

## Anodic Stripping Determination of Lead and Thallium at a Bismuth Film Electrode After Extraction of the Respective Bromide Complexes into Propylene Carbonate

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**Abstract:** In this contribution, anodic stripping voltammetric determination of lead(II) and thallium(III) in organic solvent; namely, propylene carbonate, is reported concerning a bismuth film electrode (BiFE) as the working electrode of choice. The corresponding measurements were performed directly in organic phase after gas-stirred liquid-liquid extraction from hydrochloric acid-based solution, confirming the enhancement in both sensitivity and selectivity of metal determination when employing the methods used some decades ago and combining extraction with polarographic principles. The metals of interest were determined either separately or simultaneously and for the detection of lead(II), the comparison between *in-situ* and *ex-situ* operated BIFEs had also been made and the respective differences discussed.

**Keywords:** Anodic stripping voltammetry; Bismuth film electrode; Organic solvent; Liquid-liquid extraction; Lead(II), Thallium(III).

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## Introduction

Bismuth, as environmentally less harmful element, was discovered for electrochemical stripping analysis (ESA) in a form of bismuth film electrodes (BiFEs) already more than a decade ago [1], having been soon recognized as the most promising alternative to mercury electrodes in ESA [2-4]. Typical use of BiFEs is mainly connected with the detection of heavy metals under conditions of anodic or adsorptive stripping measurement in aqueous media. So far, the electrochemical detection in non-aqueous solution was not often studied except two recent attempts of using ionic liquid [5] and propylene carbonate [6].

Nevertheless, the application of organic solvents can resolve some difficulties in selectivity often observed in aqueous media and enhance the sensitivity of metal determination as it was shown some decades ago by several effective combinations of extraction with polarographic analysis [7]. There the target metals were extracted in the form of complexes (*via* liquid-liquid extraction process) from water phase to organic phase. Then after establishing of equilibrium and separation of both phases, the metals could be directly detected in organic phase without the need of re-extraction. The undesirable slowness of common solvent extraction steps can be simplified by purging nitrogen through both phases that carries out the deoxygenation of the solution prior to analysis as well [8,9].

In this article, anodic stripping voltammetric analysis is proposed concerning the determination of Pb(II) and Tl(III) in propylene carbonate using BiFEs. The metal ions of interest originally present in aqueous phase were transferred using gas-stirred liquid-liquid extraction into organic phase (propylene carbonate) in the form of the respective bromide complexes and, then, directly determined by differential pulse anodic stripping voltammetry. This study extends the previously invented procedure with the employment of constant current stripping chronopotentiometry as the technique of choice for the determination of Pb(II) after extracting its bromide complex into propylene carbonate [6].

## Experimental

### *Chemicals, Reagents, and Solutions*

All chemicals and reagents were of analytical grade and purchased from *TCI - Tokyo Chemical Industry Co.* or *Wako Pure Chemical Industries* (both Japan). All solutions were prepared from deionized and/or distilled water; the special mixtures of water with organic solvent being specified below.

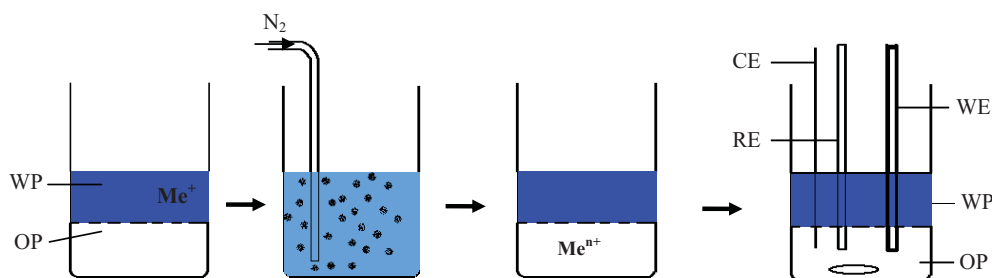
## Instrumentation

Voltammetric analyzer Model P-1000 (*Yanaco*, Japan) controlled by VoltamRec software was employed for all differential pulse stripping voltammetric measurements. A three-electrode configuration with Ag/AgCl (3M KCl) reference and a Pt-wire auxiliary electrode was used throughout the work. A plastic formed carbon disc [(PFC) *BAS*, Japan] served as the working electrode, which was additionally plated *in-situ* or *ex-situ* with a bismuth film. Extraction and subsequent electrochemical measurements were performed in a one-compartment glass cell. Whenever need, stirring was accomplished with a magnetic bar (6×2 mm) agitated at approx. 300 rpm.

## Procedures

**Preparation of Working Electrode.** Prior to electrochemical measurements, the PFC working electrode was cleaned daily by polishing with alumina slurry and then rinsed with water. Such a treated electrode was used as a substrate for plating the bismuth film either *in situ*, simply by addition of Bi(III) ions to the water phase, or *ex-situ* from external solution (0.1 M KBr + 100 ppm Bi(III)) by applying the potential of -400 mV for 120 s.

**Extraction Process.** Water phase of 2 mL consisted of 0.05 M HCl, 0.5 M KBr, the target metal ion (Pb(II) and/or Tl(III)) and in the case of *in-situ* plated BiFE also Bi(III) ions, usually 500ppb. Organic phase of 2 mL was made of propylene carbonate (PC) and 0.2 M tetrabutylammonium bromide (TBAB). The extraction was performed by purging of nitrogen through both phases for 60 s, which cause the formation of microemulsion of the two immiscible liquids, in order to extract the metal bromide complexes into the organic phase. This purging served also as oxygen removal prior to voltammetric measurements. After establishing of equilibrium between both phases, the electrochemical measurements in DPASV mode were carried out in organic phase. Whole extraction procedure with final electrodes arrangement is depicted in Fig. 1.



**Fig. 1:** The scheme of extraction procedure and the final electrode arrangement. Legend: WP – water phase, OP – organic phase, Me<sup>n+</sup> - metal cation, WE – working electrode, CE – counter electrode, RE – reference electrode.

**Differential Pulse Anodic Stripping Voltammetry (DPASV).** The preconcentration usually took place at a potential of  $-1000$  or  $-1100$  mV for 120 or 180 s (depending on the metal tested), followed by an equilibration for 20s. The detection (stripping) step was performed in the anodic direction by scanning from an initial potential,  $E_{\text{INT}} = E_{\text{DEP}}$ , to the final potential,  $E_{\text{FIN}}$ , differing according to the working electrode used (for *in-situ* plated BiFE, it was usually  $-50$  mV vs. ref., whereas for *ex-situ* plated BiFE, the respective value being  $-400$  mV). A scan rate,  $v = 20$  mV $\cdot$ s $^{-1}$ , the amplitude,  $\Delta E = 50$  mV, and the current range of  $5$   $\mu$ A $\cdot$ V $^{-1}$  then completed the instrumental parameters of choice for experimentation. When using the *ex-situ* plated BiFE, the electrochemical cleaning / regeneration at a potential of  $-450$  mV was carried out (for 30 s) before each measurement.

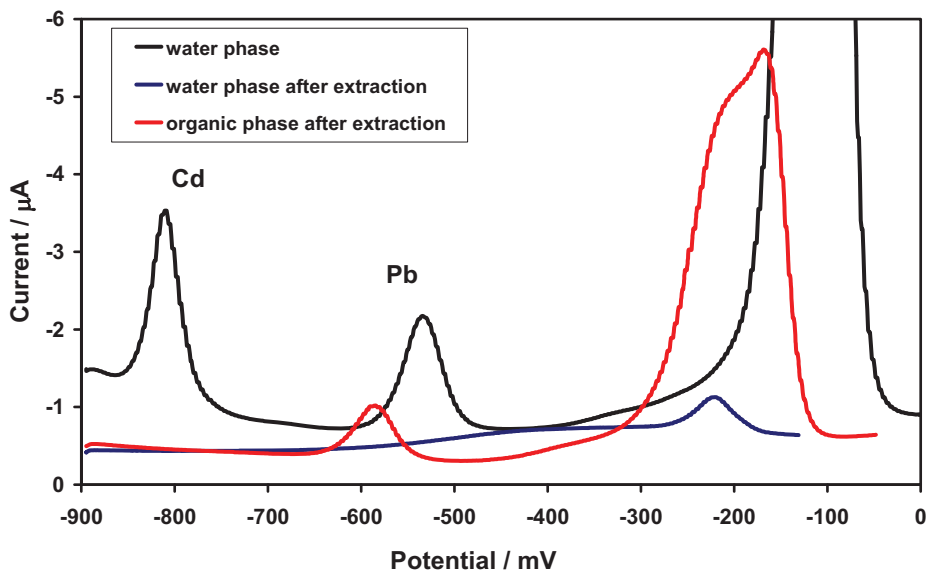
## Results and Discussion

### Determination of Lead(II) at *In-Situ* Plated BiFE

**Selectivity of Procedure via Proper Extraction Conditions.** The voltammetric behavior of lead in a form of lead(II) bromide complex, which was before extracted from water phase into propylene carbonate phase, was studied by differential pulse anodic stripping voltammetric method. Success of the extraction process relies on choosing the proper complexing agent. Some complexing agents can be used for more metals, some others are selective for certain metals or even specific for one metal. Using such an agent, the extraction into organic phase is almost specific toward the target metal.

An example of such a selective extraction is the simultaneous determination of cadmium and lead at *in-situ* plated BiFE shown in Fig. 2. In water phase, there were both metals presented in the voltammogram (black line), but after the extraction (blue line) using the agent tetrabutylammonium bromide both cadmium and lead disappeared meaning that both of them were extracted to organic phase. Only a small amount of Bi(III) left in a water phase because these ions were presented in excess and 60 s were possibly not enough to extract all ions. The red line in Fig. 2 depicts the determination in organic phase after the extraction, but only Pb(II) and Bi(III) ions are presented. This observation indicates that even if Cd(II) ions were extracted they do not form electroactive species in organic phase and therefore, they are not electrochemically detectable.

**Optimization of Key Operational Parameters.** We have optimized the deposition parameters, which influence either the formation of the bismuth film or the final stripping performance of the working electrode.



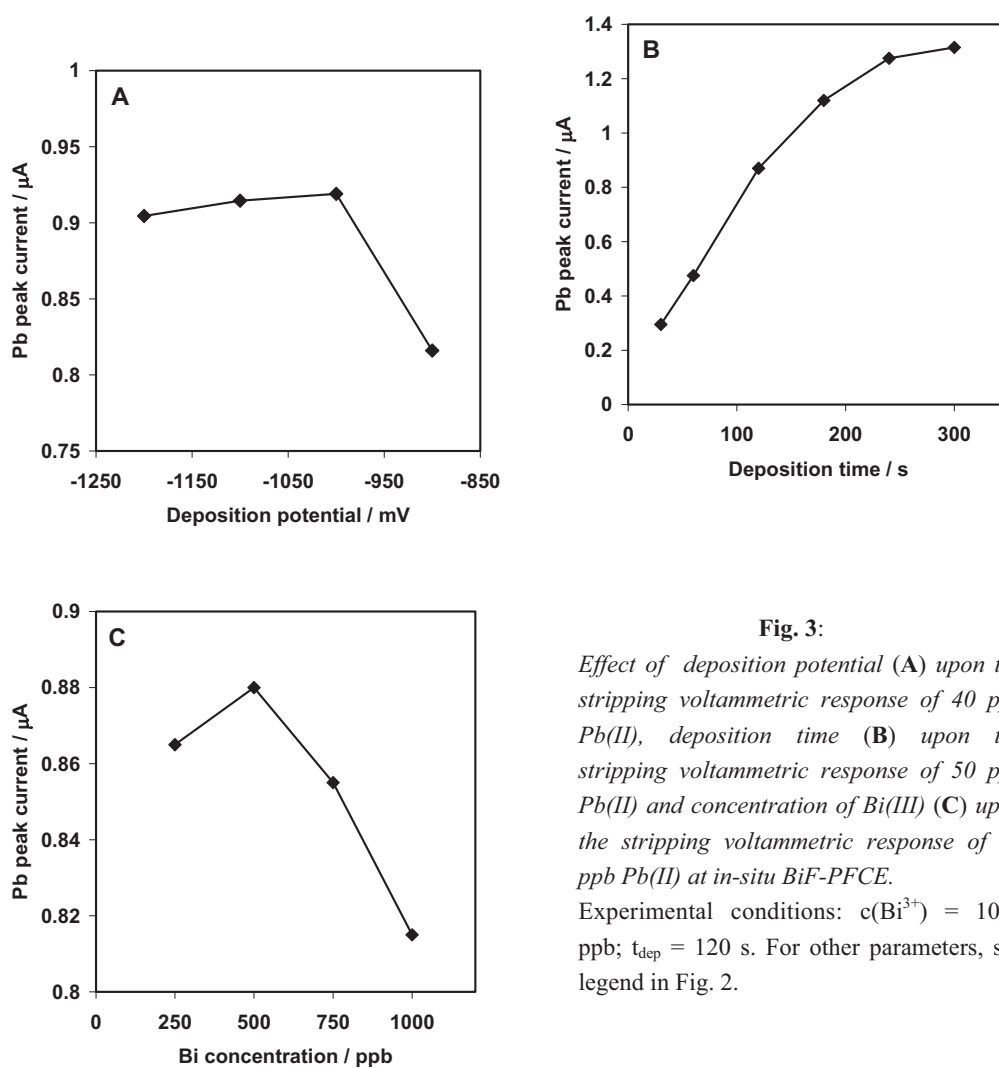
**Fig. 2:** Typical voltammograms obtained after selective extraction into polypropylene carbonate by detecting Cd(II) and Pb(II) at *in-situ* plated BiFE in (i) aqueous phase (0.05 M HCl + 0.5 M KBr; **black line**), (ii) aqueous phase after extraction (**blue line**), and (iii) organic phase (PC + 0.2 M TBAB) after extraction; **red line**). Experimental conditions: extraction time,  $t_{\text{EXT}} = 60$  s,  $c(\text{Bi}^{3+}) = 500$  ppb; deposition conditions,  $E_{\text{dep}} -1000$  mV,  $t_{\text{dep}} = 60$  s,  $t_{\text{eq}} = 20$  s; the current range:  $5 \mu\text{A}\cdot\text{V}^{-1}$ , pulse amplitude,  $\Delta E = 50$  mV, scan rate,  $v = 20$  mV/s.

The effect of the varying deposition potential on the stripping signal of lead was studied within the interval from  $-900$  to  $-1200$  mV as illustrated in Fig. 3A. The maximum peak-height was reached for the deposition potential of  $-1000$  mV. Fig. 3B shows the dependence of increasing deposition time upon the Pb-peak, with increasing deposition time the peak also increased but not linearly in the whole range tested (30 – 300 s). For higher times than 120 s it started to level off, *i.e.* to exhibit the attributes of saturation. Then, the deposition time of 120 s was chosen as optimum and used in further experiments. The third parameter under investigation was the concentration of Bi(III) ions for *in-situ* plating of the bismuth film onto the PFC substrate (Fig. 3C). In a tested range of 500 – 2000 ppb and later 250 – 1000 ppb the highest signal for Pb(II) was obtained for 500 ppb Bi.

**Calibration Curve, Reproducibility, and Limit of Detection.** With optimal operational parameters we continued our investigation of electroanalytical performance of *in-situ* plated BiFE in propylene carbonate with the examination of some analytical parameters.

As found out, the *in-situ* plated BiFE exhibited a fairly linear reoxidation current response for lead within the concentration interval from 10 to 100 ppb (see Fig. 4.), characterized with a very satisfactory correlation of  $R^2 = 0.995$ .

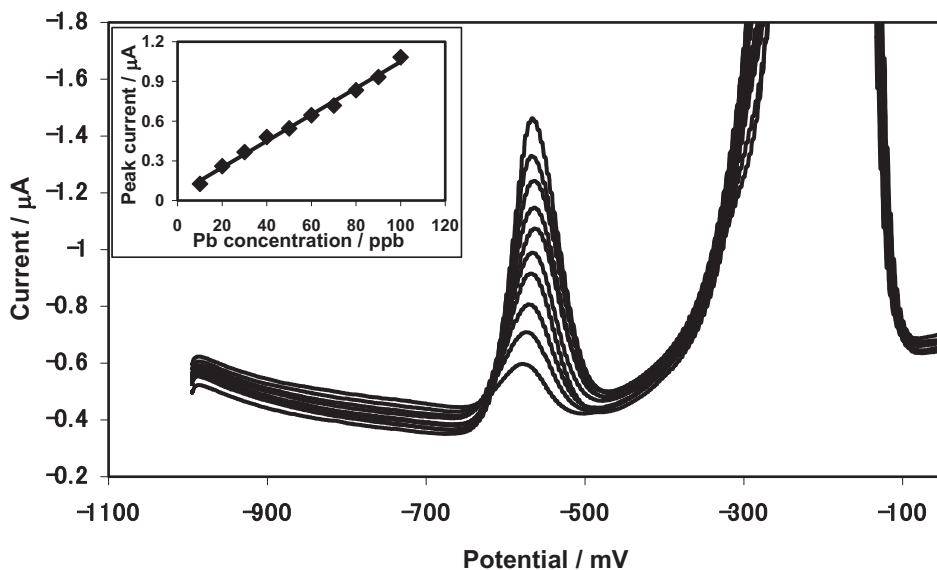
The limit of detection (LOD), estimated by means of the  $3\sigma$  criterion, was calculated to be about 1.1 ppb (when using the accumulation period for 120 s). Finally, eight replicates of typical measurements with a model concentration of 30 ppb Pb(II) have revealed good reproducibility, which could be expressed by means of the relative standard deviation,  $RSD = \pm 5.8\%$  (for  $n = 8$ ).



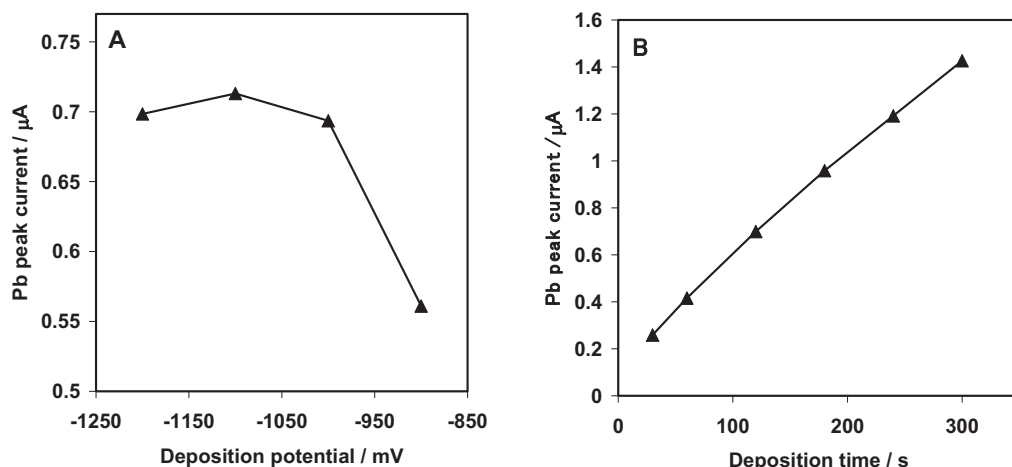
**Fig. 3:**

*Effect of deposition potential (A) upon the stripping voltammetric response of 40 ppb Pb(II), deposition time (B) upon the stripping voltammetric response of 50 ppb Pb(II) and concentration of Bi(III) (C) upon the stripping voltammetric response of 60 ppb Pb(II) at in-situ BiF-PFCE.*

Experimental conditions:  $c(\text{Bi}^{3+}) = 1000$  ppb;  $t_{\text{dep}} = 120$  s. For other parameters, see legend in Fig. 2.



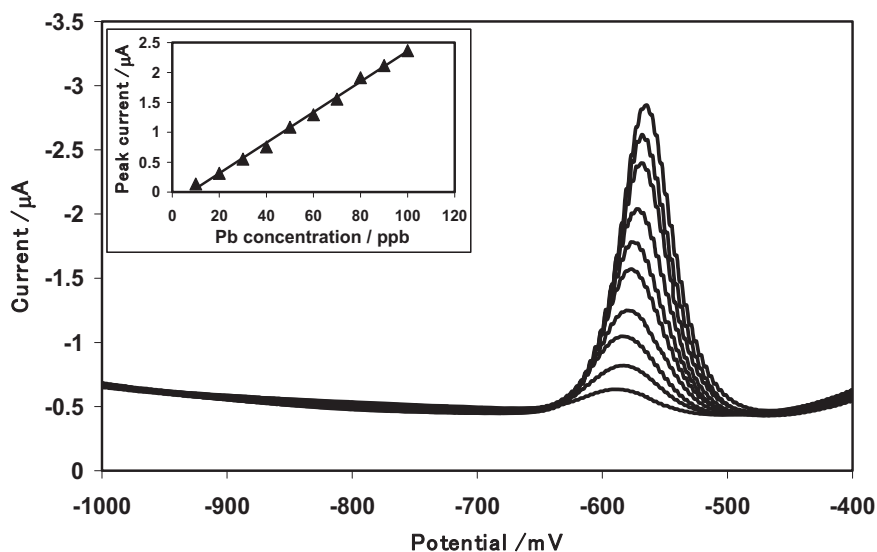
**Fig. 4:** Anodic stripping voltammograms for successive additions of Pb(II) in ten aliquots (10 ppb steps) obtained at the in-situ plated BiF-PFCE. The inset shows the corresponding calibration plot for concentration levels from 10 ppb up to 100 ppb. Experimental conditions:  $t_{\text{dep}} = 120$  s. For other parameters, see legend in Fig. 2.



**Fig. 5:** Effect of deposition potential (A) upon the stripping voltammetric response of 40 ppb Pb(II) and deposition time (B) upon the stripping response of 50 ppb Pb(II) at ex-situ BiF-PFCE. Experimental conditions:  $t_{\text{dep}} = 120$  s. For other parameters, see legend in Fig. 2.

## Determination of Lead(II) at *Ex-Situ* Plated BiFE

**Optimization of Accumulation Parameters.** Again, the operational parameters influencing the accumulation step were carefully optimized. Deposition potential was altered from  $-900$  to  $-1200$  mV and its dependence upon the Pb-peak height is shown in Fig. 5A. The maximum peak-height was obtained in this case for the deposition potential  $-1100$  mV. Fig. 5B discloses the effect of increasing accumulation time. As can be seen the Pb-peak increased almost linearly with increasing deposition time from 30 to 300 s. For further measurements the deposition time of 120 s was chosen, also for possibility of comparison between measurement at *in-situ* and *ex-situ* plated BiFE.



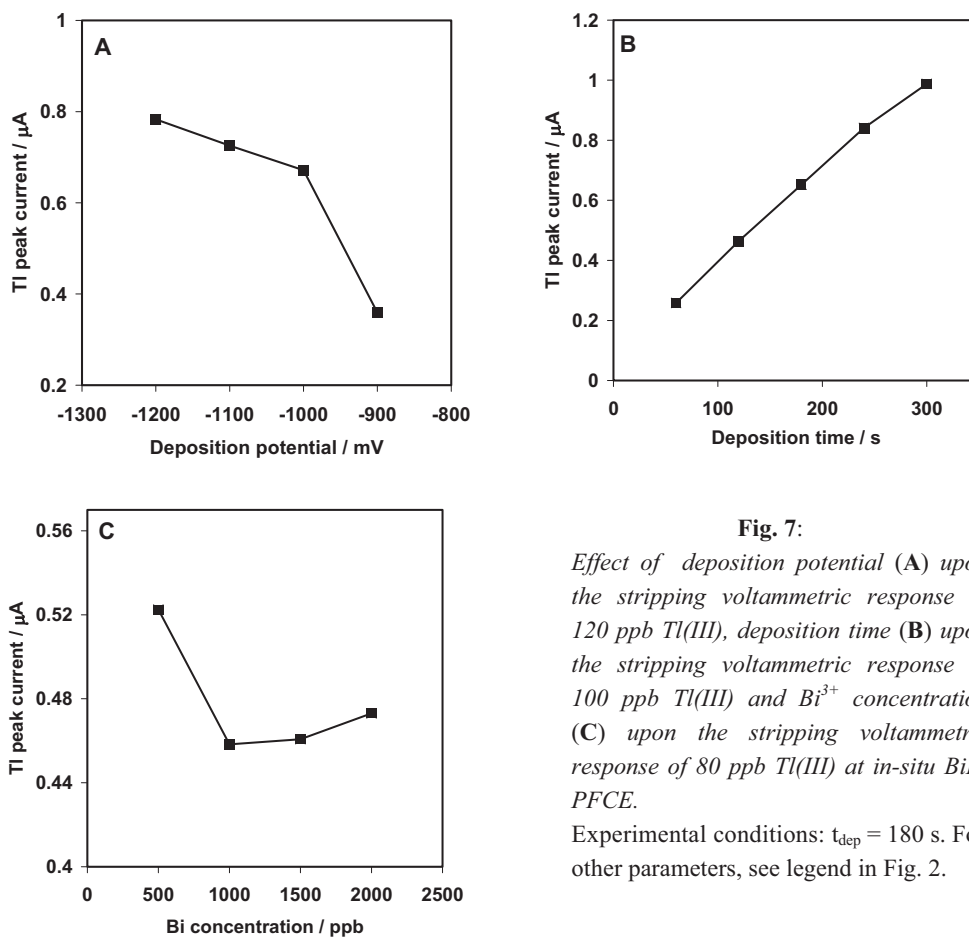
**Fig. 6:** Anodic stripping voltammograms for successive additions of Pb(II) in ten aliquots (10 ppb steps) obtained at the *ex-situ* plated BiF-PFCE. The inset shows the corresponding calibration plot for concentration levels from 10 ppb up to 100 ppb. Experimental conditions:  $E_{\text{dep}} = -1100$  mV,  $t_{\text{dep}} = 120$  s. For other parameters, see legend in Fig. 2.

**Electroanalytical Performance.** Optimized parameters were used for the investigation of analytical characterization data of *ex-situ* plated BiFE in propylene carbonate. The linear calibration curve for the increasing concentration of Pb(II) in the range 10 – 100 ppb with the correlation coefficient ( $R^2$ ) of 0.997 is depicted in Fig. 6.



The LOD (estimated again *via* the  $3\sigma$  criterion) obtained for optimal accumulation time of 120 s was about 1.4 ppb, while repetitive measurements of 30 ppb Pb(II) had resulted in a reproducibility of RSD =  $\pm 2.8\%$  (for  $n = 8$ ).

**Comparison of In-Situ and Ex-Situ Plated BiFEs for the Determination of Pb(II).** When comparing the LOD values achieved at both *in-situ* and *ex-situ* plated BiFEs for the same concentration of lead and equal deposition time, the respective number was slightly higher for *ex-situ* plated BiFE that might suggest a higher sensitivity of the *in-situ* plated BiFE. But when confronting also the slopes of calibration curves,  $S_{\text{ex-s}} = 0.0255$  at *ex-situ* and  $S_{\text{in-s}} = 0.01$  at *in-situ* plated BiFEs, the final resolution at *ex-situ* plated BiFE has been more than two times more sensitive for the determination of Pb(II) than that with *in-situ* plated variant.



**Fig. 7:**

Effect of deposition potential (A) upon the stripping voltammetric response of 120 ppb Tl(III), deposition time (B) upon the stripping voltammetric response of 100 ppb Tl(III) and Bi<sup>3+</sup> concentration (C) upon the stripping voltammetric response of 80 ppb Tl(III) at *in-situ* BiF-PFCE.

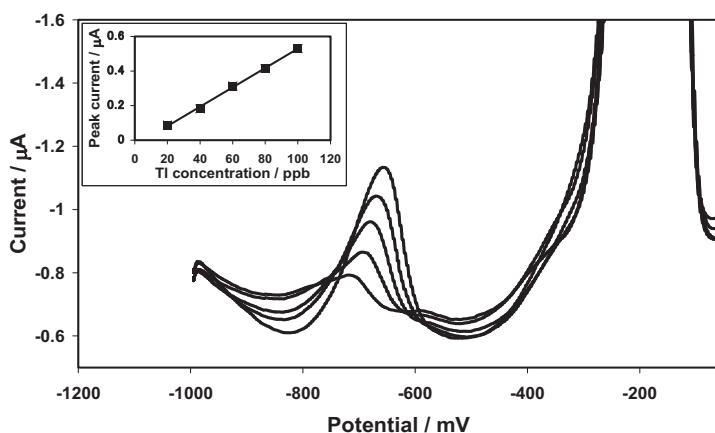
Experimental conditions:  $t_{\text{dep}} = 180$  s. For other parameters, see legend in Fig. 2.

## Determination of Thallium(III) at *In-Situ* Plated BiFE

**Optimization of the Deposition Regime.** At first sight, the use of Tl(III) can be considered as rather unusual, but this choice is logical. In contrast to thallium(I), the trivalent form can be readily complexed and hence, it is the proper choice for our method. And as confirmed previously [8,9], there is no reflection of rather strong oxidation capabilities of the  $Tl^{3+}$  ions.

The main deposition parameters, as accumulation time and potential, as well as the concentration of Bi(III), were of particular interest. Fig. 7A demonstrates the effect of deposition potential which was varied from  $-900$  to  $-1300$  mV. The respective Tl-peak had increased with more negative potential but also changed its shape becoming deformed, which was particularly evident for the depositions at  $E_{dep} = -1300$  and  $-1200$  mV. On the basis of this observation, a lower value of deposition potential,  $E_{dep} = -1000$  mV, was chosen and the further measurements already did not suffer from such deformations.

The effect of the deposition time is illustrated in Fig. 7B. The dependence of the peak-height for Tl-signal studied in four replicates at a  $t_{dep}$  from 60 to 300 s was almost linear in whole interval tested (not shown). Due to a lower sensitivity for the detection thallium(III), accumulation time of 180 s was selected as optimum for further experiments. Concerning the concentration of Bi(III) ions for *in-situ* plating and its influence upon the Tl-peak (Fig. 7C), the results were similar to those reached for Pb(II) and the final concentration of 500 ppb Bi was chosen for the next measurements.

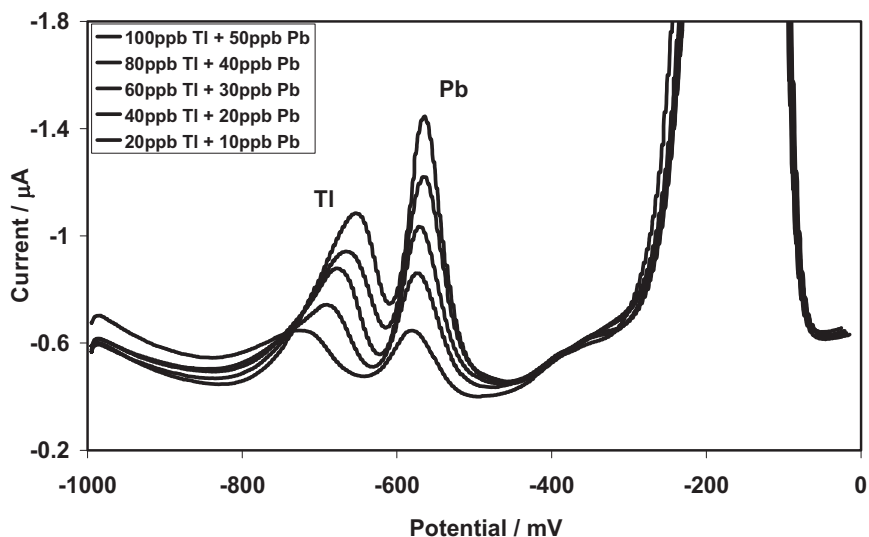


**Fig. 8:** Anodic stripping voltammograms for successive additions of Tl(III) in five aliquots (20 ppb steps) obtained at the *in-situ* plated BiF-PFCE. The inset shows the corresponding calibration plot for an interval of 20-100 ppb Me. For other parameters, see legend in Fig. 2.

**Calibration Plot, Reproducibility and Limit of Detection.** After the optimization of operational parameters we determined the analytical parameters for the detection of thallium in propylene carbonate. The *in-situ* plated BiFE revealed a linear calibration curve for the increasing concentrations from 20 to 100 ppb Tl(III) with the correlation coefficient of  $R^2 = 0.998$  (see Fig. 8). Repetitive measurements with 50 ppb Tl(III) had confirmed a very good reproducibility with  $RSD = \pm 2.6 \%$  (for  $n = 10$ ); the LOD ( $3\sigma$ ) in combination with 180 s accumulation time being estimated to be 2.3 ppb Tl(III).

### Simultaneous Determination of Lead(II) and Thallium(III) Using *In-Situ* Plated BiFE

Finally, due to similar optimal deposition parameters for determination of either Pb(II) or Tl(III), we tried to detect both metals together. As found out, this simultaneous determination was feasible under the above mentioned parameters and composition of water and organic phases, but just with qualitative resolution of both peaks; their quantitative resolution being possible only for lower concentrations, 10 or 20 ppb Me, (see Fig. 9). To ensure the sufficient resolution of both peaks also for quantitative detection at higher concentrations, new optimization of the composition of water and the organic phase would be necessary.



**Fig. 9:** Anodic stripping voltammograms for successive additions of Pb(II) and Tl(III) obtained at *in-situ* plated BiF-PFCE. Other conditions are as in Fig.7.

## Conclusions

As shown above, the *in-situ* operated bismuth film electrode can be combined with the direct voltammetric measurement and, in this way, used to determine selected heavy metals; *e.g.*, Pb(II) and Tl(III) being the subject of interest within this study. The principal step is a gas-stirred liquid-liquid extraction of their complexes, when the subsequent electrochemical detection offers satisfactory results. The two metal elements tested herein could be determined either single or in parallel; the latter with less precise results, however. Furthermore, two different configurations of the BiFE — *in-situ* and *ex-situ* operated variants — were compared for the determination of Pb(II), both providing comparable results.

It can be stated that the method proposed is simple, selective, and not very time-consuming as one would expect from the incorporation of an extraction step into the procedure. This is because of the fact that the entire extraction process, utilizing the effective purging with nitrogen, could be shortened down to one minute only and the transfer of metal complexes still remained quantitative in nature, which was confirmed by the maximal yield for both metal ions involved. Thus, so-far existing palette of methods for practical determination of Pb(II) at BiFEs [10], with similar prospects also for thallium.

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