

The Elaboration Of Amperometric Methods For The Determination Of Some Noble Metals In The Environmental Objects

Abstract

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Abstract: *The possibility of determination the electrochemical behavior of thionalide and thiourea on a platinum disk microanode is shown. The influence of background electrolytes and buffer mixtures on the conditions, course and results was studied. Based on these data methods for the amperometric determination of Pd(II) and Ag(I) using solutions of thioureas(TU) and thionalide (TNL) on a platinum rotating anode by its oxidation current, with a clear titration curve characterized by a clear endpoint were developed.*

Keywords: *amperometrical titration, palladium, silver, thiourea, thionalid, electrode, oxidation, complex-formation, the point of equivalence, the end point of titration.*

1. INTRODUCTION

In analytical chemistry organic reagents containing thionic ($=C=S$) and thiol ($\equiv C-SH$) groups are increasingly used. They are characterized by significant chemical activity and react with a large number of ions, forming colored or colorless compounds of various compositions. Their peculiarity is the ability to react with individual groups of elements in a certain range of acidity.

The high sensitivity of the reactions makes it possible to determine small amounts of metal ions with a sufficient degree of accuracy, and in some cases it is possible selectively

determination of one element in the presence of others without prior separation. Literature data have confirmed that thions and thiols form strong complexes with palladium[1-4], silver[5-6], gold [7] and other metals[8-10].

2. EXPERIMENTAL PART

Preparation of the initial Pd(II) solution. A sample of 0,266 g Pd was dissolved in a mixture of 0.1 M HCl and HNO₃ (3:1) and brought to the mark in a 250 ml flask by bidistilled water.

Preparation of the initial 0.01 M Ag(I) solution. A sample of 0.425 g of AgNO₃ was dissolved in 5-10 ml of 1,0 M HNO₃ and the volume was adjusted to 250 ml.

Universal buffer mixtures were prepared by mixing 0,04 M solutions of H₃PO₄, CH₃COOH, and H₃BO₃ with 0,2 M NaOH of various volumes [11].

For preparation 0.03 M solution of TNL, a same by mass 1,629 g was taken and dissolved in 98% acetic acid, then the total volume was adjusted to 250 ml.

A 0,1 M solution of TU was prepared by dissolving a sample of a freshly recrystallized prepurate (1,829 g) in water or 96% ethyl alcohol.

It was found that 0.005–0.1 M solutions of TNL and TU practically do not change their titer (if they are stored in the dark and on the cold) for 20-25 days.

Universal EV-74 ionometer and pH meter pH/mV/temr Meter P 25 EcoMet (South Korea) have been used in this investigation.

3. RESULTS AND DISCUSSION

The oxidation of TU (as well as many other sulfur-containing ones) begins at almost the same potential – from + 0,4 to +0,5 V. However, the nature of the TUpolarogram strongly depends on the direction of removal of the current-voltage curve. When removing the current-voltage curves of the TU in the direction of increasing the positive polarization of the electrode (curves 1 and 2), a more or less pronounced maximum was observed on the polarograms at a potential of about + 1.3 V, which is typical for cases when oxygen of surface platinum oxides participates in oxidation. From fig.1 it is the current-voltage curves of TU against the fone of sulfuric acid.

When the voltammetric curves TU in the direction of decreasing the positive electrode polarization (curves 1 and 2) polarograms have a slightly different view: maximum at +1.3 V disappeared, but another maximum at a potential of +0.9 to +1,0 V appeared and between the forward and reverse motion of the polarization curves is observed a significant hysteresis loop was observed.

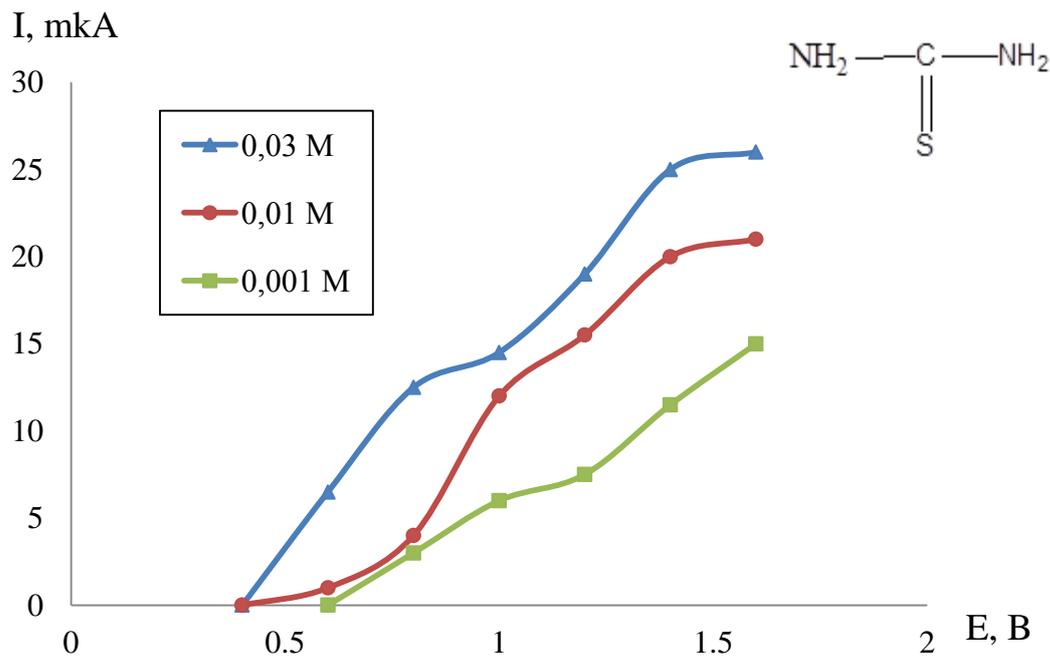


Fig. 1. Volt-ampereometric curves of 0,01 M on the fone H_2SO_4 solutions of various concentrations.

TNL is oxidized on a platinum rotating microelectrode with the formation of single horizontal platform on volt-ampereometric curve in the range of 1,05-1,25 V. The value of the diffusion current is proportional to the concentration of the reagent, owing to which it is possible to carried on volt-ampereometric titration of the investigated metal ions by the anode current. On fig. 2. the current - voltage curves of titration of TNL solutions of various concentrations on the backbone of 0,01 M of sulfuric acid are shown; the curves on the backbone of nitric and sulfuric acid salts of potassium or ammonium with the addition of acetic acid have a similar appearance. The titer of the acetic acid solution of TNL practically does not change during the month. Titration is best performed in a sulfuric acid medium.

It was found[10] that the number of electrooxidation for TNL and TU on platinum disk microanode on different acid-base properties of fonelectrolytes and buffer mixtures is equal to two. The number of elektropanorama of the investigated reagents on different by nature electrolytes and studied mediums was the same.

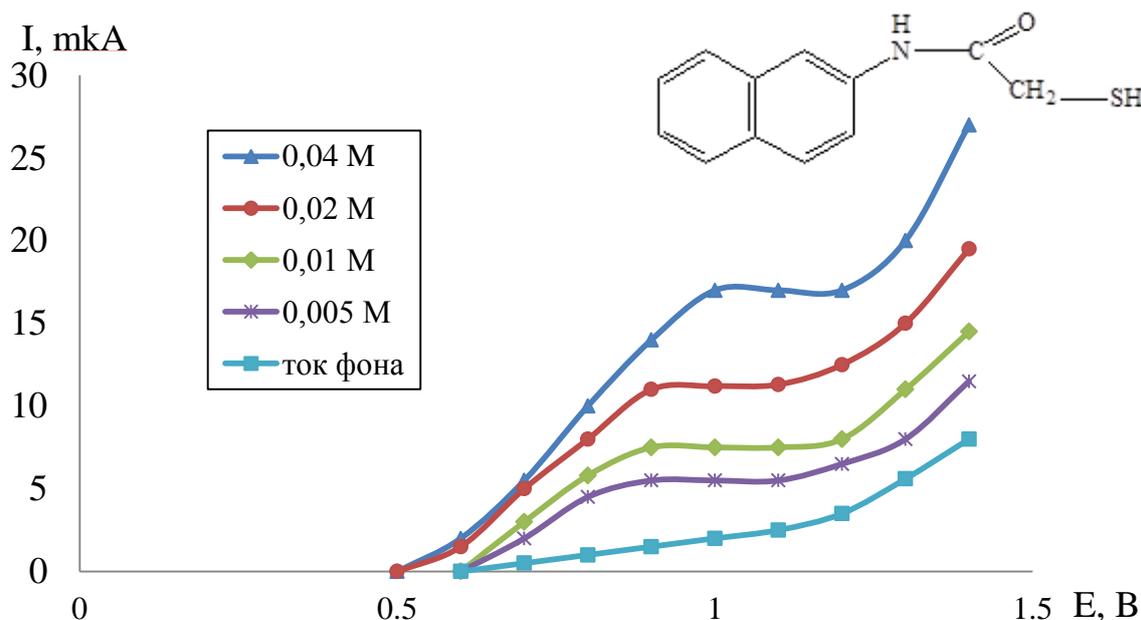


Fig. 2. Volt-ampere curves on the fone of 0.01 M H_2SO_4 of TNL solutions of different concentrations.

Since the value of the stress must also have a significant influence on the shape of the curves, conditions and results of the determination of metals therefore, first of all the nature of the influence of this factor on the titration of the palladium and silver ions with solutions of TNL and TU was studied. On the base of identified volt-ampere characteristics of TU and TNL on platinum disk microanode in the presence of various fone electrolytes in aqueous medium, it was shown that amperometric indication of CTT of various metal ions with two indicator electrodes it is necessary to be carried out at a potential of 0.65-1.10 V for TU and TNL depending on the nature of the fone electrolytes and buffer mixtures. At carrying out AT of metal ions analysis with two indicator electrodes the minimum voltage on the platinum electrodes should be 0.40 V.

The concentration of fone electrolytes and buffer mixtures should be in the region corresponding to their optimized amounts. The titrant concentration (TU, TNL) was in range 0.04 to 0.001 M, the volume of the tested solution was 10.0 ml, the temperature was about 20 °C.

TU forms strong compounds mainly with the metals, the sulphides of which are insoluble in water. In this case a coordination bond has occurred due to a pair of electrons belonging to the sulfur atom.

It is established that TU is easily oxidized on a rotating platinum microanode and the character of the volt-ampere curves was shown. These curves were obtained on the fone of sulfuric acid. At low concentrations of TU the wave height is proportional to this value, which has allowed the use of TU for direct amperometric titration of many metals.

On the base of these data, methods were elaborated for amperometric determination by using solutions of TU and TNL on a platinum rotating anode by its oxidation current, and at this the titration curve was characterized by a clear end point (Fig. 3-4).

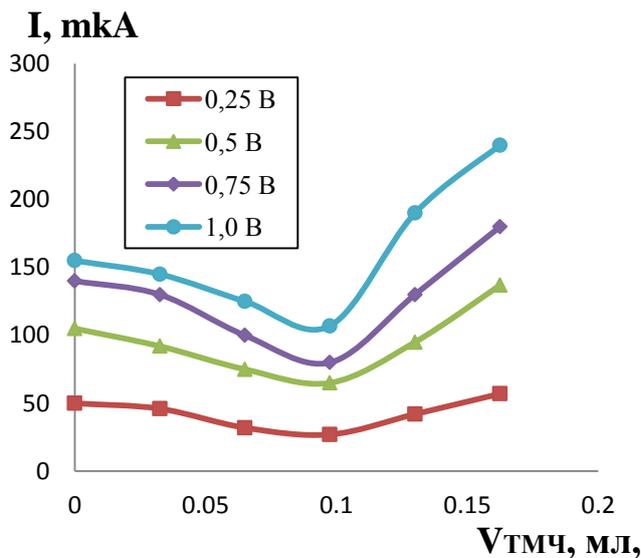


Fig. 3. Titration curves for Ag(I) 0.01 M solution TU by on the fone 0.5 M H₂SO₄ at different voltages on the indicator electrodes.

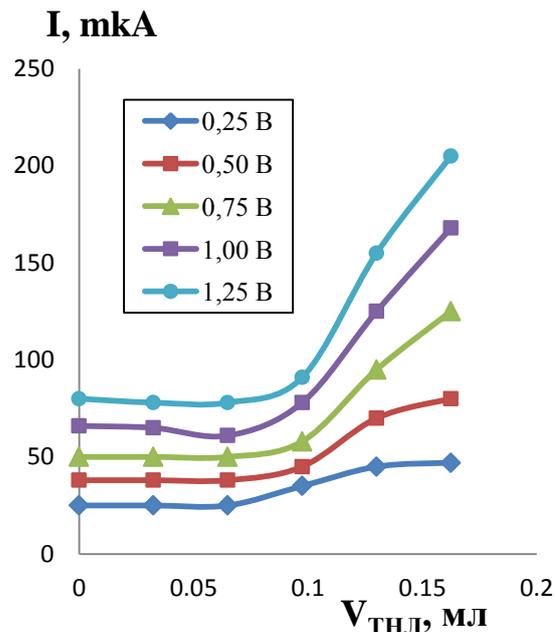


Fig. 4. Pd(II) titration curves by 0.03 M TNL solution on the fone of potassium phthalate (pH 1.58) at different voltages on the indicator electrodes.

TU and TNL are oxidized on the platinum electrode and give a wave with small maximum, which was increases proportion rally to the content of TU and TNL in the solution.

The character of the change in the current value as the addition of TU is corresponds to titration along an increasing wave (—/—-form and \—/—-form). The course of the titration curve can be explained as follows: the first portions of PMCH and TNL are spent on interaction with Pd(II) and Ag(I) ions and then the current value remained constant. After reaching the e. p., so after binding all the ions of silver, and palladium, the added excess of TU and TNL gives a current increasing with its concentration.

It titration a fairly clear titration curve with theoretically expected classical descending left and ascending right forms with a relatively small section of the curve of smooth curvature between the branches. When Pd(II) and Ag(I) are titrated the precipitator almost isn't formed, the titrated solution remains relatively transparent and the reaction products during complexation are slightly yellowish.

The character of change of value of the limiting anodic current at the addition of TNL and TU to solution is determined by the first downward left and then a rising right-branches of the curve from it is which shown that the first added portion of the reagents has required for their interaction with ions of Pd(II) and Ag(I) and therefore the value of the current limit oxidation titrant is reduced owing to binding of ions of metals with titration reagent. After reaching equivalence point and complete binding of metal ions into complexes, an excess of TNL and TU gives a growing anode current indicating on the end of titration. As an example on figure 5. the curve of amperometric titration of Pd(II) with a TU solution are presented. The first added portion of PMCH is spent on interaction with Pd(II) ions; in this case, the limit current of PMCH oxidation has decreased owing to the binding of Pd(II) ions by PMCH. After the equivalence point is reached and fully bound of Pd(II) complexes, the excess of TU gives a

growing anode current. After TU is oxidation, formamidindisulfide was formed, which was decomposed with formation thiourea, CNNH_2 cyanamide and elemental sulfur.

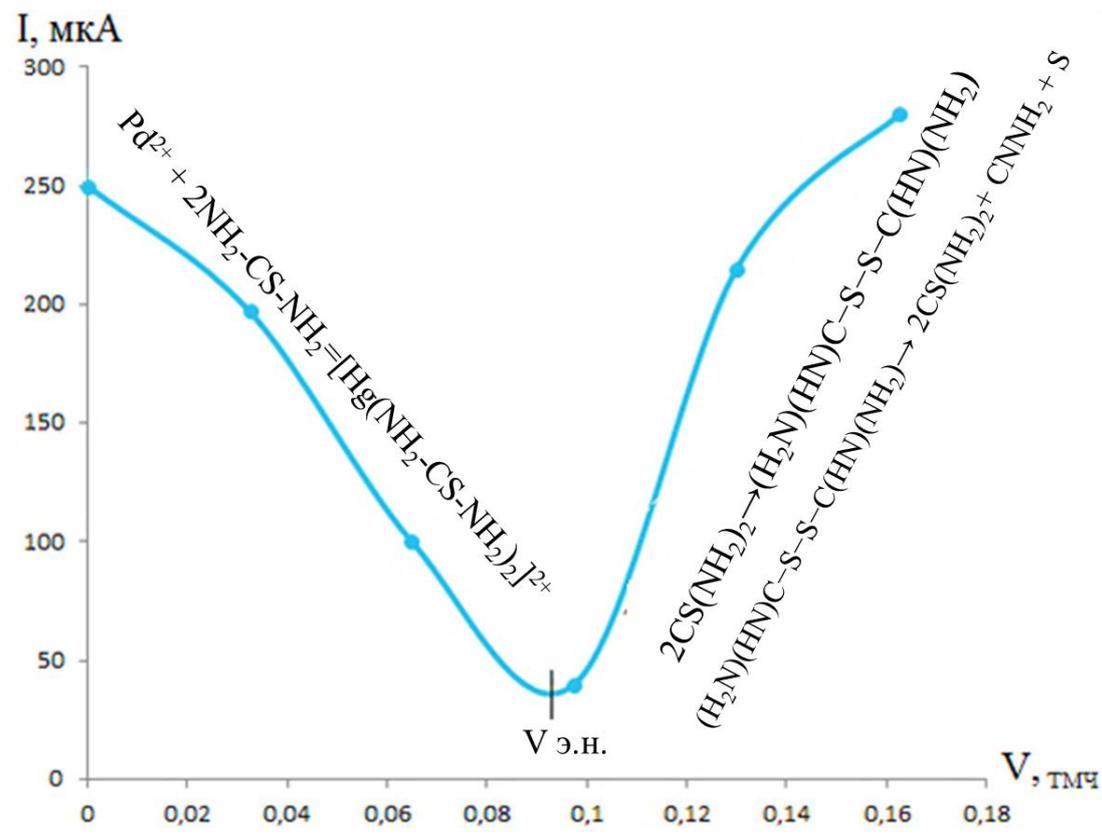


Fig. 5. Amperometric titration of Pd(II) with TU solution.

All the revealed facts [12-14] indicate that the interaction of ions of the determined metals with TNL and TU fairly well-soluble complexes were a formal that correspond to the formulas for TNL $[\text{Pd}(\text{C}_{12}\text{H}_{10})_2]$ and TU $[\text{Pd}(\text{NH}_2\text{-CS-NH}_2)_2]$, $[\text{Ag}(\text{NH}_2\text{-CS-NH}_2)]$ and corresponding to the theoretically expected.

Titration of Pd(II) and Ag(I) with solutions of TU (0,1 M) and TNL (0,03 M) was carried out using a universal Britton-Robinson buffer with a pH of in the range from 1,81 to 12,50; oxalic acid (pH 2,20), potassium tartaric acid (pH 1,68), aminoacetic acid (pH 1,50), potassium citrate (pH 1,69), potassium phthalic acid (pH 1,58) and fone electrolytes: HCl, HClO_4 , H_2SO_4 , HNO_3 , KCl, NaCl, etc. at potential difference at the electrode (e) in the range of 0,25-1,25 V. It was found that titration was carried out fairly quickly, leading to well-reproducible and correct determination results, as well as accurate titrant expense in the of course the titration point.

For statistically evaluate ion of the accuracy of the elaborated amperometric methods for determining Pd(II) and Ag(I) with solutions of TU and TNL with two platinum indicator electrodes, titrations of their various amounts were carried out with multiple parallel repetition of each determination at optimal conditions. Some of obtained data are presented in table 1.

Table 1. Results of amperometric titration of various amounts of metals by 0.03 M TNL solution under optimized conditions
(E = 0,75-1,25 В; P = 0,95)

Metal ion	Introduced metal, μg	Found $\text{Me}(\bar{x} \pm \Delta X), \mu\text{g}$	n	S	S_r
Pd(II)	10,0	$9,96 \pm 0,06$	4	0,04	0,004
	20,0	$20,32 \pm 0,40$	5	0,32	0,016
	40,0	$39,2 \pm 1,24$	4	0,78	0,020
	80,0	$78,26 \pm 2,09$	5	1,70	0,021
	160,0	$156,6 \pm 5,29$	4	3,32	0,020
Ag(I)	4,0	$3,95 \pm 0,06$	5	0,05	0,013
	8,0	$7,79 \pm 0,32$	4	0,21	0,026
	16,0	$15,49 \pm 0,78$	4	0,49	0,032
	32,0	$33,1 \pm 1,81$	4	1,13	0,034
	64,0	$62,12 \pm 2,24$	5	1,82	0,029

4. CONCLUSIONS

1. The possibility of electrolysis is shown and the conditions for the determination of Ag(I) and Pd(II) ions by sulfur-containing TNL and TU compounds are optimized.
2. It was found that under optimized conditions, the oxidation curves of the selected thionalide and thiourea reagents confirmed their suitability as analytical titrants, and the logarithmic analysis revealed the irreversible nature of the limiting anode current.
3. The diffusion nature of electrode processes is shown and the mechanism of their action is Revealed for the development of amperometric methods for determining Ag(I) and Pd(II) ions.
4. Amperometric methods for the determination of Hg(II), Ag(I), and Pd(II) ions using standard solutions of TNL and TU on various acid-base media have been developed.
5. The developed method for determining Hg(II), Ag(I) and Pd(II) by solutions of TNL and TU is applied to their individual solutions, binary, triple and more complex model mixtures (Pd(II)-1.0 ppm, Ag(I)-0.4 ppm and Hg(II)-3.2 ppm), real natural objects and industrial materials.

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