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Trace Determination of Indium by Electrolytic Preconcentration and Open Circuit Stripping via Localized Galvanic Cells

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Synopsis. A galvanic stripping analysis procedure is described for the trace determination of indium(III). The determination involves the reoxidation of predeposited indium on the mercury-film-coated glassy carbon electrode in open circuit position (in the absence of external potential or current input or oxidant in solution). The reoxidation of indium was shown to occur due to the formation of localized galvanic cells. The time of reoxidation (stripping) was found to be proportional to the concentration of indium present in the solution (1 to 100 ppb). The details of the development of such a procedure and its possible application to determination of indium in zinc deposits and aluminium alloys are discussed.

Electroanalytical techniques were widely used for the trace determination of indium. These include phase selective[1] and second harmonic[2] a.c. Polarographic, differential pulse polarographic[3] and anodic stripping voltammetric techniques.[4–10] Stripping voltammetric techniques are preferred over polarographic techniques in view of the simplicity, rapidity, and higher sensitivity of these procedures. Most of the researchers utilize halide medium in anodic stripping voltammetric studies as they offer higher sensitivity arising out of the fast reactions of indium in these media. A few of these stripping voltammetric procedures find application in the determination of 1.8 ppm of indium in zinc[6] or 0.2 to 0.7 ppm of indium in aluminium.[7] Recently, we have described a novel electroanalytical technique namely galvanic stripping analysis (GSA) which was successfully utilized for trace determination of cadmium,[11] chromium,[12] and lead.[13] This paper describes the development of galvanic stripping analysis procedure for the determination of traces of indium and its possible application to determination of indium in zinc deposits and aluminium alloys.

Experimental

Reagents. Indium(III) Solution: This solution was prepared by dissolving 0.2212 g of indium(III) chloride in 100 ml of conductivity water (0.01 mol dm^{-3}). A working solution containing 10 ng cm^{-3} of indium was prepared by suitably diluting the stock solution with conductivity water.

Acetate Buffer: This solution was prepared by dissolving 13.608 g of sodium acetate in water and adding 6 ml of glacial acetic acid, adjusting the pH to 3.5 with dilute HCl and diluting the solution to 100 cm^3.

Apparatus: A Wenking potentiostat (Model LB 75 M) coupled with a Wenking scan generator (Model VSG 72) was used for controlling the potential during preconcentration step. A Ricadenki xy/t recorder was used for obtaining galvanic stripping E-t profiles. A conventional three electrode cell consisting of mercury film coated glassy carbon working electrode (MFGCE) prepared as described elsewhere[14] (Tokai & Co., 3 mm dia.), a platinum foil counter and a normal calomel electrode (NCE) as reference was used. All the potentials were expressed with respect to NCE and measurements were made at room temperature.

Porcedure: Transfer a suitable aliquot (upto 40 cm^3) of sample solution containing $\leq$100 ppb of indium(III) into a 50 cm^3 volumetric flask. Add 5 cm^3 of acetate buffer solution and dilute to volume with conductivity water. Transfer the solution to electrochemical cell and deaerate with N_2 for 15 min. After preconcentrating electrolytically for 4 min at -1.4 V vs. NCE, the galvanic stripping E-t profiles were drawn after keeping the potentiostat in open circuit position (i.e. where the counter electrode is disconnected from the three electrode assembly) and in the absence of any external oxidant or electrical input. The E-t profiles thus obtained represent the variations of the MFGCE working electrode potential with respect to NCE. The time taken for stripping forms the analytical signal of GSA. Prepare a calibration graph for the determination of 1—100 ppb of indium(III) by the above procedure.

Results and Discussion

Figure 1 shows the stripping E-t profiles obtained after preconcentrating 0, 10, 30, and 50 ppb of indium(III) (curves A, B, C, and D respectively) onto MFGCE at -1.4 V vs. NCE for 4 min. These E-t profiles were drawn by keeping the potentiostat in open circuit mode immediately after preconcentration step and in the absence of any imposed stripping conditions viz. external electrical input (potential or current) or addition of chemical oxidants. On the other hand, when the potentiostat is kept in open circuit position after

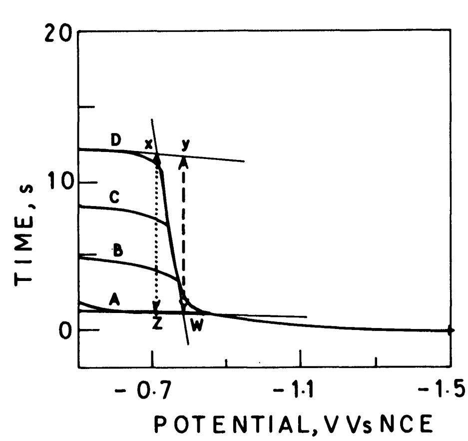

Fig. 1. Galvanic stripping E-t profiles recorded for 0, 10^{-7}, 3×10^{-7}, and 5×10^{-7} M of indium(III) between MFGCE working and normal calomel reference electrode, 0.1 M acetate buffer (pH 3.5); total volume=50 ml; deposition potential (E_d)=-1.4 V vs. NCE; deposition time (t_d)=4 min.

Table 1. Effect of Supporting Electrolyte

Sample No.	Supporting electrolyte (concentration)	Stripping time s
1	KI (0.2 M) or KBr (0.2 M) or NaCl (0.2 M)	Not resolved
2	Chloroacetate buffer (0.1 M)	0.0
3	KNO_3 (0.1 M)	0.60
4	Acetate buffer, pH 3 (0.1 M)	2.00
5	KNO_3 (0.1 M)+Acetate buffer, pH 3 (0.1 M)	0.65
6	Acetate buffer, pH 3 (0.1 M)+KSCN (0.2 M)	0.70
7	Acetate buffer, pH 3 (0.1 M)+KI (0.2 M)	0.60
8	Acetate buffer, pH 3 (0.1 M)+KBr (0.2 M)	1.60
9	Acetate buffer, pH 3 (0.1 M)+NaCl (0.2 M)	2.00

Concentration of indium=10 ppm. Deposition potential (E_d)=−1.4 V vs. NCE. Time of deposition (t_d)=4 min.

depositing for 4 min at −1.4 V vs. NCE, the potential of hanging mercury drop and glassy carbon with respect to NCE drop to −0.8 and 0.1 V vs. NCE respectively. Thus in case of MFGCE, the potential difference between In (Hg) film electrode and uncovered portions of GCE (as mercury film is known to present as fine droplets) is ≈0.9 V. Hence, the stripping profiles of Fig. 1 can be thought of as due to the formation of localized galvanic cells between indium amalgam and uncovered portions of glassy carbon electrode (GCE). Experiments were then carried out to confirm the formation of localized galvanic cells as described elsewhere.[11–13] These include a) observing the flow of current from Pt foil to MFGCE, when Pt foil and MFGCE were connected externally by placing zero resistance ammeter in between (during this experiment potentiostat is kept in open circuit position) b) stability of indium amalgam on hanging mercury drop electrode and c) unaltered GSA stripping profiles with different stirring rates. Further, the time of stripping measured as indicated for curve D in Fig. 1 (xz or yw) is proportional to indium present in solution.

Effect of Supporting Electrolyte. The effect of supporting electrolyte on the galvanic stripping analysis (GSA) signal of 10 ppb of indium using MFGCE was investigated by drawing E-t profiles in open circuit selection mode after preconcentrating for 4 min at −1.4 V vs. NCE. The results obtained are shown in Table 1, from which it is clear that the stripping signal is maximum in acetate or acetate-chloride medium compared to other media.

Effect of pH. The effect of pH in the range 2.5 to 6.0 on the GSA determination of 10 ppb of indium on MFGCE was then studied by employing 0.1 M (1M=1 mol dm^{-3}) acetate buffer as supporting electrolyte. The results obtained are shown in curve A of Fig. 2 from which it is clear that the optimum pH range is 3.0 to 3.8. pH 3.5 acetate buffered medium was chosen in further studies.

Effect of Deposition Potential. In order to ascertain optimum deposition potential, the deposition potential during 4 min preconcentration of 10 ppb of indium was varied in the range −0.8 to −1.5 V vs. NCE in steps of 0.1 V onto MFGCE. Curve B in Fig. 2 shows the time of stripping obtained from E-t profiles drawn during stripping of indium deposited at various deposition potentials. The maximum GSA stripping signal is obtained at potentials more negative to −1.4 V vs. NCE as seen from curve B of Fig. 2.

Effect of Time of Deposition. The effect of deposition time (1 to 16 min) on GSA stripping signal of 10 ppb of indium was next investigated by depositing at −1.4 V vs. NCE onto MFGCE. The results thus obtained revealed that the stripping signal is directly proportional to the time of deposition.

Calibration Graph and Precision. Linear calibration graph passing through the origin was obtained for 1—100 ppb of indium (cf. Fig. 3) with 4 min of deposition time. The relative standard deviation for 5 replicate determinations of 10 ppb of indium(III) was calculated to be 3.8%.

Analysis of Synthetic Samples. The results of the analysis of aluminium and zinc metal samples spiked with known amounts of indium are shown in Table 2. Aluminium do not interfere at all concentrations in the present procedure. But zinc do interfere by codepositing with indium which can be avoided by maintaining deposition potential at −1.05 V vs. NCE. Under these conditions the sensitivity of the procedure decreases by ≈6%. However, the calibration range

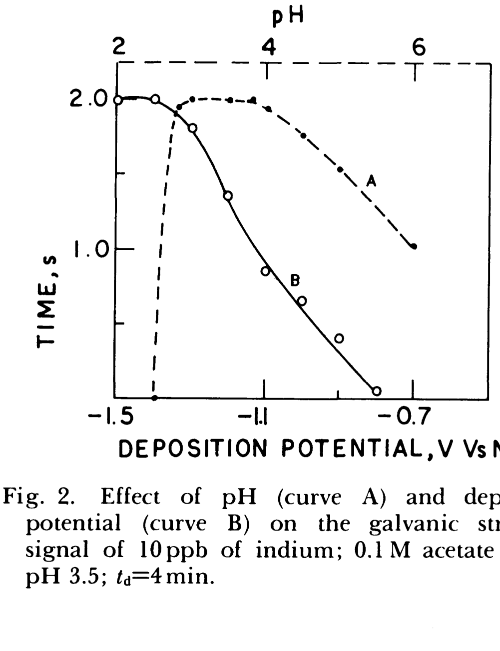

Fig. 2. Effect of pH (curve A) and deposition potential (curve B) on the galvanic stripping signal of 10 ppb of indium; 0.1 M acetate buffer, pH 3.5; t_d=4 min.

Table 2. Analysis of Synthetic Samples

Sample solution	Amount of indium(III) added	Aliquot taken	Indium(III) found	Recovery
	μg/g	ml	μg/g	%
1. Aluminium Metal	—	40	0.0	—
(5 g per 50 ml)	0.5	40	0.49	98.0
	1.0	40	1.01	101.0
2. Zinc metal[a)]	—	40	0.0	—
(5 g per 50 ml)	0.4	40	0.39	97.5
	0.8	40	0.80	100.0
	1.2	25	1.18	98.3

a) By depositing at −1.05 V vs. NCE for 4 min.

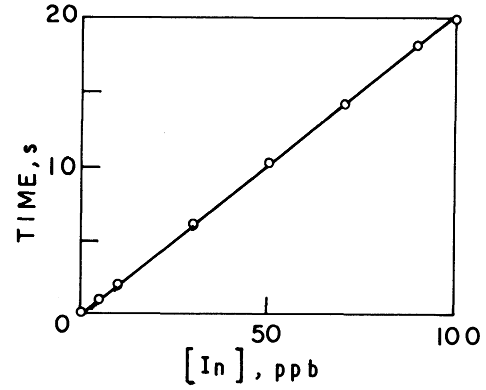

Fig. 3. Calibration graph.

remains unaffected. As the recoveries obtained were quantitative, the developed (cf. Table 3) procedure is expected to find application in ascertaining the concentration of indium in zinc deposits and aluminium alloys.

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