Electrothermal Atomic Absorption Spectrometric Determination of Trace Bismuth in Aluminium and Its Alloys without Preliminary Separation

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Abstract

Graphite-furnace atomic absorption spectrometry is used for the determination of >0.002 % of bismuth in aluminium and its alloys. The samples are dissolved in hydrochloric acid and analyzed directly after addition of slight excess of $(NH_4)_2$EDTA over aluminium. Sample and standard solutions must contain equal amounts of EDTA.

Introduction

Rapid simple methods are required for the determination of traces of metals in metallurgical materials, and electrothermal atomic absorption spectrometry (a. a. s.) is probably the best technique for this purpose. However, interferences from chloride are frequently encountered1),2), which is unfortunate, as many metals and alloys are readily dissolved in hydrochloric acid. In previous works3),4), the mechanism of halide interferences in the determination of trace elements was investigated ; the evidence indicates that these effects arise initially from metal-halide complex formation in solution. On the basis of this mechanism, ammonium-EDTA was found to be the most suitable additive for removal of the interferences, because the metal ions are masked by EDTA and the readily volatile ammonium halide is produced. It was applied to the determination of trace lead, copper, manganese, chromium, nickel, iron and beryllium in aluminium and its alloys5),6). In the present work, ammonium-EDTA is again applied to the direct determination of trace bismuth in aluminium and its alloys after dissolution of the sample in hydrochloric acid. The detection limit for this element in aluminium was found to be similar to that obtained by flame a. a. s. with liquid-liquid extraction7),8).

Experimental

Apparatus and Reagents

A Varian-Techtron model 63 carbon rod atomizer was used in conjunction with a Varian-Techtron model 1200 atomic absorption spectrometer. A tube type of graphite cell was used and the absorption was measured in a nitrogen atmosphere. The signal was recorded with a Hitachi model 056 recorder. A Hitachi bismuth hollow-cathode lamp was used as the radiation source and a Varian-Techtron deuterium lamp was used for back-

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ground correction. The applied voltage between the atomizer terminals was measured with a digital voltmeter connected in parallel; the temperature of the center of the graphite tube was measured with a platinum/platinum-rhodium thermocouple. The sample was added from a 5-μl Excalibur Autopet fitted with disposable tips.

All solutions were prepared from analytical-reagent grade chemicals and demineralized water and stored in polyethylene bottles. The 1000-μg ml^{-1} stock solution for bismuth was prepared by dissolving bismuth metal (99.99 % pure) in the minimum of nitric acid and diluting with 0.1 M nitric acid.

Procedure

The sample (ca. 1 g) was weighed accurately and dissolved in the minimum of 6 M hydrochloric acid and several drops of 30 % hydrogen peroxide by heating gently on a hotting plate. After filtration, the solution was diluted to 100 ml with water. To aliquots of the sample solution containing 0.1–35 μg of bismuth, 3.7×10^{-2} mol or slightly more $(NH_4)_2$EDTA was added per gram of metal sample. The pH was adjusted, if necessary, to a value in the range 2–10 with ammonia, and the volume was made up to 25 ml with water. Calibration solutions were prepared similarly, using the stock solution and equal amount of $(NH_4)_2$EDTA.

A 5-μl aliquot of the sample solution was deposited in the center of the graphite tube with the micropipette and then dried, ashed and atomized with nitrogen gas flowing. The instrumental conditions are summarized in Table 1. The graphite tube was fired at its maximum temperature for 4 sec after each sample to clear any residue from the tube surface. The absorption signals during the atomization step were recorded and peak heights were measured. The non-atomic absorption of the sample was measured by use of the deuterium lamp under the same conditions and a suitable correction was applied. The bismuth contents were determined from calibration graphs. The variation of furnace temperature with applied voltage was measured at the drying and ashing steps, in the absence of any salt.

Table 1 Instrumental conditions

Wavelength	306.8 or 223.1 nm
N_2 flow rate	6.0 l min^{-1}
Drying	110℃ (0.56 V) for 30 sec
Ashing	410℃ (1.4 V) for 30 or 60 sec
Atomization	5.0 V (step mode) for 3 sec

Results and Discussion

Investigation of Analytical Conditions

The concentration of bismuth in the test solution and the analytical wavelength, unless otherwise specified, were set to 1.0 μg ml^{-1} and 306.8 nm line, respectively. The effects of drying and atomization conditions and of nitrogen flow rate were examined for the solution containing aluminium chloride (0.27 mg Al ml^{-1}) and 0.01 M $(NH_4)_2$EDTA. As described previously, in the presence of EDTA, at above 500℃ of ashing temperature the atomic absorbance of bismuth decreased$^{4)}$. Accordingly, the ashing condition was set to 1.4 V (410℃) for 30 sec, and when the concentration of EDTA was above 0.02 M, the ashing time was set to 60 sec. Under the conditions shown in Table 1, the calibration graphs were linear over the range 0.1–1.4 μg Bi ml^{-1}(at 306.8 nm line) and 0.04–0.4 μg Bi ml^{-1} (at 223.1 nm line).

Prior to the examination of the effect of EDTA, the effects of aluminium chloride concentration on the atomic absorption signal of bismuth in the absence of EDTA were investigated. Plots (a) and (b) in Fig. 1 show that in the presence of 0.1 M nitric acid the bismuth signal is suppressed by >40 μg ml^{-1}aluminium (as chloride), and in the presence of 0.1 M hydrochloric acid the signal is further suppressed by this acid. Addition of masking agents such as EDTA, therefore, is necessary for the determination of traces of bismuth in aluminium and its alloys after dissolution in hydrochloric acid.

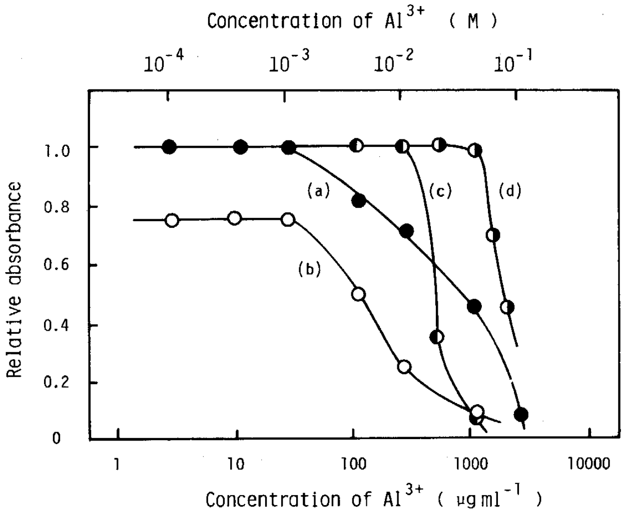

Fig. 1 Effects of aluminium concentration (as chloride) on the absorbance of bismuth (1.0 μg ml^{-1}) in the presence of (a) 0.1 M nitric acid ; (b) 0.1 M hydrochloric acid ; (c) 0.01 M $(NH_4)_2$EDTA ; (d) 0.04 M $(NH_4)_2$EDTA, relative to that when aluminium chloride is absent and 0.1 M nitric acid is present.

The effect of added $(NH_4)_2$EDTA concentration on the atomic absorbance of bismuth in the absence of aluminium chloride was investigated. As shown in Fig. 2, EDTA above

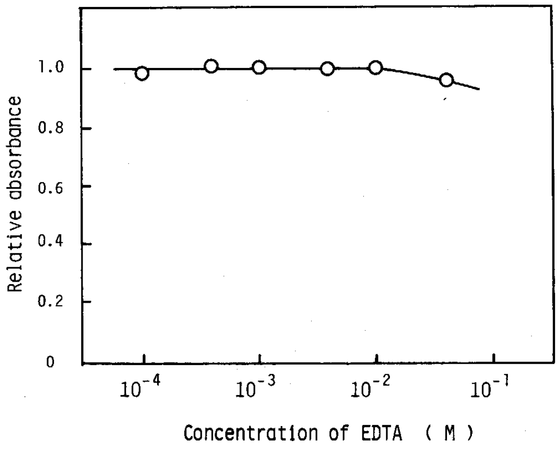

Fig. 2 Effect of $(NH_4)_2$EDTA concentration on the atomic absorbance of bismuth (1.0 μg ml^{-1}) relative to that when EDTA is absent and 0.1 M nitric acid is present.

0.01 M slightly suppresses the signal of bismuth. In the presence of above 0.01 M EDTA, the ashing operation of sample must be performed carefully, because the atomic absorption signal of bismuth was affected by ashing temperature[4]. In the presence of 0.01 or 0.04 M EDTA, the effects of aluminium chloride concentration on the atomic absorption signal of bismuth were investigated under the recommended conditions. Plots of (c) and (d) in Fig. 1 show that the interference by aluminium chloride can be completely removed by addition of an equimolar concentration of EDTA to aluminium, as in the determination of lead, copper and manganese[5] and chromium, nickel, iron and beryllium[6].

In order to standardize the amount of $(NH_4)_2EDTA$ added, all samples were regarded as pure aluminium, and the amount of EDTA added was calculated on that basis, i. e., 3.7×10^{-2} mol (or slightly more) per gram of sample. For the calibration solutions equal concentrations of EDTA were added to compensate for any interfering effects of EDTA. The maximum concentration of EDTA used in the sample solution was 0.04 M, because at higher concentration, the reproducibility of the analytical signal was invariably poor.

The effect of the pH of the test solution on the atomic absorption signal of bismuth was investigated for a synthetic sample solution containing aluminium chloride (0.27 mg Al ml^{-1}) and 0.01 M EDTA. The pH was adjusted with hydrochloric acid or ammonia. Between pH 2 and 10, no variation in absorbance of the bismuth was observed. Below pH 2, the EDTA precipitated. Therefore, the pH of the solution can be adjusted to any values between 2 and 10 with ammonia ; such a wide pH range is very advantageous.

Effect of Other Metals ; Detection Limit and Recovery

The conditions described above were used in the investigation of the effects of major metals in aluminium alloys on the recovery of the analyte. Magnesium, zinc, copper(II), iron(III), nickel, chromium(III), tin(II), manganese(II) and lead were chosen as other metals. The absorbance of bismuth was compared with two sets of solution, one having only bismuth and EDTA, and the other containing bismuth, aluminum chloride (270 μg Al ml^{-1}), EDTA and another metal chloride. For magnesium, copper and zinc, which usually form alloys with aluminium, the amount added was 10 % that of aluminium, i. e., 27 μg ml^{-1}, and for other metals, 2.7 μg ml^{-1}. The amount of added EDTA, therefore, was adjusted to be equivalent to 297 or 272.7 μg Al ml^{-1}. The results showed no significant effects of other metals on the determination of bismuth by the proposed procedure.

The detection limits for bismuth in aluminium were established by use of synthetic aluminium chloride solution. The detection limits (the concentration of analyte giving an analytical signal twice that of the background signal at the analytical wavelength) were 0.02 % (at 306.8 nm line) and 0.01 % (at 223.1 nm line) for bismuth in aluminium. These values are comparable with those obtained by flame a. a. s. using the separation with liquid-liquid extraction[7],[8].

The proposed procedure was applied to the determination of traces (0.002–0.05 %) of bismuth in several aluminium and alloy samples. When the sample contained bismuth below 0.01 %, 233.1 nm line was chosen as analytical wavelength, because the analytical sensitivity at this line was more than at 306.8 nm line. The results are presented in Table 2. They show good reproducibility, and good agreement with certificated values.

Table 2 Determination of bismuth in aluminium and its alloys

Sample	Found (%)[a]	Certified value (%)
ALCOA WA-1199-L	0.0015±0.0003	0.0018
ALCOA WA-1000-K	0.012±0.001	0.012
ALCOA WA-5005-D	0.032±0.003	0.033
ALCOA SS-2018-E (4%Cu-2%Ni-Al alloy)	0.045±0.003	0.044

[a] Mean and standard deviation calculated from five replicate measurements

Conclusions

Ammonium-EDTA is shown to be a very suitable additive for the direct determination of traces of bismuth in aluminium and its alloys by graphite-furnace a. a. s. As the specimen can be dissolved in hydrochloric acid and no chemical separation is required, the analysis is rapid and the risk of contamination of the sample is considerably reduced.

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