_4$	3.858	1.339	12.62		−0.26
	3.952	1.399	12.87		−0.01
Thallium selenate	3.775	1.229	11.84	11.60	+0.24
Tl_2SeO_4	4.390	1.401	11.60		0.00
	4.411	1.461	12.04		+0.44
Thallium sulfate	4.772	1.665	12.69	12.68	+0.11
Tl_2SO_4	3.267	1.120	12.47		−0.21
	4.129	1.422	12.52		−0.16
Thallium hydrogen tartrate	4.494	3.390	27.43	27.16	+0.27
$TlC_4H_5O_6$	3.301	2.472	27.23		+0.13
	4.145	3.137	27.52		+0.36
Ethyl benzoyl acetate thallium	4.955	1.679	12.32	12.10	+0.22
$C_{11}H_{12}O_3Tl$	3.984	1.339	12.22		+0.12
	3.769	1.263	12.18		+0.08
2(1H) Pyridone thallium	3.894	0.602	5.62	5.34	+0.28
C_5H_5NOTl	3.101	0.444	5.21		−0.13
	3.336	0.513	5.59		+0.25
(8-Quinolinolato-N,O) thallium	4.217	0.513	4.42	4.59	−0.17
C_9H_6NOTl	3.761	0.465	4.50		−0.09
	3.695	0.458	4.51		−0.08
Tris (8-quinolinolato-N,O) thallium	4.310	0.926	7.81	7.54	+0.27
$Tl(C_9H_6NO)_3$	3.356	0.710	7.69		+0.15
	4.392	0.913	7.56		+0.02

of the silica tube at the upper part of the sample boat in the sample heater and about 5 or 6 analyses caused cracks in the silica tube. The cause of the difference between the calculated and found values for oxygen may be presumed as follows: the samples such as thallium (III) oxide and thallium carbonate were decomposed by heating partly to thallium (I) oxide and the evaporation of this thallium (I) oxide formed thallium silicate at the inside wall of the silica tube; accordingly, oxygen in the samples could not be determined completely, the oxygen in the samples partly remaining in the sample boat as the thallium oxides.

Effect of Carbon Coating of the Silica Tube and Addition of Carbon Powder into the Sample Boat

In order to avoid the devitrification and cracks, the inside wall of the silica tube was coated with carbon as described in the Procedure. It was considered possible to prevent the direct reaction of thallium (I) oxide with the silica tube by the carbon coating. In order to avoid the other source of loss in oxygen content resulting from the thallium oxides remaining in the sample boat, carbon powder was uniformly sprinkled over the sample boat prior to the sample weighing and then the weighed sample was placed on the boat. The oxygen in thallium compounds was thus determined according to the Procedure, and the analytical results are given in Table I. As seen from the results in Table I, quite favorable results could be obtained with the proposed method.

The oxygen in the commercially available thallium (in the form of pellet) and in thallium powder (60—80 mesh) heated to 185° in the air was determined, and it was found that the pellet-form thallium contained approximately 0.7% oxygen and the thallium powder, prepared from the pellet-form thallium in the air, approximately 1.5% oxygen by weight.

The analytical results also disclosed that thallium was readily oxidized in the air,[6] the surface of thallium being coated with thallium (I) oxide, and that accordingly oxygen content in the thallium powder was higher than that in the pellet-form thallium. When thallium powder was heated at 185° in the air for 2 hr or 5 hr, the oxygen content in thallium powder was approximately 3.2% or 8.5%, respectively.

For oxygen determination in organic metal compounds, a series of experiments has been carried out by us on the appropriate combination of the heat of formation of metal oxides and their reducing agents to be added. It has been proved that the heat of formation of thallium (I) oxide is $\Delta H^\circ f$ -41.9 kcal/mol and that this figure is approximately the same as that of copper (I) oxide, namely, $\Delta H^\circ f$ -39.8 kcal/mol. Thus, the method using naphthalene, that was employed by us in the determination of oxygen in copper compounds, is applicable to oxygen determination in thallium compounds, but in the present experiments carbon was selected because it could be used more conveniently than naphthalene.

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[6] H. Ohnishi, "Mukikagaku Zensho X-1-2 Gallium·Indium·Thallium," ed. by S. Fujiwara, Maruzen, Tokyo, 1966, p. 150.