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Differential potentiometric precipitation titration of zinc(II) and copper(II) using carbon composite electrode

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Abstract. The article presents the results of investigation of potentiometric titration of the working solution containing Zn(II) and Cu(II) by sodium diethyldithiocarbamate (NaDEDC) using carbon composite electrode as the indicator electrode. The proposed method for the separate determination of copper ions (II) and zinc (II) under the joint presence was tested on data from titration model of binary mixtures and the real object. The titration curves were processed by the linearization method based on the transformation of a titration curve into the multiphase linear regression, whose parameters determine the equivalence point with high accuracy.

1. Introduction

Zinc and copper are metals which are widely used in various areas of industry, science and technology. The control of amount of these metals in different objects is performed by physical and physicochemical methods of analysis, many of which demand the expensive equipment, reagents and additional sample preparation step [1–4]. Electrochemical methods of analysis are advantageous because of their polyfunctional performance, high accuracy, low cost and simplicity. The efficiency of an electrochemical method is determined by the use of appropriate detection system (i.e. indicating electrode or sensor). Therefore, development of new electrode systems and their implementation in the routine analysis are prospective areas of analytical chemistry. Usually potentiometric determination of copper and zinc is carried out using metal, ion-selective, carbon and other indicator electrodes [5–9]. A new electrochemical sensor, carbon composite electrode (CCE), was previously shown to use in potentiometric determination of some heavy metals [10]. The sensor demonstrated long lifetime and ease working surface renovation; it can be modified (bulk and surface) with a conducting or insulating phase; also, it has low cost. The CCE may be used in various electrochemical techniques (e.g. coulometry, voltammetry, potentiometry, etc.) due to its polyfunctional properties.

In this work, the CCE has been proposed as a sensor for the potentiometric titration of Zn(II) and Cu(II). The conditions for the separate determination of zinc(II) and copper(II) were studied and have been optimized. The developed technique has been applied for the determination of zinc and copper in simulation solutions and in a jewelry alloy containing copper and zinc.

2. Experimental part



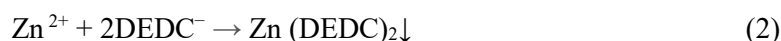
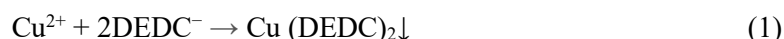
The potentiometric measurements were performed with the pH meter/ionomer Ethan (Russia). The working electrode was CCE. The CCE was made of polyethylene concentrate containing 30% carbon with uniform distribution of particles in the bulk of electrode [11]. The solution of NaDEDC was added to analyt with a pneumatic microburette. The acidity of a solution was measured with pH-meter.

The potentiometric titration of Zn(II) and Cu(II) was performed according to the following procedure. The 0.5 ml portions of a titrant were added to the solutions. The portions were reduced to 0.2 ml near the equivalence point. The electromotive force was recorded after each addition of a titrant portion and solution stirring until a stable potential is reached. All the titration curves were processing by the fragmentary linear approximation method in order to determine the equivalence point. This method was developed by Maryanov. This method helps to determine the equivalence point at any part of the titration curve. The principle of the method is to use the mathematical model to transform a titration curve into a linear regression [12].

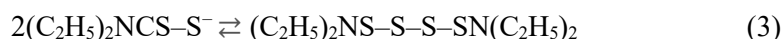
2.1 Titrant for potentiometric titration of Zn (II) and Cu (II)

Dithiocarbamates have gained widespread use in potentiometry among chelating agents for titrimetric determination of metal ions. NaDEDC in particular is widely used in analysis due to its reactivity, simple synthesis and other essential analytical properties.

It can form a low-soluble precipitate with Cu(II) - Zn(II) ions in the ratio 1:2 in a wide pH range according to Eqs. 1 and 2:



The sensitivity of the CCE and silver electrode toward DEDC^- ion may be explained by the redox properties of the titrant. The redox pair of oxidized and reductive forms of dithiocarbamate – thiuram disulfide reagent arises in NaDEDC solution (Eq. 3) and the indicator electrode exhibits its redox behavior.



2.2 The analytical response of Zn (II) and Cu (II) on CCE

The typical potentiometric curves for Zn(II) and Cu(II) with NaDEDC using CCE are shown in Figures 1 and 2. The titration curves were transformed into a linear plot by the linearization method in order to determine the equivalence point. Since there are pronounced jumps on the titration curves, the AB regions were processed for this purpose.

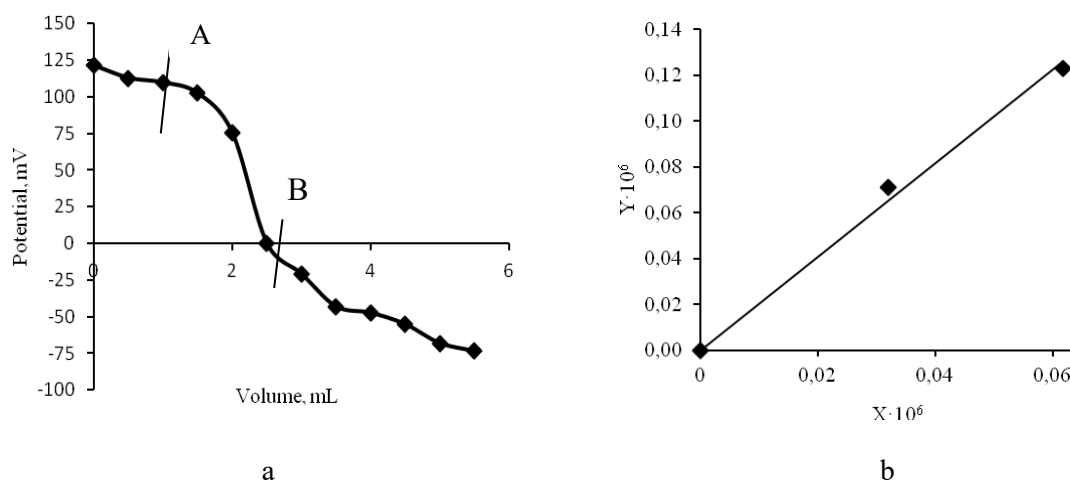


Figure 1. a – Potentiometric titration curve for the simulation solution of $2 \cdot 10^{-3}$ M Zn(II) with $2 \cdot 10^{-2}$ NaDEDC using CCE; the aliquot volume is 25 ml; b – the linear plot for AB fragment of the titration curve.

Figure 1b shows the linear plot for AB region, which is approximated by a straight line with a good correlation coefficient $r = 0.9999$; the slope $V_{eq}(\text{Zn})$ is 2.314 ± 0.043 . This demonstrates good agreement between the titration model and the experimental data. The precipitate solubility K_{sp} value of a precipitate formed has a sufficient impact on the results of potentiometric titration. The experimental solubility product of Zn(DEDCE)_2 was calculated to be 4.034×10^{-15} using a regression intercept term y_0 . Figure 2b shows the linear plot for AB region, which is approximated by a straight line with a good correlation coefficient $r = 0.9999$; the slope $V_{eq}(\text{Cu})$ is 3.322 ± 0.001 . This also demonstrates a good agreement between the titration model and the experimental data. The experimental solubility product of Cu(DEDCE)_2 was calculated to be 1.729×10^{-19} using a regression intercept term y_0 .

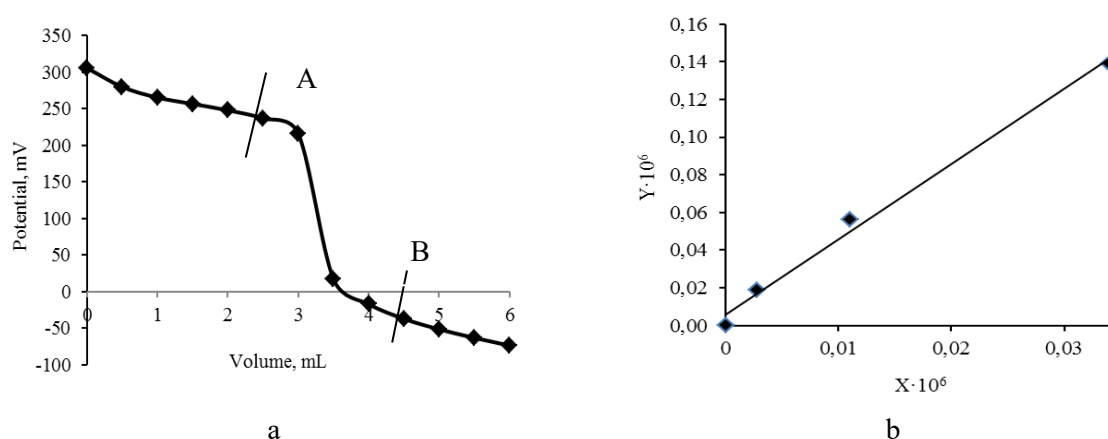


Figure 2. a – Potentiometric titration curve for the simulation solution of $2.314 \cdot 10^{-3}$ M Cu(II) with $2 \cdot 10^{-2}$ NaDEDCE using CCE; the aliquot volume is 25 ml; b – the linear plot for AB fragment of the titration curve.

2.2.1 Effect of supporting Electrolyte

Supporting electrolytes and buffer solutions were used in order to stabilize the ionic strength and to keep pH constant for better reproducibility of analysis results. It is especially necessary to add the supporting electrolyte to very dilute solutions with low conductivity in order to reach a stable electrode potential.

A decrease of the jump in potential is observed for Zn(II), with the pH increase up to 8 in ammonia buffer solution. It is impossible to conduct the potentiometric titration in strong acidic solutions at pH3 because of the decomposition of NaDEDCE in acidic solutions. The curves with the most pronounced jumps in potential were obtained at the pH range from 4 to 6 using H_3BO_3 supporting electrolyte. The solution of H_3BO_3 can stabilize the ionic strength and prevent the Zn(II) surface adsorption. Unlike zinc, copper can be titrated in an alkaline medium using ammonia buffer solution pH8. The curves with the most pronounced jump in potential were obtained at the pH range from 7 to 8 using NH_4OH supporting electrolyte.

Tables 1 and 2 present the results of titration of simulation solutions of zinc and copper with NaDEDCE.

Table 1. The results of titration of simulation solutions of zinc.

	Added (mg)	Found (mg)	Δ (%)	S_r
$1 \cdot 10^{-2}$	8.1	8.0 ± 0.1	1.6	0.007
$2 \cdot 10^{-3}$	1.6	1.57 ± 0.03	3.6	0.007
$2 \cdot 10^{-4}$	0.162	0.181 ± 0.005	11.6	0.011
$2 \cdot 10^{-5}$	0.016	0.010 ± 0.006	15.6	0.005

Table 2. The results of titration of simulation solutions of copper.

	Added (mg)	Found (mg)	Δ (%)	S_r
$2 \cdot 10^{-2}$	18.6	19.1 ± 0.1	2.6	0.0027
$2 \cdot 10^{-3}$	1.86	1.83 ± 0.03	2.0	0.0068
$2 \cdot 10^{-4}$	0.186	0.179 ± 0.002	3.1	0.0044
$2 \cdot 10^{-5}$	0.0186	0.0203 ± 0.0004	9.4	0.0098

An error of Zn(II) and Cu(II) potentiometric determination using CCE is increased with the solution dilution, which may be attributed to the decrease of the jump in potential near the equivalence point.

The stability of some complex ions of a metal with NaDEDC is as follows [13]:

Hg(II) > Pd(II) > Ag(I) > Cu(II) > Ni(II) > Bi(III) > Co(II) > Pb(II) > Cd(II) > Tl(I) > Zn(II) > In(III) > Sb(III) > Fe(III) > Te(IV) > Mn(II).

In potentiometric titration of a mixture of ions, the ion with the lowest precipitate solubility is first being precipitated. The lowest value of $K_{sp} = 1.729 \times 10^{-19}$ corresponds to Cu(EDDC)_2 . The possibility of the separate determination of ions is limited by the value of the precipitate solubility. The strong difference in the value of precipitate solubility of the ions increases the possibility of their separate determination.

2.3 Simulation solutions of Zn (II) and Cu (II)

The titration of the simulating solutions containing zinc(II) and copper(II) with various ratios with NaDEDC has been done. The titration curve (Figure 3a) has a jump in potential corresponding to the simultaneous precipitation of Zn(EDDC)_2 and Cu(EDDC)_2 , so the separate determination of copper and zinc ions is impossible under these conditions.

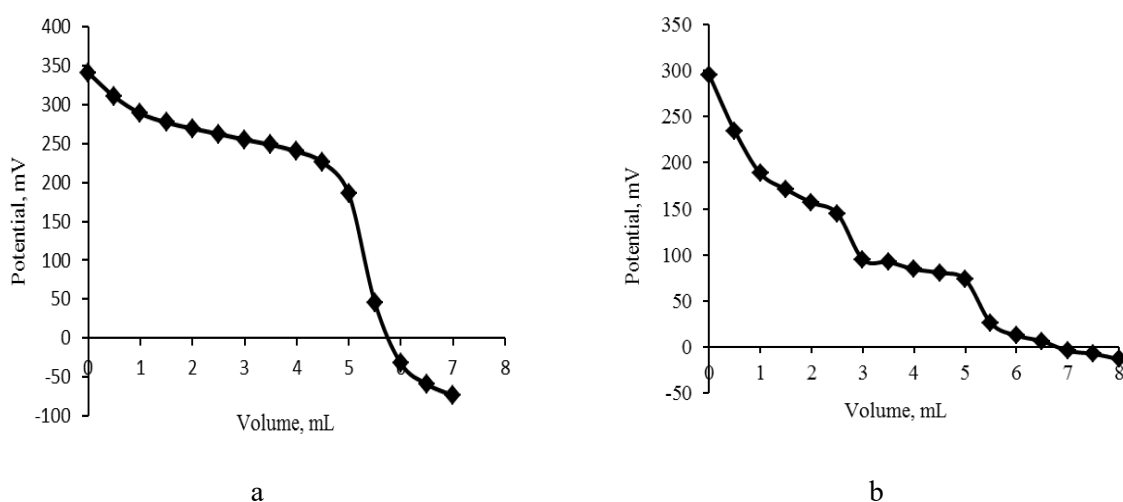


Figure 3. - Potentiometric titration curves of 25 ml solution containing $2 \cdot 10^{-3}$ M of zinc(II) and $2.3 \cdot 10^{-3}$ M copper(II) with 0.02 M NaDEDC using CCE; a - without addition of the supporting electrolyte, b - with an addition of the supporting electrolyte.

It has been shown that the separate determination of copper(II) and zinc(II) ions by potentiometric titration with CCE is possible using EDTA as a background electrolyte. The medium alkaline pH7-8 was maintained with ammonia buffer solution. This helped to avoid ion hydrolysis and significantly affect the solubility constant for the copper and zinc complexes obtained. A sufficient difference in the conditional constants makes it possible to carry out the differential titration. The titration curve (Figure 3b) contains two jumps in potential. The first jump correlates with copper(II) titration whereas the second one correlates with the total precipitation of zinc(II) and copper(II) ions.

Table 3 presents the results of the titration of simulation solutions containing Zn(II) and Cu(II) with various ratios with NaDEDC titrant using CCE.

Table 3. The results of the titration of simulation solutions containing Zn(II) and Cu(II) with various ratios with NaDEDC titrant using CCE ($P = 0.95$, $n = 3$).

	Ratio of the components	Added (mg)	Found (mg)	Δ (%)	S_r
Cu	1	1.86	1.89±0.05	1.86	0.011
Zn	1	1.58	1.5±0.1	4.13	0.026
Cu	2.5	4.64	4.82±0.02	3.86	0.0017
Zn	1	1.58	1.46±0.15	7.96	0.043
Cu	5	1.86	1.78±0.01	3.94	0.0024
Zn	1	0.32	0.347±0.002	9.5	0.0275

Table 3 shows that the increase of the difference in the ratio of the components leads to the increase of error which may reach 10%. A larger error for zinc ion determination compared to the one for copper ions can be explained by a partial co-precipitation of the second component of a mixture onto the first component precipitate. The method of differential determination of copper and zinc ions has been developed and tested in the analysis of a jewelry alloy containing copper and zinc. The results were in a good agreement with those obtained by X-ray fluorescence within random error, and the total content of zinc and copper correlated with the sample weight. Relative standard deviation for the copper and zinc determination was typical for potentiometric titration analysis.

3. Summary

The basic characteristics of a new sensor for potentiometric analysis have been studying. The conditions for Zn(II) and Cu(II) titration in working solutions (composition of supporting solution and pH) have been optimized, and the procedure for Zn(II) and Cu(II) determination by potentiometric precipitation titration has been developed. The conditions of differentiated determination of copper ion (II) and zinc (II) from a single solution by potentiometric titration with computer processing results of fragmentary linearization method were studied. The random errors for the titration of $1 \cdot 10^{-2}$ – $1 \cdot 10^{-4}$ M solutions are the range of 2-10%, S_r is 0.003–0.01. The developed procedure has been successfully tested in the analysis of a jewelry alloy, which has demonstrated that the results meet the expected values within the confidence interval and are confirmed by precipitation titration and X-ray fluorescence.

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