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Determination of Cadmium in Mixtures With Metal Ions

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A method for the determination of cadmium microamounts in mixtures with metallic ions with $E_{1/2}$ near to $E_{1/2}$ of cadmium is discussed. For higher selectivity cadmium was extracted in the form of the pyridin—thiocyanate complexes prior to polarography.

(Keywords: Cadmium, determination of; Liquid—liquid extraction; Polarography)

Bestimmung von Cadmium(II) neben anderen Metallionen

Es wird eine polarographische Methode zur Bestimmung von Cd(II) neben anderen Metallionen mit $E_{1/2}$ nahe $E_{1/2}$(Cd) diskutiert. Zur Erhöhung der Selektivität und Genauigkeit wird eine Pyridin—Thiocyanat-Extraktion vorgeschalten.

As known from literature cadmium yields well-defined polarographic waves corresponding to two-electron reduction in acidic, neutral, and basic solutions in the presence of inorganic or organic complex forming reagents. The half-wave potential of the cathodic reduction of cadmium ions varies between 550 and 1,350 mV (SCE) depending on the reaction conditions. Recent literature often mentions the extraction-polarographic determination of elements in mixtures[2,3].

Experimental

The polarographic measurements were carried out on the polarograph LP 7 (LP Prague). As an indicative electrode served a mercury drop electrode $t = 2.1\,s^{-1}$ in $1M$-KCl solution; flow rate of mercury $m = 1.5\,mg\,Hg \cdot s^{-1}$, *Smoleř* type[4]. A saturated calomel electrode was used as reference electrode (SCE). It was used for compensation of the rest currents of $0.45\,\mu A \cdot V^{-1}$ or $0.21\,\mu A \cdot V^{-1}$ as well as for the damping of the galvanometer.

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The ions of interest were extracted from the samples in 50 ml to 500 ml volumes using a 5% pyridine reagent in chloroform solution in the following way: a sufficient amount of NH_4SCN solution (20%) was added into a slightly acidic solution of a sample, then the *pH* was modified to 5.0 by adding acetate buffered solutions; this solution was extracted by two doses (5 and 7 ml) of 5% pyridine reagent. The mixed extracts were washed with the same amount of 20% NH_4SCN solution. Then the extracted complex was decomposed by hydrochlorid acid by evaporation to dryness. The residue (after dissolving in the necessary amount of 1*M*-hydrochloric acid) was neutralized partially with sodium carbonate and after the addition of 2-3 ml of tartaric buffer solution neutralization was completed: *pH* 5.4, 10 ml volume. The polarographic waves varying from 0 to —900 mV registered after removing oxygen from the solution. The concentration of cadmium in the analyzed solutions was calculated from the wave height corresponding with the limit current of Cd using a calibration curve.

Results and Discussion

The half-wave potential of the cathodic reduction of Cd(II) ions is relatively positive and allows the direct determination of Cd(II) in addition to cations being reduced with more negative half-wave potentials. The determination of Cd(II) in various materials by this method is important and in many cases simple. Nevertheless, Cd(II) determination in trace amounts becomes problematic in the presence of elements with more positive half-wave potentials of the cathodic reduction relative to $E_{1/2}$Cd(II). Especially Cu, Ag, Hg, Bi, Tl and Pb(In) were taken into consideration.

Regarding the mentioned interfering elements, the Ag and Hg reductions appear in the anodic part of the polarographic wave, their $E_{1/2}$ corresponding to the cathodic reduction being relatively different from that one of Cd(II); but they disturb the determination of μg amounts of Cd(II) by rising the zero line of the galvanometer expecially if an excess of these ions is present in solution. The sensitivity and accuracy of the polarographic cadmium determination is then essentially decreased. The influence of Bi and Tl whose cathodic reduction $E_{1/2}$ is similar to that of Cd(II) can be eliminated by introducing extraction procedures of Cd(II). No disturbing influence of Tl or of Bi was observed when using extraction with the aid of pyridine—thiocyanate complexes. Since copper and lead are extracted together with cadmium they can be determined in tartaric buffer solutions (*pH* 4.6-5.4).

Fig. 1 illustrates an example of the polarographic behaviour of copper(II), lead(II) and cadmium(II) ions in tartaric buffer solution. The pyridine—thiocyanate complexes were decomposed with hydrochloric acid and not with HNO_3[5]. Using HNO_3 irreproducible polarographic waves were observed. Reproducibility was very good using

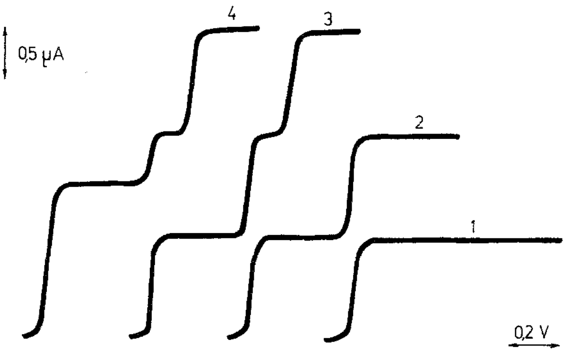

Fig. 1. Cathodic reduction of copper, lead and cadmium(II) ions in tartrate buffer solution—*pH* 5.4; registration: 0-900 mV (SCE). *1* 55 μg Cu, *2* 55 μg Cu + 150 μg Pb, *3* 55 μg Cu + 150 μg Pb + 80 μg Cd, *4* 80 μg Cu + 80 μg Pb + 80 μg Cd

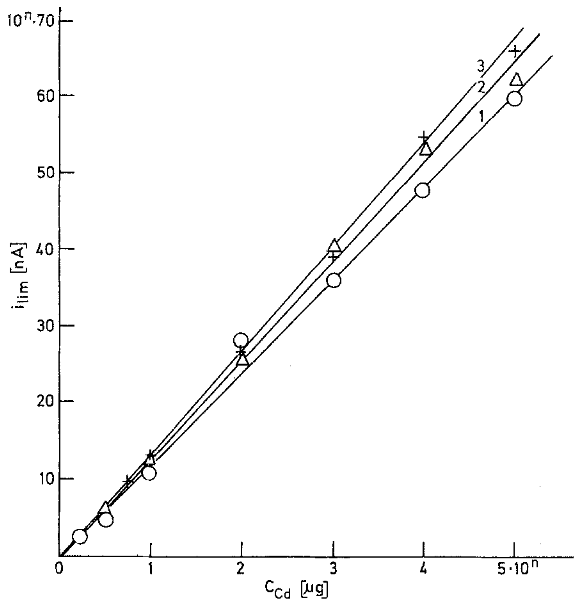

Fig. 2. Cadmium(II) ions limit current vs. concentration in ionic buffer solutions. *1* 0-5 μg Cd, $n = 0$, *2* 0-50 μg Cd, $n = 1$, *3* 0-500 μg Cd, $n = 2$

hydrochloric acid in spite of the very fast decomposition and evaporation to dryness.

The most positive $E_{1/2}$ (Fig. 1, curve 1) corresponds to the two-electron cathodic reduction of Cu(II) (~ -0.1 V; SCE). At more negative $E_{1/2}$ (~ 0.48 V; SCE) a wave corresponding to the two-electron reduction of Pb(II) is obtained (Fig. 1, curve 2). At the most negative $E_{1/2}$ (~ -0.64 V; SCE) a wave corresponding to the two-electron reduction of Cd(II) is observed. Curves 1-3 were registered with such ion concentrations that the wave heights were equal (equimolar conditions). Curve 4 was registered with non-equimolar conditions.

Fig. 1 shows that the polarographic method is most sensitive for copper and less for lead. Further the excellent sensitivity of the extraction-polarographic method for cadmium and the linearity of the *Ilkovic* relation could be demonstrated. The limiting current corresponding to the cathodic reduction of cadmium(II) ions was found to correspond to the equation within the range of 0.25 μg to 500 μg.

$$i_{\mathrm{lim}} = 0.01329\ (\pm\ 0.00005) \cdot \mu\mathrm{g\,Cd} + 0.0026\ (\pm\ 0.0068)$$
$$n = 68; \quad r = 0.9994; \quad S = 0.00014$$

where n is the number of analyses and r is the correlation coefficient, S is residual scattering.

As seen from the correlation coefficient (0.9994) the relation is proved to be strictly linear. It can be shown from the slope value ($\rho = 0.01329\ \mu\mathrm{A}/\mu\mathrm{g}$), taking into consideration the sensitivity of the apparatus 10^{-10} A/l, that less than 1 μg of Cd can be polarographically determined in the analyzed solution.

Taking into account the low costs and the simplicity of the extraction-polarographic method for cadmium determination even in presence of other elements, it might be successfully used instead of the photometric method.

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