AMPEROMETRIC TITRATION OF NOBLE METALS WITH SOLUTIONS OF NITROGEN-SULPHUR-CONTAINING REAGENTS IN NON-AQUEOUS AND MIXED MEDIA

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Abstract: The article shows the conditions and the possibility of amperometric titration of noble metals with 4 – methoxyphenylcarboxymethyl-diethyldithiocarbamate (MPhCMDETK) and 4 – methoxyphenylcarboxymethyl - diethyldithiocarbazone solutions (MPhCMDFDTK) in non-aqueous media (acetic acid, n-propanol, DMFA, DMSO) and their mixtures with background electrolytes having different acid-base properties. The methods of amperometric titration of micrograms of the quantities of noble metals ions in the presence of foreign ions containing ions

Key words: palladium, platinum, silver, gold, IFCMDETK, IFCMDFTK, solution, acetic acid, n-propanol, DMFA, DMSO, background electrolytes.

Аннотация: В статье показаны условия и возможность амперометрического титрования благородных металлов растворами 4-метоксифенилкарбоксиметилдиэтилдитиокарбамата (MPhCMDETK) и 4-метоксифенилкарбоксиметилдиэтилдитиокарбазона (MPhCMDFDTK) в неводных средах (уксусная кислота, н-пропанол, ДМФА, ДМСО) и их смесях с фоновыми электролитами, обладающими различными кислотно-основными свойствами. Разработаны методы амперометрического титрования микрограммовых количеств ионов благородных металлов в присутствии посторонних ионов, содержащих ионы.

Ключевые слова: палладий, платина, серебро, золото, IFCMDETK, IFCMDFTK, раствор, уксусная кислота, н-пропанол, ДМФА, ДМСО, фоновые электролиты.

Annotatsiya: Maqolada 4-metoksifenilkarboksimetil dietilditiokarbamat (MPhCMDETK) va 4-metoksifenilkarboksimetil dietilditiokarbazon (MPhCMDFDTK) eritmalari bilan asal metallarni amperometrik titrlash shartlari va maqsadga muvofiqligi ko'rsatilgan. DMSO) va ularning turli kislota-asos xususiyatlariga ega fon elektrolitlari bilan aralashmalari. Ionlarni o'z ichiga olgan begona ionlar ishtirokida asil metal ionlarining mikrogram miqdorini amperometrik titrlash usullari ishlab chiqilgan.

Kalit so‘zlar: palladiy, platina, kumush, oltin, IFCMDETK, IFCMDFTK, eritma, sirka kislotasi, n-propanol, DMF, DMSO, fon elektrolitlari.

Introduction.

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Amperometric titration of metal ions in non-aqueous and mixed media with various complexants makes it possible to expand their analytical capabilities and simplify the solution of many complex analytical problems [1, 2]. First, this is due to the fact that the nature of the solvent strongly affects the strength of the resulting complex, and it is not the same for different cations, which determines the selectivity and rapidity of the method. [Complex compounds in analytical chemistry complex compounds in analytical chemistry [3,4]. In addition, non-aqueous complexometry methods make it possible to successfully solve the problem of accurate and selective determination of metals in objects of organic origin, as well as directly in extracts obtained by their concentration. All this determines the urgency of the problem of searching for new complexing titrants that allow amperometric titration to be carried out [5–7].

The aim of this study is to optimize the conditions for the amperometric titration of a number of precious metal ions, in particular, silver, gold, platinum, and palladium, using newly synthesized complexing titrants - solutions of 4-methoxyphenylcarboxymethyl-diethyldithiocarbamate (MPKMDETK) and 4-methoxyphenylcarboxymethyldiethyldithiocarbamate (MPKMDFTK) in non-aqueous and mixed media (acetic acid, n-propanol, DMF, DMSO) and their mixtures with background electrolytes with different acid-base properties. The formulation of such a problem is also due to the fact that these titrants were synthesized only recently and information about their use in the analysis of noble and precious metals has not been adequately reflected in the scientific literature [8, 9].

Methods. The initial 0.002 M solutions of Na_2PdCl_4, K_2PtCl_6, $AuCl_3$, and $AgNO_3$, as well as 0.01 M solutions of MFCMDETC and MFCMDFTC, were prepared by dissolving the corresponding weighed portions of these reagents in acetic acid (n-propanol, DMF, and DMSO). Amperometric titration was carried out on a setup with two platinum wire electrodes rotating (1000 rpm) on a common axis. The equipment used, the design of the electrochemical cell equipped with an automatic piston microburette and rotating disk electrodes are described in detail in [10].

Results and its discussion. Earlier, using voltammetric research methods, we studied the electrochemical behavior of MFCMDETK, MFCMDFTK and other participants in electrochemical processes on platinum electrodes and showed that amperometric titration of noble metal ions should be carried out at an electrode polarization voltage of 0.75-1.15 V, depending on the nature and concentration of the background electrolyte (acetates, nitrates, chlorides, perchlorates of alkali metals and ammonium) [11]. In this case, the indicator current arises beyond the

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equivalence point (ie) due to the oxidation of the free reagent and the reduction of dissolved oxygen in the air.

The experimental data showed that in the studied media and background electrolytes with concentrations of 0.15-0.40 M, the titration of noble metal ions with solutions of MFCMDETK and MFCMDFTK proceeds quite smoothly and quickly, and the shape of the curve coincides with the expected one: a certain constancy of the current at the beginning of titration followed by a sharp jump (kink) at the end point of the titration (CTT).

Determination of noble metal ions in individual solutions. It has been established that during the titration of ions of palladium (II) and platinum IV), the molar ratio of Me:reagent is: Pd:reagent 1:2 and Pt:reagent 1:4. The titratable solution acquires a reddish-brown color. When passing from acetate to perchlorate backgrounds, the shape of the titration curve for noble metal ions deteriorates significantly, which ultimately leads to a decrease in the reproducibility and correctness of the results. This is explained by an increase in the acidity of the analyzed medium upon passing from acetates to perchlorates [11]. Some of the obtained experimental data are shown in Table 1.

The results of determining various concentrations of noble metal ions with a solution of MFCMDETK in 10.0 ml of the test solution under optimal conditions indicate a good accuracy of the developed technique. The influence on the correctness and reproducibility of the titration of noble metal ions of additives to acetic acid, n-propanol, DMF, DMSO, and some reagents most commonly used as extractants, such as chloroform, carbon tetrachloride, benzene, toluene, hexane, methyl ethyl ketone, dioxane and etc. The conditions are the same as for the titration of noble metal ions in their individual solutions, with the only difference that the content of the protolytic solvent in the analyzed sample was regulated in strict accordance with the volume of the added extractant.

Table-1.

Results of amperometric titration of various amounts of palladium (II) and platinum (IV) ions with a solution of MFCMDETC in DMSO against the background of 0.20 M lithium perchlorate

Entered Me, mcg	Found Me, mcg (P=0,95; x±ΔX	n	S	S_r
Pd 15,44	15,42±0,16	3	0,06	0,004
Pt 30,88	30,91±0,12	4	0,05	0,002
Pd 61,75	61,79±0,18	3	0,03	0,001

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Pt 123,50	123,61±0,20	4	0,10	0,001
Pd 247,00	246.91±0,41	4	0,21	0,001
Pt 493,10	493,80±0,52	3	0,62	0,001
Pd 740,71	739,45±1,43	4	0,91	0,001
Pt 998,10	987,91±1,54	4	0,63	0,001

Due to the decrease in the solubility of the background electrolyte under these conditions to values less than 0.2 M under the influence of large additions of an inert solvent, the background concentration (from 40-50 vol.% of an inert solvent) must be continuously reduced down to values of the order of 0.05 M. The addition of any of the above solvents in an amount of 10-20 vol.% (depending on the nature of the solvent) have practically no effect on the shape of the titration curve, the graph of which, however, becomes less steep with respect to the volume axis (V). For the same reason, at solvent contents above 50-60 vol.%, the reproducibility and accuracy of the determinations of noble metal ions deteriorate.

The revealed nature of the influence of inert solvents on the shape of the titration curve is explained by a sharp decrease in the electrical conductivity of the titrated solution at a high content of the inert solvent in the protolytic medium.

Determination of silver (I) and gold (III) ions in model mixtures. The possibility of amperometric titration of silver (I) and gold (III) with a solution of MFCMDFTK was tested on various artificial mixtures of salts (simulating natural and industrial materials) containing large amounts of other metals, often and widely accompanying these metals in nature.

Determination of silver (I) and gold (III) ions can be carried out in two ways [12, 13].

1) directly in an aliquot of the analyzed sample with strict observance of all optimization conditions when assessing the degree of influence of various foreign cations, which also form strong complexes with the reagent under study [14],

2) a combination of preliminary extraction separation of silver (I) and gold (III) ions from other elements with their subsequent titration with a standard solution of MFCMDFTK in an aliquot of the obtained extract after the destruction of the extraction reagent and complex in it, as well as adding the necessary amounts of protolytic solvent and background [15].

The results of amperometric titration of silver (I) and gold (III) ions in model mixtures using a 0.01 M solution of MFCMDFTK as a titrant are shown in Table 2.

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Table-2

Results of amperometric titration of various amounts of silver (I) and gold (III) ions with MPKMDFTK solution

Composition of the mixture, %	Found Me, mcg (P=0,95; x±ΔX	n	S	S_r
Au (0,684)+Os(0,329)+Cd(39,42)+ Ni(48,18)+Co(10,06) +Ru(1,327)	Au, 0,684±0,224	3	0,09	0,133
Ag (0,342)+Ru(0,664)+Ir(0,954)+ Cu(59,81)+Mn(28,37)+Ti(9,86)	Ag, 0,341±0,075	4	0,03	0,089
Au(1,027)+Ru(0,534)+Ir(0,419)+ Cu(32,05)+ Mn(12,58)+Zn(53,39)	Au, 1,026±0,111	3	0,07	0,066
Ag(0,664)+Os(03,31)+Cd(39,40)+ Ni(48,20)+Co(10,03) +Ru(1,33)	Ag, 0,663±0,223	4	0,09	0,129

The results of amperometric titration of silver (I) and gold (III) ions with a solution of MFCMDFTK shown in Table 2 show high selectivity and reproducibility of the analysis with a relative standard deviation not exceeding 0.133.

Conclusions.

1. The possibility of using the new synthesized nitrogen-sulfur- containing reagents 4-methoxyphenylcarboxymethyl- diethyldithiocarbamate (MPKMDETK) and 4-methoxyphenylcarboxymethyldiethyldithiocarbamate (MPKMDFTK) as titrants in amperometric titration was studied.
2. The conditions for the implementation of amperometric titration of noble metals: platinum, palladium, silver and gold.
3. It has been experimentally established that the amperometric titration of silver (I) and gold (III) ions with a solution of MFCMDFTK shows high selectivity and reproducibility of the analysis with a relative standard deviation not exceeding 0.133.
4. The results obtained make it possible to apply the developed methods for the determination of precious metals by the method of amperometric titration in the practice of factory and research laboratories.

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