Determination of Indium in Aluminum Alloy by Electrothermal Atomic Absorption Spectrometry with a Tungsten-Coated L'vov Platform Tube

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The determination of trace amounts of indium, especially involved as an impurity in aluminum and its alloys, is important, since these are used as new technical materials in the field of electronics and mechanical industries, and the impurities cause often serious problems.¹ For this purpose, several methods, such as graphite-furnace atomic absorption spectrometry (GFAAS)^{1,2}, flame-emission spectrometry³, X-ray fluorescence analysis⁴, and neutron-activation analysis⁵, have been used.

Although GFAAS is one of the most useful methods for the determination of indium, there is a lack of sensitivity for indium. The poor sensitivity is mainly due to the loss by vaporization of the molecular species of indium during the heating process.^{6,7} To overcome the insufficiency of sensitivity and to eliminate interference from the matrix, various techniques of preconcentration by extraction⁸, adsorption⁹, and coprecipitation², as well as of chemical modification¹⁰ have been used. Another technique is to coat the graphite furnace with metals, such as tungsten, tantalum, and zirconium.¹¹⁻¹³

In our previous paper¹⁴, a simple and rapid tungsten-coating method without soaking a tube in a tungstate solution was proposed for graphite tubes. The pretreated tubes were found to greatly increase the sensitivity for tin.

The present manuscript describes a sensitive method for the determination of indium by GFAAS using the L'vov platform technique coupled with a tungsten-coating pretreatment and its application to the analysis of indium in an aluminum rod which had been treated by zone melting.

Experimental

Apparatus

A Perkin Elmer (Model 5000; Norwalk, CT, USA) atomic absorption spectrometer equipped with a

graphite-furnace atomizer (Model HGA-500) and an autosampler (Model HGA-40) was used. An Oki Electronics personal computer (Model if 800-50; Tokyo) was used to record the absorbance-signal profiles at 303.9 nm (In I). The graphite furnaces used were of pyrolytic L'vov platform graphite (PPG) tubes (Part No. Bo. 11260; Lot No. VI/29/32403 and IV/114/85202) purchased from Perkin Elmer.

Reagents

An indium(III) stock standard solution for AAS (1000 mg dm⁻³ indium(III) in 1.0 mol dm⁻³ nitric acid; Katayama Chemical, Osaka) was diluted with 0.05 mol dm⁻³ nitric acid as required. A 10 mmol dm⁻³ tungsten(VI) solution used for coating the tubes was prepared by dissolving 0.33 g of sodium tungstate dihydrate (Kanto Chemical, Tokyo) in water and making the volume to 100 cm³. A chemical modifier solution was prepared by dissolving 3.48 g of aluminum nitrate monohydrate (Kanto Chemical) in 100 cm³ of 0.05 mol dm⁻³ nitric acid.

Tungsten coating procedure

A 100 mm³ aliquot of the coating solution was placed on the PPG tube incorporated into the furnace atomizer; the tube was then heated according to the temperature program listed in Table 1. This coating procedure was repeated five times.

Table 1 Atomization temperature program

	Step No.		
	1	2	3
Temperature/°C	150	500	2300
Ramp time/s	15	20	0
Hold time/s	10	10	3
Argon gas flow/cm ³ min ⁻¹	300	300	20

Fig. 1 Reproducibility of indium atomic absorption for a 25 mm³ sample of a standard solution containing 40 ng cm⁻³ of indium(III). A, W-PPG tube; B, PPG tube.

Sample digestion procedure

First, 500 mg of aluminum pieces, which had been prepared by cutting a fixed part of an aluminum-rod sample, was soaked in 10 cm³ hydrochloric acid overnight at room temperature; then it was heated at 150°C for *ca.* 4 h. After being treated with a small portion of nitric acid, the digest was diluted as required.

Results and Discussion

Preparation of tungsten-coated tubes

The maximum and reproducible atomic-absorption signal of indium was obtained when the tungsten-coating treatment was repeated at least three times. Therefore, five times of the coating treatment were adopted. The tungsten-coated PPG (W-PPG) tube enhanced the sensitivity to be four times higher than that obtained with the PPG tube. Figure 1A shows an example of the coating effect when a series of 25-mm³ samples of a solution each containing 1.0 ng of indium(III) was injected into the W-PPG tube. It was found that the W-PPG tube gave stable signals for at least 450 firings without recoating tungsten. The durability of the tungsten coating was as long as the lifetime of the original L'vov platform tube (Fig. 1B).

Analytical performances

The effects of foreign cations and anions on the atomization of indium were investigated. Tolerable amounts of foreign ions, which gave less than a 10% error for the determination of indium, were evaluated for both the W-PPG and PPG tubes. As Table 2 shows, the tolerance limits of other ubiquitous ions were improved by the tungsten coating.

As an example, although an added amount of silicon(IV) equal to that of indium(III) suppressed the signal to approximately 50%, this interference was appreciably eliminated with the W-PPG tube. Moreover, when aluminum(III) as a chemical modifier was deposited on the surface of the W-PPG tube, the inter-

Table 2 Permissible amounts of foreign ions for the determination of indium (results within 10% error)

Ion	Weight ratio ^a Ion/In ³⁺			Ion	Weight ratio ^a Ion/In ³⁺		
	W-PPG tube ^b	W-PPG tube	PPG tube		W-PPG tube ^b	W-PPG tube	PPG tube
Na ⁺	>1000 ^c	600	600	Ag ⁺	>1000 ^c	820	870
K ⁺	>1000 ^c	800	640	Zn ²⁺	850	850	540
Mg ²⁺	>1000 ^c	690	490	B ^{III}	900	800	600
Ca ²⁺	850	530	570	Sn ²⁺	>1000 ^c	950	810
Cr ^{VI}	900	550	310	Si ^{IV}	>1000 ^c	760	<1 ^d
Mn ²⁺	>1000 ^c	520	530	Pb ²⁺	>1000 ^c	650	520
Fe ³⁺	>1000 ^c	780	380	NO ₃ ⁻	>4000 ^c	>4000 ^c	>4000 ^c
Co ²⁺	>1000 ^c	790	610	Cl ⁻	>4000 ^c	>4000 ^c	>4000 ^c
Ni ²⁺	>1000 ^c	620	650	SO ₄ ²⁻	>4000 ^c	>4000 ^c	>4000 ^c
Cu ²⁺	>1000 ^c	750	550				

a. In³⁺, 1.0 ng.

b. Al³⁺ added, 5 µg.

c. Maximum amount tested.

d. Minimum amount tested.

ference was completely overcome. It was found that by adding 5 µg of aluminum(III), the sensitivity was enhanced by approximately 2.5-fold compared to that without aluminum(III). The indium sensitivity was maximum and independent over the range of 1 – 100 µg aluminum(III) as a chemical modifier.

The detection limit (3σ) of 8 pg was achieved by using the W-PPG tube with aluminum(III) as the chemical modifier. The range of linearity was up to 2 ng of indium(III). The performance can allow the determination of indium in aluminum-based alloy samples.

Application to practical samples

The proposed method was applied to an analysis of the indium distribution in an aluminum-rod sample. The preparation of the aluminum rod was as follows: a known amount of metallic indium (148.5 mg) was added to an edge of an aluminum rod (1.6 cm o.d.×48.8 cm long, 99.999% purity); then, the rod was treated four times by a zone-melting procedure, starting from the edge *in vacuo*.

The concentration of indium(III) was determined by the calibration-curve method using a series of standard indium(III) solutions, of which the matrices were nearly adjusted to those of each sample solution. The resulting solutions contained a sufficient amount of aluminum(III), which served effectively as the chemical modifier. Therefore, none of the amount of aluminum(III) was added to the sample solutions. The analytical results are illustrated in Fig. 2. The indium content was found to abruptly increase beyond a distance of 35 cm (45.8 cm in total length) from the starting edge.

The proposed method is applicable to the determination of indium in such samples as the aluminum alloy.

Fig. 2 Analytical results of an aluminum rod after a zone-melting treatment. A 148.8 mg amount of indium was added to an edge of the aluminum rod before zone melting. The location in the abscissa means the distance from the edge, to which a known amount of metallic indium was initially added.

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