

## DETERMINATION OF CHLORINE, BROMINE AND IODINE IN ORGANIC SUBSTANCES IN THE PRESENCE OF THE PLATINUM METALS

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Received December 18th, 1974

A procedure has been proposed for the determination of the chlorine, bromine and iodine contents in organic substances containing the platinum metals (Ru, Rh, Pd, Os, Pt). In order to eliminate interference from the platinum metals in the subsequent argentometric titration, the substances were mineralized with a mixture of magnesium and magnesium oxide, during which the platinum metals are reduced to the elemental form.

When chlorine, bromine and iodine are determined in substances used as homogeneous or pseudohomogeneous catalysts, which usually contain some of the platinum metals (Ru, Rh, Pd, Os, Pt), the common combustion methods cannot be employed without certain modifications<sup>1-4</sup>. After combustion, most of the platinum metals present are transferred to the titrated liquid in the form of soluble halogenocomplexes. The bond between the platinum metal and the halide is so strong that the formation of these complexes plays an important role as a side reaction during precipitation of a silver halide or the formation of a mercury halide. Therefore, the platinum metal in the liquid obtained on combustion in the oxygen flask must be suitably reduced. However, it is sometimes difficult to reduce the platinum metal, *e.g.* Os or Ru, quantitatively<sup>5,6</sup>; moreover, the reducing agent may also contain a halide and its excess may interfere in the subsequent argentometric or mercurimetric titration.

In the present work, in the determination of chlorine, bromine and iodine in organic substances containing noble metals, mineralization by ignition with a mixture of pulverized magnesium and magnesium oxide was employed. This mineralization was described earlier by Schöniger<sup>3</sup> in the determination of the halogens and was employed by Jureček and coworkers in the determination of arsenic<sup>7,8</sup>, phosphorus<sup>9</sup>, antimony<sup>10</sup> and iodine<sup>11</sup> in organic substances. We assumed that the platinum metals will be reduced by magnesium to the elemental form in the course of this mineralization procedure and would thus be readily removed from the aqueous extract of the reaction mixture. The conditions for the treatment of this aqueous extract enabling the subsequent argentometric determination of chlorine, bromine and iodine have been found.

## EXPERIMENTAL

## Chemicals

A 1 : 2 (weight) mixture of magnesium and magnesium oxide (Lachema, Brno) was prepared. Platinum and palladium sponges were prepared from the appropriate chlorides or potassium salts of the chloro complexes (Safina, Vestec) by reduction with zinc (*p.a.* Lachema, Kralupy) in an acidic medium, by thorough washing of the filtered preparation with hot water and drying in the air. Rhodium and ruthenium metals were obtained by decomposing  $\text{RhCl}_3$  and  $\text{RuCl}_3$  (Fluka AG, Buchs, Switzerland) by ignition with a mixture of  $\text{Mg} + \text{MgO}$  and extraction, similar to the procedure described below. Osmium tetroxide was obtained from Safina, Vestec and its purity was not specified.

Chloranil (*I*) and *o*-chloroacetanilide (*II*) were chemically pure (Lachema, Brno) and were recrystallized from methanol and dried *in vacuo* at room temperature before use. 5,7-Dibromoxyquinoline (*III*) (Fluka, Buchs, Switzerland) was sublimated *in vacuo* before use. 7-Iodo-8-hydroxyquinoline-5-sulphonic acid (*IV*) was analytically pure (Koch-Light, London, England) and its purity was verified by determining the sulphur content. The halogeno complexes of palladium, platinum and rhodium with organic phosphine- or nitrogen-containing ligands (*V-X*) were kindly supplied by the workers from the department of Homogeneous Catalysis of the Institute and their purity was first verified by determining the content of the noble metal and phosphorus or nitrogen (Table III). All the other chemicals were common commercial substances of *p.a.* purity.

The argentometric titrations were indicated using a Precision pH-meter OP-205 with a silver indicator and mercurous sulphate reference electrode (Radelkis, Budapest).

## Procedure

About 2—50 mg of a solid, non-volatile sample are accurately weighed into a hard glass test-tube ( $10 \times 0.8$  cm, wall thickness of c. 1 mm), thoroughly mixed with c. 0.6 g of the  $\text{Mg} + \text{MgO}$  mixture and about 2—2.5 g of the latter mixture are placed on top. The test-tube orifice is then

TABLE I

Determination of Chlorine, Bromine and Iodine in Organic Substances

*I* Chloranil; *II* *o*-chloroacetanilide; *III* 5,7-dibromoxyquinoline; *IV* 7-iodo-8-oxyquinoline-5-sulphonic acid

Substance analyzed	Halogen, %		Number of determinations	Relative standard deviation <sup>14,15</sup> , %
	found	calculated		
<i>I</i>	57.65	57.68	9	0.24
<i>II</i>	20.96	20.91	9	0.38
<i>III</i>	52.76	52.75	11	0.25
<i>IV</i> <sup>a</sup>	36.09	36.14	7	0.31

<sup>a</sup> Hydrogen sulphide was expelled by 10-minute boiling after acidification with acetic acid.

drawn into a capillary with an inner diameter of c. 0.1 mm; the test-tube is fixed in a vertical position. The test-tube content is then ignited with a glass-blowing burner until it is red-hot; the flame is slowly moved from the upper layer downwards. After thorough ignition of the whole test-tube content, the still-hot test-tube is transferred to a tall dry 250 ml beaker, which is covered with a watch glass, and is carefully sprayed with a thin stream of distilled water; the walls of the test-tube crack. After cooling, the test-tube is crushed into large pieces using a thick glass rod and 10 ml of water mixed with 5 ml of glacial acetic acid are added to the pieces. After dissolution of magnesium and magnesium oxide (in cold solution), the suspension of soot and reduced platinum metal is removed by filtration through a large-pore paper filter, rinsing the pieces in the beaker with 10 ml of water and then with several portions with a total volume of approx. 80 ml. The filtrate is acidified with about 5 ml of 70% perchloric acid (free of  $\text{Cl}^-$  ions) and titrated with a 0.01M solution of  $\text{AgNO}_3$ . The blank is determined for all the chemicals used in each series of determinations; its value amounted to 0.11 ml of 0.01M- $\text{AgNO}_3$  with the chemicals specified above. The analysis requires about 30 minutes.

The accuracy and precision of the whole procedure was checked by repeated analysis of 5–15 mg samples of chloranil, *o*-chloroacetanilide and dibromooxyquinoline. The results of these analyses are given in Table I.

## RESULTS AND DISCUSSION

Argentometric and mercurimetric titration of chloride and bromide ions with visual or electrometric indication fails when the stability constants of the halogeno complexes of the metals present in the solution titrated are high enough to compete with the main reaction. This occurs when *e.g.* soluble compounds of Pt(II), Pt(IV), Rh(III), Pd(II), Ru(III), Ru(IV), Os(IV) and Os(VI) are present in the solution titrated, as follows from comparison of the few stability constants published for the halogeno complexes of the above metals with the solubility products of silver halides and the stability constants of mercuric halides<sup>12</sup>.

Preliminary experiments with the potentiometric argentometric determination of chlorine, bromine and iodine in pure palladium halides and in pure alkali halogenoplatinates led to poorly reproducible results, which were 5–70% lower than the theoretical values, depending on the experimental conditions. In the combustion<sup>3</sup> of organic substances containing Pt, Pd and Rh fixed through functional amino or phosphino groups to the basic polystyrene–divinylbenzene or polymethacrylate skeleton, it was found that the platinum metal is always present in the resultant liquid titrated in the form of soluble compounds. Therefore, reduction of the platinum metal ions with zinc or aluminium metal was first attempted in weakly or strongly acidic media. Neither procedure was successful, owing to either slow or incomplete reduction. Attempts to decompose the halides or halogeno complexes of the platinum metals or organic compounds with metallic sodium in sealed glass ampoules<sup>13</sup> were also unsuccessful, chiefly due to very violent reactions during mineralization and to difficulties in preparation of the aqueous extract of the reaction mixture.

TABLE II

Determination of Chlorine, Bromine and Iodine in the Presence of the Platinum Metals

Substance analyzed	Platinum metal compound added	Halogen <sup>b</sup> found, %	Number of determinations
<i>I</i>	Pt <sup>c</sup>	100.3 ± 0.6	4
<i>III</i>	Pt <sup>c</sup>	100.4 ± 0.8	3
<i>IV<sup>a</sup></i>	Pt <sup>c</sup>	100.1 ± 0.7	3
<i>I</i>	Pd <sup>c</sup>	99.1 ± 3.1	3
<i>III</i>	Pd <sup>c</sup>	99.9 ± 0.5	3
<i>IV<sup>a</sup></i>	Pd <sup>c</sup>	100.6 ± 1.7	3
<i>I</i>	OsO <sub>4</sub>	100.0 ± 0.4	4
<i>III</i>	OsO <sub>4</sub>	99.4 ± 1.0	3
<i>IV<sup>a</sup></i>	OsO <sub>4</sub>	98.8 ± 2.6	3
<i>I</i>	RuCl <sub>3</sub>	98.9 ± 3.6	4
<i>III</i>	Ru <sup>c</sup>	99.9 ± 0.6	3
<i>IV<sup>a</sup></i>	Ru <sup>c</sup>	101.3 ± 1.9	4
<i>I</i>	RhCl <sub>3</sub> ·4 H <sub>2</sub> O	100.2 ± 0.8	4
<i>I</i>	Rh <sup>c</sup>	100.0 ± 0.3	4
<i>III</i>	Rh <sup>c</sup>	99.8 ± 0.9	3
<i>IV<sup>a</sup></i>	Rh <sup>c</sup>	99.8 ± 1.2	3
<i>I</i>	K <sub>2</sub> PtCl <sub>4</sub>	100.6 ± 1.6	3

<sup>a</sup> See Table I; <sup>b</sup> The error was calculated according to Dean and Dixon<sup>5</sup>; Preparation see p. 2016.

TABLE III

Test Substances

Substance	Composition	Found (calc.), %		
		Me <sup>a</sup>	P or N	X <sup>b</sup>
<i>V</i>	CH <sub>2</sub> =CHNH <sub>3</sub> PtCl <sub>3</sub>	54.6 (54.3)	3.90 (3.89)	29.33 (29.57)
<i>VI</i>	(CH <sub>2</sub> =CHCH <sub>2</sub> PdCl) <sub>2</sub>	58.0 (58.2)	—	19.11 (19.35)
<i>VII</i>	[Rh(CO <sub>2</sub> )Cl] <sub>2</sub>	52.2 (52.9)	—	18.32 (19.24)
<i>VIII</i>	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub> RhCl	11.1 (11.1)	10.20 (10.04)	3.88 (3.83)
<i>IX</i>	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub> RhBr	10.5 (10.6)	9.53 (9.58)	8.16 (8.24)
<i>X</i>	[P(C <sub>6</sub> H <sub>5</sub> ) <sub>3</sub> ] <sub>3</sub> RhJ	10.0 (10.1)	9.21 (9.14)	12.70 (12.48)

<sup>a</sup> Me represents a platinum metal; <sup>b</sup> X represents a halogen.

In mineralization of platinum-containing organic substances, the above procedure must be observed in order that the whole analysis be performed rapidly, with precise and accurate results. When aqueous extracts of the ignited mixture were acidified with acetic acid alone, it was impossible to locate the inflection point on the potentiometric titration curve. If the whole of the reaction mixture is dissolved by treatment with a strong acid, *e.g.* sulphuric or perchloric acid in the atmosphere, the danger that part of the platinum metal sponge will dissolve due to the presence of atmospheric oxygen and will cause distortion of the titration results, must be born in mind. If the ignited reaction mixture is extracted with dilute acetic acid, the extract contains all of the chlorine, bromine or iodine contained in the sample, in the form of the anions,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ ; soot and the reduced platinum metal, formed during the pyrolysis in the presence of magnesium, remain as a readily filterable suspension. Colloidal basic magnesium acetates are converted into an ionized form in the filtrate and the solution obtained then behaves analogously to a solution of an alkali halide alone in the subsequent argentometric titration.

The procedure described was tested on model substances I–IV, to which dried Pt, Ru and Rh sponge-like powders (for their preparation see Experimental), or  $\text{RhCl}_3 \cdot 4 \text{H}_2\text{O}$ ,  $\text{K}_2\text{PtCl}_4$ ,  $\text{RuCl}_3$  or  $\text{OsO}_4$  (Table II); were added before mineralization. In addition, substances V–X were analyzed employing the procedure described; their calculated and determined compositions are given in Table III. It is evident that chlorine, bromine and iodine can be determined with sufficient precision and accuracy using the procedure proposed, even in the presence of Pt, Pd, Rh, Ru and Os.

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Translated by M. Štulíková.