

Differential pulse adsorptive stripping voltammetric determination of nickel and cobalt in high purity aluminium

M. M. Palrecha

Analytical Chemistry Division,
Bhabha Atomic Research Centre, Bombay-400 085, India

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Abstract. A sensitive method for the simultaneous determination of trace amounts of nickel and cobalt in pure aluminium has been described using differential pulse adsorptive stripping voltammetry (DPASV) by adsorptive accumulation of the dimethyl glyoxime (DMG) complex on the hanging mercury drop electrode (HMDE). As supporting electrolyte 0.1 mol/l ammonia buffer, pH 9.0, containing ammonium citrate and 5×10^{-4} mol/l DMG has been used. The determination limit obtained has been as low as 0.5 $\mu\text{g/g}$ for Ni and 0.2 $\mu\text{g/g}$ for Co (using about 100 mg sample) with a relative standard deviation of 13% and 22%, respectively.

Introduction

Adsorption voltammetric methods based on the adsorption accumulation of the dimethyl glyoxime complex of Ni or Co on a stationary electrode such as the hanging mercury drop electrode [1–10] has found wide applications in trace analysis. Recently, an adsorptive voltammetric method has been applied for the determination of Co in high purity aluminium after separating it from the matrix by anion exchange resin [11]. Here, a simple DPASV-method is described for the simultaneous determination of Ni and Co in high purity aluminium without separating these elements from the matrix.

Experimental

A polarographic analyser EG & G PARC 174 A, in conjunction with a static mercury drop electrode (303 A) was used. *Experimental conditions* see as indicated in Fig. 1.

Reagents. Stock standard solutions of Ni and Co both 1 g/l in 0.2 mol/l HNO₃ were prepared from Titrisol ampoules (Merck) and standards of lower concentrations were obtained by appropriate dilution with doubly distilled water. Analytical grade reagents and solvents were used unless otherwise noted.

Procedure. About 0.5 g high purity aluminium sample was dissolved in 10 ml conc. HCl and the solution was then made up to 50 ml in a standard flask with double distilled water. A similar reagent blank was also prepared. A known amount of sample aliquot (5 ml) was taken in a cleaned beaker. To this 2 ml of citrate, ammonia buffer (0.01 mol/l) and, DMG (5×10^{-4} mol/l) were added and the pH was adjusted to 9 and the volume was made up to 10 ml. The solution was transferred to the polarographic cell, deoxygenated for 5 min and subjected to DPASV. The adsorbed complex was then reduced. The Ni and Co contents were evaluated by the standard addition method (Fig. 1).

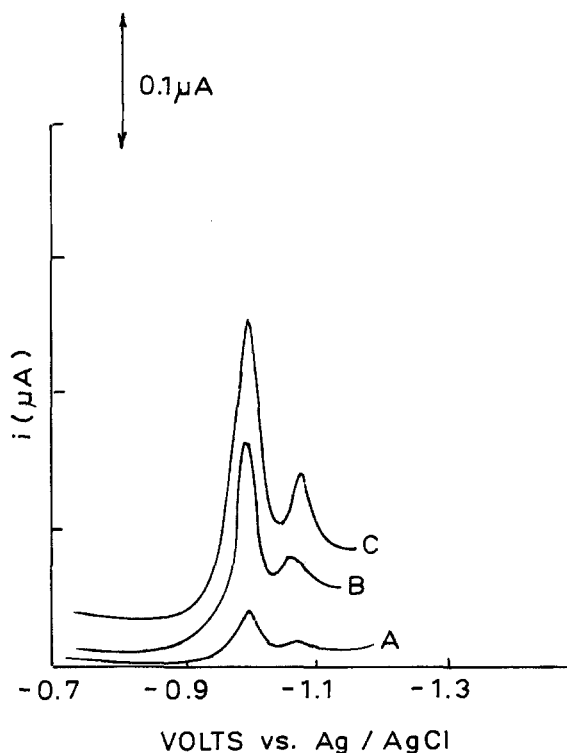


Fig. 1. DPASV of Ni and Co in aluminium. A, reagent blank; B sample; C sample + standard addition (Ni –2.1 ng/ml, Co –0.6 ng/ml). Media : 0.01 mol/l NH₃ buffer + 1×10^{-4} mol/l DMG + 0.2 mol/l citric acid; pH = 9.0; scan rate: 2 mV/s; pulse amplitude: 50 mV; adsorption potential: –0.7 V (vs Ag/AgCl); adsorption time: 120 s; equilibration time: 30 s; sample solutions were deoxygenated with nitrogen

Results and discussion

Zinc generally interferes with the determination of cobalt as the peak potentials of Zn and Co in ammonia buffer are very close to each other (–1.1 V). Moreover, the Ni/Co ratio also affects the sensitivity in the determination of cobalt.

Ni and Co as DMG complexes in aluminium samples could not be determined in ammonia buffer (pH = 9) because at pH 9, aluminium would get hydrolysed resulting in the formation of Al(OH)₃ precipitate which might block the surface of the mercury drop during stirring of the solution and there is a risk of losing Ni and Co by adsorption on or occlusion in Al(OH)₃ precipitate. To suppress the hydrolysis of aluminium citrate was added and then the pH was adjusted to 9 by ammonia. Citrate minimises also the Zn interference especially for the determination of Co as the Zn-citrate reduction potential shifted to a more negative potential (–1.25 V) than that of the Co(DMG)₂ complex.

Using these experimental conditions, Ni and Co could be determined in presence of an excess of Zn of about 500 times Co and at a Ni/Co ratio of maximum up to 15. The most probable other impurities like As, Pb, Cu, Cd, Cr, Fe, Mn, Mo, Se, Ga Tl, V occurring in the ultra trace range in high purity aluminium did not interfere with the determination of Co and Ni as evidenced by the accuracy of replicate analysis of aluminium samples. The results obtained by the proposed method and GFAAS are presented in Table 1.

Detection limits for Ni and Co depend on the reproducibility of the procedural blank rather than on the instrumental

Table 1. Concentration of Ni and Co in different samples determined by DPASV and GFAAS

S. No	Voltammetry ^a		GFAAS ^a	
	Ni ^b μg/g	Co ^c μg/g	Ni μg/g	Co μg/g
1	2.1	0.3	2.5	0.5
2	7.2	1.2	6.9	1.1
3	5.1	1.0	5.4	1.3

^a n = 4^b r.s.d. 13% (Ni)^c r.s.d. 22% (Co)

noise. The blank has been estimated for Ni at 0.3 ± 0.05 ng/ml and for Co at 0.05 ± 0.01 ng/ml (n = 6). These results yield detection limits (3σ) of 0.10 ng/ml for Ni and 0.03 ng/ml for Co.

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Determination of impurities in strontium titanate ceramics by inductively coupled plasma mass spectrometry

Shoji Kozuka, Yukari Yokote, Kazuhide Abe, Masaru Hayashi, Hideki Matsunaga

Environmental Engineering Laboratory, Research and Development Center, Toshiba Corporation, 1, Komukai-toshiba, Saiwai, Kawasaki 210, Japan

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Abstract. The determination of impurities in SrTiO₃ by ICP-MS was investigated. The sample was decomposed with hydrochloric and hydrofluoric acids in a PTFE pressure vessel. The internal standard method using Au was selected to eliminate an ion count suppression by the Sr and Ti matrix. Impurities at sub μg/ml level in SrTiO₃ were determined. The detection limits were in the range of 0.008 to 0.01 μg/g.

Introduction

A strontium titanate ceramic (SrTiO₃) has been employed as insulation film in dynamic random access memories or as dielectric material in hybrid integrated circuits. It is important to measure the impurities in that material, because they are known to significantly affect the electrical characteristics such as leakage current. The impurities in barium titanate ceramic (BaTiO₃), which was used as well as SrTiO₃, has been determined with inductively coupled plasma atomic emission spectrometry by Morikawa [1] and Farinas [2]. However, an analytical method for SrTiO₃ has not yet been reported. The objective of the pre-

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sent work is to establish a method to precisely determine impurities in SrTiO₃ by inductively coupled plasma mass spectrometry (ICP-MS).

Experimental

Apparatus. ICP-MS measurements were carried out with an SPQ-6500 (Seiko Instruments, Inc.). The ion lenses and mass resolutions were set by tuning so as to yield maximum responses for cobalt, barium, and lead. Acid pressure decomposition of the sample was carried out in a stainless pressure vessel using polytetrafluoroethylene (PTFE) inserts of 50 ml volume.

Reagents. Stock solutions (10 μg/ml) were prepared by diluting a single element standard stock solution (for use in atomic absorption spectrometry, Kanto Chemical Co., Inc.). The working standards were obtained by mixing aliquots of 10 μg/ml stock solutions. All of the acids used were of super-analytical grade (Tama Pure AA-1000, Tama Chemical, Inc.). Distilled deionized water was used throughout.

Procedure. A sample of 100 mg was heated with 10 ml of 30% hydrochloric acid and a few ml of 38% hydrofluoric acid in a PTFE pressure vessel at 200° C for 4 h. After cooling, the solution was almost completely dried to evaporate the hydrofluoric acid. The residue was dissolved in 10 ml of 30% hydrochloric acid and was then added to 0.5 ml of 10 μg/ml gold solution as an internal standard. The solution was diluted to 100 ml and measured by ICP-MS.

Results and discussion

SrTiO₃ is one of the most difficult materials to be decomposed with acids and usually alkali fusion is selected for decomposition. This procedure, however, is not suitable for the determination of trace impurities due to a possible contamination from the atmosphere during fusion and from the platinum crucible. We therefore decomposed the sample with hydrochloric and