

# Anodic stripping determination of Pt(IV) based on the anodic oxidation of In from electrochemically deposited Pt–In alloy phases

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Received: 1 November 2011 / Revised: 1 December 2011 / Accepted: 2 December 2011 / Published online: 28 December 2011  
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**Abstract** A simple, rapid, and sensitive anodic stripping voltammetric method for the determination of Pt (IV) is described. It is based on depositing an intermetallic indium–platinum alloy phase on the surface of a modified graphite electrode, and recording the oxidation peak of indium from that alloy phase with the help of linear scan voltammetry. A systematic study of the behavior of different In–Pt phases revealed that the peak potential of indium oxidation from the different phases can be explained on the basis of simple thermodynamic considerations. Different alloy phases have characteristic peak potentials. For the purpose of analysis, it is possible to choose such conditions that only one specific alloy phase forms, viz. PtIn. This is the case for a concentration (milligrams per liter) ratio of In (III)/Pt(IV)=50,000:1, at least.

**Keywords** Indium · Platinum · Intermetallic compound · Binary alloy · Stripping voltammetry

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## Introduction

Determination of platinum in the mineral raw materials is an important analytical task. For this purpose the voltammetric methods can be used as methods of analysis. These methods allow determining micro amounts of various metals with great accuracy and sensitivity. Although platinum is reduced at the electrode surface, it does not give an electro-oxidation peak in the voltammograms.

When platinum is determined by means of stripping voltammetric methods [1, 2], normally a coprecipitation with other metals, e.g., copper, lead, mercury, etc. happens. However, because of their toxicity, we did not choose these metals, but—in order to develop a stripping analytical method—decided to study the coprecipitation with indium. The analytical determination of platinum in mineral raw materials is an important task, and if one decides for a coprecipitation with In, it is necessary to study the electrochemical formation and behavior of the formed indium–platinum alloy phases.

The determination of platinum is complicated, as the formation of several intermetallic phases (In–Pt) affect the voltammograms.

There are several different possibilities for the determination of platinum, e.g., stripping voltammetry, atomic absorption spectroscopy, ICP MS, etc. The advantage of stripping voltammetry as compared to the other techniques is its sensitivity.

Since indium and platinum form a range of different alloy phases under stripping voltammetric conditions, and each phase exhibits its own anodic stripping peak, it was the goal of this paper to find such conditions that only one peak is observed.

Here we show that it is possible to determine platinum in the geological material by anodic stripping voltammetry using indium as co-depositing metal.

## Experimental part

### Reagents and chemicals

All chemicals used were of analytical or pharmaceutical grade and solutions were prepared with deionized water. Platinum, indium, and hydrochloric acid were supplied by Merck.

### Electrochemical measurements

Voltammetric measurements were carried out with the analyzer TA-4 (“Tom’analit”, Tomsk). A conventional three-electrode system was used and special quartz beakers of  $V=20$  ml as voltammetric vessels. A polyethylene-impregnated graphite electrode produced according to [3] was used as working electrode. A saturated silver/silver chloride electrode served as reference and another silver/silver chloride electrode served a counter electrode. Platinum (IV) and indium (III) were deposited from solutions containing chlorides of these metals at the potential of  $-1.2$  V. The graphite electrode was electrochemically cleaned by keeping it at  $1.05$  V for 60 s.

## Results and discussion

Indium (III) was deposited on the graphite electrode surface from a solution containing  $1 \text{ mol l}^{-1}$  hydrochloric acid at the potential  $-1.2$  V. The anodic peak of indium was observed at  $-0.75$  V. When platinum and indium are electrochemically deposit together, one observes several peaks, the peak potentials and currents of which are depending on the concentrations of both platinum (IV) and indium (III) in the solution.

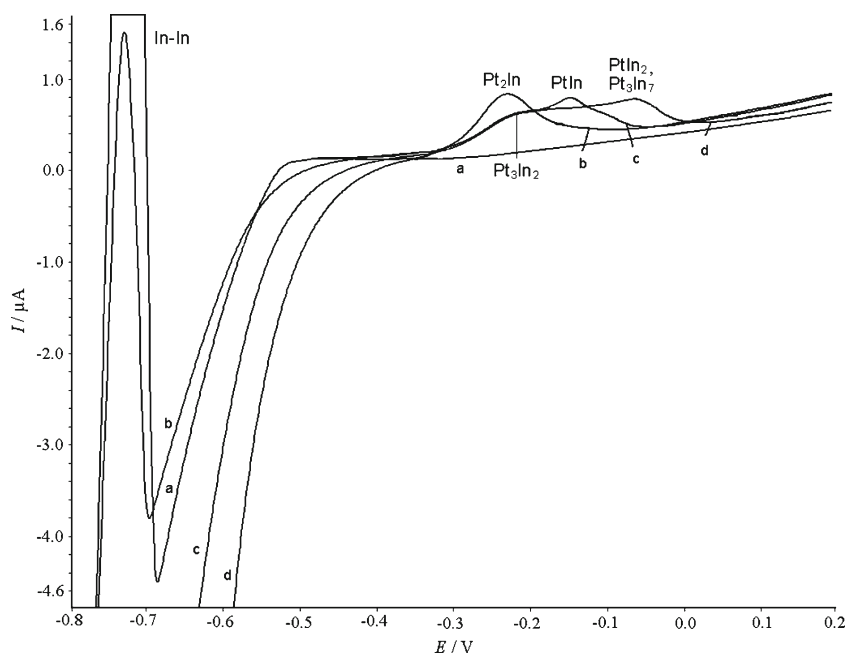
Figure 1 shows the voltammograms of indium oxidation from indium–platinum alloys. The ratio of indium(III) to platinum(IV) concentrations (in milligrams per liter) in the solution was 5,000:1 to 5,000:5.

By varying the amount of platinum in the alloy, several peaks (phases of In–Pt) appear associated with the electro-oxidation of indium from these alloys.

When the In(III) and Pt(IV) contents of solution varies, the individual peak currents (and charges underneath) of the individual intermetallic phases also vary, but the peak potentials of these peaks remain constant. This is a strong indication of the invariant composition of these intermetallic phases (constancy of composition).

It can be expected that the electrochemical oxidation of indium from different Pt–In phases (intermetallic compounds) will occur at anodic peaks at different potentials. According to the literature data [4, 5], indium and platinum form the following intermetallic phases:  $\text{Pt}_3\text{In}$ ,  $\text{Pt}_2\text{In}$ ,  $\text{Pt}_3\text{In}_2$ ,  $\text{PtIn}_2$ ,  $\text{PtIn}$ ,

**Fig. 1** Voltammograms of electrochemical oxidation of the indium–platinum alloys. Experiment conditions:  $1 \text{ mol l}^{-1}$  hydrochloride solution deposition time  $t_c=100$  s, scan rate  $v=80 \text{ mV s}^{-1}$ : *a* anodic stripping voltammogram of a pure In solution ( $5,000 \text{ mg l}^{-1}$ ), *b* anodic stripping voltammogram recorded after first addition of platinum (i.e.,  $5,000 \text{ mg l}^{-1}$  In (III),  $1 \text{ mg l}^{-1}$  Pt(IV)), *c* after second addition of platinum ( $3 \text{ mg l}^{-1}$ ), *d* after third addition of platinum ( $5 \text{ mg l}^{-1}$ )



**Table 1** Comparison of the calculated and experimentally determined values of the potentials of the peaks of selective indium electro-oxidation from IMC containing platinum

Potential of an anodic peak of indium	Composition of IMC							
	Pt <sub>3</sub> In, <i>X<sub>i</sub></i> =0.25	Pt <sub>2</sub> In <i>X<sub>i</sub></i> =0.33	Pt <sub>3</sub> In <sub>2</sub> <i>X<sub>i</sub></i> =0.4	PtIn <i>X<sub>i</sub></i> =0.5	Pt <sub>13</sub> In <sub>9</sub> <i>X<sub>i</sub></i> =0.59	Pt <sub>2</sub> In <sub>3</sub> <i>X<sub>i</sub></i> =0.6	PtIn <sub>2</sub> <i>X<sub>i</sub></i> =0.67	Pt <sub>3</sub> In <sub>7</sub> <i>X<sub>i</sub></i> =0.7
<i>E<sub>calc</sub></i> , V	-0.32	-0.26	-0.2	-0.15	-0.199	-0.093	-0.063	-0.053
<i>E<sub>exp</sub></i> , V	No	-0.23	-0.215	-0.148	No	No	-0.076	-0.043

Pt<sub>2</sub>In<sub>3</sub>, Pt<sub>13</sub>In<sub>9</sub>, Pt<sub>3</sub>In<sub>7</sub>. The total charge consumed per mole indium should remain constant for all these phases.

It has been shown earlier [6] that the peak potential shift for the electrochemical oxidation of the less noble component of intermetallic phases can be described by a general equation, which can be written in the special case of In–Pt as follows:

$$\Delta E_{\text{paIn}} = E_{\text{paIn}} - E_{\text{paIn}}^m = \frac{RT}{zF} \ln X_{\text{In}} - \frac{(1 - X_{\text{In}})}{zF} \varepsilon_m, \quad (1)$$

where  $\Delta E_{\text{paIn}}$  is the anodic peak potential of pure indium (-0.75 V);

$E_{\text{paIn}}^m$  is the anodic peak potential of oxidation of indium from the In–Pt alloys

$\varepsilon_m$  is the integral mixing heat of the compounds forming the intermetallic phases

$X_{\text{In}}$  is a mole fraction of In.

The mixing heats of alloy formation can be approximately calculated from the energies of formation of covalent bonds between the metals using Pauling’s correlation equation [6]:

$$\varepsilon_m = \frac{1}{2} (\varepsilon_{\text{A-A}} + \varepsilon_{\text{B-B}}) + 100(\chi_{\text{A}} - \chi_{\text{B}})^2 - 6,5(\chi_{\text{A}} - \chi_{\text{B}})^4, \quad (2)$$

where  $\varepsilon_{\text{A-A}}$ ,  $\varepsilon_{\text{B-B}}$  are the energies of formation of the metallic bonds between A and B atoms, respectively;  $\chi_{\text{A}}$ ,  $\chi_{\text{B}}$  are the electronegativities of the alloy components. The energy of the formation of metallic bonds and the electronegativity values of elements are taken from the published data [7, 8]. The mixing heat of indium and platinum calculated from these data is 140.189 kJ mol<sup>-1</sup>. To calculate the energy of mixing the partial energies of formation of the metallic bonds  $\varepsilon_{\text{In-In}} = 103.81$  kJ mol<sup>-1</sup>,  $\varepsilon_{\text{Pt-Pt}} = 164.04$  kJ mol<sup>-1</sup>, and the electronegativities of metals were used.

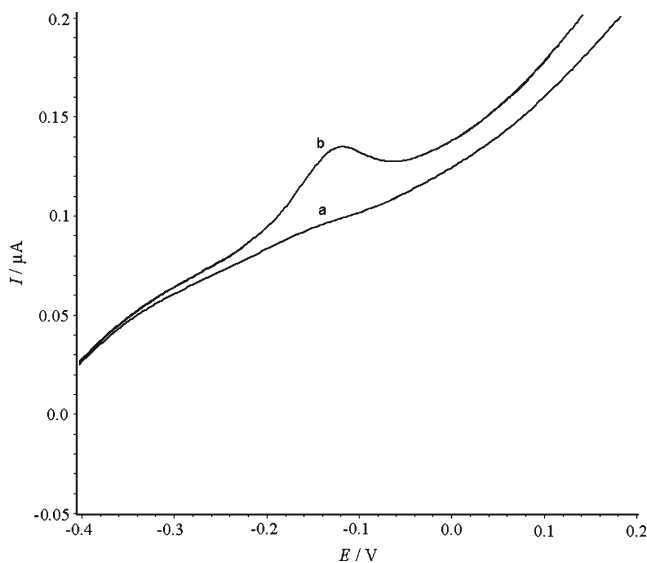
With the help of Eqs. 1 and 2, one can calculate the peak potentials of indium oxidation from the different intermetallic phases and one can compare these data with the experimentally obtained data: Table 1 shows the comparison.

Since it is inconvenient to determine the Pt(IV) content of solutions by evaluation of several peaks in one voltammogram, a condition had to be found for which only one peak occurs: as Fig. 2 proves this is a ratio of In(III)/Pt(IV)=10,000:1.

Figure 2 shows that the peak potential of indium oxidation is -0.14 V, indicating that the composition of the intermetallic phase is PtIn. This peak is useful for the determination of platinum ions in solutions by stripping voltammetry.

**Conclusion**

The results presented here show that it is possible to determine Pt(IV) in solutions by recording the anodic stripping voltammograms of indium oxidation when the In–Pt alloy phase is deposited from appropriate solutions. The method is applicable for the analysis of ores of different composition (sulfide ores, polymetallic ores, etc.)



**Fig. 2** Voltammogram of electrochemical oxidation of indium from an indium–platinum alloy: *a* is a background curve (1 mol l<sup>-1</sup> hydrochloride solution), *b* anodic stripping voltammogram of indium from a In–Pt alloy, when the solution contained In/Pt=50,000: 1. The absolute concentrations were: 0.44 mol l<sup>-1</sup> In(III), 5.1 μmol l<sup>-1</sup> Pt(IV)

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