FORMATION OF THIOUREA COMPLEXES BY PLATINUM AND PALLADIUM AND AMPEROMETRICAL METHOD

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Abstract. Ability of ions of platinum and palladium determination was shown and also conditions of their complex-formations with thiourea solution were determined. Influence of phone electrolytes and buffer mixtures on the conditions and results of titration was investigated. Determination of platinum ions in mixtures imitated some real objects and also in platinum and palladium catalysts and concentrates was carried out by titration by solution of thiourea. Elaborated method was valued from the point of metrology and it was shown it’s rightness and reproduction (relative standard deviation Sr=0,33)

Key words: amperometrical titration, platinum and palladium, thiourea, electrode, oxidation, complex-formation, the point of equivalence, the end point of titration

Introduction

Organic reagents containing tionaic (=C=S) and tiolic (≡CBSH) groups are used wide in analytical chemistry. They have possessed by high chemical activity and have reacted with different ions of metals with forming coloured and non-coloured compounds of different composition. Their peculiarity is an ability to react with separate groups of metals in definite interval of acidity. High sensibility of above mentioned reactions has allowed to determine a small quantities of ions of some metals with sufficient degree of precision, in some cases possible an election determination ions only one metal in the presence of other ions without preliminary division (Songina and Bessarabova, 1973).

Sulfer-containing reagents including thiourea (TU) have been used in amperometrical method at determination of cations of noble metals (Shaponikova and Tarayan, 1972; Gavva, Zakharov and Songina, 1982; Usatenko and Tolubara, 1975; Gevorgyan et al., 2013).

Using of platinum wire as indicator electrode has allowed to apply currents of reduction of determined metal’s ions and current of oxidation of TU what has widen possibilities of amperometrical determinations.

Experimental part

Solutions of ions of different metals, reagent, buffer solutions and phones were prepared on the bidistilled water.

Preparation of 0,01 M solution of Pd(II): 0,5 g of Pd was dissolved in mixture 0,1 M HCl and 0,1 HNO₃ (3:1) and volume of solution was carried to 250 ml.

Preparation of 0,01 M solution of Pt(IV): 0,2 g of Pt was dissolved in mixture 0,1 M HCl and 0,1 HNO₃ (3:1) and volume of solution was carried to 100 ml.

Universal buffer mixtures and phone electrolytes were prepared according to literature date (Gevorgyan et al., 2013).

0,1 M solution of TU was prepared by dissolution of its 1,829 g after purification by recrystallisation in water or in 96 % ethanol. It was determined that 0,005-0,1 M solutions of TU haven’t changed practically their titer during 20-25 twenty-four hours (at condition their storage in darkness and on the coldness) (Gevorgyan et al., 2013, p. 4).

Universal ionomer EV-74 and pH-metr pH/mV/TEMP Meter P25 EcoMet (South Korea) were used in this investigation.

Results and their discussion

Determination of Pt(II) and Pt(IV) by solution of thiourea.

Since nature and concentration of phone electrolyte and buffer mixture have influenced in grate degree on the conditions and results of titration it was necessary to investigate influence of these parameters in first
turn. Experiments have shown that on phones of HCl and H₂SO₄ titration of Pt(II) and Pt(IV) by solution of TU was impossible since interaction of TU with these ions has carried out very slowly and because of constant increasing of oxidation current of TU. On the phone of HNO₃ interaction of Pt(II) and Pt(IV) with TU has carried out enough rapidly and it was shown clearly expressed the end point on the titration curve. In case of Pt(II) titration the end point was determined at molar ratio Pt(II):TU 1:4 and solution has acquired yellow-green colouring what has indicated on the formation of complex [Pt(SCN₂H₄)₂]²⁺. In the case of titration of Pt(IV) the same colouring was observed but molar ratio of Pt(IV):TU in the end point of titration was equaled 1:6, on the base of this fact conclusion was carried out about reduction of Pt(IV) by TU to Pt(II) with following formation of above-mentioned complex which is electro-chemically active and by this reason type of amperometrical curve has depended on potential of the indicator electrode. At potentials 0,5-0,6 V this complex on the anode didn’t oxidized and titration curves have an usual V-figurative type but at potentials +0,7-1,0 V this complex has oxidized and on the titration curve before achievement of the end point the some increasing of current was marked. The optimal conditions of titration of Pt(II) and Pt(IV) by solution of TU were following: phone-HNO₃, potential of the indicator electrode +0,6 V and time fixation of current strength after addition of next portion titrant-45-60 s. At these conditions the limit of determination of Pt(II) and Pt(IV) was equaled 5 mkg/ml. Results of titration of Pt(II) and Pt(IV) in factitious solutions containing H₂PtCl₆ and H₂PtCl₄ are presented in table 1.

<table>
<thead>
<tr>
<th>Introduced of Pt(II), mkg/ml</th>
<th>Determined of Pt(II), mkg/ml</th>
<th>S</th>
<th>Sr</th>
<th>Introduced of Pt(IV), mkg/ml</th>
<th>Determined of Pt(IV), mkg/ml</th>
<th>S</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>5,0</td>
<td>4,98 ± 0,08</td>
<td>0,07</td>
<td>0,13</td>
<td>5,0</td>
<td>4,97 ± 0,18</td>
<td>0,16</td>
<td>0,032</td>
</tr>
<tr>
<td>10</td>
<td>10,02 ± 0,11</td>
<td>0,10</td>
<td>0,010</td>
<td>10,0</td>
<td>9,90 ± 0,29</td>
<td>0,25</td>
<td>0,026</td>
</tr>
<tr>
<td>20</td>
<td>19,95 ± 0,19</td>
<td>0,16</td>
<td>0,008</td>
<td>20,0</td>
<td>19,86 ± 0,18</td>
<td>0,48</td>
<td>0,024</td>
</tr>
<tr>
<td>40</td>
<td>39,9 ± 0,38</td>
<td>0,33</td>
<td>0,008</td>
<td>40,0</td>
<td>39,92 ± 0,69</td>
<td>0,60</td>
<td>0,015</td>
</tr>
</tbody>
</table>

It is shown from the date of table 1 that determined quantities of ions Pt(II) and Pt(IV) have corresponded to their introduced quantities and don’t go out behind limits of confidence interval was has conformed high precession of elaborated amperometrical method of determination of platinum ions by solution of TU with relative standard deviation (Sr) 0,032.

For determination of Pt(II) and Pt(IV) by solution of TU in model mixture and some real natural objects the influence of some outside cations accompanying them in nature and often meeting in alloys ores and industrial materials was investigated. It was shown that to determination of Pt(IV) at quantities 5,0-20,0 mg/ml don’t prevent 15-multiple quantities of Rh(III) and Ir(III); 500-multiple quantities of Ni(II) and Al(III). Such cations as Ir(IV), Ru(IV), Au(III), Fe(III), Hg(II), Ag(I), Cu(II), Se(IV) have prevented to determination Pd(II) and Pd(IV) can be titrated differentially and by this reason on the amperometrical curve two point equivalence were marked: the first has ended of reaction of TU with Pd(II) and second has ended reaction with Pt(IV). Differentiation titration of Pd(II) and Pt(IV) has given the best results at potential +0,8 V. Results of determination of Pt(IV) in the presence of some outsider cations are presented in table 2.

Amperometrical determination by TU was used for analysis of platinum-palladium catalysts and some obtained results are presented in table 3.

<table>
<thead>
<tr>
<th>Outside cation, mg/ml</th>
<th>Determined Pt(IV), mkg/ml</th>
<th>n</th>
<th>S</th>
<th>Sr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rh (0,075 mg/ml)</td>
<td>4,86 ± 0,22</td>
<td>4</td>
<td>0,14</td>
<td>0,028</td>
</tr>
<tr>
<td>Ir (0,075 mg/ml)</td>
<td>5,12 ± 0,19</td>
<td>4</td>
<td>0,12</td>
<td>0,024</td>
</tr>
<tr>
<td>Ni (2,5 mg/ml)</td>
<td>4,91 ± 0,11</td>
<td>5</td>
<td>0,08</td>
<td>0,018</td>
</tr>
<tr>
<td>Al(2,5 mg/ml)</td>
<td>5,23 ± 0,29</td>
<td>5</td>
<td>0,24</td>
<td>0,046</td>
</tr>
</tbody>
</table>
Table 3

<table>
<thead>
<tr>
<th>Composition of catalyst</th>
<th>Quantity of cations of Pt(IV) and Pd(II) by passport, %</th>
<th>Determined quantities, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
<td>Pd</td>
</tr>
<tr>
<td>Pt-Al-Pd</td>
<td>40,75</td>
<td>9,83</td>
</tr>
<tr>
<td>Pt-Al-Pd</td>
<td>60,10</td>
<td>10,20</td>
</tr>
<tr>
<td>Pt-Pd</td>
<td>50,82</td>
<td>49,18</td>
</tr>
<tr>
<td>Pt-Al</td>
<td>74,52</td>
<td>-</td>
</tr>
<tr>
<td>Pt-Al</td>
<td>86,45</td>
<td>-</td>
</tr>
</tbody>
</table>

Carrying-out of determination. 0,2-0,5 g of catalyst was dissolved in mixture HCl and HNO₃ (1:3), which twice was steamed by HCl (1:1) for removal of nitrogen oxides and solution was carried in measuring flask by capacity 100 ml and solution volume was carried to marking by distilled water. To aliquant of solution (2 ml) 2 M solution of HNO₃ was added to volume 10,0 ml and titration by 0,1 solution of TU at potential of the indicator electrode +0,8 V was carried out. Results of catalysts analysis are presented in table 3.

Determination of Pd(II) by solution of TU. Experiments have confirmed literature date that TU has oxidized on the platinum electrode and has given wave with small maximum which has increased proportionally to TU content in solution. Character of changing of current value at addition TU has corresponded to titration by increasing wave (V-form). This type of titration wave can be explain by following manner: the first portions of TU were expended on the interaction with ions of Pd(II) and by this reason current value has remain constant. After achievement of point of equivalent that is after connecting all Pd(II) adding surplus of TU has given current which has increased with increasing of regent concentration.

Such changing of current in process of titration is accompanied by characteristic changing in solution. At following addition of TU yellow coloration of solution caused by present of ions [PdCl₄]²⁻ gradually has increased and then has become an orange, then red-orange and at Pd(II) content more than 5,0 mg/ml less has appeared in solution, after which red-brown precipitation has precipitated. After achievement of equivalent point partial dissolution of participation has began; a coloration of solution has become more light-yellow and then it’s intensity coloration has became constant.

Type of curve of amperometrical titration at addition of large surplus of TU has presented on figure 1.

![Fig. 1. Titration of 5 mkg/ml Pd(II) by 0,01 M solution of TU at its surplus on following phones: 1-0,5 M H₂SO₄, 2.-3 M H₂SO₄](image_url)

It is shown from this figure that addition of first portions of TU the current has remain constant because these portions are spent on the participation of Pd(II) (part AB on the curve). After achievement of equivalent point which has corresponded to molar ratio Pt(II):TU=1:2 the partial dissolution of participation has began with simultaneous formation of complexes Pd(II):TU with composition 1:3 and 1:4 (part BC on figure). Sharp raising of current on this part was caused by accumulation of complexes with composition 1:3 and 1:4 in
solution with simultaneous oxidation of them on the electrode. After achievement of point corresponding to
formation of complexes of composition Pd(II)-TU=1:4 (part CD on the figure) the current value slightly has
decreased what is caused with some suppression of dissociation of these complexes in presence of TU
surplus.

Influence of different accompanying ions on the determination of Pd(II) by solution of TU was
investigated. Obtained data have shown that to determination of Pd(II) and Pd(IV); quantities of ions of Rd,
Se, Cu, Co, and Sn at relation of Pd(II) and these ions 1:400; ions of Ti, As, Bi, Al, Zn and Cr at relation
1:500; ions of Ni, Fe, Pb and Mn at relation 1:1000.

At concentration HNO₃ in solution more than 0.05 N results of determination of Pd(II) were slightly
overstated. The presence of HCl has distorted the normal type of titration curve and has caused to erroneous
estimation of Pd(II) contend in solution. Ions of Ag(I) and Au(III) also have prevented to Pd(II) determination
because they simultaneously are titrated with Pd(II) by TU and titration curve in this case shown the summary
quantities of all three ions.

Method of amperometrical determination of palladium by titration of solution of TU with using of
platinum electrode was applied to analysis of some industrial materials including some platinum-palladium
concentrate, which is complex by composition product. The main advantage of method of amperometrical
titration is a possibility of rapid determination Pd(II) in the presence of considerable quantities of
accompanying ions of different metals what has allowed to simple a scheme of analysis and to quicken it’s
conducting.

Practically to determination of Pd(II) only ions of Ag and Au have prevented and by this reason the new
scheme of analysis must except only these ions.

Carrying-out of analysis. For determination of palladium in platinum-palladium concentrate method of
division of components was used in which after dissolution of sample of analyzed material they obtained
solution was treated at definite pH by NaNO₃ and at this all ions of non-noble metals and Au precipitated but
ions of noble metals remained in solution as complex nitrates which were distracted by evaporation with HCl;
remainder was dissolved in bidistillate and obtained solution was acidified by HCl and was transferred in
measured flask. Aliquot of obtained solution was picked out in glass for titration and quantity of Pd(II) was
determined by the elaborated amperometrical method.

Method of amperometrical titration also was used for palladium determination in standard allows which
has bounded included stage of extraction separation of palladium from other metal’s ions including ions of
platinum.

Method of amperometrical titration for Pd(II) determination in standard allows and different mixtures is
characterized has increased precision of analysis owing to its objectivity and exception of arrows bonding
with considerable number of operations at its carrying-out. Such new amperometrical method of rapid
determination of Pt(II), Pt(IV) and Pd(II) in different objects especially at determination their small quantities
has been elaborated.

References
Bardin, M., Balandina, N. and Todorova, G. (1964). Amperometriceskoye opredeleniye palladiya pri
pomoshli tiosochevnii s primenieneniem vrashayushyegosya platinoavgogo elektroda. Zhurnal Analiticheskoy
Himi, 19(10), pp.1228-1232.
blagorodnii i toksichnii metallov razlichnimi tiolami. Uchebno-metodicheskaya razrabotka. Tashkent.
Kuzmin, N. and Songina, O. (1973). Issledovaniye sostava tiosochevnii kompleksov serebra,