Square-wave polarographic determination of copper, lead, and cadmium in zinc oxide

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The content of Cu, Pb, and Cd in ZnO was determined by using square-wave polarography in the medium of nitric acid of 0.3 mol dm^{-3} concentration and the method of standard additions. As we found by simultaneous determinations considerable interactions between cations (especially influencing of Pb(II) by Cd(II)), we recommended to determine individual components in separate portions of the sample solution. Thus we found (10.7 ± 0.8) μg Cu, (360.6 ± 10.0) μg Pb, and (42.7 ± 1.0) μg Cd in 1 g ZnO.

С использованием квадратноволновой полярографии в среде азотной кислоты с концентрацией 0,3 моль $дм^{-3}$ мы установили содержание Cu, Pb и Cd в ZnO посредством метода стандартных добавок. Поскольку при одновременном определении было обнаружено значительное взаимное влияние катионов (особенно Cd(II) на Pb(II)), мы рекомендуем проводить определение индивидуальных компонентов в отдельных порциях раствора образца. В 1 г ZnO найдено $(10{,}7 \pm 0{,}8)$ мкг Cu, $(360{,}6 \pm 10{,}0)$ мкг Pb и $(42{,}7 \pm 1{,}0)$ мкг Cd.

The application of zinc white under industrial conditions necessitates to verify its chemical purity. We concentrated our attention on the determination of Cu, Pb, and Cd. As the mass fractions of these components are approximately equal to 1×10^{-3} % Cu, 3.6×10^{-2} % Pb, and 4.4×10^{-3} % Cd and these elements belong among typical electroactive elements, we applied square-wave polarography to their determination. Thus we used methods allowing the determination of all three components in dilute nitric acid without separation or screening.

Experimental

Instruments

The polarographic measurements were performed with a square-wave polarograph OH 104 (Radelkis, Budapest) in two-electrode connection within the range of sensitivity of

$(6—12) \times 10^{-9}$ A/mm. A dropping mercury electrode with the drop time of 3.1 s at the height of mercury column of 80 cm was used for these measurements. The mercury on the bottom in polarographic vessel functioned as a reference electrode. The amplitude of the superimposed voltage was equal to 20 mV.

Working procedure

Zinc oxide (0.4 g, 1 g or 2 g) was dissolved in cool isothermally distilled HNO_3 (10 cm^3). After dissolution, the sample was diluted to 100 cm^3 with water obtained by threefold distillation. The following solutions containing nitric acid in 0.3 mol dm^{-3} concentration were used for polarographic measurements: For determination of Cu, 2 cm^3 of the stock solution (2 g ZnO/100 cm^3) were pipetted and diluted with 2 cm^3 of water. For determination of Pb or Cd, the stock solution (concentration of ZnO was 4×10^{-3} g cm^{-3} or 1×10^{-2} g cm^{-3}) was diluted in the same manner. After preceding removal of oxygen with a stream of nitrogen, the solutions thus prepared were subjected to polarographic analysis in the region of potentials 0 V— − 1.2 V. The determination of concentration was carried out by the method of standard additions using five 50 mm^3 additions (pipette from Eppendorf, GFR) of 10^{-4} mol dm^{-3} or 2×10^{-4} mol dm^{-3} concentration. The standard solutions were obtained by diluting 10^{-2} m[illegible] dm^{-3} solutions of the salts, *i. e.* $Pb(NO_3)_2$, $CuSO_4 \cdot 5H_2O$, and $CdSO_4 \cdot 8H_2O$ dried to constant mass beforehand. The results were processed by linear regression with a calculator TI 59 on the basis of simple programs.

Results and discussion

The electrochemical methods, especially d.c. and a.c. polarography or electrochemical stripping analysis (e.s.a.) are most frequently used for determining Cu(II), Pb(II), and Cd(II) in the presence of one another. These methods are able to utilize electrochemical activity of cations, high solubility of metals in mercury as well as their reversible electrochemical behaviour in most noncomplex-forming electrolytes [1—3]. Owing to mass fractions of the determined components (10—360 ppm), we chose a.c. polarography with superimposed rectangular voltage, *i.e.* square-wave polarography among the above-mentioned methods. This method represents the medium sensitive method from among the three mentioned methods, but its sensitivity is sufficient for our aim. Its use enables us to avoid the drawback due to greater tediousness as well as formation of intermetallic alloys manifesting itself in electrochemical stripping analysis by the fact that the current signal does not change linearly with concentration in numerous mixtures of cations.

We chose the medium of nitric acid ($c(HNO_3) = 0.3$ mol dm^{-3}) from various media and ground electrolytes. In this medium the signals of all three components are reversible and the value of half-width of a peak corresponds approximately to 45 mV. The fundamental component, *i.e.* Zn(II) does not show itself in this

medium. The solutions of HNO_3 do not exhibit any complex-forming properties and the distance between cathodic peaks of the determined cations is sufficient: $E_p(Cu) = -210$ mV, $E_p(Pb) = -650$ mV, and $E_p(Cd) = -820$ mV against Hg on the bottom of the polarographic vessel (Fig. 1).

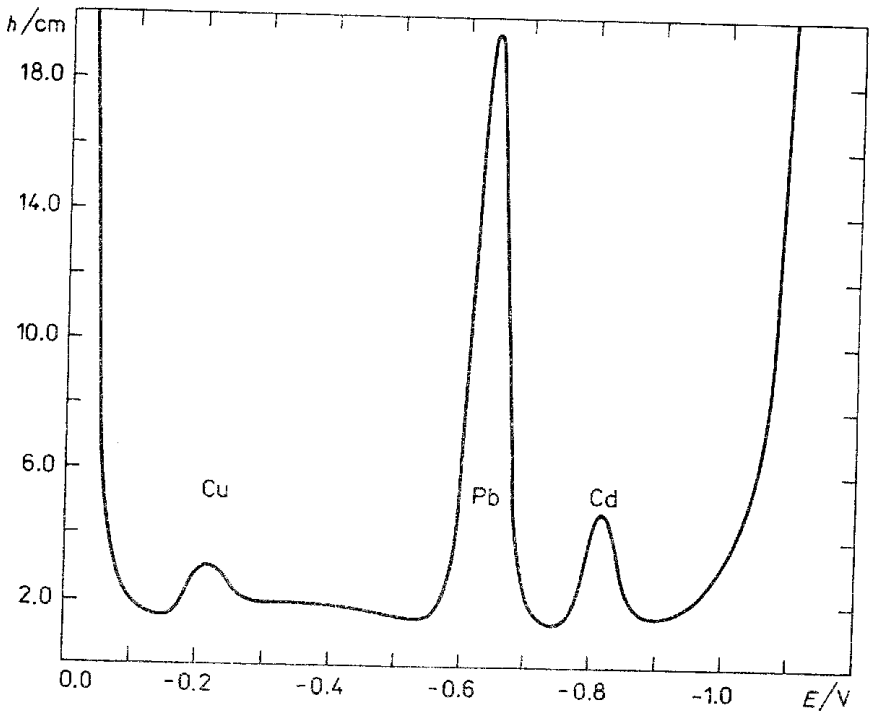

Fig. 1. Square-wave polarographic record of the solution obtained by dissolving 2 g of ZnO in 100 cm^3.

This medium is proper because it has been obtained by dissolution of ZnO and does not contain any contaminating substances owing to high purity of isothermally distilled nitric acid. Other frequently used medium is represented by the acetate or ammonia buffer solution [3]. As for these ground electrolytes, we examined the medium containing the NH_4^+-buffer solution prepared *in situ* by adding isothermally distilled ammonia. The increasing concentration of NH_4OH (increasing pH) brings about that $E_p(Cu)$ very rapidly shifts to more negative potentials as far as the peaks of Cu(II) and Pb(II) conjoin. *Doležal* and *Musil* [3] employed the medium of mineral acids for determining Cu, Pb, and Cd in different materials. *Lysenko* and *Lisitsina* [4] used the medium of HCl and its salts of 1 mol dm^{-3} concentration for polarographic determination of these elements in ores and ascertained that Cu could be determined in the presence of 1000-fold excess of Pb(II) and cadmium in the presence of 1000-fold excess of Cu(II) or Pb(II), while the determination of Pb(II) was feasible only in the presence of 500-fold excess of Cu(II) at most. The determination of Cu (2×10^{-5} mass %), Pb (2×10^{-4} mass %), and Cd (4×10^{-5} mass %) in pure zinc using the medium of

dilute H_2SO_4 is described in publication [5]. The square-wave signals were evaluated on the basis of the method of standard additions. In paper [6], we determined Pb in the presence of Zn and Fe in the medium of H_2SO_4 on the basis of a linear relationship between the square-wave polarographic peak and concentration of standard additions.

Cu, Pb, and Cd in ZnO were determined individually so that only one cation was always determined in the investigated solution and a new portion of solution was taken for the determination of another one. By using the method of five standard additions, the linear regression expressing the relationship between the height of peak and concentration under these conditions gave high values of correlation coefficients (0.9992—0.9997) at the relative standard deviation of 1.0 %—3.2 % (Fig. 2).

Simultaneous determinations gave varying results, which was caused by mutual influencing of individual components. This method also brings about experimental difficulties resulting from different proportions of the determined substances as well as necessity to use different sensitivities and additions of standard solutions of various concentration. The mutual influencing is most conspicuous in the determination of Pb which follows the determination of Cd in the same portion of solution (Table 1). Provided Pb in ZnO was determined as the first element, we obtained

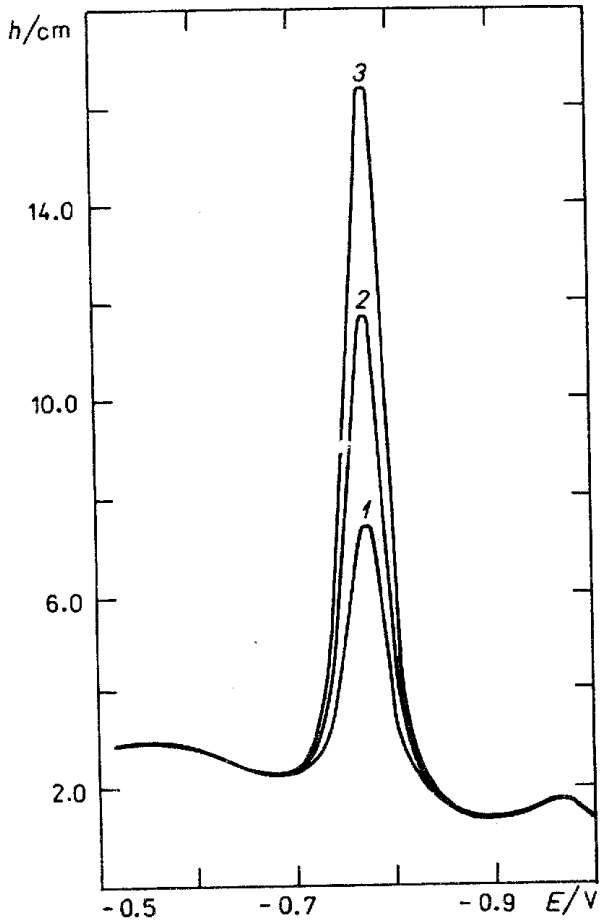

Fig. 2. Square-wave polarographic peak corresponding to the reduction of Pb(II) in the medium of HNO_3 of 0.3 mol dm^{-3} concentration. Composition of solution: 2 cm^3 of solution containing ZnO ($\varrho(ZnO) = 4 \times 10^{-3}$ g cm^{-3}) + 2 cm^3 of water. Amplitude 20 mV, sensitivity 6×10^{-9} A/mm.
1. Peak: Pb(II) in the sample of ZnO; 2., 3. Peaks: after 100 mm^3 additions of Pb(II) solution ($c(Pb(II)) = 2 \times 10^{-4}$ mol dm^{-3}).

Table 1

Results of the determination of Cu, Pb, and Cd in ZnO
Tabulated values are mass fractions in ZnO

w_i/ppm					
Cu	Pb	Pb[a]	Cd	Cd[b]	Cd[c]
9.5	347.0	282.3	42.3	42.7	42.3
10.3	362.6	271.9	44.3	44.0	42.4
9.5	383.3	268.1	45.0	41.0	
11.3	375.5	266.8	41.3	43.0	
11.1	349.6	270.9	43.0		
12.2	383.3		39.3		
11.9	360.0		42.2		
10.3	367.8		42.7		
9.1	344.5		44.0		
11.3	370.4		41.0		
	347.0				
	366.7				
$\{\bar{w}\} = 10.7$	$\{\bar{w}\} = 360.6$	$\{\bar{w}\} = 272$	$\{\bar{w}\} = 42.7$	$\{\bar{w}\} = 42.7$	
$s_r/\% = 3.2$	$s_r/\% = 1.3$	$s_r/\% = 1.0$	$s_r/\% = 1.0$	$s_r/\% = 1.4$	
$\{L_{1,2}\} = 10.7 \pm 0.8$	$\{L_{1,2}\} = 360.6 \pm 10$	$\{L_{1,2}\} = 272 \pm 8$	$\{L_{1,2}\} = 42.7 \pm 1$	$\{L_{1,2}\} = 42.7 \pm 2$	

a) Pb determined after Cd(II) addition; *b*) Cd determined after Cu(II) addition; *c*) Cd determined after Pb(II) addition; s_r — relative standard deviation of arithmetic mean; $L_{1,2}$ — calculated for 95 % probability.

the value 360.6 ppm while the determination of Pb following Cd(II) additions gave a considerably lower result (272 ppm) with almost equal precision (1.0 %—1.25 %). This observation is so much more surprising that the content of interfering Cd(II) is eight-times lower in comparison with the determined Pb(II).

The results listed in Table 1 show that the influence of Pb(II) and Cu(II) on the determination of Cd(II) is negligible. This table contains the results of determination of individual elements in ZnO: (10.7 ± 0.8) ppm Cu, (360.6 ± 10.0) ppm Pb, and (42.7 ± 1.0) ppm Cd, which means that we determined the contaminants in ZnO under the described conditions with better precision than 3.2 %.

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