Redox Substoichiometry in Activation Analysis I.

Application to the Determination of Antimony in Metallic Zinc

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Redox substoichiometry in activation analysis of antimony was investigated. The procedure involves substoichiometric oxidation of trivalent antimony with permanganate, followed by quantitative separation of trivalent antimony from pentavalent antimony. The BPHA extraction was used in the separation of trivalent and pentavalent antimony. The substoichiometric procedure was applied to the determination of antimony in metallic zinc. From the analytical results obtained the method is found to be simple, rapid and exact. Such redox substoichiometry of antimony might be applicable to activation analysis of antimony in various metals or alloys.

Introduction

Substoichiometry in activation analysis has been developed by investigating isolation procedures in which constant amounts of the element to be determined are always separated with high precision and reproducibility. The substoichiometric separation has been carried out by extraction\(^{11-16}\), electrolysis\(^9\), ion exchange\(^{10}\), and adsorption\(^{13}\) methods, etc. Recently, Polak applied coprecipitation procedures to the separation necessary in isotope dilution analysis after the oxidation or reduction of the substoichiometric amounts of element to be determined\(^{12,13}\).

As to the separation of antimony (III) from antimony (V) the BPHA (N-benzoyl-N-phenylhydroxylamine) extraction has been found to be most reliable and excellent\(^{14}\). The authors have succeeded in quantitative extraction of antimony (III) with BPHA in chloroform, after the substoichiometric oxidation of antimony (III) to antimony (V) with potassium permanganate.

In the present paper, the procedure and results of substoichiometric radioactivation analysis of antimony in metallic zinc are described.

Experimental

Reagents: All chemicals used were of reagent grade. A 0.1 M BPHA solution in chloroform was used as the extracting agent. Reagent grade Sb\(_2\)O\(_3\) was used as the activation standard.

Tracer experiment for substoichiometry: Five ml of Sb(III) solution (9.5 mg Sb/ml) in 6 M HCl labelled with \(^{125}\)Sb(III) were diluted to 2 M HCl with dil. HCl. Different aliquots of the solution (4-9 ml) were transferred into separating funnels. By adding 1 ml of 0.0508 N KMnO\(_4\) to each solution, substoichiometric amounts of Sb(III) were oxidized to Sb(V). Each solution was diluted to 1 M HCl (19 ml) with dil. HCl. The diluted solution was shaken with 6 ml of 0.1 M BPHA (in CHCl\(_3\)) for 1 min to separate Sb(III) and Sb(V). A 5 ml aliquot of the aqueous phase was taken out and counted by a scintillation counter (NaI). The same procedure of the oxidation and the separation was also inves-
tigated in the presence of zinc (1–10 mg).

Neutron irradiation: Appropriate amounts of the sample and the standard were packed in polyethylene tubes separately. After being packed in a polyethylene rabbit, they were irradiated for 30 min at a thermal neutron flux of $2.75 \times 10^{13} n/cm^2 \cdot sec$ in the pneumatic tube facilities (Pn-2) of Kyoto University Reactor (KUR).

Apparatus: Measurements of gamma-ray spectra were carried out by using a 30 ml Ge (Li) detector coupled to a Nuclear Data 1024 channel pulse height analyzer. The area under the peak was evaluated according to the method of Covell1115.

Analytical procedure for irradiated zinc: An accurately weighed amount of irradiated zinc sample (ca. 50 mg) was dissolved with 10 ml of 6 M HCl containing 2 ml of 30% H$_2$O$_2$ in a 50 ml volumetric flask and diluted to the mark with 6 M HCl. From the solution 10 ml aliquots were taken and diluted to 3 M in HCl with 10 ml of 0.1 M HCl. Sulfur dioxide gas was bubbled through the solution for 20 min in order to complete the reduction of Sb(III) to Sb(II), while heating gently the solution. After being evaporated to 2 ml, the solution was diluted to 2 M in HCl (optimum concentrations of hydrochloric acid range from 2 M to 3 M16) with 5 ml of 0.4 M HCl. An Sb(II) carrier solution (3.0 mg Sb/ml in 2 M HCl, 2 ml) was added to the solution which was then cooled with ice. Thereafter substoichiometric amount of Sb(III) was oxidized by addition of 1 ml of 0.0508 N KMnO$_4$. After the substoichiometric oxidation, the solution was diluted to 1 M in HCl with 9 ml of 0.1 M HCl and transferred into a separating funnel. It was then shaken with 6 ml of 0.1 M BPHA (in CHCl$_3$) for 1 min. A 5 ml aliquot of the organic phase was taken for activity measurement. The antimony standard was treated in the same way.

Results and Discussion

The results of substoichiometric oxidation of Sb(III) followed by BPHA extraction separation are shown in Fig. 1. It shows the linear increase of Sb(V) amount separated until the amount of Sb(III) added reaches the substoichiometric quantity, after which the amount of Sb(V) present in the solution remains constant. The same experiment was performed in the presence of target material, zinc. It was found that the presence of zinc shows no interfering effects. It is thus concluded that the substoichiometric oxidation of Sb(III) with KMnO$_4$ followed by BPHA extraction is quantitative. Hence, this technique is considered to be applicable to activation analysis of antimony in zinc with good accuracy.

In the substoichiometric separation procedures from the neutron irradiated zinc target, first of all it was necessary to reduce all antimony to trivalent state. The complete reduction was found to be achieved by bubbling sulfur dioxide gas through the solution for at least 20 min, as shown in Fig. 2. The result of this tracer experiment is shown in Table 1, from which it can be seen that the values obtained are in good agreement with the calculated ones.

The determination of antimony in metallic zinc was carried out by the proposed method. The comparison method was applied for determination of the antimony content. In this case the ordinary formula17,
Fig. 2 Effect of the bubbling time of SO₂ gas on the reduction of pentavalent antimony.
Acidity: 3 M hydrochloric acid
Amount of antimony (II): 20 mg

Table 1 Substoichiometric determination of antimony, using 125Sb as the tracer

<table>
<thead>
<tr>
<th>µg</th>
<th>found, µg</th>
<th>in the presence of zinc (10 mg)</th>
<th>in the absence of zinc</th>
</tr>
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<tbody>
<tr>
<td>12.0</td>
<td>12.4±0.4</td>
<td>12.3±0.4</td>
<td></td>
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</table>

Ten mg of metallic zinc were used for analysis.

was used for the substoichiometric analysis:

\[ x = \frac{A_2}{A_1} y \]

where \( x \) is the amount of the element to be determined, \( y \) the known amount of standard antimony, \( A_1 \) activity of antimony of substoichiometric amount separated from the standard and \( A_2 \) activity of that separated from the sample.

The results obtained are given in Table 2, together with those obtained by some other methods for the comparison. It can be seen that these values agree with each other within experimental errors and the determination of amounts down to 0.2 µg antimony is possible with good accuracy.

For the present analysis, the photo-peak of gamma-rays, 0.564 MeV, was used for the determination of antimony. It is very close to that of 76As, 0.559 MeV. However, no additional separation of the antimony and the arsenic was considered to be necessary, because the extraction of As(II) and As(V) with the BPHA from dilute hydrochloric acid is negligible and also in the substoichiometric oxidation after the addition of large amounts of Sb(III) carrier, the oxidation of As(II) present in trace with KMnO₄ is considered to be negligible.

The redox substoichiometry applied for the activation analysis of antimony in zinc is found to be reliable, simple and rapid. Such a substoichiometric procedure is considered to be applicable to the activation and isotope dilution analyses of antimony in various metals or alloys.

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References

1) N. Suzuki: Proc. 2nd Conf. Radioisotopes (Japan), 151 (1958)
2) J. Ruzicka, J. Stary and A. Zeman: Talanta, 11, 1151 (1964)
4) K. Kudo: Radioisotopes, 15, 209 (1966); ibid., 16, 199 (1967)
6) B.M. Tejam and B.C. Haldar: ibid., 9, 19, 77, 189 (1972)


