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AMPEROMETRIC TITRATION OF MERCURY (II) WITH MPHCMDEDTC – A NITROGEN-AND-SULFUR- CONTAINING REAGENT

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Abstract. The article describes the determination of the dissociation constant of 4-methoxyphenyl- carboxymethyl- diethyl- dithiocarbamate (MPHCMDEDTC) (pKa1 = 2.84). The reagent manifests depolarization properties on a graphite electrode in a wide range of acidity of background solutions. The linear dependence of the wave height on the concentration of the complexing agent is determined in the range from 2.5.10–6 M – 5.0.10–4 M. MPHCMDEDTC forms a soluble complex with mercury (II) with a 1:1 ratio on backgrounds of 0.1 M of CH3COOH, CH3COOK, KNO3 and KCl potassium acetate, nitrate and lithium chloride. A rapid method has been developed for the determi- nation of 0.25–90.0 μg/ml of mercury (II) in wastewater of non-ferrous metallurgy and petrochemical enterprises.

Keywords: 4-methoxyphenyl-carboxymethyl- diethyl- dithiocarbamate, solution, acetic acid, graphite electrode, electrolyte, reagent, concentration, complex, mercury (II), method, amperometric determination.

Introduction. Complexing agents are widely used in analytical chemistry. EDTA, also known as Trilon B (sodium ethylenediaminetet- raacetate) is widely used as a titrant (including use in ampero- metric titration method) [1]. The use of EDTA as a titrant for the amperometric determination of mercury (II) is described in [2]. However, the lower limit of the determined contents in this case is very high – 4 μg/ml, also Cu(II), Ti(IV), Pb(II), Fe(III), Mo(VI) interfere with the determination of mercury. In recent years, analytical chemists have been interested in complexing agents containing heteroatoms, including nitrogen and sulfur. Data on the use of nitrogen-and-sulfur-con- taining complexing agents in amperometric titration method are limited. Data are given for determining the composition of the complexes of a number of metals 1-morflino-4-meth- ylhexin-2-ol-4 and ethylene glycol-bis (ethylthioacetic acid) [3; 4]. The use of dithiodiacetic acid for the amperometric determination of a number of metals, including mercury (II), by the current recovery of the reagent at the dropping mer- cury electrode [5] has also been described [5]. We found that the selectivity of the determination of mercury using the nitrogen-sulfur-containing complexing agent MPHMDEDT(4-methoxyphenylcarboxymethyldiethyldithiocarbamate) is higher than during the titration of EDTA. Therefore, the use of nitrogen-and-sulfur-containing compounds in the method of amperometric titration is of undoubted interest.

This paper is devoted to the study of the possibility of amperometric titration of mercury (II) with two indicator electrodes with solution of 4-methoxyphenylcarboxymethyl diethyldithiocarbamate (MPHCMDEDTC) in a wide range of aprotic bipolar solvents used in electrochemical studies, such as dimethyl sulfoxide (DMSO) and dimethylformamide (DMF), which show weak basic properties.

We tried to find the optimal conditions for the ampero- metric titration of mercury (II) with MPHCMDEDTC solu- tions in non-aqueous protolytic media on different acid-base properties of background electrolytes. The literature has no data on the amperometric titration of mercury (II) and ions of various metals with MPHCMDEDTC solutions, since it was synthesized relatively recently [6] and, apart from biological activity, their other properties have not yet been studied [7].

Materials and methods The reference 0.002 M mercury (II) nitrate solution was prepared by dissolving a sample of Hg(NO). HO (CP) in polarographs with recorders: ЛКД4–003 (LKD4–003) and ПДП4–002 (PDP4–002), using a three-electrode cell, design of which is described in [9] and amperometric titration with two indicator rotating platinum electrodes was performed on the previously described equipment. The titrant was dosed with a piston microburette to the accuracy of 0.0005 ml the final volume of the solution prepared for the titration was 10.0 ml.

Results and discussion. Electrochemical oxidation of MPHCMDEDTC has been studied in a wide acidity range of background solutions. Against the background of 0.1 M CH3COOH and ammonium-acetate backgrounds of pH 3.35–5.50 MPHCMDEDTC gives one clear oxidation wave with a current limiting area in the potential range of 1.25–1.45 V that decreases with the increase of pH background electrolytes and disappears at pH $\geq$ 7.0. At the 0.01 M H2SO4 background no oxidation wave of MPHCMDEDTC was detected, however, oxidation takes place (anodic shift). At the limiting current potential on all backgrounds, the dependence of the current on the reagent concentration is linear. It is established that the limiting current is directly proportional to the concentration of the depo-DMSO or DMF and standardized by aqueous solution. Solutions of lower concentrations were obtained by diluting the reference solution immediately before their use. MPHC- MDEDTC (5.10–2 M) solutions were prepared by accurately weighing the reagent. Mercury (II) solutions were prepared by dissolving a portion of CP mercury nitrate in distilled water, standardization was carried out on sodium chloride [8]. Working solutions of lower concentration were prepared by sequential dilution of the initial solution. On the curve of potentiometric titration MPHCMD- EDTC a potential jump is observed after addition of two moles of alkali. The acid dissociation constants pKa1 and pKa2 were calculated equal to 2.84 and 4.75, respectively. 0.1 M solutions of CH3COOH, CH3COOK, KNO3 and KCl were used as backgrounds solutions. Volt-ampere curves of MPHCMDEDTC in the anodic polarization region of the platinum microdisk electrode were recorded using the ППТ-1 (PPT-1) and ПУ-1 (PU-1) larizer in the range of 2.5.10–4 – 5.0.10–4M.

The complexation reaction of mercury (II) with MPHC- MDEDTC, was studied using the method of amperometric titration on different acidity backgrounds at E = 1.25–1.45 V by the current of reagent oxidation. At pH > 6.5 fuzzy titration curves were obtained, the end point of the titration is difficult to determine, since under these conditions the height of the ti- trant oxidation wave decreased. Distinct titration curves with a pronounced kink were obtained on the backgrounds of 0.1 M CH3COOH, CH3COOK, KNO3, KCl as well as using ammonium acetate mixtures with pH 3.35–5.50.

Data on the titration of reference mercury (II) solution with a reagent lead to a conclusion, that complex of molar ratio of mercury (II) and MPHCMDEDTC is formed at a ratio of 1:1 on titration backgrounds. The results of the titration of mercury (II) with the solution MPHCMDEDTC presented in table 1. The data show that the lower limit of the determined content of mercury (II) is 0.25 µg/ml.

Table 1.– The results of the determination of various amounts of mercury (II) with a solution of MPHCMDEDTC in acetic acid

Introduced Hg (II), µg	**Found metal, µg (P = 0.95; $x \pm DX$)**	**n**	**S**	**Sr**
25.48	25.43±	3	0.21	0.008
50.96	51.23±	3	0.11	0.002
101.9	101.4±	4	0.34	0.003
231.4	234.0±	4	0.26	0.001
462.7	462.8±	3	0.36	0.001

The possibility of selective determination of mercury (II) in the presence of a number of related elements has been studied. The results are presented in (table 2). It has been established that any amounts of Cd, Zn, Co, Ni, Al, Cu, Pb, Ca, Mg do not interfere with the amperometric determination of mercury (II).

Table 2.– The results of amperometric titration of mercury (II) with a solution of MPHCMDEDTC in acetic acid on the background of 0.25 M of potassium acetate in model mixtures

Analyzed mixture composition, µg	**Found Hg, µg (P=0.95; $x \pm DX$)**	**n**	**S**	**Sr**

Hg(25.07)+Cd(4.85)	25.42±	5	0.32	0.013
Hg(25.07)+Mg(20.55)	24.65±	4	0.28	0.011
Hg(50.14)+Cd(35.62)+Zn(10.58)	50.51±	4	0.45	0.009
Hg(50.14)+Mg(6.45)+Ni(28.50)	49.85±	5	0.53	0.011
Hg(75.21)+Cd(10.45)+Ca(15.63)+Al(144.57)	75.96±	5	0.45	0.006
Hg(75.21)+Zn(150.40)+Al(16.55)+Pb(2.75)	74.71±	5	0.67	0.009

At high chromium (III) concentration, the results of mercury (II) determination were lowered, which may be due to the formation of a complex of chromium (III) with MPHCMDEDTC and a change in the slope of the titration curve after the equivalence point [3]. Silver (I) content of up to a 50-fold excess does not affect the results of the mercury determination. The determination of mercury (II) in the presence of manganese (II) is difficult because of the high and unstable initial current, which is the result of the oxidation of manganese (II) at a given potential. The pos- sibility of amperometric determination of mercury (II) in the presence of a 10-fold excess of vanadium (V) and iron has been established.

Methods of analysis: 0.2 g of mesityl oxide is added to an aliquot of the analyzed solution containing 5–75 µg of mercury (II), then the pH is adjusted to 4.5–5.0 with caustic potassium and hydrochloric acid, the solution is diluted to 50 ml and extracted mercury (II) for 1 min with 10 ml of mesityl oxide. After separation of the phases, the extract is destroyed by heating with chromic anhydride or hydrogen peroxide, then collected in a 25 ml flask, and brought to the mark, an aliquot of the analyzed solution is taken (2–5 ml), create optimal con- ditions for conducting amperometric titration (2.0 ml 0, 25 M potassium acetate and the required amount of acetic acid) and titrate the mercury (II) with a solution MPHCMDEDTC.

The results of the titration of mercury (II) with a solution of MPHCMDEDTC in the extracts are given in (Table 3). As can be seen from the data in the tables, the developed methods for amperometric titration of mercury (II) with MPHCMD- EDTC solution in various artificial mixtures of salts after its extraction separation are distinguished by relatively high accuracy and very good selectivity.

Table 3.– The results of the amperometric titration of mercury (II) with the MPHCMDEDTC solution directly in the extracts (extraction reagent – mesityl oxide; backgrounds – potassium acetate, nitrate and lithium chloride, (ΔE = 0.75 B)

Analyzed mixture composition,%	**Found Hg, µg (II),% (P=0.95;** x = DX **)**	**n**	**S**	**Sr**
Hg(3.154)+Bi(5.60)+Sn(91.24)	3.162 ± 0.079	4	0.05	0.016

Hg(1.072)+Au(0.56)+Cd(98.36)	1.077 ± 0.063	4	0.04	0.037
Hg(5.275)+Ir(14.62)+Cu(80.10)	5.259 ± 0.025	5	0.02	0.004
Hg(0.294)+Bi(11.40)+Ir(0.36)+Zn(87.94)	0.304 ± 0.016	4	0.01	0.033
Hg(0.435)+Ni(56.31)+Sn(28.65)+Mg(14.60)	0.421 ± 0.032	4	0.02	0.047
Hg(1.150)+Cd(65.12)+Pt(0.53)+Bi(33.20)	1.140 ± 0.048	4	0.03	0.026
Hg(0.684)+Co(45.18)+Os(0.47)+Cd(48.34)	0.675 ± 0.025	5	0.02	0.030
Hg(1.027)+Zn(12.43)+Pb(50.66)+Ni(34.44)	1.017 ± 0.018	4	0.03	0.029
Hg(0.342)+Mn(31.12)+Cd(0.88)+Sn(0.65)	0.335 ± 0.025	5	0.02	0.060

As shown by the data in the tables, amperometric titration of the studied metals with a solution of MPHCMDEDTC results in fairly accurate and reproducible results. In all cases, the found contents correspond to the introduced quantities and do not exceed the limits of the confidence intervals, and the relative standard deviation does not exceed 0.06.

Conclusion. The results of the titration of mercury (II) with a solution of MPHCMDEDTC in the extracts are given in. As can be seen from the data in the tables, the developed methods for amperometric titration of mercury (II) with MPHCMD- EDTC solution in various artificial mixtures of salts after its extraction separation are distinguished by relatively high accuracy and very good selectivity. As shown by the data in the tables, amperometric titration of the studied metals with a solution of MPHCMDEDTC results in fairly accurate and reproducible results.

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