

HYBRID EXTRACTION-AMPEROMETRIC DETERMINATION OF W(VI) AND Sb(III)

Yakhshieva Zukhra¹, Bakakhonov Anvar², Kalonov Rustam³

¹Doctor of Chemical Sciences, Professor, Jizzakh State Pedagogical Institute. 130100. Avenue Sh. Rashidova JSPI. Uzbekistan

²Doctoral Candidate, Jizzakh State Pedagogical Institute. 130100. Avenue Sh. Rashidova JSPI. Uzbekistan

³Teacher, Jizzakh State Pedagogical Institute. 130100. Avenue Sh. Rashidova JSPI. Uzbekistan

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ABSTRACT: Methods of hybrid extraction amperometric determination W(VI) and Sb(III) by solutions of tioacetamide and thionalide in water, mixed and non-water mediums have been elaborated. These methods were used at carrying out of analysis of binary, triple and more complex model mixtures imitated some industrial materials and natural objects.

KEYWORDS: amperometrical, titration, thionalid, tioacetamid.

I. INTRODUCTION

Actuality of problem. In practical relation electroanalytical chemistry has promoted to solution of such problem as extraction-amperometric titration of ions of different metals directly in extracts excluding reextraction; increasing a sensibility, selectivity and also expression of carrying out of determinations.

Titration in water, mixed and non-water mediums in principle must be an fundament or ground for metals determination in extracts obtained at extraction division or concentration elements and also in organic materials which badly solute in water.

The intensive development and widespread use of amperometric titration methods is due to high accuracy indicators, sensitivity, selectivity and expressness, which allow to successfully and quickly solve the tasks of analytical control (monitoring) of technological processes, environmental objects, biological products, clinical materials, sanitary facilities and numerous industrial facilities. The growing industry needs for tungsten and antimony, which are distinguished by their hardness, heaviness and refractoriness, make the problem of analyzing environmental objects with a micro-content of these metals topical.

This, with all the obviousness, implies the relevance of the presented article devoted to the development of scientific and methodological foundations for the targeted determination of microconcentrations of tungsten and antimony ions in environmental objects and food products in the field.

II. EXPERIMENTAL PART

Voltammograms were shot on polarimeters PPT-1 and PU-1 with self-records: LCD 4-003 and PDP 4-002, with a three-electrode cell. To optimize the titration conditions of W (VI), the pH of the medium was determined using a universal EV-74 ionomer and a pH / mV / TEMP Meter P 25 EcoMet pH meter. The initial solution (1 mg / ml) of W (VI) and Sb (III) was prepared by dissolving weighed portions of 2 g of their "chemically pure" salts. A sample of the sample (1.0-5.0 g) was weighed on an analytical balance, after which it was placed in a special heat-resistant glass, 4.0-5.0 ml conc. HCl and the same 5% solution of H₂O₂ were heated at a temperature no higher than 80–90 ° C for 5–10 min. The resulting solutions were diluted with bidistilled water in a volumetric flask (250 ml).

New variant of amperometrical titration of ions of different metals after extraction separation of them as diethylditiocarbaminates or ditizonates has been elaborated. This method consists from following stages: to aliquate part of extract an anhydrous acetic acid (also propanol), little quantity of non-water solution of suitable strong oxidizer (Cr₂O₃, KMnO₄, H₂O₂ or O₃) was added and then the mixture was heated for full destruction of complex and extraction reagent. After cooling analysed solution phone electrolyte (CH₃COOK or LiClO₄) was added and after this titration by Ethylenediaminetetraacetic acid (or by other similar titrant) solution was carried out.

The base stage of analysis is destruction of extracted complex and surplus of reagent by strong oxidizer satisfied to following demands: at first it must fast and fully to destruct of the extracted complex and secondly neither itself nor its products of reduction must not interact with titrant tioacetamid, thionalide and titrating ions and also don't participate in electrode processes. It was determined that the best oxidizers corresponded to above mentioned demands are solutions of Cr₂O₃, KMnO₄, H₂O₂ in protolytical solvents with

concentration neither more 0,001M because at this demands titrants practically don't undergo to oxidation and also amperometrical titration of ions of different metals has carried out smoothly as well in absence of oxidizers. But it is necessary to avoid more high concentrations of oxidizers because at these the curves of titration are less clear and results of titration are overstated.

Method of carrying out of analysis: aliquates of analyzed solution containing about 200 mkg of Pb(II) were placed in fannel, acidified by 0,2 M solution of HCl, than 5 ml of 0,1 M solution of Ethylenediaminetetraacetic acid and 2 ml of 1,0 % water solution of sodium salt of dimethylglyoxime were added and obtained mixtures were mixed and after 10 min Pd(II) was extracted by two portion (5,0 ml) of chloroform during 1 minute. United extracts were transferred in glass for titration than 5 ml acetic acid was added and obtained mixture was heated to beginning of boiling was destructed by addition of 30-40 drops of saturated solution of KMnO4 in acetic acid. Then 5 ml of 2,0 M solution of LiCl in acetic acid was added and heating was carried out during several minutes for fully reduction of metals. Results of W(VI) determination are presented in table and they have witnessed about rightness and reproduction of the proposed methods.

Titration of the W(VI) and Sb(III) after it's extraction separation was carried out by solution of thionalide. Thus new extraction-amperometrical method of Pd(II) determination in mixture with noble metals based on the extraction of W(VI) and Sb(III) in chloroform at pH=8-9 by mezithelen oxide, destruction of extracting reagent and complex of W(VI) and Sb(III) by strong oxidizer (Cr₂O₃, O₃, H₂O₂) with following titration by thionalide, was elaborated.

Method of carrying out of analysis: to aliquate of analyzed solution containing 5-75 mg Pb(II) mezithelen oxide (0,2 g) was added then with help of KOH or HCl the pH was established in range 4,5-5,0. Then mixture was deluted to volume 50 ml and was extracted during 1,0 min by 10 ml of phases extract was destructed at heating by chromic or hydrogen peroxide after which collected in flash(25 ml). Aliquate of obtained solution was placed and optimal condition, were carried out for amperometrical titration of Pd(II) (2,0 ml 0,5 M CH₃COOH and necessary quantity of DMCO or n-propanol) and then Pd(II) was titrated by thionalide.

Table Results of extraction amperometrical determination of Sb(III) and W(VI) by solutions thioacetamide and thionalide in artificial mixtures

Nature and quantity of metals, %	Reagent	Founded of Me (P=0,95; x ± ΔX)	n	S _r
Sb(0,102) + Ni(4,88) + Sn(10,09) + Os(0,03)	TAA	0,101 ± 0,019	4	0,118
Sb(0,102) + As(10,73) + Al(1,51) + Ni(0,06)		0,104 ± 0,022	5	0,170
W(0,353) + Ag(0,907) + Ni(21,54) + Bi(47,63)	TA	0,350 ± 0,211	3	0,249
W(0,306) + Ni(0,813) + Bi(0,129) + Sn(0,071)		0,301 ± 0,101	5	0,269

As shown from data of table the elaborated methods of amperometrical titration of W(VI) and Sb(III) by solutions of thioacetamide and thionalide in different artificial mixtures of salts after extraction separation are characterized by high selectivity.

Taking account importance of task and also fact that thionalid and thioacetamid can oxidized on anod in n-propanol that is amperometrical titration by these reagents can be carried by arising anodic current it was necessary to determine a possibility their using for titrametrical determination ions metals W(VI) and Sb(III) in propanol and it's mixtures with inert solvents in which reactions of formation thionalid complexes of these metals are carried on marked rapidly than in water mediums.

Influence of outer tension. For determination of influence of value of giving on electrodes tension on the conditions of titration, form of curves and results of amperometrical titration of metals ions by solutions by thionalid and thioacetamid corresponding determinations were carried out on the phones: 0,20 M perchlorate of litium and 0,25 M acetate of potassim.

Experiments have shown that titration of W(VI) and Sb(III) can be carried out at values of tension in interval 0,53 – 1,00 V. It is necessary to note at tensions smaller than 0,30 V it was noted increasing of dropping of steepness of right branch of curve of titration wat has carried out to worsening of reproduction and rightness of obtained results of titration.

Optimal tension of titration of ions W(VI) by solution of thionalid with two platinum indicator electrodes is interval of potent ions 0,55-0,80V.

Influence of nature and concentration of phone electrolyte. Hight soluble in n-propanol and having acid-base properties salts: perchlorate, chloride and nitrate of litium and also acetates of potassium and ammonium were used as phones electrolytes. These phone electrolytes are enumerated in order of decreasing their acid properties.

Experiments have shown that results of titrations of ions of W(VI) and Sb(III) by solutions of thionalid and thioacetamid were best of all at using as carried phone perchlorate and nitrate of litium. On the phone of acetates

of potassium and ammonium possessing by sharp basic properties results were in some degree understated owing to solvolysis of W(VI) and Sb(III) also owing to acceleration of oxidizing of titrant by oxygen in base medium. The best by form curve of titration branches of which have a large steepness and the most extensive rectilinear parts was obtained at using lithium perchlorate. By the quality to it curve obtained on the phone of lithium nitrate right branch of which was less steepness is yielded. Besides the rate establishment of equilibrium after each addition of titrant on the nitrate phone is markedly lower. On the lithium chloride curve was formed with almost horizontal right branch and process of titration has slow down. These factors can be explain by fact that under influence of high concentration of chloride-ions a strength complexes with W(VI) and Sb(III) have been formed waves of reduction of which are displaced in range of more negative potentials. Thus it is possible to conclude that lithium perchlorate is the best phone electrolytes at titration of W(II) and Sb(III) by thionalid.

Influence of water additions. Investigation has been carried out on the example of titration of W(II) and Sb(III) by solutions of thionalid and thioacetamid. Titration in the presence of variable quantities of water has been carried out at the same conditions that titration of individual ions in propanol but at these quantity of n-propanol has been varied by content of added water.

Small quantities of water (before 10-15%) practically didn't influenced on form of titration curves of W(VI) and Sb(III) at titration by solution of thionalid.

Thus small quantities of water which can present in n-propanol don't prevent to determination of ions of above-mentioned metals by solutions of thioacetamid and thionalid.

For metrological value of elaborated amperometrical methods and obtained experimental data the correlation analysis of results.

Calculations of the correlation coefficients were carried out by following equations (1:5) [3]:

$$r = \frac{n \cdot \sum x_i y_i - \sum x_i \sum y_i}{\left(\left[n \cdot \sum x_i^2 - (\sum x_i)^2 \right] \cdot \left[n \cdot \sum y_i^2 - (\sum y_i)^2 \right] \right)^{1/2}} \quad (1);$$

$$r = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\left[\sum (x_i - \bar{x})^2 \sum (y_i - \bar{y})^2 \right]^{1/2}} \quad (2);$$

$$r = \frac{1}{n} \sum (x_i - \bar{x})(y_i - \bar{y}) : (S_x S_y) = \left(\frac{1}{n} \sum x_i y_i - \bar{x} \bar{y} \right) : (S_x S_y) \quad (3);$$

$$S_x^2 = \frac{1}{n} \sum (x_i - \bar{x})^2 \quad (4);$$

$$S_y^2 = \frac{1}{n} \sum (y_i - \bar{y})^2 \quad (5)$$

where: n- number of experimental points; x-concentration of determined cation, mkg/ml; x-average determined value of component concentration; y₁-equivalent point of titrated cation; y- average determined value of heights of voltamperogramm.

It is known [4] that strong correlation bond don't obligatorlly designate causel bond between parameters "x" and "y"

Results of determination of the correlation coefficient for Sb(III) are presented in table.

Calculation of the correlation coefficient "r" at amperometrical titration of Sb(III) was carried out by following formular:

$$r = \frac{5 \cdot 315 - 100 \cdot 14}{\left(\left[5 \cdot 2250 - (100)^2 \right] \cdot \left[5 \cdot 44,1 - (14)^2 \right] \right)^{1/2}} = 1,0$$

Table Metrological characteristics using for calculation of the correlation coefficient (r) of determination of Sb(III)

№	x_i	y_i	$x_i \cdot y_i$	x_i^2	y_i^2
1	10	1,4	14	100	1,96
2	15	2,1	31,5	225	4,41
3	20	2,8	56	400	7,84
4	25	3,5	87,5	625	12,25
5	30	4,2	126	900	17,64
Σ	100	14	315	2250	44,1

As shown from obtained data the determinate correlation coefficients “r” in all cases don’t exceed 1,0 what is in accordance with theoretical literature data. Obtained values of “r” have indicated about rightness and reproduction of elaborated amperometrical methods of determination of Sb(III) by solution of thioacetaldehyde. Thus these methods are suitable for analysis of different by nature standart samples of ores, minerals, tails and some other materials because the low limits of determinate quantities of investigated elements and also their limits of detection (sensibleness) are on the level of concentration limit and lower.

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