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## Short Communication

# Determination of Thallium at A Silver-Gold Alloy Electrode by Voltammetric Methods in Plant Material and Bottom Sediment Containing Cd and Pb

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## Abstract

The applicability of the subtractive anodic stripping voltammetry (SASV) using the square-wave mode at the silver-gold alloy electrode has been studied for thallium determination in the presence of large amount of lead and cadmium in natural samples. 10 mmol L<sup>-1</sup> perchloric acid was found as the most suitable supporting electrolyte for determination in synthetic solutions. The thallium peak was separated about 200 mV from Cd + Pb peak. Diethylenetriaminepentaacetic acid addition was necessary to determine thallium at the silver-gold alloy electrode in digested plant and sediment. The determination limit was equal to 1.4 µg L<sup>-1</sup>. The method was validated by the inter-method comparison (ICP-MS).

**Keywords:** Thallium, Silver-gold electrode, Subtractive anodic stripping voltammetry, Plant and sediments, DTPA

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During our previous study [1, 2], differential pulse anodic stripping voltammetry for Tl determination in the presence of Pb and Cd was established and the method was applied for samples of sewage waters, plants and bottom sediments collected near "Bolesław" Zn-Pb smelter. Voltammetric determinations of Tl were successfully carried out using HMDE in supporting electrolyte containing diethylenetriaminepentaacetic acid (DTPA) and acetate ions [1]. Toxicity of mercury caused that the use of non mercury electrodes is very attractive for environments purpose. Several solid electrodes were shown to be useful for such determinations: silver [3] and gold electrode [4], bismuth-coated carbon electrodes [5], silver-coated electrode [4, 6]. Based on undertaken studies, Bonfil et al. [4,6,7] concluded that the silver-gold alloy (50:50) seemed to be the most suitable solid electrode for the quantitative determination of thallium in the presence of lead and cadmium. The signal of Tl recorded in supporting electrolyte containing 10 mmol L<sup>-1</sup> HNO<sub>3</sub> and 10 mmol L<sup>-1</sup> NaCl was well-defined and appeared at a distance of 200 mV from those of the two other elements. Peaks of Cd and Pb overlapped. Subtractive anodic stripping voltammetry (SASV) in the square-wave (SW) mode at a silver-gold electrode without removal of oxygen has been used to thallium determination in synthetic solution [7]. In the presented work, the Ag-Au alloy electrode has been applied for Tl determination in bottom sediment and plant material collected from polluted region of Poland. The sampling area bellows to the region of the highest heavy metals concentration. The thallium concentration in biotopes reaches even mg kg<sup>-1</sup> level [1, 2]. It is shown that

SASV in SW mode using a silver-gold alloy electrode without removal of oxygen (0.02 mol L<sup>-1</sup> DTPA and 0.024 mol L<sup>-1</sup> NaAc adjusted to pH 5.5) is suitable for quantification of the total amount of thallium in plant material and bottom sediment samples collected in the thallium polluted region. However, the determination using SASV method could only be performed when the Tl concentration is equal or higher than 1.4 µg L<sup>-1</sup> and the excess of interfering ions is not higher than 1000-fold for Pb and 450-fold for Cd. It should be also noted that prior analysis, samples after digestion with nitric acid had to be evaporated till nearly dry residue as interferences from nitric ions are observed.

During the first step of experiments, studies in synthetic solutions were performed. Experiments carried out in 10 mmol L<sup>-1</sup> HNO<sub>3</sub> and 10 mmol L<sup>-1</sup> NaCl solution containing similar concentration of Tl, Cd and Pb showed that Tl peak appeared in more negative potential, about 200 mV than overlapped signals of Cd and Pb (Cd + Pb). But we have found that 2-times higher concentration of Cd than Tl interferes its signal due to nitrate reduction catalyzed by Cd adatoms. That is in accordance with Bonfil et al. [7] who suggested that 10 mmol L<sup>-1</sup> HCl solution is better for Tl determination than nitric acid. Due to that, HNO<sub>3</sub> was replaced by hydrochloric acid. Recorded Tl and Cd + Pb peaks were well defined and separated ( $\Delta E = 200$  mV), when the concentration of metals were similar. Further addition of Cd caused the increase height of peak at potential -200 mV and also the decrease of Tl peak recorded in slightly more positive potential. But it should

Table 1. Results of Tl, Pb, and Cd determination in the studied samples. The data are presented as mean  $\pm$  SD ( $n=3$ ) in  $\text{mg kg}^{-1}$  d.m.

Sample	SASV	ICP-MS		
	Tl	Tl	Pb	Cd
Moss	$2.85 \pm 0.15$	$2.62 \pm 0.07$	$4030 \pm 105$	$92 \pm 2$
Bottom sediment	$15.1 \pm 1.0$	$14.1 \pm 1.8$	$5070 \pm 257$	$110 \pm 3$

be noted that the real samples contain at least 40-times more Cd than Tl (Table 1). The application of  $10 \text{ mmol L}^{-1} \text{HClO}_4$  was also investigated as supporting electrolyte. This acid does not contain complexing ions. Tl and Cd + Pb peaks were also separated about 200 mV, till concentration of interfering metals was not more than the thallium one. While Cd and Pb content was higher than Tl, the overlapping of those peaks was observed. In  $\text{HClO}_4$  solution the sensitivity of proposed method was slightly better than in nitric or hydrochloric acids solution. Unfortunately, the voltammogram recorded for moss sample was not suitable for analytical purpose. The signal represented the sum of Tl, Cd and Pb oxidation currents. So, in the next step of experiments, the voltammetry determination with addition of DTPA as a complexing agent, at the Ag-Au alloy electrodes was performed. DTPA forms very stable complexes with  $\text{Me}^{2+}$  ions and their stability constants are fifteen orders of magnitude greater than the one of  $\text{Tl}^+$  complex [8]. The applied supporting electrolyte contained  $0.02 \text{ mol L}^{-1}$  DTPA. The used concentration of complexing agent was high enough to guarantee molar excess of ligand [1, 2]. As pH plays a crucial role in metal complexation, shape and height

of Tl peak were tested within pH range 4.5 and 6.5. Our investigations have proved that the pH should be adjusted to the values  $5.5 \pm 0.2$ . Also it was found that prior analysis, samples after wet decomposition with nitric acids had to be evaporated till nearly dryness. Additionally the deposition potential within range  $-600 \text{ mV}$  and  $-1100 \text{ mV}$  and the deposition time within range 60 s and 600 s were examined. The most suitable conditions for Tl ( $10 \mu\text{g Tl L}^{-1}$ ) determination were as follows: deposition potential:  $-800 \text{ mV}$ , deposition time: 250–400 s. The signal of Tl oxidation was observed at  $-460 \text{ mV}$ . The typical voltammogram recorded for moss sample is presented on Figure 1. The quantitative determination was done by double standard addition method, the plots were recorded twice. Our previous study indicated that Cd could strongly interfere the Tl determination [1]. Therefore the effect of interfering ions on Tl signals was investigated, the Cd:Tl and Pb:Tl ratios ranging from 400:1 to 1200:1 were tested. These ratios represent the predictable relations between amount of Cd, Pb and Tl in analyzed samples. According to the results of the significance test, the current of Tl measured at the Pb – to – Tl ratio equal to 1100:1 and at the Cd to Tl ratio equal to 470:1 differed significantly from that obtained in absence of Pb and Cd ( $P=95\%$ ,  $n-1=3$   $t_{\text{crit}}=2.78$ ,  $t_{\text{exp(Pb)}}=2.98$ ,  $t_{\text{exp(Cd)}}=2.91$ ). Detection and determination limits for Tl were estimated from the calibration plot prepared for five independent thallium determinations in the concentration within range 0.2 and  $1 \text{ ng mL}^{-1}$ . Detection and determination limits were defined as 3- and 10-times the standard deviation of the calibration plot intersection with the X-axis, respectively. They amounted to 0.6 and  $1.4 \mu\text{g L}^{-1}$ , respectively. In order to verify the electrochemically ob-

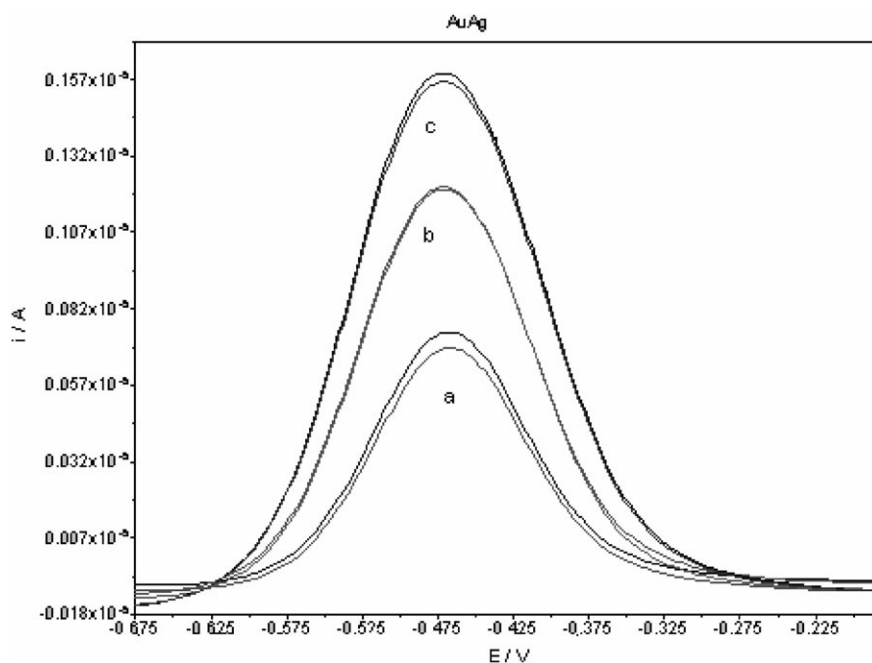


Fig. 1. Determination of Tl in moss sample by the method of standard additions: the plot a) for sample, the plot b) for 20 ng of Tl addition, and the plot c) for 40 ng of Tl addition. Supporting electrolyte:  $0.02 \text{ mol L}^{-1}$  DTPA and  $0.024 \text{ mol L}^{-1}$  acetate buffer pH 5.5. Conditions: deposition potential of:  $-0.8 \text{ V}$ , deposition time: 300 s, SW amplitude: 10 mV, step potential: 2.5 mV, frequency: 25 Hz.

tained results, Cd, Pb and Tl were also determined by ICP-MS method (Tab. 1). Both series of data were averaged and compared by subjecting them to the two-tailed significance *t*-test ( $P = 95\%$ ,  $n - 1 = 3$ ,  $t_{\text{crit}} = 2.78$ ). Both sets of results did not differ significantly ( $0.84 < t_{\text{exp}} < 2.40$ ).

During our studies we have found that the purity of alloy Ag-Au used as electrode material plays a crucial role. One of the prepared electrodes incidentally contained 11% of copper in others Cu content was less than 0.1%. Applicability of such Ag-Au-Cu electrode was also checked. During experiment it was found that higher amount of Cu in electrode materials causes higher determination limit for Tl and the overlapping of Tl, Cd and Pb signals was observed for lower concentration of the interfering ions.

### Experimental

The moss (*Entodon schreberi*) and bottom sediment samples were collected in summer 2004. The plant material was washed with DI water and dried in open air at 50 °C in a laboratory dryer. Then ground in agate balls mill. The sediment sample was dried in open air over 24 h and then in a laboratory dryer at 50 °C over 7 hours. After grounding in laboratory mill (Fritsch, Germany) the samples were digested in microwave system Paar Physica (Germany). The pressure microwave assisted decomposition with a mixture of hydrochloric, nitric and hydrofluoric acids heated inside a Teflon vessel was chosen, previously applied for sediment digestion before Pb and Tl determination [2]. For measurements  $\mu$ Autolab II (Eco-Chemie, BV, Netherlands) with an electrode system: 663 VA Stand (with 3 mol L<sup>-1</sup> Ag/AgCl as a reference electrode) (Metrohm, Switzerland) and Coupled Plasma Mass Spectrometer SCIEX "Elan 6100 DRC" Perkin Elmer (USA) were used. Scanning electron microscope (Zeiss, type LEO 435 VP) combined with an energy-dispersive spectrometer (Röntec, type M1, Germany) for electrode characterization (the elemental composition of the alloys) was used. The following reagents were used: 68% HNO<sub>3</sub> ( $d = 1.42$  g mL<sup>-1</sup>), 70% HClO<sub>4</sub> ( $d = 1.67$  g mL<sup>-1</sup>) 30% HCl ( $d = 1.15$  g mL<sup>-1</sup>) Ultranal (Chemian, Poland), NaCl (58.44 g mol<sup>-1</sup>) Suprapur (Merck), NaAc ( $M = 82.03$  g mol<sup>-1</sup>), 30% NaOH ( $d = 1.33$  g mL<sup>-1</sup>), 96% HAc ( $d = 1.06$  g mL<sup>-1</sup>) Suprapur (Merck), diethylenetriaminopentaacetic acid – DTPA ( $M = 393.35$  g mol<sup>-1</sup>) pro analysis (Merck). The Merck standards of the metal concentration 1 g L<sup>-1</sup> were diluted to obtain appropriate concentration for standard solutions of Cd, Tl and Pb employed in the experiments. All solutions were prepared

using deionized water from Milli-Q-Water-System (Millipore, USA).

SASV determinations in the SW mode carried out with or without subtraction of blank current (recorded at 0 s deposition time) were done. The following experimental parameters were set: wave amplitude: 10 mV, step potential: 2.5 mV, frequency: 25 Hz, deposition potential:  $-0.80$  V (versus Ag/AgCl) and deposition time in the range of 150–450 s. The solution was stirred during deposition step. The working electrode was prepared by melting exactly weighed quantities of silver and gold in a quartz tube, than the alloy cylinder was formed ( $\varnothing 3$  mm). A freshly prepared electrode was polished. A 10 mL quartz crucible was used as a cell equipped with a three-electrode configuration: working electrode-Ag-Au (50:50); counter-Pt and reference-Ag/AgCl electrode. It was stated that analysis could be performed without removal of oxygen. To control the quality of obtained electrochemical results, inter-method comparison was applied. The measurements of Tl, Cd and Pb by ICP-MS were performed applying the following experimental parameters: sweep 5; number of replicates 5; dwell time: 0.1 s; ICP RF power: 1100 W; lens voltage: 12 V; nebulizer gas flow: 0.95 L min<sup>-1</sup>; plasma gas flow: 13.3 L min<sup>-1</sup>; and monitored isotopes: Cd 114, Pb 206 and Tl 203. Quantitative Analysis program was used to automatically correct the intensities of interfering isobaric and molecular ions.

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