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Method development and optimization for the determination of benzene, toluene, ethylbenzene and xylenes in water at trace levels by static headspace extraction coupled to gas chromatography–barrier ionization discharge detection

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ABSTRACT

Benzene, toluene, ethylbenzene, and xylenes, more commonly named BTEX, represent one of the most ubiquitous and hazardous groups of atmospheric pollutants. The goal of our research was the trace quantification of BTEX in water by using a new simple, low-cost, and accurate method, based on headspace (HS) extraction and gas chromatography (GC) coupled to barrier ionization discharge detector (BID). This water application dealt with simple matrices without protein, fat, or humic material that adsorb target analytes, thus the external standard calibration was suitable to quantify each compound. The validation steps included the study of linearity, detection and quantification limits, and accuracy. LODs and LOQs varied from 0.159 to 1.845 $\mu\text{g/L}$ and from 0.202 to 2.452 $\mu\text{g/L}$, respectively. The recovery was between 0.74 ± 0.13 and 1.15 ± 0.09 ; relative standard deviations (% RSDs) were less than 12.81% ($n = 5$) and 14.84% ($n = 10$). Also, GC performance was evaluated in term of efficiency, peak tailing and resolution. Preliminary results from practical applications to analyses of real samples are presented. The results indicate that static HS coupled to GC–BID is a successful method for BTEX analysis in water samples at the $\mu\text{g/L}$ levels, provided that hydrocarbons interference occur at similar concentration levels. GC–BID may become a routine reference method alongside the official analytical techniques for quality control purposes of contaminated waters. Moreover, the new method is amenable to automation by using commercial HS units.

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1. Introduction

Benzene, toluene, ethylbenzene, *m/p*-xylene, and *o*-xylene (BTEX) have been shown to cause a variety of adverse health effects, including potential carcinogenicity [1]. Their leakage, during fuels storage and transfer, can contaminate both ground and surface water, as well as the soil and the atmosphere [2]. The U.S. Environment Protection Agency (EPA) has defined BTEX as priority pollutants in water and established a maximum contaminant level in drinking water of 5 $\mu\text{g/L}$ for benzene, 1000 $\mu\text{g/L}$ for toluene, 700 $\mu\text{g/L}$ for ethylbenzene and 10,000 $\mu\text{g/L}$ for xylenes [3]. The current Italian environmental regulation on water quality is the

Legislative Decree April 3, 2006 no. 152 (D.L. 152/2006) [4], which imposes stricter limits for BTEX in groundwater: the maximum permissible levels of benzene, toluene, ethylbenzene, and xylenes are 1, 15, 50 and 10 $\mu\text{g/L}$, respectively. Therefore, in order to protect people's health, it is necessary to establish an effective and convenient quantification method for monitoring BTEX in water, below the maximum permitted levels [5]. In literature, the analysis of BTEX in water requires preconcentration and clean-up of the analytes through multiple solventless extraction techniques such as purge and trap (P&T), static or dynamic headspace (HS), and solid-phase microextraction (SPME) [6,7]. Among them, HS sampling has been adopted by the Environmental Protection Agency (EPA) in many protocols thanks to its advantages [8,9]: it is not expensive, it does not require complicated instrumentation and the use of a large volume of organic solvents, and it shows an enhanced sensitivity for BTEX compared to direct aqueous injection (DAI) techniques [10]. Gas chromatography (GC) plays a crucial role for

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the identification and quantification of such volatile organic compounds [5,11]. In order to monitor BTEX at $\mu\text{g/L}$ levels, numerous detectors are available but the most commonly used are flame ionization detectors (FID), photoionization detectors (PID) and mass spectrometry (MS) [12]. The significantly limited capabilities for water monitoring in many developing countries, which are affected by serious water quality problems, led to the development of alternative and/or additional simple and sensitive methods for BTEX determination.

The main aim of this study was to develop and optimise an adequately sensitive and reliable analytical method to be applied in routine monitoring of BTEX by using the static headspace and an economically accessible system, such as gas chromatography with a barrier ionization discharge detector (GC-BID), instead of the traditional GC-FID, GC-PID and GC/MS systems. The BID detector, based on helium discharge plasma ionization, enables the sensitive detection of all volatile compounds including analytes with a poor or no response in the FID, except for He and Ne [13–17]. The proposed analytical method was validated in terms of limits of detection, limits of quantitation, linearity, trueness, and precision according to the European Action in Chemistry (EURACHEM) guidelines [18]. The contamination of water samples with petroleum hydrocarbons was simulated under laboratory conditions and the validated method was applied for trace detection of BTEX.

2. Material and methods

2.1. Chemicals and standard solutions

The standard BTEX compounds used in this paper were benzene (Carlo Erba, Rodano, Milano, Italy; purity: 99.5%; density: 0.879 g/mL), toluene (Carlo Erba, Rodano, Milano, Italy; purity: 99.5%; density: 0.867 g/mL), ethylbenzene (Sigma-Aldrich, Schnelldorf, Germany, purity: 99%; density: 0.867 g/mL) and xylenes (Sigma-Aldrich, Schnelldorf, Germany, histological grade, density: 0.860 g/mL). The stock solutions of 1 g/L benzene, 1 g/L toluene, 1 g/L ethylbenzene and 1 g/L xylenes were prepared by dissolving appropriate amounts of each pure substance in methanol (Carlo Erba, Rodano, Milano, Italy). Appropriate amounts of the stock solutions were added to ultrapure water to give final concentration for the static HS optimization procedure, chromatographic and validation studies, as described in Sections 2.2–2.4 respectively. Dilutions were performed with class A volumetric glassware. All calibration solutions were equilibrated at 20 °C before preparation and use. Revised PVOC mixture (UltraScientific, California, USA), consisting of $1002 \pm 5 \mu\text{g/mL}$ of benzene, $1003 \pm 5 \mu\text{g/mL}$ of toluene, $1004 \pm 5 \mu\text{g/mL}$ of ethylbenzene, $1002 \pm 5 \mu\text{g/mL}$ of *o*-xylene, $1003 \pm 5 \mu\text{g/mL}$ of *m*-xylene and $1005 \pm 5 \mu\text{g/mL}$ of *p*-xylene in methanol (Lot CP-0864), was used for the assessment of trueness by means of the recovery evaluation on blank samples and simulated contaminated water samples.

2.2. Static headspace procedure

The BTEX extraction by static HS is influenced by several parameters: temperature, stirring, sample volume, heating time and ionic strength, which have been studied individually keeping the other parameters constant [7]. The BTEX concentration was 50 $\mu\text{g/L}$ for each analyte and all solutions were analysed by changing the parameters under study, one at a time as discussed below. The analyses were performed in triplicate ($n=3$) and all parameters were kept constant for each of the three replicates. The liquid samples were transferred in 40 mL vials tightly sealed with polytetrafluoroethylene silicone septa (Supelco; Milano, Italy) and the vials were placed on a stirrer hot plate at a controlled temperature. The

temperature effect in extraction using static HS was studied by analysing 50 $\mu\text{g/L}$ standard solution of each analyte, under the same conditions (20 mL, 30 min, 200 rpm) at different temperatures (20, 40, 60 and 80 °C). The effect of sample volume in 40 mL vial on peak areas of 50 $\mu\text{g/L}$ BTEX in water, produced by HS for 30 min at 80 °C and 200 rpm, was studied by changing solution volume between 5 mL and 25 mL. The stirring effect was investigated by changing the rates per minutes (rpm) from 0 to 400 rpm, while keeping the other parameters constant. Finally, the effect of ionic strength on BTEX determination was studied through the saturation of 20 mL sample volume with 8 g of NaCl (Carlo Erba, Milano, Italy) and performing headspace sampling after 30 min at 80 °C and 200 rpm. The results are expressed as mean \pm standard deviation (Mean \pm SD). The Student's *t*-test (SPSS 19.0 for Windows; IBM SPSS Statistics, Armonk, NY, USA) was used to assess the presence of significant differences ($p < 0.05$) among the results obtained for static HS conditions, thus choosing the best one.

2.3. GC-BID conditions

A Shimadzu system (Kyoto, Japan) consisting of a barrier ionization discharge (BID) detector equipped with a 2010 Plus Tracera gas chromatograph (GC) with a split/splitless injector was used for the quantification and confirmation of the aromatic hydrocarbons. Headspace gaseous phase sampling was performed with 25 mL gas-tight syringe (Sigma Aldrich Milano, Italy) and injected into GC-BID system through 500 μL sample loop at 70 °C, while the pressure drop was kept constant by using a 10–100 cc/min scale RMA-150-BV rotameter (Rometec, Roma, Italy) [15]. The flow control at the loop output eliminated pressure variability and improved sample-to-sample precision of manual injection. The injector port was maintained at 200 °C, and a 500 μL volume of headspace was injected in split mode (split ratio 90:10). A Restek Rtx-624 fused silica capillary column (6% Cyanopropyl-phenyl 94% Dimethyl polysiloxane; 20 m \times 0.18 mm I.D.; film thickness 1.00 μm) was employed with He 6.0 (SIAD Corporation, Bergamo, Italy) as the carrier gas at a flow rate of 1.0 mL/min. The column temperature was programmed as follows: constant 30 °C for 1 min, increasing to 70 °C at 10 °C/min and holding for 10 min; finally the temperature was increased to 200 °C at 15 °C/min and holding for 5 min. The effluent from the GC column was transferred via a 50 mL/min discharge gas flow into the BID detector at 250 °C. Data acquisition and processing were done by using the LabSolution (Shimadzu, Kyoto, Japan) software.

2.4. Analytical method validation

In order to validate the method for the determination of the BTEX analytes by HS GC-BID system, the following parameters were assessed: GC performance (i.e., efficiency, tailing factor and resolution), linearity, trueness, precision, limits of detection (LODs), limits of quantification (LOQs) and uncertainties. Owing to their co-elution (see Fig. 3), *m*-xylene and *p*-xylene were identified and quantified together.

2.4.1. GC performance

The evaluation of GC performance is important for the comparison with the official analytical techniques. GC separation was assessed in terms of efficiency, peak tailing and resolution, which are calculated with LabSolution software.

The number of theoretical plates (NTP), and the height equivalent to theoretical plate (HETP), are indices used to determine the column efficiency, and are calculated from the width at half the peak height ($W_{0.5}$) at a specific retention time (t_r).

The resolution was calculated by using the half-height method because it is easier to measure the half-height width than the base-

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