Neutron Activation Analysis of Arsenic, Antimony and Cadmium in Metallic Zinc

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Studies were made to establish a rapid and simple radiochemical procedure for the determination of antimony, arsenic and cadmium in metallic zinc by neutron activation analysis. The procedure involves short time irradiation, rapid dissolution of the target and one-step separation of each nuclide (^{122}Sb , ^{76}As and $^{111\text{m}}\text{Cd}$) from the target nuclides (^{65}Zn and $^{69\text{m}}\text{Zn}$).

The irradiated target was rapidly dissolved with hydrochloric acid in the presence of potassium bromate. ^{122}Sb was separated by DEHPA extraction from concentrated hydrochloric acid and ^{76}As by As_2S_3 precipitation in a 6M hydrochloric acid solution. $^{111\text{m}}\text{Cd}$ was freed from zinc activities by ethyl ether extraction of zinc thiocyanate complex. About half an hour was enough to separate each nuclide from the target. The limits of detection are ca. 30 ppb for antimony, ca. 15 ppb for arsenic and ca. 120 ppb for cadmium by short time irradiation of small amounts of the zinc sample.

Introduction

Trace analysis of antimony, arsenic and cadmium in metallic zinc is very important for the study on electrolytic refining of zinc. The radionuclide characters of the three elements¹⁾ show that the non-destructive neutron activation analysis is not suitable for the determination of individual element, i.e., the Compton continuum of zinc matrix causes much difficulties in the determination of $^{111\text{m}}\text{Cd}$, and also, very close photo-peaks (^{76}As and ^{122}Sb) can not be completely resolved from each other. Therefore, it is apparent that these elements should be chemically separated before counting.

The mutual separation of antimony and arsenic has been investigated by ion exchange method²⁾, distillation method³⁾, precipitation method^{4),5)}, and solvent extraction method^{6)~8)}. The solvent extraction and precipitation methods are considered to be a more rapid and simple separation procedure than the other methods. The use of amine

extractants such as tri-benzylamine (TBA) was proposed for the rapid and simple separation of antimony and arsenic, but it could not be achieved in concentrated hydrochloric acid solutions⁹⁾. Recently, di-2-ethylhexylphosphoric acid (DEHPA) has widely been used as an extractant and some comprehensive investigations have been made on extraction of a number of elements from mineral acid at the concentrations above $1M$ ⁹⁾.

From rapidity, simplicity and completeness of separation, it is considered to be advantageous if each antimony, arsenic and cadmium can be freed from the zinc matrix by one-step separation based on the solvent extraction or the precipitation method. In this paper, we describe a rapid and simple radiochemical procedure for each determination of the elements in metallic zinc together with the results of the determinations.

Experimental

Reagents: All chemicals used were of

reagent grade. Di-2-ethylhexylphosphoric acid* (DEHPA) dissolved in equal volume of *n*-heptane was used as the extracting agent. The activation standards of ^{122}Sb , ^{76}As and $^{111\text{m}}\text{Cd}$ were prepared by neutron irradiation of reagent grade Sb_2O_3 , As_2O_3 and CdO , respectively.

Neutron irradiation: Appropriate amounts of the samples and the standards were packed with paraffin papers separately, and each of them was sealed in a polyethylene bag. After being packed in a polyethylene rabbit, they were irradiated for 10~15 min at a neutron flux of $2.75 \times 10^{13} \text{ n/cm}^2 \cdot \text{sec}$ in the pneumatic tube facilities (Pn-2) of Kyoto University Reactor (KUR).

Apparatus: Measurements of gamma-ray spectra were carried out with a 30 cc Ge(Li) detector connected to a Nuclear Data 512-channel pulse height analyzer. The area under the photo-peak was calculated by a computer, OKITAC 5090, using the KUR program¹⁰⁾ including the area determination by the Covell method¹¹⁾.

Separation procedure for cadmium: The zinc sample (approximately 25 mg) irradiated was dissolved with 2 ml of conc HCl to which 100 mg KBrO_3 and 1 mg CdO carrier had been added. To the solution was added 8 ml of distilled water, 10 ml of 4M NH_4SCN and 20 ml of ethyl ether, and the mixture was vigorously shaken for 3 min to extract the zinc thiocyanate complex¹²⁾. After the phase separation, 10 ml of the aqueous phase was transferred to a 50 ml Erlenmeyer flask, to which 10 ml of ethyl ether was added. The ethyl ether extraction of the thiocyanate complex was repeated. 5 ml of the aqueous phase was transferred to a polyethylene tube and counted. From the gamma-ray spectra obtained each area under 151 and 245 keV photo-peaks of $^{111\text{m}}\text{Cd}$ was determined. The amounts of cadmium were calculated by using the comparative method, i.e., the area under the 151 keV or 245 keV photo-peak for the sample was compared with the corresponding area of the standard with the correction for $^{111\text{m}}\text{Cd}$ decay being made¹³⁾.

Separation of antimony: The irradiated

zinc sample (ca. 50 mg) was dissolved with 10 ml of conc HCl containing 100 mg KBrO_3 and 1 mg Sb_2O_3 carrier. The solution was vigorously shaken with 10 ml of DEHPA solution (1:1) in *n*-heptane for 3 min to extract antimony. 5 ml of the organic phase was counted. From the gamma-ray spectrum obtained, the area under the 564 keV photo-peak of ^{122}Sb was computed.

Separation of arsenic: The irradiated zinc sample (ca. 50 mg) was dissolved with 10 ml of 6M HCl containing 100 mg KBrO_3 and 5 mg As_2O_3 carrier. After 1 g $\text{NH}_4\text{OH} \cdot \text{HCl}$ was added to the solution for the reduction of As(V) to As(III), 1 ml of 2% thioacetamide was added and heated to precipitate arsenic as sulfide. The precipitate was filtered, washed with a 3M HCl solution and then dissolved in 10 ml of an ammonium sulfide solution. The gamma-ray spectrum of the solution was measured. The area under the 559 keV photo-peak of ^{76}As was computed.

Preparation of the standards: The irradiated standards (1~2 mg As_2O_3 , Sb_2O_3) were dissolved with about 6M HCl in a 1,000 ml volumetric flask to which 50 mg KBrO_3 had been added. The standard of CdO (1~2 mg) irradiated was dissolved in 10 ml of 6M HCl in a 250 ml volumetric flask and diluted to the mark with distilled water. Appropriate amounts of these solutions were transferred to polyethylene tubes and counted. The gamma-ray spectra of the separated fractions and the standards were measured under identical conditions.

Tracer experiment: The analytical procedures proposed as mentioned above were tested by using 25~50 mg zinc (almost equal amounts used in the practical analysis) and the tracers of ^{65}Zn , ^{115}Cd , ^{124}Sb and ^{74}As .

Results and Discussion

It was found by the tracer studies that the zinc sample could be rapidly dissolved with negligible loss of ^{124}Sb or ^{74}As . The

* Obtained from Tokyo Kasei Co., Ltd.; it contained MEHPA (15%) and other alkyl phosphate (5%).

$\text{HCl} + \text{KBrO}_3$ dissolution method is found to be a better method than the ordinary aqua regia dissolution method¹⁴⁾.

As to the isolation of cadmium activity from the zinc matrix the ethyl ether extraction yield of zinc was found to be more than 99% at 1.2M HCl and 2M NH_4SCN , whereas that of cadmium was less than 0.1%, i.e., no correction for the chemical yield was needed.

The results of DEHPA extraction of antimony and arsenic are shown in Fig. 1. The results show no extraction of arsenic from concentrated hydrochloric acid solutions into DEHPA containing some other alkylphosphoric acid, indicating that the use of such DEHPA gives far better results than that of pure DEHPA for separation of antimony from arsenic according to the synergistic effect. As to the separation of arsenic from antimony arsenic can be quantitatively precipitated from 6M HCl, whereas antimony showed little coprecipitation.

Fig. 1 Effect of HCl concentration on the extraction of Sb(V) and As(V) ions into DEHPA (obtained from Tokyo Kasei Co., Ltd., not pure).

The dotted line shows the results of the extraction of Sb(V) with pure DEHPA according to Levin, et al.¹⁵⁾

From the results of the tracer experiments as mentioned above, it was found that the determinations of cadmium, antimony and arsenic in metallic zinc could be performed by one-step separation procedure of each element based on extraction or precipitation.

The gamma-ray spectra of the fractions isolated from the activated zinc target showed clearly that the mutual separation of antimony, arsenic and cadmium can be achieved by application of the scheme. The results are shown in Table 1. These values were in good agreement with those obtained by the colorimetric method with brilliant green¹⁶⁾ for antimony, by the standard addition method¹⁷⁾ in neutron activation analysis for arsenic and by the polarographic method¹⁸⁾ for cadmium.

Table 1 Determinations of antimony, arsenic and cadmium in zinc*

Element	Sp. grade (ppm)	1st grade (ppm)	Sample** (ppm)
Antimony	1.03±0.18	19.2±1.9	2896±110
	—	19.5±1.1 ^{a)}	—
Arsenic	0.37±0.10	1.09±0.27	51.4±7.6
	—	—	48.5±6.1 ^{b)}
Cadmium	340±34	5090±940	1046±15
	341±25 ^{c)}	5110±314 ^{c)}	1074±82 ^{c)}

The value is the average of at least five determinations and the error is the standard deviation of them.

* K. Chemical Co., Ltd.

** Obtained from Zinc Manufacture Co.

a) Colorimetric method with brilliant green; b) Standard addition method in neutron activation analysis; c) Polarographic method

The time for carrying out the separation scheme proposed for each determination of antimony, arsenic and cadmium is about 40 min, including irradiation of the sample. Dissolution of the target and chemical separation for element are simple, rapid and quantitative. The limits of detection are estimated to be ca. 30 ppb for antimony, 15 ppb for arsenic and 120 ppb for cadmium by neutron irradiation (10 min for cadmium, 15 min for antimony and arsenic) with the counting time of 400 sec.

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要 旨

金属亜鉛中のヒ素、アンチモン、カドミウムの中性子放射化分析

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金属亜鉛中のヒ素、アンチモン、カドミウムについて、迅速かつ簡便な定量法として中性子放射化分析法を検討した。すなわち、試料の短時間照射、迅速溶解法、ターゲットから目的元素の迅速分離法などが検討された。

ターゲットの溶解は臭素酸カリウムの塩酸溶液を用い、ターゲットよりアンチモンの分離は濃塩酸溶液より DEHPA により抽出、カドミウムの分離は 1.2M HCl, 2M NH₄SCN 溶液より亜鉛をロダン錯体としてエーテルに抽出、ヒ素は 6M HCl 溶液より硫化ヒ素として沈殿分離させた。これら分離に要する時間は約30分ときわめて迅速であり、また、アンチモン、ヒ素の同時定量も可能であることがわかった。