

Short Communication

Preconcentration by coflotation for the polarographic determination of traces of heavy metals in water

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Preconcentration by coflotation is employed to improve the detection limits for the determination of parts per billion levels of heavy metal ions such as copper(II), lead(II), cadmium(II), zinc(II), nickel(II) and cobalt(II) in natural and sea water by differential pulse polarography (DPP). Trace amounts of these ions in water are coprecipitated on colloidal aluminium hydroxide and the precipitate is floated with the aid of sodium oleate and a stream of nitrogen bubbles. Experimental conditions are optimized to obtain maximum recovery of these ions by coflotation. The effect of surfactant on the DPP peak currents of these ions in the supporting electrolyte used in this work is studied.

There is an increasing need for the development of methods for the estimation of trace amounts of heavy metal ions such as copper, lead, cadmium, zinc, nickel and cobalt in natural waters. Many instrumental methods lack the necessary sensitivity and hence preconcentration is required. Coflotation has an advantage over the other conventional preconcentration techniques like coprecipitation, solvent extraction and ion exchange as it can deal with large volumes of sample in a short duration of time. Various flotation techniques used for the separation of many such elements has already been reviewed¹⁻³. An adsorbing colloid flotation technique has been used to separate Cu(II) and Zn(II) from sea water using ferric hydroxide as collector⁴. A combination of adsorbing colloid flotation and differential pulse polarography (DPP) has also been described to determine traces of molybdenum in water⁵. This paper presents the studies on coflotation for the simultaneous preconcentration of these heavy metal ions prior to their determination by polarography.

Experimental procedure—The polarograph as well as the flotation apparatus were described earlier⁵. All

reagents used were of AR grade except the surfactant. Sodium oleate (SO) was obtained from Loba Chemie. The stock solutions (1000 ppm) of copper, lead, cadmium, zinc, nickel and cobalt were prepared either by dissolving the pure metal in nitric acid or by dissolving the nitrate salt in water. A stock solution of aluminium (10 mg/mL) was prepared from aluminium sulphate. Sodium oleate (4 mg/mL) was prepared by dissolving the reagent in 80% (v/v) ethanol. Dimethyl glyoxime (1%) was prepared in ethanol.

Water samples were stored in precleaned polyethylene bottles after acidification to pH 2 with hydrochloric acid. All analytical determinations were performed within one week of collection of samples.

The flotation of the water samples was carried out by the procedure described earlier⁵. After adding 5 mL Al(III) solution to 1 L water sample, pH was adjusted to 9.0 ± 0.2 with aqueous ammonia and the solution was stirred for 5 min. 5 mL of sodium oleate solution was added and the solution was floated by bubbling nitrogen through the solution for 2 min. The froth was dissolved in 10 mL of 2 M HCl, heated to reduce the volume and made up to 10 mL with water.

Polarograms of copper, lead, cadmium and zinc were recorded in a supporting electrolyte (S.E.) of 0.2 M KCl and 0.25% ascorbic acid at pH 2.5–3.0 from –0.05 to –1.20 V with respect to SCE. Similarly, the polarograms of nickel and cobalt were recorded in a S.E. of 0.1 M ammonium tartrate at pH 8.8 and 0.01% dimethyl glyoxime (DMG) from –0.80 to –1.50 V with respect to SCE. The metal ion concentrations were determined by standard addition method.

Results and discussion—Aluminium hydroxide was chosen as the collector since aluminium(III) did not interfere with the polarographic determination of the other metal ions. Sodium oleate (SO) is able to float aluminium hydroxide completely in the pH range of 7.0–9.2 and hence it was chosen as the surfactant.

The effect of pH on the recoveries of these ions from a solution of low ionic strength ($\mu < 0.01$) by coflotation was carried out in the pH range of 7–9.5. The results are shown in Fig. 1. It is observed that the pH ranges for maximum recovery are 7.0–9.2 for Cu(II), Pb(II) and Zn(II) and 8.8–9.2 for Ni(II), Co(II) and Cd(II), thus, it may be concluded that simultaneous and complete recovery of all the six

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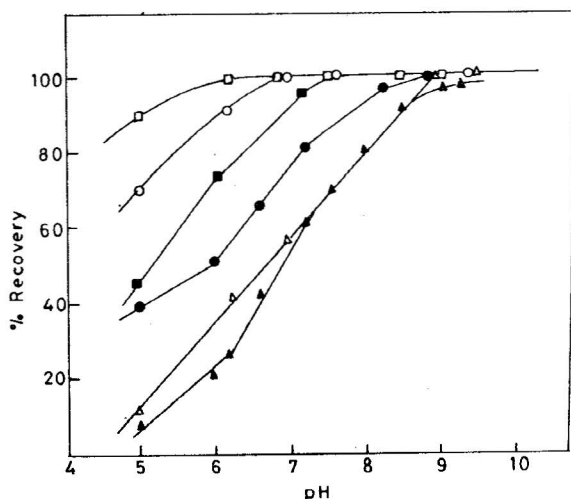


Fig. 1—Effect of pH on the recoveries of Cu(II), Pb(II), Cd(II), Zn(II), Ni(II) and Co(II) by coflotation using aluminium hydroxide as collector and SO as surfactant. [Cu(II)] = [Pb(II)] = [Cd(II)] = [Zn(II)] = [Ni(II)] = [Co(II)] = 0.2 ppm (○) copper; (□) lead; (△) cadmium; (■) zinc; (●) nickel; (▲) cobalt

elements could be achieved in the pH range 8.8 – 9.2. Therefore, a pH of 9.0 ± 0.2 was chosen for the preconcentration of these elements by coflotation using aluminium hydroxide as collector and SO as surfactant.

The optimum concentrations of collector and surfactant required to obtain maximum recovery at pH 9.0 were found to be 50 ppm and 10 ppm, respectively. It was also found that a short time of 3 to 5 min was sufficient to bring about the complete recovery of all the six elements.

For the simultaneous polarographic determination of Cu(II), Pb(II), Cd(II) and Zn(II) in the preconcentrated sample, addition of ascorbic acid was helpful in overcoming the interference of Fe(III). It was also found that the peak current of copper was enhanced by 45% in the presence of ascorbic acid. The determination of Ni(II) and Co(II) was based on the dimethyl glyoxime enhancement of DPP peak current⁶. The enhancement in sensitivity was about 12 for nickel and 10 for cobalt [at $t = 0.5$ s]. At a higher droptime [$t = 2.0$ s], the enhancement factor was found to be about 25 to 30.

The effect of variation of SO concentration on the DPP peak currents of these heavy metal ions has been studied and the results obtained for Cu(II), Pb(II), Cd(II) and Zn(II) in a S.E. of 0.2 M KCl and 0.25% ascorbic acid are shown in Fig. 2. It is seen that the peak currents of lead and cadmium are not affected by up to 80 ppm SO. The peak current of copper increased initially with increase in SO concentration up to 40 ppm SO and decreased thereafter. The peak current of zinc is not affected by up to 40 ppm SO but

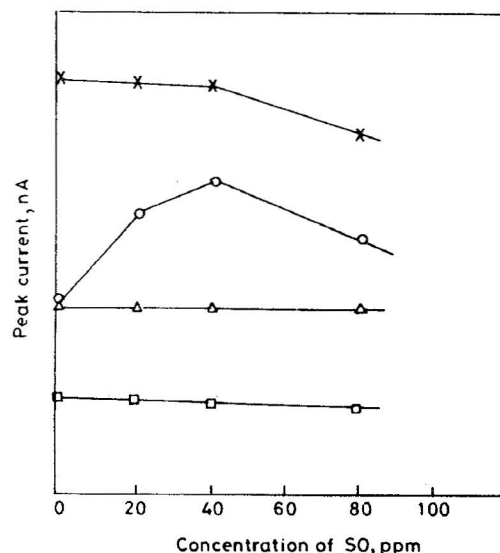


Fig. 2—Effect of variation of SO concentration on the DPP peak currents of Cu(II), Pb(II), Cd(II) and Zn(II). S.E.: 0.2 M potassium chloride + 0.25% ascorbic acid. [Cu(II)] = [Pb(II)] = [Cd(II)] = [Zn(II)] = 0.4 ppm. DPP conditions: $t = 2.0$ s; $\Delta E = 50$ mV; $h = 75$ cm; (○) copper; (□) lead; (△) cadmium; (×) zinc

decreased above this level. The effect of SO on the DPP peak currents of nickel and cobalt in ammonium tartrate buffer containing DMG was examined. There was no change in peak currents of Ni(II) and Co(II) up to 40 ppm SO. A slight increase (5 to 7%) in peak current was observed for Ni(II) and Co(II) at 80 ppm SO. It was also seen that the SO present in the floated sample did not interfere in the polarographic determination of these ions.

The sensitivities of these ions under the DPP conditions used in this work [$t = 2$ s; $\Delta E = 50$ mV; $m = 2.20$ mg/s and $h = 75$ cm] were 240, 130, 200, 290, 5000 and 5200 nA/ppm for Cu(II), Pb(II), Cd(II), Zn(II), Ni(II) and Co(II), respectively. The detection limits were lowered 50 times by using the combination of coflotation and DPP. Experimental values of detection limits were 0.6, 0.8, 0.4, 0.5, 0.2, and 0.08 ppb for these six ions in the same order as given above. Synthetic water samples were prepared by adding 1, 5 and 10 μ g each of these metal ions to 200 mL distilled water and these were analysed by the coflotation-DPP method under the standardized experimental conditions. It was found that the recoveries of the heavy metal ions were 95 to 100%.

Flotations with anionic surfactants are generally sensitive to the presence of anions^{7,8}. Usually, the flotation efficiency and the recoveries of ions are adversely affected by multiple charged anions like sulphate, phosphate and silicate. Natural water samples often contain small amounts of anions like chloride, sulphate, silicate and phosphate. The effect

of these anions on the coflotation has been investigated by adding known amounts of anions to the solution before coflotation using aluminium hydroxide as collector and SO as surfactant. It was seen that the flotation and recoveries of elements were incomplete above 3 ppm phosphate and 5 ppm silicate. Chloride, nitrate and sulphate could be tolerated up to a concentration of 0.2, 0.2 and 0.05 M, respectively.

Fresh water samples and sea water were analysed using this coflotation - DPP procedure. It was found that the values of relative standard deviation (RSD) for five replicate measurements were 2-3% and 5-7% for the recoveries of these elements from fresh water and sea water, respectively. The samples were acidified to pH 2 with nitric acid and subjected to ultra-violet irradiation for 4 h to destroy dissolved

organic matter and analyzed by coflotation and DPP. The results were found to be independent of the presence or absence of the UV irradiation step. Thus the total heavy metal content in the water samples could be determined by this method.

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