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Instructions for use

Determination of Cu, Pb, Cd and Zn in Seawater by Anodic Stripping Voltammetry

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Abstract

Analytical conditions to determine considerably low concentrations of heavy metals in seawater by anodic stripping voltammetry were examined. This method can prevent a sample from becoming contaminated by metals, and also determine the metals with small amount of a sample. The precision of Cu, Pb, Cd and Zn, of which the concentrations are 50, 40, 30 and 700 ng/l, were 27, 22, 19 and 11 % respectively.

Introduction

As to the concentration of heavy metals in seawater, recently reported values have been decreased by factors of one-tenth to one-hundredth (Boyle & Edmond, 1975; Sclater et al., 1976; Boyle et al., 1976; Moor & Burton, 1976; Moor, 1978; Bruland et al., 1978-a, 1978-b; Danielsson, 1978; Bruland, 1980; Knauer & Martin, 1981; Schaule & Patterson, 1981; Heggie, 1982). The reason for this is assumed to be the development of new sampling bottles to prevent samples from being contaminated by metals, and of highly sensitive analytical instruments. With the development of the highly sensitive analytical instruments, it has been possible to detect the metals that have been contaminated by a sampler or a storage bottle. For studying the biochemical or geochemical cycles of the metals, it is important to determine the reliable concentration of the metals in seawater.

Analytical techniques are broadely divided into flameless atomic absorption spectrophotometry (FAAS) and anodic stripping voltammetry (ASV). The former is widely used by many investigators and the latter only by Heggi (1982), Spencer et al. (1982) and Batley (1983).

As FAAS is not so sensitive, the metals must be concentrated from large amounts of samples. It is very difficult to do this, however, without the metals becoming contaminated. On the other hand, ASV is highly sensitive, so the metals can be determined by using small amounts of samples.

In this paper, an analytical method for determining the metals in seawater by ASV is described.

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Experiment

Apparatus and reagents

A Yanako P–1000 Voltammetric Analyzer was used with a hanging mercury drop electrode (Metrohm EA 290), a platinum wire electrode and a saturated calomel electrode as a reference electrode. A polarogram was recorded by a Watanabe X-Y recorder.

Mercury and water were purified using a vaccum distiller and a quartz glass distiller respectively. Deoxgenation was carried out with highly pure nitrogen gas.

Procedure

Transfer 40 ml of a sample solution to an electrolysis cell, and deoxgenate with nitrogen gas for 20 min with stirring. Preelectrolyse the metals at –1.3 V for 15 min (1 min for Zn) with stirring at 400 rpm. Stop stirring and allow to stand for 20 sec. Scan the electrode potential from –1.3 to 0.0 V at a scan rate of 20 mV/sec with a 50 mV pulse amplitude and record the polarogram. Determine the concentration of Cu, Pb, Cd and Zn by the standard addition method.

Analytical conditions

Analytical conditions were examined with a solution containing a concentration of 500 ng/l in seawater of each metal.
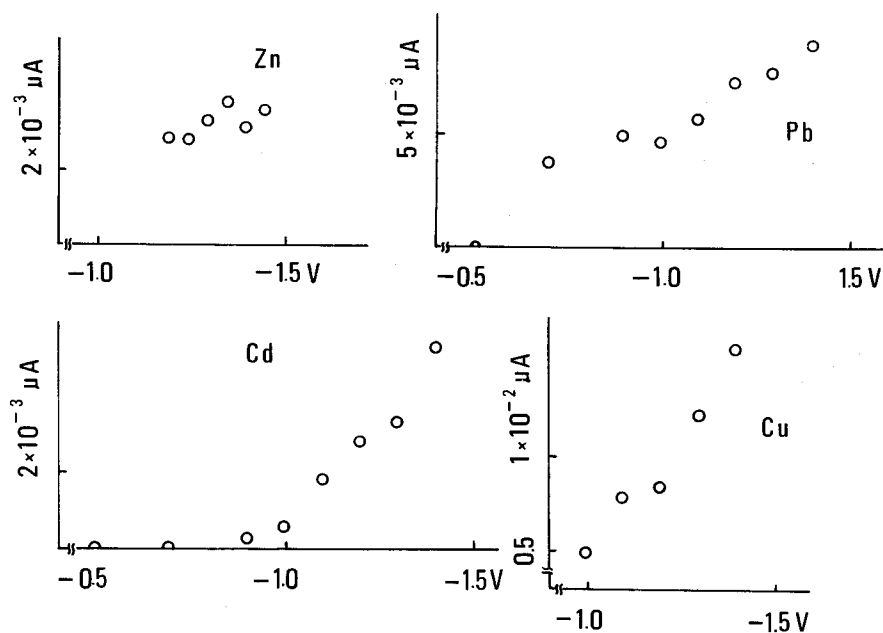

Fig. 1.   Effect of preelectrolysis potential on peak current

Effect of preelectrolysis potential on peak current

All peak currents of the metals increased with rising potential in the negative direction (Fig. 1). However, the reduction of the hydrogen ion began at about -1.5 V and disturbed the peak currents of the metals. Therefore, the most favorable preelectrolysis potential was -1.3 V.
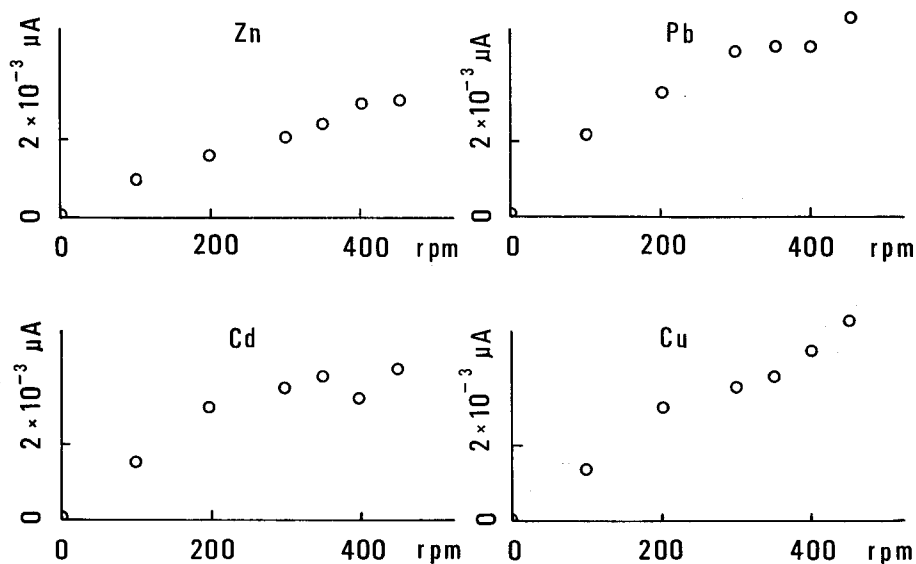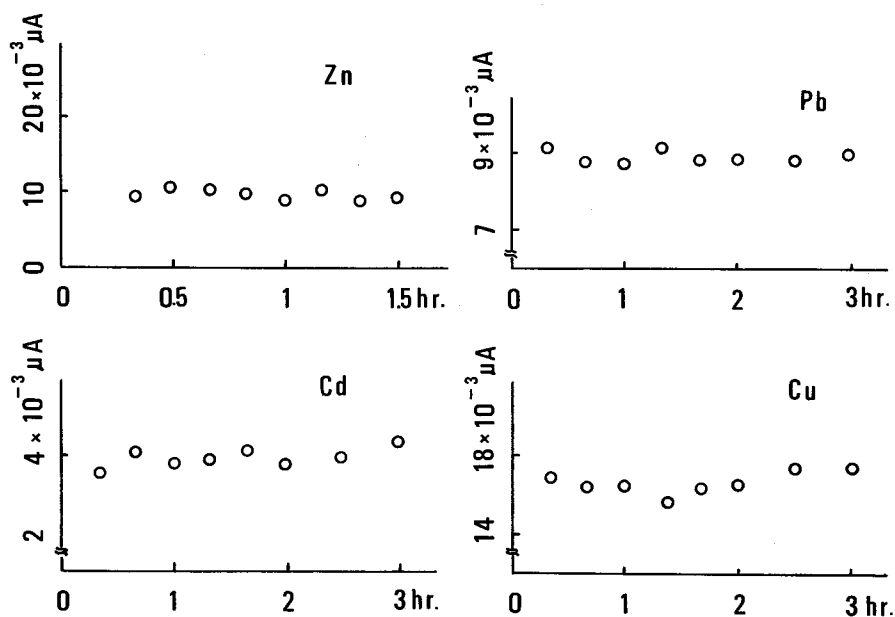
Fig. 2. Effect of stirring rate on peak current

Fig. 3. Adsorption of the metals on the walls of an electrolysis cell

Table 1. Precision for Zn

		Zn(ng/l)
1.	y=0.0145 X+11.3	782
2.	y=0.6158 X+11.0	697
3.	y=0.0163 X+12.9	791
4.	y=0.0163 X+10.8	662
5.	y=0.0165 X+11.0	666
Slope	μ=0.0158±0.0010	
	6.4% (α=0.05)	
Concentration	μ=716±78 (ng/l)	
	11% (α=0.05)	

Table 2. Precision for Cd

		Cd(ng/l)
1.	y=0.110 x+2.83	25.4
2.	y=0.093 x+3.30	35.5
3.	y=0.102 x+2.70	26.3
4.	y=0.100 x+2.60	25.9
5.	y=0.112 x+3.00	26.7
Slope	μ=0.103±0.0097	
	9.4% (α=0.05)	
Concentration	μ=27.9±5.3 (ng/l)	
	19% (α=0.05)	

Table 3. Precision for Pb

		Pb(ng/l)
1.	y=0.0408 x+1.61	39.0
2.	y=0.0356 x+1.60	44.8
3.	y=0.0397 x+2.00	50.3
4.	y=0.0335 x+1.80	46.7
5.	y=0.0422 x+1.52	30.7
Slope	μ=0.0394±0.0032	
	8.2% (α=0.05)	
Concentration	μ=42.3±9.5 (ng/l)	
	22% (α=0.05)	

Table 4. Precision for Cu

		Cu(ng/l)
1.	y=0.0435 x+2.04	46.8
2.	y=0.0463 x+3.40	73.4
3.	y=0.0495 x+3.20	64.5
4.	y=0.0483 x+2.60	53.7
5.	y=0.0516 x+2.20	56.1
Slope	μ=0.0478±0.0038	
	8.0% (α=0.05)	
Concentration	μ=56.1±14.9 (ng/l)	
	26% (α=0.05)	

Effect of stirring rate on peak current

The peak currents of the metals increased as the stirring rate increased (Fig. 2). It was difficult, however, to hold a mercury drop on the hanging mercury drop electrode at a stirring rate of more than 500 rpm.

Adsorption of the metals on the walls of an electrolysis cell

A sample was allowed to stand in the cell for several hours to test the adsorption of the metals in the sample on the walls. As shown in Fig. 3, it was found that the metals did not adsorb on the walls within 3 hr.

Precision

The reproducibility of the method was determined by addition of the metals to seawater. The concentration of each metal was determined from an intercept of a working curve.

The relative standard deviations of the concentration of each, and the slopes of the working curves for 5 replicate determinations, are shown in Tables 1–4.

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