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## VOLTAMMETRIC DETERMINATION OF IRIDIUM IN ALLOYS USING XYLENOL ORANGE

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*Received: February 23, 2011 / Revised: March 11, 2011 / Accepted: May 31, 2011*

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**Abstract.** The possibility of iridium(IV) voltammetric determination using threephenylmethane dye (xylenol orange) has been investigated. The proposed technique has been tested using model solutions and in the process of iridium alloys analysis.

**Keywords:** iridium, voltammetric determination, threephenylmethane dye, xylenol orange.

### 1. Introduction

The scientific and technological advance stimulates the usage of materials having iridium among their components. The wide use of the mentioned metal is connected with its specific physico-chemical properties. The high efficiency of the products containing iridium in most cases is explained by its synergism with other components of platinum group. Therefore the tight control of the products quality, namely their macro- and micro-components content is an urgent problem. The problem may be solved using different types of spectrophotometric analysis. However, their main drawback is low selectivity [1-4]. Voltammetric analysis is simple, express, accurate, and reproducible; it does not demand complicated pretreatment of the samples. All these facts make voltammetric analysis competitive among other physico-chemicals methods. The development of modern methods of polarographic analysis, namely oscillographic type, as well as the use of organic reagents, allow to develop the techniques with improved chemical-analytic characteristics. Xylenol orange is one of threephenylmethane dyes used in voltammetry and other physico-chemical methods of analysis [5-8].

### 2. Experimental

#### 2.1. Starting Reagents

All reagents were of analytical grade. The solution of xylenol orange was prepared using the certified reagent of HemaPol firm.

To obtain the chloride solution of iridium(IV) the method of metal iridium with oxidative mixture  $\text{NaNO}_3 + \text{NaOH}$  alloying was used. Then the obtained alloy was dissolved in chloride acid. The solutions were identified by the comparison of their absorption spectra with absorption spectra of Ir(IV) described in the literature [9-10]. Because of mechanical losses the iridium content was controlled using titration method (iodometry) [3].

The analyzed alloys were synthesized and their crystal structures were determined at the Department of Inorganic Chemistry of Ivan Franko National University of Lviv [11].

#### 2.2. Equipment

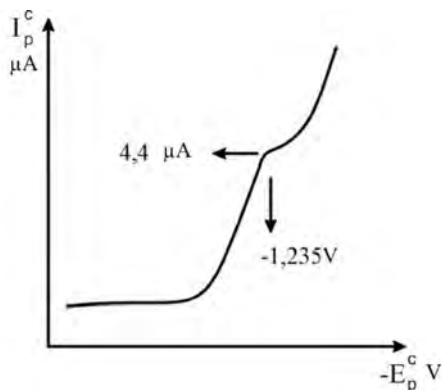
Voltammetric investigations were carried out using CLA-03 oscillograph in three-electrode thermostated cell: electrode-indicator, cathode – drop mercury electrode (d.m.e.); reference electrode, anode – mercury chloride (saturated calomel) electrode (m.c.e.) and auxiliary electrode – platinum. The values of peak potentials in the maxima were determined using digital voltammeter B7-21 with the accuracy of  $\pm 1$  mV. The dissolved oxygen was removed from the the investigated solutions by argon passed for 15 min. The medium acidity was controlled using pH-150 M pH-meter with combination glass electrode.

### 3. Results and Discussion

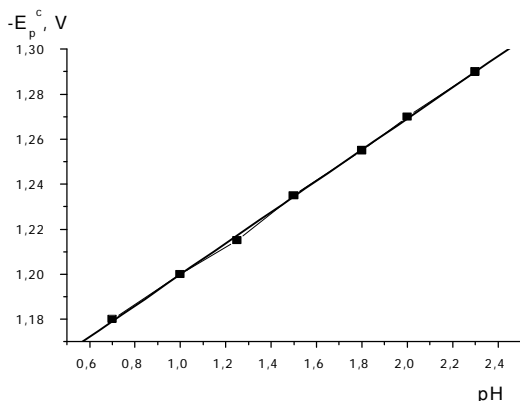
Ir(IV) solutions were investigated using oscillograph voltammetry within the concentration range of  $8.0 \cdot 10^{-3}$  to  $1.0 \cdot 10^{-7}$  mol/l. The results are represented in Fig. 1.

There are polarograph peaks in aqueous solutions of Ir(IV) in the range to pH 2.3, which disappear with the further increase of pH. We connect this fact with the formation of electroinactive forms of platinum metal ions as a result of aquatic and hydrolysis processes. The dependence of potential of the reduction peak upon the

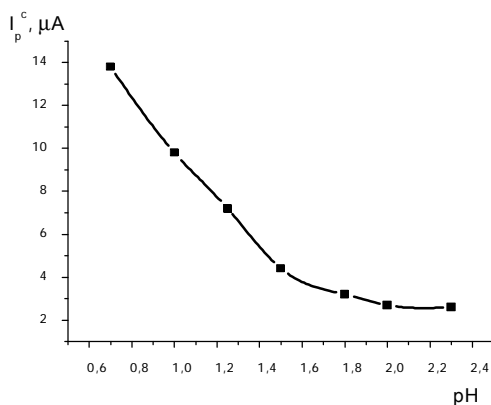
medium acidity has a linear character with a straight slope of 69 mV/pH indicating the hydrogen ions participation in the electrochemical process (Fig. 2a).



**Fig. 1.** Voltammetric characteristic of Ir(IV) solution reduction.  $C_{Ir(IV)} = 1.0 \cdot 10^{-4}$  M;  $C_{NaClO_4} = 0.16$  M; pH is 1.5



a



b

**Fig. 2.** Dependence of voltammetric characteristics of Ir(IV) ions reduction: peak potential (a) and current strength (b).  $V = 0.5$  V/s,  $C_{Ir(IV)} = 1.0 \cdot 10^{-4}$  M;  $C_{NaClO_4} = 0.16$  M

The rate criterion (Table 1) shows that slope angle tangency of the dependence  $\lg(I_p^c/S) - \lg V$  is less than 0.5 indicating the diffusive nature of current with kinetic limits. The effect of kinetic limits increases with the decrease of the medium acidity. The slope angle tangency of the rate criterion decreases with the decrease of solution pH indicating the priority of a chemical reaction over. Such reaction preceding the electrochemical process may be protonization, aquatation, hydrolysis, or polymerization of Ir(IV) complexes.

Table 1

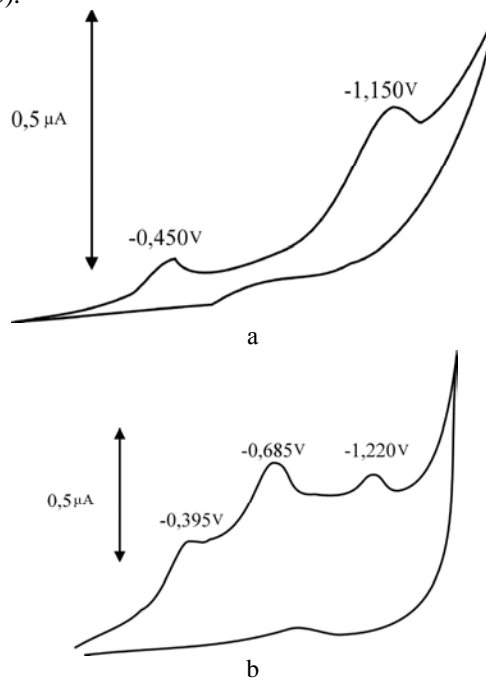
**Dependence of rate criterion upon the medium acidity for Ir(IV) solutions reduction**

background \ pH	1.0	1.5	2.0	2.3
$(Na^+ + H^+) + Cl$	0.33	0.29	0.27	0.15

Note:  $C_{Ir(IV)} = 1.0 \cdot 10^{-4}$  M;  $C_{NaClO_4} = 0.16$  M

The dependence of reduction current strength upon Ir(IV) ions concentration has a linear character. This fact was used for the development of analytic technique.

Xylenol orange (XO) is reduced at d.m.e. by two or three stages depending upon polarographic conditions (Fig. 3).



**Fig. 3.** Voltammetric characteristic of xylenol orange reduction in aqueous solutions: pH = 2.0 (a) and pH = 7.1 (b).  $C_{XO} = 1.0 \cdot 10^{-3}$  mol/l

During the introduction of the dye into the solution with Ir(IV) ions the “exaltation” of cathode

current of metal reduction takes place. The maximum increase in current is observed at the ratio Me:HR ≈ 1:2. Cathode current increases three times giving the possibility to improve the metrological characteristics of platinum metal determination (Table 2) at pH 1.0.

Table 2

**Metrological characteristics of voltammetric determination of Ir(IV) ions using xylenol orange**

Linearity limits of $I_p^c$ (μA) from $C_{Ir}$ (mol/l)	$5.0 \cdot 10^{-4} - 1.0 \cdot 10^{-6}$
Equation of graduated diagram	$I_p^c = 0.11 + 3.03 \cdot 10^5 C$
Correlation coefficient $R$	0.9969
Lower limit of $C_{min}$ determination, mol/l	$7.52 \cdot 10^{-7}$

Researches of the selectivity of voltammetric determination of Ir(IV) using xylenol orange (Table 3) show that ions of non-platinum metals, as well as two hundred-fold excess of osmium and fifty-fold excess of palladium do not impede the determination. Instead, the technique is characterized by low selectivity concerning Ru(IV), Rh(III) and Pt(IV).

Table 3

**Selectivity of Ir (IV) voltammetric determination using xylenol orange**

Ion	Ir(IV) : ion	Ion	Ir(IV) : ion
Pb(II)	1:50	Ru(IV)	1:1
Zn(II)	1:40	Rh(III)	1:0.1
Cd(II)	1:50	Pt(IV)	1:1
Ca(II)	1:200	Os(IV)	1:200
Mg(II)	1:200	Pd(II)	1:50
Al(III)	1:50	Cl <sup>-</sup>	1:500
Fe(III)	1:50	I <sup>-</sup>	1:50
Ni(II)	1:20	NO <sub>3</sub> <sup>-</sup>	1:500
Cu(II)	1:50	ClO <sub>4</sub> <sup>-</sup>	1:500
Co(II)	1:20	BrO <sub>3</sub> <sup>-</sup>	1:50
Ga(III)	1:20	SCN <sup>-</sup>	1:100
Tb(III)	1:20	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	1:100
Gd(III)	1:30	CH <sub>3</sub> COO <sup>-</sup>	1:500

**3.1. Technique of Ir(IV) Voltammetric Determination Using Xylenol Orange**

2.0 ml of NaCl solution (concentration 2.0 mol/l) and Ir(IV) solution (calculated in such a way that the end concentration of Ir(IV) ions were within  $5.0 \cdot 10^{-4} - 1.0 \cdot 10^{-6}$  mol/l) are loaded into a 25 ml flask. Then 1.0 ml of green solution of threphenylmethane dye with the concentration of  $1.0 \cdot 10^{-3}$  mol/l is added. Distilled water is poured till the total volume becomes ~ 20 ml. The pH is

established as 1.0 using HCl and NaOH solutions (not entering the alkaline area!) and distilled water is added to the mark. The medium acidity is controlled by pH-meter and more exact pH value is established if necessary. The difference between pH for parallel experiments must be ≤ 0.1. The investigated solution is transferred into an electrolyzer and dissolved oxygen is removed by a barbotage of purified argon through the cell for 15 min. Then the voltammetric curves are obtained at the polarizing range of (-0.5)–(-1.5) V and the polarization voltage rate of 0.5 V·s<sup>-1</sup>.

**3.2. Technique Approbation**

The correctness of Ir(IV) voltammetric determination was verified using the “introduced-determined” method on model solutions. One can see from Table 4 that the technique is characterized by good reproducibility and determination correctness.

Table 4

**Correctness of Ir(IV) voltammetric determination using xylenol orange ( $C_{XO} = 1 \cdot 10^{-3}$  M;  $C_{backgr.} = 0.16$  M; pH = 1.0;  $V = 0.5$  V/s;  $n = 5$ ;  $p = 0.95$ )**

Composition of matrix solution	Introduced Ir(IV), μg	Found Ir(IV), mcg	
		m(Ir(IV)), μg	$S_r$
350 μg Co(II) 250 μg Fe(III) 30 μg Pd(II)	10.0	9.80	0.019
		9.75	
		9.92	
		9.83	
		9.91	
350 μg Cd(II) 250 μg Ni(II) 250 μg Zn(II)	10.0	9.87	0.015
		9.84	
		9.93	
		9.96	
		9.81	
250 μg Ca(II) 350 μg Al(II) 250 μg Pb(II)	10.0	9.88	0.017
		9.92	
		9.79	
		9.80	
		9.92	

**3.3. Ir(IV) Voltammetric Determination in Alloys**

0.10-0.05 g of alloy is dissolved in 10 ml of HCl+HNO<sub>3</sub>(1:1) mix. The obtained solution is evaporated to wet salts and again dissolved in 50 ml of HCl (3.0 mol/l). If the alloy dissolves incompletely sintering of the new sample with NaOH+NaNO<sub>3</sub> (1:3) oxidative mix is carried out. The obtained alloy is dissolved in HCl of 3.0 mol/l concentration. Then it is placed in 250 ml

volumetric flask and distilled water is added to the mark. If necessary, the solution with iridium lower concentration is prepared. The aliquot of concentrated solution is placed in 100.0 ml flask and HCl solution (1.0 mol/l) is added to the mark.

For the analysis 2.0 ml of NaCl solution (2.0 mol/l) and aliquot of the analyzed solution are placed into 25.0 ml flask. The amount of the analyzed solution is calculated to obtain Ir(IV) ions concentration of  $1.0 \cdot 10^{-6}$ – $5.0 \cdot 10^{-4}$  mol/l. Fresh solution of xylenol orange is added to reach 5-10-fold molar excess. The voltammetric determination is the same as for iridium determination in model mixtures.

Table 5

**Ir(IV) determination  
in alloys using xylenol orange**

Sample mass, g	Ir content, %	$S_r$
<b>Tb<sub>2</sub>Ir<sub>3</sub>Al<sub>9</sub> (50.70 %)</b>		
0.0790	50.62	0.020
0.0630	50.73	0.018
<b>Ga<sub>2</sub>Ir<sub>3</sub>Al<sub>9</sub> (60.13 %)</b>		
0.0585	60.22	0.019
0.0880	60.20	0.018

#### 4. Conclusions

The possibility of iridium (IV) voltammetric determination using triphenylmethane dye – xylenol orange – has been examined. It has been established that base metals do not hinder the determination. Moreover, Ru(IV), Rh(III) and Pt(IV) ions show some catalytic

effect. The investigation results were tested on the model solutions and during iridium alloys analysis.

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**ВОЛЬТАМПЕРОМЕТРИЧНЕ ВИЗНАЧЕННЯ  
ІРИДІЮ У СПЛАВАХ ЗА ДОПОМОГОЮ  
КСИЛЕНОЛОВОГО ОРАНЖЕВОГО**

*Анотація.* Досліджено можливість вольтамперометричного визначення іридію(IV) за допомогою трифенілметанового барвника – ксиленолового оранжевого. Проведено апробацію запропонованої методики на модельних розчинах та при аналізі іридієвих сплавів.

*Ключові слова:* іридій, вольтамперометричне визначення, трифенілметанові барвники, ксиленоловий оранжевий.