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Analysis of tetrabromobisphenol A and other phenolic compounds in water samples by non-aqueous capillary electrophoresis coupled to photodiode array ultraviolet detection

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Abstract

Non-aqueous capillary electrophoresis (NACE) with large-volume sample stacking injection using the electroosmotic flow pump (LVSEP) has been developed for the determination of tetrabromobisphenol A (TBBPA) and other phenolic compounds in environmental matrices. Methanol has been used as run buffer solvent to reduce the electroosmotic flow (EOF). Identification and quantification of the analytes was performed by photodiode array ultraviolet detection. LVSEP–NACE improved sensitivity of the peak height by 90–300-fold. The method developed was applied to the analysis of TBBPA in river water and wastewater samples, using solid-phase extraction (SPE) as sample pretreatment process. The average recoveries of the analytes were in the range of 96–106% and 73–103% for 1 L of river water and 0.5 L of wastewater samples, respectively. When the method was based on off line SPE–LVSEP–NACE, sensitivity was improved by 3300–4500-fold and 1600–2200-fold for river water and wastewater samples, respectively.

Keywords: Brominated flame retardants; Bromophenols; Tetrabromobisphenol A; Tetrachlorobisphenol A; Solid-phase extraction; Non-aqueous capillary electrophoresis; Large-volume sample stacking; Water analysis

1. Introduction

Some organic halogenated compounds are widely used by industry as flame retardant additives in different polymeric materials, like plastics, electronic applications, . . ., to protect products from catching fire. Halogenated flame retardants represent about 45% of the world-wide production [1], and within this group, tetrabromobisphenol A (TBBPA) is the most commonly used, as well as some brominated phenolic compounds, such as 2,4,6-tribromophenol (2,4,6-TriBP) and pentabromophenol (PeBP).

These chemicals can be released to the environment during industrial processes, during the entire life-time of the flame-retarded product and after disposal [2]. Recently, they have been received attention from chemists and biologists because they are both lipophilic and persistent, some of them are either known or suspected endocrine disruptors, and have the ability to bioaccumulate in the food chain, being a potential environmental and human health problem [3].

Chromatographic techniques have been employed for the analysis of polymer additives, being gas chromatography preferred [4,5]. Due to the low concentrations as additives present in a large variety of environmental matrices, different sample pretreatment processes, like extraction and preconcentration, are needed before its separation, detection and quantification.

Capillary electrophoresis (CE) has been proven to be an efficient technique for the separation of charged species. The application of organic solvents in CE as an alternative to aqueous solutions has been constantly increasing [6,7]. This analytical technique usually permits the use of simpler sample

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pretreatments than others, although CE applications are often limited by sensitivity. To overcome this problem, some authors use CE with sample concentration directly on the capillary (on-column stacking). These techniques include field-amplified methods that are based on conductivity differences between the sample and the electrophoretic medium, such as large-volume sample stacking injection using the EOF pump (LVSEP) [6,8,9]. This on-column concentration could stack trace amounts of negatively charged species without polarity switching, and enhanced the sensitivity in comparison with hydrodynamic injection. The electrophoretic mobility of the sample ions must be greater than and opposite to the EOF during both sample stacking and subsequent separation processes, so that they can proceed consecutively under the same voltage [8].

In this work, a new method for the determination of TBBPA and other phenolic compounds in environmental matrices by non-aqueous capillary electrophoresis (NACE) coupled to photodiode array ultraviolet detection has been developed. It has been used LVSEP, with methanol as the run buffer solvent to reduce the EOF. Finally, to test the applicability of the developed method, river water and wastewater samples extracted by SPE were analysed.

2. Experimental

2.1. Reagents and materials

Methanol (HPLC gradient grade), ethyl acetate (for liquid chromatography), acetone (for gas chromatography), hexane (for organic trace analysis), and acetic acid glacial were obtained from Merck (Darmstadt, Germany), dimethyl sulfoxide (DMSO) (HPLC gradient grade) from Aldrich (Madrid, Spain), and hydrochloric acid from Prolabo (Fontenay-Sous-Bois, France). 2,4,6-Tribromophenol (99%), pentabromophenol (96%), tetrabromobisphenol A (97%) and tetrachlorobisphenol A (TCBPA, 98%) were obtained from Aldrich. 2,6-Dibromophenol (2,6-DiBP, 97%) was from Fluka (Buchs, Switzerland). Sodium tetraborate decahydrate and sodium hydroxide were supplied by Merck (Darmstadt, Germany). Ultrapure water was obtained from a Milli-Q system purchased from Millipore (Bedford, MA, USA).

Stock solutions of each phenol derivative were prepared at 4000 μg/mL in methanol. Chemical mixture standards for calibrations were dissolved in methanol to appropriate concentration levels. All solutions were refrigerated at 4 °C and protected against daylight. These solutions were used to make daily working standards solutions by appropriate dilution.

Cellulose ester membrane filters (SMWP, 47 mm, 5 μm; HAWP, 47 mm, 0.45 μm), Durapore membrane filters (GVHP, 47 mm, 0.22 μm), and Durapore Millex syringe filters (SLHV, 25 mm, 0.45 μm) were supplied from Millipore. Oasis SPE cartridges (HLB, 60 mg, 3 mL) were obtained from Waters (Milford, MA, USA).

2.2. CE analysis

Capillary electrophoresis was performed using a HP^{3D} system (Hewlett-Packard, Waldbronn, Germany) equipped with an on-column diode array detection (DAD) system. Absorbances at 210 and 230 nm (direct UV detection) were monitored for the detection of the analytes. The migration order was determined by injecting the individual solution of each compound and by the spectral comparison of each peak in electropherograms with an UV spectra library.

Uncoated narrow-bore silica capillary (supplied by Composite Metal Services, UK) with an effective/total length of 61.5/70 cm and 75 μm i.d. was used. The capillary was thermostated to 25.0 °C. A Chrompack RTE-110B external water bath was used for thermostating the samples to 25 °C.

Standards and samples were injected hydrodynamically by applying a pressure of 50 mbar for 2 s and 300 s, depending on the experiment, and the applied voltage for separation was −30 kV, unless otherwise stated.

New capillaries were rinsed with 1 M sodium hydroxide for 20 min. Before injections, capillaries were conditioned by washing them with 0.1 M sodium hydroxide for 5 min, Milli-Q water for 5 min, and 15 min with the separation electrolyte. After each run (once the electrophoretic separation has finished) the capillary was flushed with organic solvent corresponding to the electrophoretic medium for 5 min and with Milli-Q water for 5 min. The inlet and outlet of the capillary were kept overnight in Milli-Q water.

Methanol was assayed as solvent for non-aqueous background electrolyte preparation. Sodium tetraborate, being readily soluble in methanol, was used as electrolytic salt. The apparent pH (pH_{app}) [10] of the solution was 9.4, adjusted by addition of a sodium hydroxide solution, and measured using a Metrohm 654 pH-meter (Herisau, Switzerland) calibrated with aqueous standard buffer solutions. This solution was prepared freshly each two days, sonicated in a P-Selecta ultrasonic bath (Barcelona, Spain) for at least 4 min and filtered through a membrane of 0.22 μm pore size. Every day all remaining solutions were filtered through a 0.45 μm syringe filter before use.

Data acquisition was done by means of HP^{3D} ChemStation Software (Rev. A.06.01[403]) (Hewlett-Packard, Waldbronn, Germany). Statistical analysis of the response variables were supported by the statistical graphics software system Statgraphics Plus 3.3 (STSC, Rockville, MD, USA).

Oasis SPE cartridges were dried using a Turbo-Vap II Nitrogen Evaporator supplied by Zymark (Hopkinton, MA, USA).

2.3. Sample preparation

An off-line solid-phase extraction (SPE) step was used to cleanup and preconcentrate the samples before analysis. Environmental water samples were collected in a river and a wastewater-treatment plant near Santiago de Compostela (NW Spain).