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Determination of mercury (II) by precipitation potentiometric titration

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Abstract. The article presents the results of potentiometric titration of the solution containing Hg (II) with the solution of sodium diethylditheocarbamate (NaDEDC). The efficiency of electrochemical analysis is defined by the presence of the most appropriate indicator system. The possibility of using carbon composite electrode (CCE) as a sensor for mercury ions determination has been explored. The conditions for potentiometric determination of Hg (II) (titrant, indicating electrode, pH, response time, range of concentrations, and background electrolyte) were studied. Titration curves were processed by the linearization method.

1. Introduction

Mercury contamination is one of the most serious environmental issues worldwide. Long-term accumulation of heavy metals in the body may results in neurological degenerative processes. Repeated long-term contact with certain heavy metals or their compounds may even damage nucleic acids, cause mutation, and eventually lead to cancer [1]. Among the various analytical methods [2-5], electrochemical methods have been widely used because of their advantages such as apparatus low cost, sensitivity, and simplicity. The promising area in electrochemistry is development and improvement of electrodes. To address various challenges, metal electrodes, metal-oxide electrodes and ion-selective electrodes are used. Chemical, mechanical, and electrochemical modification of electrode surfaces leads to electrochemical characteristics improving response time reduction, reproducibility and selectivity enhancement, as well as detection limit lowering. However, the development of multifunctional electrodes designed for the analysis of multicomponent systems remains a challenging task. New carbon composite electrodes (CCEs) have many attractive properties that make them a suitable alternative to other electrodes [6, 7]. In this work, CCEs were examined because of their advantages and possible application in various electrochemical techniques. Additionally, the authors have studied the conditions for Hg (II) determination and the effect of interfering ions.

The present work is aimed to develop technique for potentiometric determination of mercury (II) in solutions with the presence of interfering ions with new carbon composite electrode.

2. Experimental part

2.1. Reagents



PFSD 2021

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The solution of Hg (II) was prepared by dissolving accurately weighed metallic mercury in diluted nitric acid with subsequent serial dilution. The titrant for potentiometric analysis was the solution of sodium diethyldithiocarbamate (NaDEDC). The NaDEDC salt was initially purified by recrystallization in ethanol. The concentration of NaDEDC solution was kept constant for two weeks when stored in cool and dark place. Simulating solutions of NaDEDC, Cd (II), Pb (II), Zn (II), and Cu (II) were prepared by dissolving their salts in distilled water with subsequent serial dilution.

2.2. Processing of results

In order to determine the equivalence point, the measurement processing was conducted by titration curves transformation into a linearity by the fragmentary linear approximation method. This method was developed by Boris M. Marianov. This method allows determining the equivalence point and physicochemical parameters at any part of the titration curve with high accuracy by mathematical model [8]. Computational algorithm was implemented by DIFT TITR software in the Pascal programming language.

2.3. Sensor for potentiometric analysis

The efficiency of potentiometric titration method is determined by proper indicating system. In this work, the authors investigated the capability of using CCE for mercury determination. The obtained CCE characteristics (response time, linear range) illustrate the advantages of a new sensor. The curve shape varies slightly with a response time increase whereas curve shifting does not occur.

2.4. Effect of response time

Research on the response time effect has shown that the optimal time for measurement varies from 60 to 90 seconds. The greater time intervals do not provide clearer results and are considered to be irrelevant.

Sodium diethyldithiocarbamate (NaDEDC) was chosen as a titrant for providing potentiometric titration. $C_5H_{10}NS_2$ -Na⁺ is a reagent with high chelating ability because of donor thiol group (–SH) and thione group (>C=S). NaDEDC is capable of forming poorly soluble compounds with a wide range of cations [9].

2.5. Effect of interfering ions

It is known from the literature that NaDEDC forms compounds with varying stability [4]: Hg(II)>Pd(II)>Ag(I)>Cu(II)>Tl(III)>Ni(II)>Bi(III)>Co(II)>Pb(II)>Cd(II)>Tl(I)>Zn(II)>In(III)>Sb(III)>Fe(III)>Te(IV)>Mn(II).

2.6. Titrant for the potentiometric titration of Hg (II)

NaDEDC forms a poorly soluble white precipitate (Hg(DEDC)₂) with Hg (II) ions in the ratio 1:2, and reaction proceeds stepwise. Firstly, the complex in ratio 1:1 is formed followed by the formation of a complex in ratio 1:2. As a result of Hg (II) titration with NaDEDC, two pronounced titration curve slopes are observed in acidic medium.

Figure 1 shows the titration curve of simulating solution containing 1.38×10^{-3} M Hg (II) with 0.07 M NaDEDC using CCE without adding of background electrolyte (pH=2.3).

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Figure 1. Potentiometric titration curve for the simulation solution of 1.38×10^{-3} M Hg (II) with 0.07 M NaDEDC using CCE, pH=2.3; the aliquot volume is 25 ml.

The precipitate formed in the process of titration has a low solubility product constant (Ksp).

2.7. Effect of pH

According to the values of titration curve slopes, with pH increasing, there has been a decrease in slope value and its shift because of hydrolysis. While providing titration in alkaline medium, hydrolysis of ions results in a significant error. The potentiometric titration of strongly acidic solutions also leads to the shift of titration curve and the increase in the determination error because of titrant decomposition. These processes affect the damage of mathematical model underlying the linear approximation method.

2.8. Effect of background electrolytes

Phosphate (pH=3.5), acetate (pH=4.4), ammonium (pH=8.0) and K-Na tartrate buffer systems were used as background electrolytes to stabilize the ionic strength and to keep pH constant for a better reproducibility of potentiometric analysis results. It is necessary to add the background electrolyte to highly diluted solutions, which results in the optimal composition of Hg (II) solution for the potentiometric titration with NaDEDC.

2.9. Range of concentrations

The study on linear range of Hg (II) working concentrations with CCE as a sensor have shown that a large amount of flocculent precipitate with effective surface is settled in the area of high concentrations $(10^{-1}-10^{-2} \text{ M})$. While settling, a part of the precipitate adsorbs on the electrode surface. Cations and anions adsorption onto the precipitate provides the analysis results aberration. The processes described lead to a significant increase in measurement errors in the area of high Hg (II) concentrations.

Concentration, Hg, M	Added mass Hg (II), m (mg)	m±Δm	Relative error, %	Sr
1.4×10 ⁻²	28.08	27.940±0.810	0.5	0.012
1.4×10 ⁻³	2.81	2.790 ± 0.070	0.8	0.010
7.0×10 ⁻⁴	1.75	1.750 ± 0.060	0.4	0.013
1.4×10 ⁻⁴	0.28	$0.270 {\pm} 0.003$	1.8	0.004

Table 1.	The	results	of Hg (l	I) po	tentiom	etric	titration	with	NaDE	DC ı	using	CCE,
				(P = 0.9	5, n=:	5).					

1969 (2021)012030 d01.10.1088/1/42-0390/1989/1/0120
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7.0×10 ⁻⁵	0.14	$0.138 {\pm} 0.008$	1.8	0.022
1.4×10 ⁻⁵	0.04	$0.035{\pm}0.001$	0.6	0.029

The proposed titrant can also interact with other cations forming stable complexes. In case of metal ions complex systems, total determination is possible. With the difference between Ksp values of precipitates increasing, the probability of separate ions determination increases. Different techniques are used for mutual elimination of interfering ions effect: precipitation under different pH, adding masking agents, etc. Based on theoretical calculations, it is possible to predict the effect of each interfering ion [4]. Conditions and possibility of separate determination of certain two-component mixtures (Hg-Pb, Hg-Cu, Hg-Cd, Hg-Zn) were identified by this method.

The conditions for potentiometric titration of simulating solutions, containing Pb (II), Cu (II), Cd (II), and Zn (II) with NaDEDC as a titrant were determined. Simulating solutions of two-component mixtures were prepared in different ratios from 1:1 to 1:10. Figure 2 presents the titration curve for solution containing 0.0014 M Hg (II) and 0.0014 M Pb (II) in ratio 1:1 and a linear plot of curve fragment.

The titration curve has two slopes corresponding to the precipitation of $Hg(DEDC)_2$ and $Pb(DEDC)_2$ respectively, therefore, the separate determination of mercury (II) and lead (II) ions is possible under these conditions.



Figure 2. Potentiometric titration curve for the simulation solution of 0.0014 M Hg (II) and 0.0014 M Pb (II) in ration 1:1 with NaDEDC, using CCE; the aliquot volume is 25 ml.



X·10^(-8)

Figure 3. The linear plots for AB fragment respectively of the titration curve.

Figure 4. The linear plots for CD fragment respectively of the titration curve.

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It was found that separate determination of mercury and other ions is possible in components ratio 1:10. If mercury concentration is more than 5:1, the total determination occurs exclusively. According to Table 2, the results are obtained within confidence intervals. The results demonstrate a good agreement with the values added into solution.

They also demonstrate a good agreement between the titration model and the experimental data. Relative error is lower than 5%, and Sr is 0.004-0.039.

Table 3. The results of Hg(II) and Cu (II) mixture potentiometric titration in different ratios with
NaDEDC, using CCE (P =0.95, n=3)

Ratio of Hg:Cu	Concentration of Hg (II) and Cu (II), M	Added mass of Hg (II) and Cu (II), mg	m±∆m, mg	Relative error, %	Sr
1:1	0.0028	7.02	6.84±0.36	2.60	0.021
	0.0028	2.22	2.13 ± 0.05	4.10	0.009
1:2	0.0014	3.51	3.51 ± 0.06	0.01	0.007
	0.0028	2.22	2.24 ± 0.09	0.60	0.016
2:1	0.0028	7.02	6.99±0.71	0.50	0.004
	0.0014	1.11	1.10 ± 0.06	1.00	0.022
1:5	0.00056	1.40	$1.39{\pm}0.14$	0.85	0.039
	0.0028	2.22	2.21 ± 0.02	0.50	0.004
1:10	0.00056	1.12	1.13 ± 0.06	2.60	0.021
	0.0056	3.56	3.55±0.06	0.37	0.070

3. Results

The conditions for Hg (II) potentiometric titration in simulating solutions have been optimized. Optimal pH range for providing mercury (II) titration with NaDEDC is 3.5–5.0, and phosphate and K-Na tartrate solutions as background electrolytes. The response time of the CCE does not exceed 90 sec. The effect of interfering ions (Pb, Cu, Cd, and Zn) for mercury ions determination was studied. It was shown that on condition of components ratio is 1:10 (Hg:Pb, Cu, Cd, Zn), interfering ions do not contribute significantly to the determination result.

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