USE OF ANODIC STRIPPING VOLTAMMETRY FOR DETERMINATION OF ANTIMONY IN SOILS

ZASTOSOWANIE WOLTAMPEROMETRII ANODOWEJ DO OZNACZANIA ANTYMONU W GLEBACH

Summary: Conditions of determination of antimony(V) using anodic stripping voltammetry with differential pulse technique and hanging mercury drop electrode have been analyzed. Antimony was extracted from soils with HCl+HNO₃ mixture (3:1). Deposition time was 15÷30 s, deposition potential –0.5 V and supporting electrolyte 3 M HCl. In the above conditions Sb(V) peak height vs its concentration dependence is linear up to 7·10⁻⁵ M antimony. The accuracy and precision of the proposed method is also satisfactory. The relative standard deviation for 1.5·10⁻⁷ M Sb(V) equals 7.5% and for 4·10⁻⁷ M Sb(V) equals 14.3%). The method has been applied to study the degree of contamination of soils in the vicinity of Huta Głogów copper smelter with antimony.

Keywords: antimony, anodic stripping voltammetry, soil samples

The development of the metallurgic industry causes a continuous increase in the concentration of antimony in natural environment. It is used in anticorrosion alloys as well as in the production of car batteries, paints and enamels. Significant emission of antimony is also caused in copper processing. Since antimony belongs to those elements which are characterized by good phytoassimilation, its concentration in soil should be controlled [1].

Stripping voltammetry is one of the more sensitive methods used in trace analysis. It has also some advantages comparing to classical methods (eg spectrometric) because cost of the equipment used in electroanalytical methods is relatively low. Antimony determination is usually made using adsorptive stripping voltammetry (AdSV) [2-6] and by differential pulse anodic stripping voltammetry (DPASV) [6-18]. As can be seen from this literature DPASV method is more sensitive comparing with AdSV.

The aim of the present paper is to:
- determine optimal conditions for antimony(V) determination using hanging mercury drop electrode (HMDE) and differential pulse anodic stripping voltammetry (DPASV),
- antimony determination in soil samples from the area under direct Huta Głogów Smeltery as well as a Kórnik reference area.

Experimental

Reagents

Nitric(V) acid, hydrochloric acid ("Suprapur", Merck), hydrogen peroxide (POCh, Poland). Standard solution of Sb(V) (1 g·dm⁻³) was prepared by dissolving the appropriate amount of K[Sb(OH)₄] in water. Solutions with concentrations below 10⁻³ M were prepared just before use. Water was doubly distilled in quartz still.

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Voltammetric measurements were carried out using a µAUTOLAB analyzer (ECO CHEMIE, Netherlands). A hanging mercury drop electrode (HMDE), having the surface of 3 mm\(^2\), produced by Laboratorní Přístroje (Czech Republic), was the working electrode, KCl saturated calomel electrode (SCE), produced by Radiometer (Denmark), was the reference electrode, and Pt wire served as the counter electrode.

Soil samples were taken from the top layer of soil from 0 to 20 cm. The soil was dried then homogenized and sieved through a mesh of 1 mm pore size. Samples of about 2.5 g each were treated with aqua regia (9 cm\(^3\) HCl + 3 cm\(^3\) HNO\(_3\)) and heated for 2 h [18]. The hot extract was filtered, and at the end of evaporation, 30% H\(_2\)O\(_2\) was added to mineralize organic compounds contained in the sample. The precipitated sediment was dissolved when hot in several drops of concentrated HCl solution. Solution was transferred to a measuring flask and made up with water to 25 cm\(^3\).

From the extract a proper amount was taken to keep Sb(V) concentrations between 5\(\times\)10\(^{-8}\) and 2\(\times\)10\(^{-7}\) M. The residue was diluted in 3 M HCl.

20 cm\(^3\) of solution was transferred into a measuring vessel. After deaeration of the solution with purified nitrogen the antimony was deposited on the surface of electrode for 15 to 30 s (depending on the expected antimony content) at –0.50 V in stirred solution. 5 s after the stirrer was stopped the voltammetric anodic curves were recorded within the potential range from –0.35 to –0.125 V. This cycle was repeated thrice. Sb(V) concentrations were determined using triple standard addition.

DPASV method can be used for quantitation of antimony in +3 as well as +5 oxidation state but under conditions for determining Sb(III) compounds antimonates are electrochemically inactive [7, 9, 14-18]. As antimony from soil samples extracted with aqua regia form antimonates in the present work a method for Sb(V) determination has been developed.

As can be found in the literature electroreduction of Sb(V) should be performed in a strongly acidic solution. In the present paper use of HCl solutions for this purpose was examined (Fig. 1). Diagram shows that an increase in HCl concentration causes significant increase in Sb(V) peak current. Choice of the base electrolyte concentration was made taking into account toxicity of concentrated HCl solutions and 3 M HCl was found optimal for further research. At this concentration satisfying results were already obtained.

Using literature and present examination results optimal conditions for Sb(V) determination have been found:

- The base electrolyte: 3 M HCl
- Deposition potential –0.5 V
- Initial potential –0.35 V
- End potential –0.125 V
- Deposition time 15÷30 s
- Amount of the soil extract added: 0.2 to 0.4 cm\(^3\).
In the above conditions Sb(V) peak height vs its concentration dependence in the presence of 0.4 cm³ of soil extract is linear up to $7 \cdot 10^{-5}$ M Sb(V).

![Graph showing the dependence of the peak current for Sb(V) on the HCl concentration. Sb concentration $5 \cdot 10^{-7}$ M. Deposition potential –0.5 V. Deposition time 15 s](image)

Experiments show, that Cu(II) produced peak near that of Sb(V) under the described conditions. Cu interference was examined in the previous papers [10, 12]. Depending on Cu concentration these interferences were removed using ion exchange chromatography [12] or by shifting start potential towards more positive value [10]. In the present paper effectiveness of the second approach was analyzed. The procedure consisted of electrochemical preconcentration at –0.5 V and then potential being shifted to –0.35 V. This method preserved the height of antimony peak even at $1 \cdot 10^{-5}$ M Cu(II).

The developed method was statistically evaluated by estimating the precision and recovery antimony determined in the presence of soil extracts from Kórnik area (Table 1). The recovery of added metal was very good and the precision was satisfactory (the relative standard deviation for $1.5 \cdot 10^{-7}$ M Sb(V) equals 7.5% and for $4.0 \cdot 10^{-7}$ M Sb(V) equals 14.3%).

**Table 1**
Recovery and precision of the determination of Sb(V) in the analytical procedure

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>I</td>
<td>$1.5 \cdot 10^{-7}$</td>
<td>$1.47 \cdot 10^{-7}$</td>
<td>98</td>
<td>$1.1 \cdot 10^{-8}$</td>
<td>7.5</td>
</tr>
<tr>
<td>II</td>
<td>$4.0 \cdot 10^{-7}$</td>
<td>$3.81 \cdot 10^{-7}$</td>
<td>95</td>
<td>$5.43 \cdot 10^{-8}$</td>
<td>14.3</td>
</tr>
</tbody>
</table>

**Table 2**
Antimony content in soil samples

<table>
<thead>
<tr>
<th>Sampling regions</th>
<th>Research area</th>
<th>Sb(V) content [μg g⁻¹]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper mining area</td>
<td>20 m south of Huta Głogów copper smelter</td>
<td>15.9</td>
</tr>
<tr>
<td>300 m south of Huta Głogów copper smelter</td>
<td>10.9</td>
<td></td>
</tr>
<tr>
<td>600 m north of Huta Głogów copper smelter</td>
<td>14.5</td>
<td></td>
</tr>
<tr>
<td>800 m north of Huta Głogów copper smelter</td>
<td>5.8</td>
<td></td>
</tr>
<tr>
<td>3000 m north of Huta Głogów copper smelter</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>Kórnik (reference area)</td>
<td>Experimental Forest Zwierzyniec</td>
<td>2.6</td>
</tr>
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</table>
The method has been applied to study the degree of contamination of soils in the vicinity of Huta Głogów copper smelter with antimony (Table 2).

Average antimony content in unpolluted soils is 0.3–0.8 µg/g getting higher in soils containing more organics. However, antimony accompanies non-ferrous metals deposits. Processing of these deposits can increase antimony content up as much as to 200 µg/g [1]. Results show that soil from the copper basin is highly polluted with antimony.

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References


ZASTOSOWANIE WOLTAMPEROMETRIII ANODOWEJ DO OZNACZANIA ANTYMONU W GLEBACH

Streszczenie: W pracy opracowano metodikę oznaczania Sb(V) w ekstraktach glebowych, wykorzystując w tym celu woltamperometrię anodową. Antymon z gleb ekstrahowano mieszaniną HCl+HNO₃ (3:1). Pomiary dokonano w technice różnicowej pulsowej, stosując wiszącą ręczową kropelową elektrodę. Elektrolitem podstawowym był 3 mol·dm⁻³ HCl. Czas zatęśania wynosił 15÷30 s, potencjał zatęśania −0,5 V wzgl. NEK. W tych warunkach krzywa kalibracji ma przebieg prostoliniowy aż do 7·10⁻⁶ mol·dm⁻³ Sb(V). Dokładność i precyzja opracowanej metodyki są zadowalające (względne odchylenie standardowe dla 1,5·10⁻⁷ mol·dm⁻³ Sb(V) wynosi 7,5%, dla 4,0·10⁻⁷ mol·dm⁻³ Sb(V) 14,3%). Opracowaną metodykę wykorzystano do oceny stopnia zanieczyszczenia antymonem terenów usytuowanych w zagłębiu miedziowym w pobliżu Huty Głogów.

Słowa kluczowe: antymon, anodowa woltamperometria, próbki gleb