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Determination of tributyltin at parts-per-trillion levels in natural waters by second-order multivariate calibration and fluorescence spectroscopy

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ABSTRACT

This work presents a non-sophisticated approach for the trace determination of tributyltin, the most toxic organotin species, in very interfering environments, combining fluorescence measurements of its morin complex and the selectivity of second-order chemometric algorithms. The power of MCR–ALS (multivariate curve resolution/alternating least-squares) to quantify tributyltin through fluorescence excitation–emission matrices in the presence of its main degradation products and of a pool of additional twenty-three metal ions is demonstrated. The applied algorithm successfully faces the challenge of solving the strong overlapping among the spectra of the several sample components. The proposed methodology was applied to tap, river, lagoon and seawater spiked samples, obtaining satisfactory results at ng L^{-1} levels, after a pre-concentration step on a C18 membrane, demonstrating the analytical potential of the proposed methodology.

1. Introduction

Due to its widespread use as an antifouling agent in boat paints, highly toxic tributyltin (TBT) is a common contaminant of marine and freshwater ecosystems [1,2]. Exposure to water and sediments contaminated with TBT induces its accumulation on marine biota, and leads to biological effects such as shell malformation in oysters [3], mortality of mussel larvae [4], and imposex of gastropods [5] Potential harmful effects on human health may also result from consumption of contaminated seafood or drinking water [6]. For these reasons, several constraints have been imposed to TBT industrial applications, and the European Union has decided to specifically include TBT compounds in its list of priority compounds in water [7]. Unfortunately, present and future restrictions will not immediately remove TBT and its degradation products, monobutyltin (MBT) and dibutyltin (DBT) from aquatic environments since these compounds are retained in the sediments where they persist [7,8].

Several analytical methodologies have been proposed to quantify organotin compounds, most of them requiring hyphenated techniques, involving a combination of extraction, separation and detection steps [9]. Various pre-concentration procedures have been proposed based on liquid–liquid extraction [10,11], solid-phase extraction (SPE) [12], solid-phase micro-extraction [13,14] and liquid-phase micro-extraction [15,16]. Following this analytical phase, most reported methods combine a separation technique such as gas chromatography (GC) with detection including atomic absorption spectrometry, flame photometry, pulsed flame photometry or inductively coupled plasma mass spectrometry [7,9]. In the case of GC, an additional derivatization step must be included, in order to transform organotins into volatile and thermally stable compounds. Although the analytical performance of these methodologies is widely recognized, allowing the analysis of complex samples containing several unknown components and interferences, they are complex, require a substantial experimental work and skilled analysts, and are difficult to implement for routine analysis.

Modern multivariate calibration methods, especially those based on second-order calibration, constitute an attractive alternative to cope with these situations, even when the processed instrumental data arise from analytical techniques which are intrinsically less selective than chromatography [17]. Certain second-order multivariate algorithms have the property of predicting the concentration of an individual component in the presence of any number of unsuspected constituents, a property commonly named as 'second-order advantage' [18,19]. Usual algorithms employed to analyze second-order data achieving this property are parallel factor analysis (PARAFAC) [20], multivariate curve resolution-alternating least squares (MCR–ALS) [21,22] and some latent-structured methods, such as unfolded partial least-squares (U-PLS) [23] and multiway PLS [24], both combined with residual bilinearization [25,26]. These chemometric methods have been scarcely used for organotin speciation analysis in environmental samples. Only a single work devoted to the quantitation of triphenyltin in seawaters has been reported [27]. However,

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this latter method does not include TBT as analyte, and only seawater matrices were evaluated.

In the present report, a new analytical method is proposed for quantitation of TBT, which is the most toxic organotin [28–30], based on the measurement of excitation–emission fluorescence matrices (EEFMs) processed by second-order multivariate calibration based on MCR–ALS. Fluorescent detection is possible thanks to the reaction between tributyltin and 3,5,7,2′,4′-pentahydroxyflavone (morin) in a Triton X-100 micellar medium, which yields a fluorescent complex. The feasibility of determining TBT in real matrices is demonstrated by applying the proposed methodology to tap, river, lagoon and sea water samples.

2. Experimental

2.1. Apparatus

Fluorescence measurements were performed on an Aminco Bowman (Rochester, NY, USA) Series 2 luminescence spectrometer equipped with a 150 W xenon lamp and using 1.0 cm path length quartz microcells and slit widths of 4 nm for both monochromators. All measurements were performed at 20 °C with a thermostated cell.

The excitation–emission fluorescence matrices were collected exciting samples in the range of 380–460 nm (each 5 nm) and obtaining the corresponding emission spectra in the range of 510–600 nm (each 5 nm), resulting in a data matrix size 19×17 for sample.

All glassware was rinsed with deionized water, decontaminated overnight in a 20% (v/v) nitric acid solution (Merck, Darmstadt, Germany) and then rinsed again with deionized water.

2.2. Reagents and standards

High quality water (18 MΩ) obtained from a Barnstead Easypure II (Thermo, Dubuque, MA USA) was used to prepare the solutions. The organotin standards, such as monobutiltin trichloride (MBT, 95%), dibutyltin dichloride (DBT, 96%) and tributyltin chloride (TBT, 96%) were obtained from Sigma-Aldrich (St. Louis, M.O., USA). Stock solutions of these reagents (1000 mg L^{-1} of Sn) were prepared in methanol and stored at −20 °C in the dark. Working standards were obtained by dilution with water. This was done on a weekly basis for solutions containing Sn at 5 mg L^{-1} and daily for solutions containing Sn at 10–100 μg L^{-1}.

An ethanolic solution 4.2×10^{-3} M of morin (Sigma-Aldrich, Munich, Germany) was prepared every day, while a stock solution 8.3% (w/v) of Triton X-100 (Fluka Chemika, Buchs, Switzerland) and a buffer solution pH 4.7 of succinic acid (Merck, Darmstadt, Germany) 0.5 M were prepared weekly.

For metal additions, a Certipur® ICP multi-element standard solution IV was purchased from Merck (Darmstadt, Germany). This standard includes 23 elements (Ag(I), Al(III), B(III), Ba(II), Bi(III), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Fe(III), Ga(III), In(III), K(I), Li(I), Mg(II), Mn(II), Na(I), Ni(II), Pb(II), Sr(II), Tl(I), Zn(II)) at 1000 mg L^{-1} dissolved in diluted nitric acid.

2.3. Synthetic samples

A set of nine TBT calibration solutions with analyte concentrations was built: eight of them contained equally spaced levels between 0 and 350 μg L^{-1} (based on Sn content). They were prepared adding adequate volumes of the standard solution (5 mg L^{-1}) in a calibrated 10.00 mL vessel. Subsequently, 200 μL of morin solution, 1.0 mL of buffer and 0.84 mL of Triton X-100 solution were added. Finally, completion to the mark was achieved with deionized water and the EEFMs were registered.

For validation, two different sets of solutions were prepared including potential interferences in environmental aqueous samples. The first set involved eight solutions containing random concentrations of TBT and their degradation products DBT and MBT, all in the range of 30–110 μg L^{-1} of Sn. Other organotin compounds, such as Triphenyltin (TPhT) and DPhT, were evaluated but they are not significant fluorescence in presence of morin, according to a previous report [31]. The second set consisted of seven solutions with random concentrations of TBT and metals in the range of 32–90 and 38–120 μg L^{-1}, respectively.

It should be noticed that, if these validation samples were subjected to the pre-concentration procedure described below, the lowest concentrations would have been 500 times lower than those quoted above, i.e., in the order of ng L^{-1}, and compatible with the needs of determining TBT at environmental levels.

2.4. Real samples

Tap and river samples were collected from the Rosario city drinking water system and Paraná River (Santa Fe, Argentina), respectively, while the remaining samples were collected from Curauma lagoon and Baron harbor, both placed in the Province of Valparaiso (Valparaiso, Chile). All samples were filtered using a nylon membrane (0.22 μm) and stored at 4 °C until analysis. TBT concentration was determined by GC with pulsed flame photometric detection [11,32], and was found to be below the detection limit. Therefore, aliquots of these samples were spiked with known amounts of TBT, reaching TBT concentrations ranging between 20 and 120 ng L^{-1}. Solid-phase extraction (SPE) using a C18 extraction membrane (Empore, Supelco, Belleponte, P.A., USA) was applied before sample analysis. The disks were loaded into a 13 mm stainless steel filter syringe kit (Alltech, Deerfield, IL, USA) and placed into a syringe. Prior to sample analysis, the disk was conditioned with methanol. Aliquots of either 100 or 200 mL of aqueous samples were passed through the membrane under vacuum pump, with a flow rate of about 10 mL min^{-1}. After elution of the retained organic compounds with 500 μL of methanol, the solvent was evaporated by using dry nitrogen and reconstituted with 400 μL of the fluorogenic solution. This implies a degree of preconcentration of 250 or 500, depending on the sample volume. Finally, the EEFM was measured for each sample and the TBT concentration was estimated using second-order multivariate calibration.

2.5. Theory

2.5.1. PARAFAC

The theory of PARAFAC is well-known [20]. In some of the presently studied systems, this method was employed to successfully decompose the three-way arrays built with the fluorescence data matrices. However, PARAFAC could not be applied with equal success to samples containing uncalibrated interferents having excitation spectra which are strongly overlapped with those of the calibrated components. This has been previously shown to be a strong challenge to PARAFAC [33,34]. The general problem of second-order calibration under strong profile overlapping in one of the data dimensions can be solved using MCR–ALS, which is thus described in detail in Section 2.5.2.

2.5.2. MCR–ALS

In this second-order multivariate method, an augmented data matrix is created from the test and calibration data matrices. The matrices are all of size $J \times K$, where J is the number of excitation wavelengths and K is the number of emission wavelengths. Augmentation can be performed in either direction, depending on the type of experiment being analyzed and also on the presence of severe overlapping in one of the data modes [18,35]. In the presently studied case, the excitation spectra of some of the various sample components are very similar, and hence it is useful to implement augmentation in this direction, creating a row-wise augmented matrix **D** by