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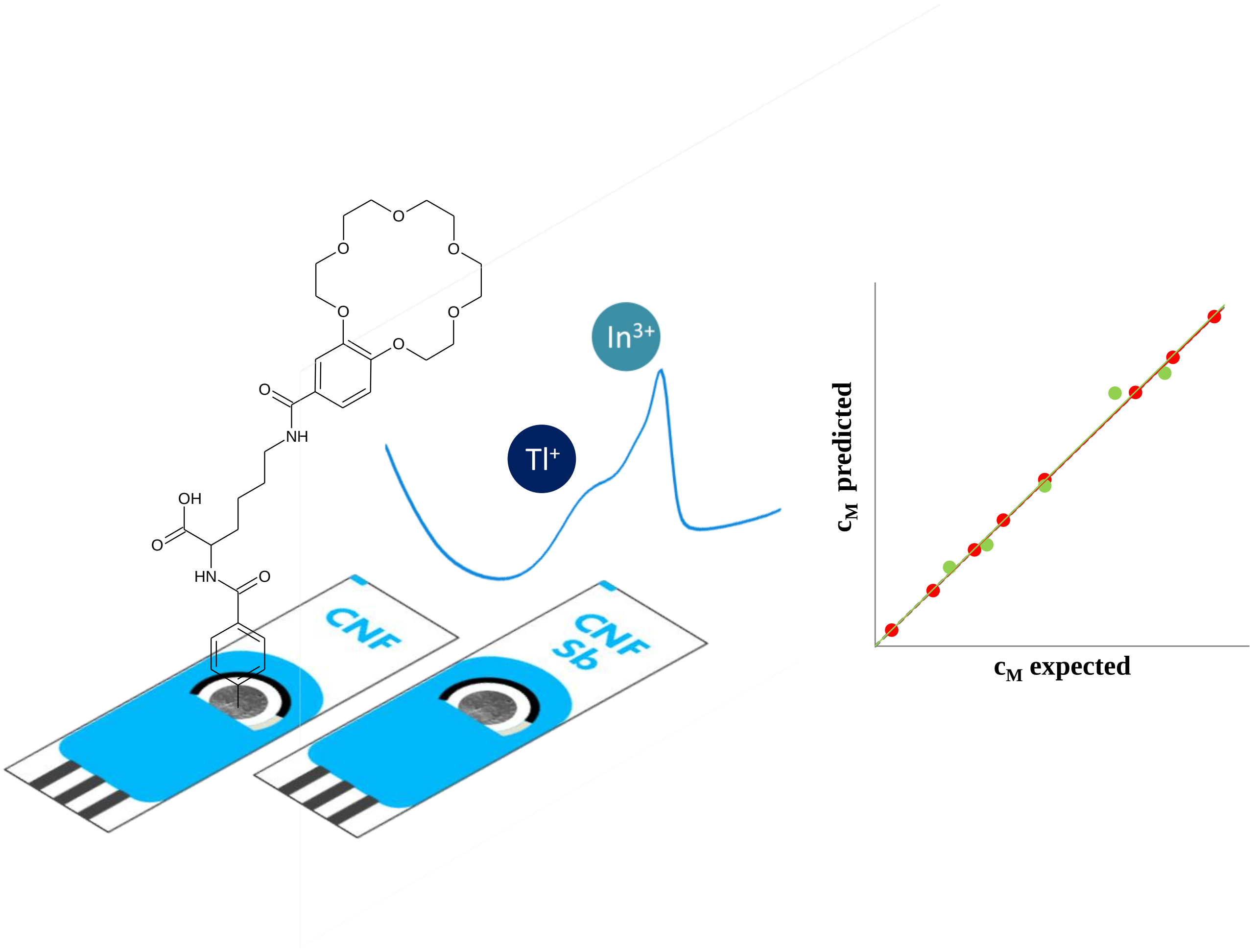
Graphical Abstract (for review)



Simultaneous determination of Tl(I) and In(III) using a voltammetric sensor array

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ABSTRACT

A sensor array consisting of a chemically modified sensor in which 4-carboxybenzo-18-crown-6 was immobilized onto a screen-printed carbon nanofiber-modified electrode (crown-6-SPCNFE) and an *ex-situ* antimony film deposited on a screen-printed carbon nanofiber-modified electrode (*ex-situ*-SbSPCNFE) was applied for the resolution of the strong overlapped signals resulting from the simultaneous determination of Tl(I) and In(III) by stripping voltammetry. A Partial Least Squares model was constructed and good calibration curves of predicted *vs.* expected concentrations of the considered metal ions, with correlation coefficients higher than 0.98 for both training and test sets, were obtained. These results provided by the sensor array were compared with those obtained by a single electrode. Moreover, this sensor array was successfully applied for the voltammetric determination of both Tl(I) and In(III) in tap water, providing comparable results to those obtained by ICP-MS measurements.

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1. INTRODUCTION

Thallium and indium are relatively rare metals that do not have any essential biological role but have been shown to be highly toxic. Due to their unique chemical properties, the use of these metals has increased in the last years. Indium is mostly used for alloys and solders whereas thallium is used for switches and closures. In addition, the use of both indium and thallium has recently been expanded in medical procedures and electronics industry [1,2].

Different techniques such as inductively coupled plasma mass spectrometry (ICP-MS) or inductively coupled plasma atomic emission spectroscopy (ICP-OES) have been used for the analysis of thallium and indium [3,4]. Electroanalytical techniques, and voltammetric stripping techniques in particular, can also be a good alternative, since they are low cost, highly reproducible, selective and sensitive, and they present capability to multielement analysis and excellent detection and quantification limits [5]. However, when traditional working electrodes like mercury are used, the simultaneous determination of indium and thallium is problematic because of their overlapping stripping signals. More promising results regarding the separation of thallium and indium peaks were achieved using alternative working electrodes such as an *in-situ* antimony film deposited onto a glassy carbon electrode [6]. Classical solid electrodes though, require continuous and tedious cleaning processes that can be avoid by using screen-printed electrodes (SPE). In fact, SPEs have recently undergone great advances, allowing the mass production of reproducible and low-cost devices. In addition, SPEs usually incorporate the whole electrode system (working, reference and auxiliary) which, coupled with their miniaturized size and their ability to be connected to portable instrumentation, makes them more suitable for *on-site* analysis. [7–10].

SPEs can also be further modified following different strategies such as electrodeposition of metal films or covalent modification through electrografting using aryl diazonium salts [11]. Particularly for metal ion determination, in the first case, good results have been reported for both bismuth film electrodes [12] and antimony film electrodes [13] whereas in the second case different ligands can be immobilized onto the electrode surface, i.e. good results have been reported using peptide related structures [14–18] or crown ethers [19,20] as ligands.

In both strategies of modification, the substrate is also an important aspect that has to be taken into account during the preparation of these modified sensors. It is well-known that the use of carbon- based nanomaterials such as carbon nanotubes (CNT), carbon nanofiber (CNF) or graphene (GPH) enhance the effective surface and improve the electron-transfer kinetics. In particular, it has been reported that sensors with better analytical performance can be obtained if a carbon nanofiber modified screen-printed electrode (SPCE-CNF) is used as electrode substrate [15,21], since CNFs are easier to functionalize and simultaneously provide mechanical and electrical property enhancements.

These chemical sensors can be used as single-electrode sensors for the voltammetric determination of metal ions in samples of biological, food and environmental origin but for some analytes it is difficult to obtain sensors with appropriate selectivity and sensitivity. In some cases, the analysis of unresolved signals obtained by electroanalytical techniques has been successfully carried out using different chemometric tools such as partial least squares (PLS) or multivariate curve resolution by alternating least squares (MCR-ALS) [22]. However, in the event of a strong signal overlapping or interactions between different analytes, better results can be achieved by combining the signals obtained from different sensors grouped in a sensor array. In this array approach each electrode is modified with different compounds in search for a multivariate response. Although a sensor array requires longer manufacturing time, a multichannel potentiostat to control the potential and the use of chemometric tools to process the more complex data, the information obtained by the sensor array is much better than that provided from a single sensor [23,24]. Therefore, this sensor array allows the combination of several less specific sensors with cross-selectivity to obtain multivariate data sets that can be further analyzed by chemometric methods.

Thus, in this study a sensor array formed by the combination of an *ex-situ* antimony film deposited on a screen-printed carbon nanofiber-modified electrode (*ex-situ*-SbSPCNFE) and a chemically modified sensor in which 4-carboxybenzo-18-crown-6 was immobilized onto a screen-printed carbon nanofiber-modified electrode (crown-6-SPCNFE) is presented. The obtained data-set was further analysed using PLS, which successfully allowed the simultaneous voltammetric determination of thallium and indium ions in water samples.

2. EXPERIMENTAL SECTION

2.1. Chemicals and Solutions.

All chemicals used were of analytical grade. Sb(III) 1.000 mg L^{-1} atomic absorption standard solution, 2-(N-morpholino)-ethanesulfonic acid (MES), potassium ferrocyanide $K_4[Fe(CN)_6]\cdot 3H_2O$, hydrochloric acid, nitric acid, acetic acid, and sodium acetate were supplied by Merck (Merck (Darmstadt, Germany). Sodium nitrite, *N*-hydroxysulfosuccinimide (sulfo-NHS), 4-aminobenzoic acid (ABA), *N*-(3-dimethylaminopropyl)-*N'*-ethylcarbodiimide hydrochloride (EDC), perchloric acid, methanol, potassium dihydrogen phosphate, and sodium monophosphate were purchased from Sigma-Aldrich (St. Louis, MO, USA). Potassium ferricyanide $K_3[Fe(CN)_6]$ and 4-carboxybenzo-18-crown-6 were provided by Panreac (Barcelona, Spain) and Acros (Geel, Belgium) respectively.

In(III) and Tl(I) stock solutions 10^{-3} mol L^{-1} were prepared from $In_2(SO_4)_3.5H_2O$ and TlCl respectively, supplied by Sigma-Aldrich. Stock solution concentrations were determined by ICP-MS. Ultrapure water (Milli-Q plus 185 system, Millipore) was used in all experiments.

Tap water sample was collected in the laboratory from the local water distribution network, managed by Agbar Company (Barcelona; http://www.agbar.es/eng/home.asp) and mostly using water coming from Llobregat River.

2.2. Instrumentation.

Differential pulse anodic stripping voltammetric (DPASV) measurements were performed in an Autolab System PGSTAT12 (EcoChemie, The Netherlands), in its multichannel configuration and using GPES Multichannel 4.7 software package (EcoChemie).

Ag|AgCl|KCl (3 mol L^{-1}) supplied by Metrohm (Switzerland) was used as reference electrode and an *ex-situ* antimony film and a 4-carboxybenzo-18-crown-6 modified electrode, both prepared using a commercial carbon nanofiber modified screen-printed disk electrode (ref. 110CNF, DS SPCE) of 4 mm diameter provided by Dropsense (Oviedo, Spain) as substrate, were used as working electrodes. The carbon counter electrode from one of the SPEs was used as counter electrode and two flexible cables (ref. CAC, DropSens) were used to connect the SPEs to the Autolab System.

A Crison micro pH 2000 pH-meter was used for pH measurements.

All measurements were carried out at room temperature (20 °C) and a purified nitrogen atmosphere (Linde N50) was used for the antimony film preparation.

Inductively coupled plasma mass spectrometry Perkin-Elmer model NexIon 350 D with a collision cell (helium) (USA) was used for ICP-MS measurements.

2.3. Preparation of modified SPEs.

2.3.1. Crown-6 modified electrode (Crown-6-SPCNFE)

The immobilization of 4-carboxybenzo-18-crown-6 on the surface of SPCE-CNF was based on a procedure previously reported [19], with slight modifications. Briefly, the aryl diazonium salt was generated *in-situ* by adding 4 mmol L^{-1} of $NaNO_2$ to a cooled solution of 146 mmol L^{-1} of ABA in 1 mol L^{-1} HCl. This solution was mixed in an ice bath for 30 min before the electrochemical grafting process was conducted. For this purpose, the SPCE-CNF was immersed in the diazonium salt solution and 30 cyclic voltammetry (CV) cycles from 0 V to −1 V at 0.2 V s^{-1} were applied. The electrodes were rinsed with water and ethanol and the carboxylic groups were activated by dropping 10 µL of a 35 mmol L^{-1} sulfo-NHS and 26 mmol L^{-1} EDC solution in 0.1 mol L^{-1} MES buffer (pH 4.5) onto the electrode surface and leaving it for 1 h. In order to conjugate the activated carboxylic groups with the carboxy-modified ligand, a lysine spacer was intercalated in between them by incubating 2.9 mg of 4-carboxybenzo-18-crown-6 with 100 µL 5 mM lysine in 0.1 M MES buffer / ethanol (10%) for 3 h at 4 °C. Then 10 µL of this solution were dropped onto the functionalized electrode surface and left to react overnight at 4 °C.

The electrochemical characterisation of the crown-6-SPCNFE was carried out using 2 mmol L^{-1} ferrocyanide/ferricyanide as redox probe in 100 mmol L^{-1} phosphate buffer (pH 7.4) at each functionalization step by cyclic voltammetry (CV) leading voltammograms that confirm the modifications taking place on the electrode surface (Figure not shown).

2.3.2. Ex-situ antimony film electrode (ex-situ-SbSPCNFE)

The SPCE-CNF was immersed, together with the reference and auxiliary electrodes, into a 0.01 mol L^{-1} HCl solution containing 50 mg L^{-1} of Sb(III). This solution was dearated for 10 min and an E_d of -0.5 V was applied with stirring for 300 s, followed by a rest period of 20 s, without stirring. Finally, the electrode was rinsed with water. This methodology was previously tested, showing a very high repeatability and reproducibility [25].

2.4. Voltammetric measurements.

DPASV determinations of Tl(I) and In(III) using crown-6-SPCNFE and *ex-situ*-SbSPCNFE were performed at a deposition potential (E_d) of -1.4 V, applied with stirring, during a deposition time (t_s) of 120 s and followed by a rest period (t_r) of 5 s. Determinations were done by scanning the potential from -1.4 to -0.5 V, using pulse amplitudes of 100 mV, a step potential of 5 mV, and pulse times of 50 ms.

The remaining bound metals from both working electrodes were eliminated through a cleaning step, which consisted in applying a conditioning potential (E_{cond}) of -0.3 V for 15 s in 0.1 mol L^{-1} $HClO_4$ after each measurement.

In order to obtain the linear calibration plots for the separate determination of Tl(I) and In(III), metal ion concentrations were increased in 0.1 mol L^{-1} acetate buffer solution at pH 4.5.

For the simultaneous determination of Tl(I) and In(III) a total set of 14 samples, distributed among training (9) and test (5) subsets, were prepared from appropriate dilution of stock solutions. Training samples were distributed in a square design and test samples where distributed along the experimental domain (Figure 1). It should be noted that central point is included in both training and testing subsets.

In addition, the suitability of the sensor array for the simultaneous determination of In(III) and Tl(I) in natural samples was tested by measuring 3 replicates of a spiked tap water sample with Tl(I) and In(III) concentrations distributed in the range of the calibration curves.

2.5. Sample preparation.

Water samples collected from the local water distribution network were spiked with 225 μg L^{-1} of Tl(I) and 75 μg L^{-1} of In(III). These values were further determined by ICP-MS. For voltammetric determinations, an aliquot of spiked water sample was diluted with acetate buffer to pH 4.5 resulting in solution concentrations of 145.5 μg L^{-1} of Tl(I) and 48.5 μg L^{-1} of In(III).

2.6. Data processing.

Data matrices were built from stripping voltammograms measured for all samples with crown-6-SPCNFE as a single-sensor or with the sensor array consisting of an *ex-situ*-SbSPCNFE and a crown-6-SPCNFE. Prior to building the PLS model different pre-processing steps were applied, including baseline correction, smoothing Savitzky-Golay, 1st derivative Savitzky-Golay, reference correction and autoscale.

Pre-processing of the data matrices, variable selection and construction of PLS model were made using Matlab®[26] with PLS-toolbox[27].

3. RESULTS AND DISCUSSION

As the most novel aspect of the present work is the part concerning Tl(I) and In(III) sensing using the crown-6-SPCNFE this was studied in detail. Once stablished the working conditions, the crown-6-SPCNFE was analytically characterized for the determination of Tl(I) and In(III) given that there are no previous studies in this regard. *Ex-situ*-SbSPCNFE response towards Tl(I) and In(III) was already studied in a previous work, involving the simultaneous voltammetric determination of Cd(II), Pb(II), Tl(I), In(III), Zn(II), and Bi(III) [28]. Table 1 summarizes the calibration data of both crown-6-SPCNFE and *ex-situ*-SbSPCNFE for the analysis of Tl(I) and In(III).

3.1. Analytical performance of crown-6-SPCNFE

The effect of deposition potential was firstly tested in order to ensure the maximum separation between Tl(I) and In(III) peaks. For this purpose, voltammetric measurements applying different E_d ranging from -1.6 V to -1.3 V for 120 s were performed in a solution containing 100 µg L^{-1} Tl(I) and In(III) at acetate buffer pH 4.5 on crown-6-SPCNFE (Figure 2A). As it can be observed, the best separation is obtained at -1.4 V. More negative potentials result in a decrease of In(III) peak in comparison to Tl(I) peak whereas more positive potentials results in smaller peaks for both Tl(I) and In(III) ions.

Individual calibrations of Tl(I) and In(III) by stripping voltammetry applying the optimized potential of -1.4 V and a t_d of 120 s were then carried out. For this purpose, thirteen standard solutions with increasing concentrations of Tl(I) or In(III) within the range 1.2-270.3 and 1.8-300.4 µg L^{-1} respectively were measured, obtaining comparable responses that allowed the determination of both metal ions in the considered concentration ranges. Calibration data are summarized in Table 1. Both In(III) and Tl(I) showed good linear responses of peak area *vs* metal ion concentration and the sensitivity, obtained from the slope of the calibration curve, was higher in the case of indium(III). Regarding the limits of detection (LOD), calculated as 3 times the standard deviation of the intercept over the slope of the calibration curve of each metal, were at the level of µg L^{-1} for both metal ions, being slightly better in the case of thallium(I).

The effect of having Tl(I) and In(III) in different proportion was also evaluated. Figure 2B shows the stripping measurements obtained by applying an E_d of -1.4 V during 120 s for several solutions containing different concentrations of Tl(I) and In(III) at acetate buffer pH 4.5. A high interaction between both metal ions can be observed. The best peak separation is achieved when similar concentrations of Tl(I) and In(III) are considered whereas a strong overlapping can be observed when one metal ion concentration is much higher than the other. This is especially problematic because different environmental studies carried out in the Antarctica, Sweden and Japan have reported that usually thallium(I) is found at higher concentrations than indium(III) [3,29,30]. The strong overlapping observed at these metal ion proportions prevents the use of univariate calibration for the determination of Tl(I) and In(III) on crown-6-SPCNFE. Therefore, a multivariate calibration approach was considered.

3.2. Multivariate calibration studies

For the simultaneous voltammetric determination of Tl(I) and In(III) on crown-6-SPCNFE, a PLS model was constructed. For this purpose, calibration and validation sets constituted by 9 (64 %) and 5 (36 %) samples respectively (Figure 1) were considered. Taking into account that in real samples thallium(I) is usually found at higher concentrations than indium(III), the experimental design was conceived so that most samples contained more Tl(I) than In(III). More specifically, Tl(I) concentration ranged from 9.7 to 199.5 µg L^{-1} whereas In(III) concentration ranged from 3.8 to 79.3 µg L^{-1}.

A key step in the construction of PLS models is data pretreatment. In this sense, baseline was firstly corrected by fitting a polynomial curve to points which were known to be part of the baseline. Following baseline correction, smoothing and first derivative Savitzky-Golay were applied and data were autoscaled. Pretreated data were studied by PCA and one outlier was detected and therefore removed from the training set. Then,

PLS-1 models were built for the determination of both Tl(I) and In(III). The number of latent variables (LVs), selected by the results provided by both training and test subsets, was 3 for both Tl(I) and In(III). Comparison graphs of obtained *vs* expected concentrations for In(III) and Tl(I) are shown in Figures 3A and 3B respectively, whereas Table 2 shows the main parameters of the regression lines, as well as the root mean square error (RMSE) obtained for calibration and validation. Good results were obtained in the calibration of both In(III) and Tl(I), with slopes and correlation coefficients close to 1, intercepts close to 0 and really small RMSE values. Validation for thallium(I) was also quite good, although in this case higher prediction errors were obtained. Validation for indium(III) however, was not successful since a linear response could not be obtained, which suggest that the calibration model was overadjusted. It should also be pointed out that the sample containing the lowest concentration of In(III) could not be fitted by the model. Therefore, although quite good results were obtained for Tl(I), the simultaneous determination of Tl(I) and In(III) could not be successfully carried out using only crown-6-SPCNFE as working electrode.

3.3. Sensor array

As it was mentioned above the use of crown-6-SPCNFE as working electrode is not good enough for the simultaneous determination of In(III) and Tl(I). However, in these cases much better results can be obtained if two sensors with different responses are combined in a sensor array [23,24]. In this sense, an *ex-situ* antimony film was selected as a second working electrode. This electrode was previously characterized for the determination of both In(III) and Tl(I) [28] and it showed a distinctive (cross)response from crown-6-SPCNFE, with sensitivities of 0.75 and 1.10 a.u. μg^{-1} L for In(III) and Tl(I) respectively (Table 1). The voltammetric performance of *ex-situ*-SbSPCNFE for the simultaneous determination of Tl(I) and In(III) in the selected concentration range provides even more highly overlapped signals than crown-6-SPCNFE (Figure 4), that make not possible neither the univariate calibration nor the achievement of satisfactory results by means of a multivariate calibration. However, the cross-selectivity observed for crown-6-SPCNFE and *ex-situ*-SbSPCNFE makes them good candidates for the sensor array. Thus, a new PLS model was constructed following the same steps as before for the crown-6-SPCNFE but this time a matrix containing the responses of both sensors was used as input. In this case the LVs used were 3 for Tl(l) and 5 for In (III). The comparison graphs of obtained *vs.* expected concentrations for In(III) and Tl(I) using the sensor array constituted by crown-6-SPCNFE and *ex-situ*-SbSPCNFE are shown in Figure 5A and B respectively and the main parameters of the regression lines are summarized in Table 3. Good calibration models are still obtained for both In(III) and Tl(I) and predictions are much better than the ones obtained with only crown-6-SPCNFE although, in the case of the In(III) model the sample containing the lowest concentration could not either be fitted by the model. Using the sensor array good linear responses are achieved for obtained *vs.* predicted concentrations, with slopes and intercepts close to 1 and 0 respectively. Furthermore, much lower RMSEs are obtained for both metal ions. Therefore, the sensor array constituted by crown-6-SPCNFE and *ex-situ*-SbSPCNFE can successfully be applied for the simultaneous determination of In(III) and Tl(I) . These results suggest that this sensor array could also be successfully applied to the simultaneous determination of these metal ions in natural waters.

3.4. Real sample analysis

At the view of the previous results, the sensor array formed by crown-6-SPCNFE and *ex-situ*-SbSPCNFE was considered for the simultaneous determination of Tl(I) and In(III) in natural waters and its applicability was tested on a spiked tap water. In this sense, three replicates of the tap water were analysed by voltammetric stripping voltammetry with the sensor array, using the same experimental conditions and obtaining voltammetric signals that behave in a similar way to those from training and test sets.

The previously calibrated PLS model was employed to calculate Tl(I) and In(III) concentrations. A good concordance of metal ions concentration, inferred by the obtained RSD%, was achieved between the different replicates, especially in the case of Tl(I) (Table 4). In order to test the accuracy of the proposed method the sample was also analysed by ICP-MS, a well-established technique for the determination of metals, and the results obtained from both techniques were statistically compared. In this sense, a two-tailed t-test (equal variances) was performed and it was concluded that the sensor array and ICP-MS provide statistically similar results for a confidence level of 95%.

Therefore, these results confirm that the combination of crown-6-SPCNFE and *ex-situ*-SbSPCNFE in a sensor array coupled with an appropriate PLS model is successfully capable for the simultaneous determination of Tl(I) and In(III) in real samples.

Furthermore, this sensor array is proposed as an interesting and cheaper alternative to more conventional techniques such as ICP-MS.

4. CONCLUSIONS

Taking advantage of the good characteristic of the nanomaterial modified screen-printed electrodes, in this paper the immobilization of 4-carboxybenzo-18-crown-6 assisted by lysine on aryl diazonium salt monolayers anchored to the surface of a screen-printed carbon nanofiber-modified electrode (crown-6-SPCNFE) was applied for the determination of Tl(I) and In(III). The individual analytical characterization provided detection limits at levels of μg L^{-1} for both metal ions and wide linear ranges. However, the overlapped character of the voltammetric signals obtained in the simultaneous determination of both metal ions hinders the univariate calibration and also, in the case of In(III), the multivariate calibration.

Taking into account the complementary response provided by *ex-situ*-SbSPCNFE for these metal ions, this sensor was considered for the combination with crown-6-SPCNFE in a sensor array approach. The data provided by the sensor array were treated by a PLS model and successful results were obtained for both training and testing, with predicted *vs.* expected concentrations calibration curves with slopes and correlation coefficients close to 1 and intercepts close to 0. This study confirms that the use of a sensor array approach represents a great improvement of the results (specially for In(III)) with respect of a single-electrode, in the fact that it allows the resolution of these strongly overlapped signals with a good prediction of both metal ion concentrations. Moreover, the simultaneous determination of Tl(I) and In(III) in a spiked tap water was also satisfactory achieved, providing comparable results to those obtained by ICP-MS measurements.

5. AKNOWLEDGMENTS

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Table 1. Calibration data for the separate determination of In(III) and Tl(I) on crown-6-SPCNFE and *ex-situ*-SbSPCNFE modified electrodes at E_d of -1.4 V using a t_d of 120 s at acetate buffer pH 4.5.

	In(III)	**Tl(I)**
Crown-18-SPCE-CNF		
Sensitivity (a.u. µg^{-1} L)	0.57 (0.01)	0.30 (0.01)
R^2	0.998	0.998
LOD (µg L^{-1})	13.7	10.9
***Ex-situ*-SbSPCE-CNF**		
Sensitivity (a.u. µg^{-1} L)	0.75 (0.01)	1.10 (0.02)
R^2	0.999	0.999
LOD (µg L^{-1})	6.3	8.6

Table 2. Main parameters of the regression lines obtained in the comparison between predicted *vs.* expected values of the training and test subsets for In(III) and Tl(I) (ranges calculated at the 95% confidence level) for crown-6-SPCNFE. The standard deviations are denoted by parenthesis.

	In(III)	**Tl(I)**
Training set		
Slope	1.000 (0.002)	1.00 (0.02)
Intercept (μg L^{-1})	0.0 (0.1)	0 (2)
R^2	1.000	0.999
RMSE[a] (μg L^{-1})	0.11	2.44
Test set		
Slope	0.2 (0.4)	0.84 (0.07)
Intercept (μg L^{-1})	32 (20)	10 (6)
R^2	0.123	0.980
RMSE[a] (μg L^{-1})	15.96	11.52

[a] RMSE: root mean square error

Table 3. Main parameters of the regression lines obtained in the comparison between predicted *vs.* expected values of the training and test subsets for In(III) and Tl(I) (ranges calculated at the 95% confidence level) for the sensor array. The standard deviations are denoted by parenthesis.

	In(III)	**Tl(I)**
Training set		
Slope	1.00 (0.02)	1.000 (0.003)
Intercept (µg L^{-1})	0 (1)	0.0 (0.4)
R^2	0.997	0.999
RMSE[a] (µg L^{-1})	1.20	0.49
Test set		
Slope	1.07 (0.10)	1.00 (0.08)
Intercept (µg L^{-1})	-5 (5)	0 (9)
R^2	0.984	0.981
RMSE[a] (µg L^{-1})	2.60	6.55

[a] RMSE: root mean square error

Table 4. Total concentrations of Tl(I) and In(III) determined in tap water samples by DPASV on the multisensor array formed by Crown-6-SPCNFE / *Ex-situ*-SbSPCNFE modified electrodes and by ICP-MS.

		Tl(I)	**In(III)**
DPASV	c (μg L^{-1})	219.4	80.5
	RSD (%)	2.8	9.2
ICP-MS	c (μg L^{-1})	223.5	74.7
	RSD (%)	0.8	1.8

n=3 for RSD (%)

Caption to figures

Figure 1. Experimental design used for training (●) and testing (○) subsets. Central point is included in both training and testing subset.

Figure 2. DPASV voltammograms on crown-6-SPCNFE at acetate buffer pH 4.5 A) of a solution containing 100 µg L^{-1} Tl(I) and In(III) and applying a t_d of 120 s and an E_d of -1.6 V (a), -1.5 V (b), -1.4 V (c) and -1.3 V(d) and B) of solutions containing different concentrations of Tl(I) and In(III) applying and E_d of -1.4 V.

Figure 3. Comparison graphs of predicted *vs.* expected concentrations obtained on crown-6-SPCNFE for In(III) (A) and Tl(I) (B) for training set (●,—) and test set (○,—). Dashed line represents theoretical diagonal line (y=x).

Figure 4. DPASV voltammograms on *ex-situ*-SbSPCNFE at acetate buffer pH 4.5 of solutions containing different concentrations of Tl(I) and In(III) applying and E_d of -1.4 V.

Figure 5. Comparison graphs of predicted *vs.* expected concentrations obtained on the sensor array for In(III) (A) and Tl(I) (B) for training set (●,—) and test set (○,—). Dashed line represents theoretical diagonal line (y=x).

Figure 1

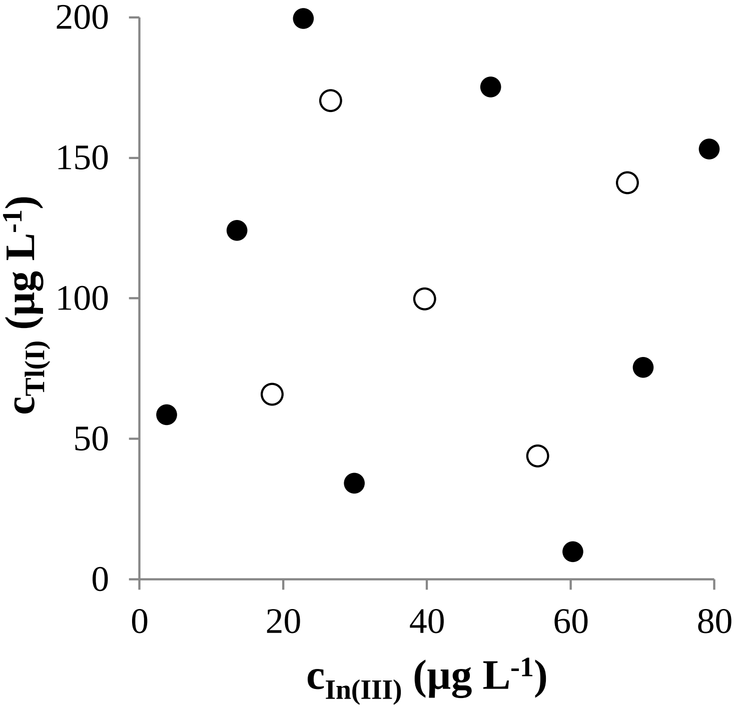


Figure 2

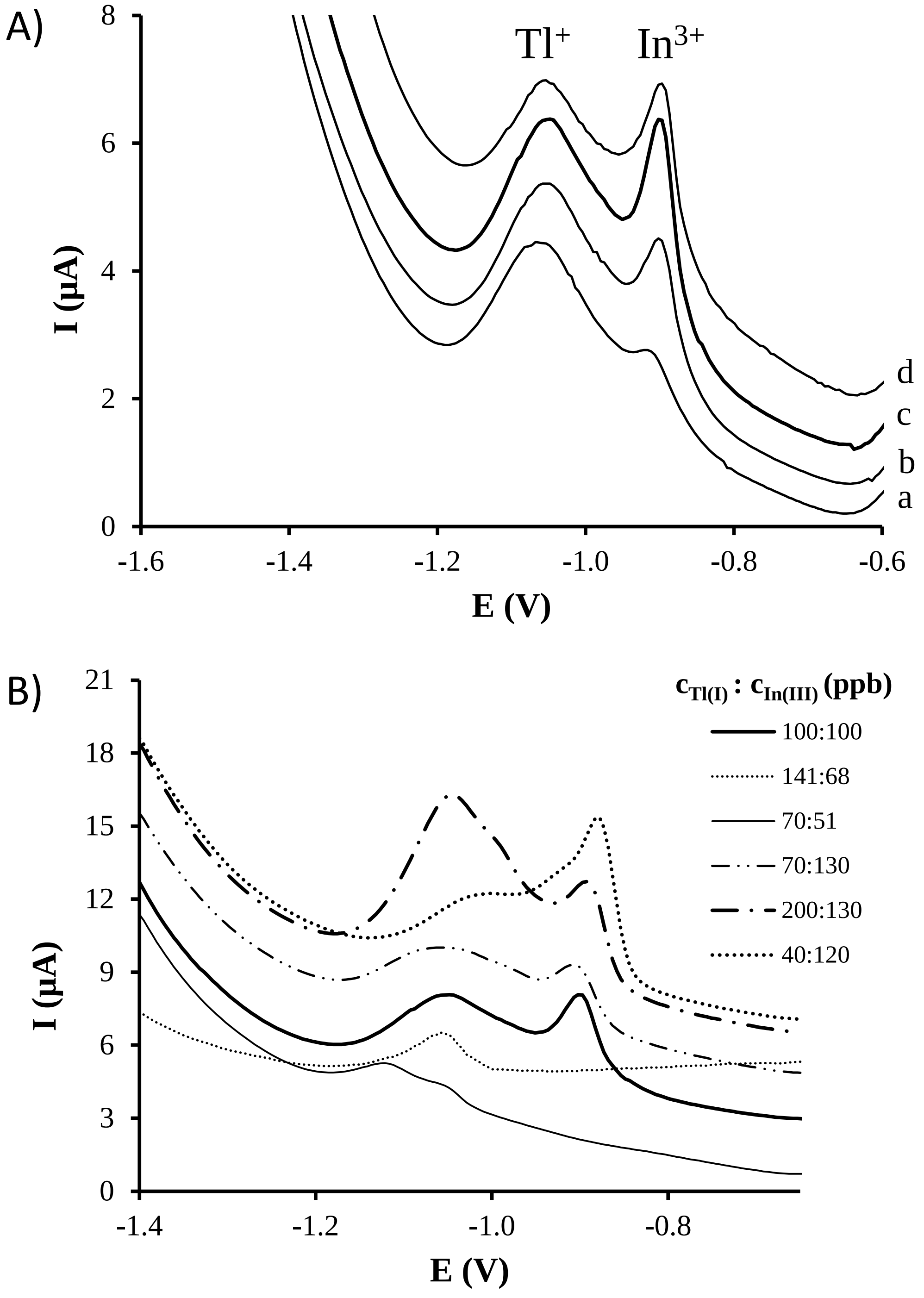

A)
8
6
4
2
0
I (µA)
Tl⁺
In³⁺
d
c
b
a
-1.6
-1.4
-1.2
-1.0
-0.8
-0.6
E (V)
B)
21
18
15
12
9
6
3
0
I (µA)
c_Tl(I) : c_In(III) (ppb)
100:100
141:68
70:51
70:130
200:130
40:120
-1.4
-1.2
-1.0
-0.8
E (V)

Figure 3

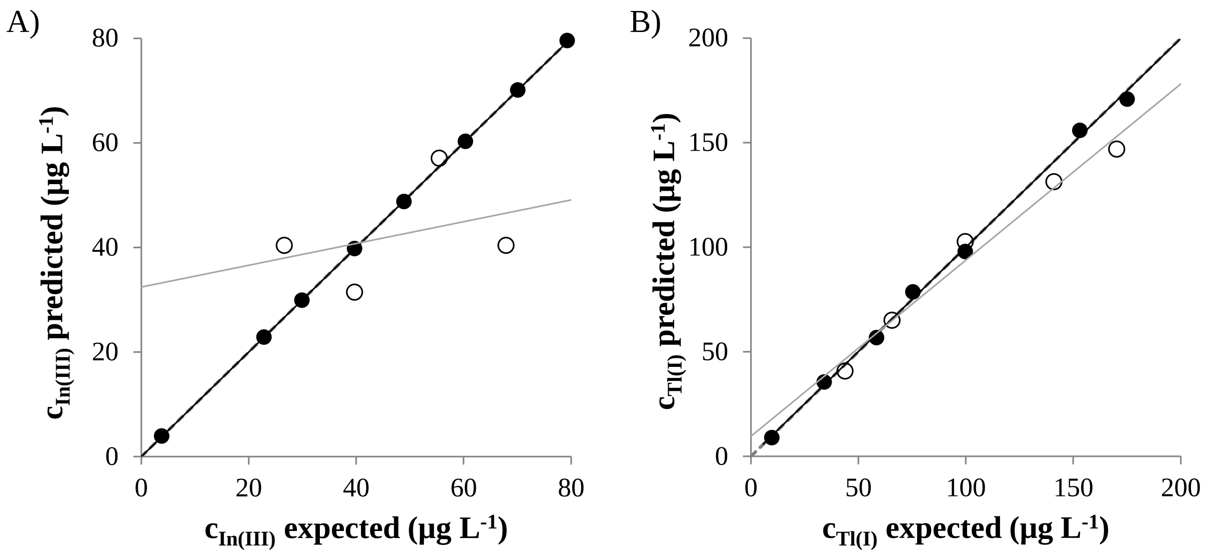

A)
80
60
40
20
0
0
20
40
60
80
$c_{In(III)}$ predicted (µg L^{-1})
$c_{In(III)}$ expected (µg L^{-1})
B)
200
150
100
50
0
0
50
100
150
200
$c_{Tl(I)}$ predicted (µg L^{-1})
$c_{Tl(I)}$ expected (µg L^{-1})

Figure 4

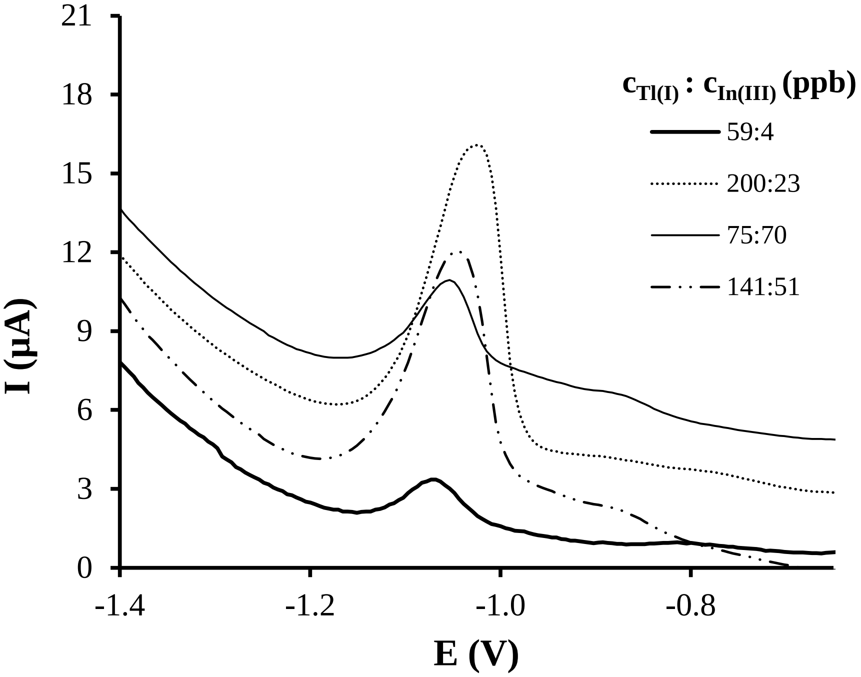
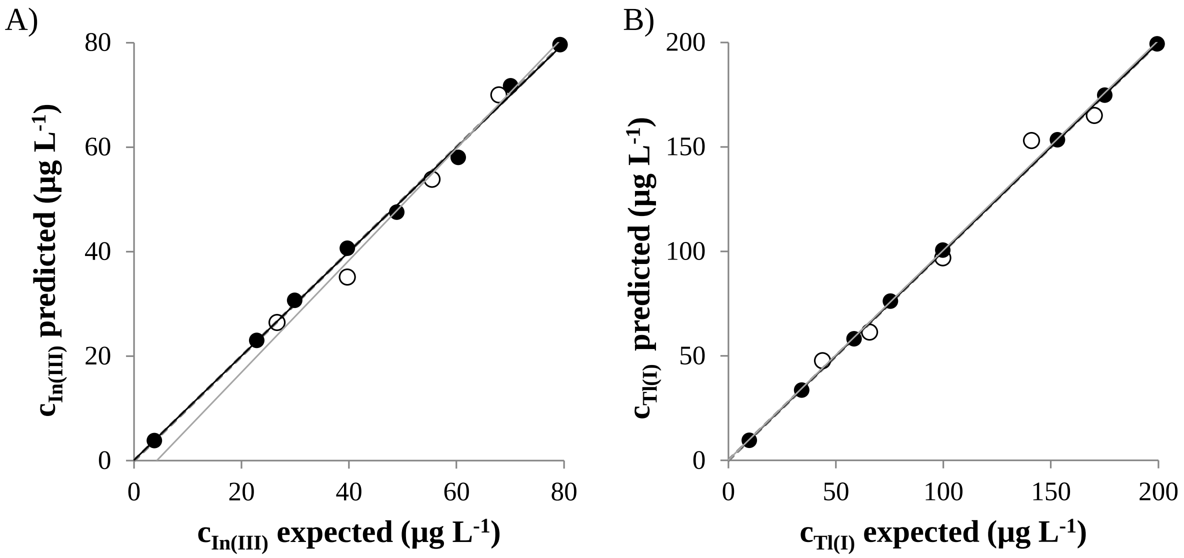

21
18
15
12
9
6
3
0
I (µA)
-1.4
-1.2
-1.0
-0.8
E (V)
$c_{Tl(I)} : c_{In(III)}$ (ppb)
59:4
200:23
75:70
141:51

Figure 5


A)
B)
$c_{In(III)}$ predicted (µg L^{-1})
$c_{In(III)}$ expected (µg L^{-1})
$c_{Tl(I)}$ predicted (µg L^{-1})
$c_{Tl(I)}$ expected (µg L^{-1})
0
20
40
60
80
0
50
100
150
200