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Ion-pair single-drop microextraction versus phase-transfer catalytic extraction for the gas chromatographic determination of phenols as tosylated derivatives

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ABSTRACT

The environmental fate of phenols represents a diachronic scientific consideration mainly due to their high toxicity and diverse physicochemical properties rendering them difficult to be analyzed as unity. Ion-pair-assisted extraction and microextraction techniques in association with a dedicated derivatization reaction are possible to lead to enhanced selectivity and sensitivity in gas chromatography. Phase-transfer catalytic liquid–liquid extraction–derivatization and ion-pair-assisted single-drop microextraction with in-drop derivatization are successfully employed for the analysis of 15 phenolic compounds. The analytes that react at room temperature with *p*-toluenesulfonyl chloride into the bulk of the organic phase are subsequently determined by GC–MS in selective-ion monitoring mode. Aiming at maximizing the derivatization yields obtained from the 15 analytes in a reasonable time period, the optimum experimental parameters were established along with the figures of merit of the methods. The limits of detection ranged from 0.48 to 1.5 ng/ml and from 0.20 to 0.28 ng/ml respectively, while the limits of quantitation ranged from 1.4 to 4.5 ng/ml and from 0.59 to 0.84 ng/ml for the two methods with the techniques under study. The overall procedure presented satisfactory analytical features with the liquid–liquid extraction protocol being easier to carry out while the single-drop one, presented higher sensitivity and significant reduction of the organic solvent employed. By comparison with other methods for the analysis of phenols, the proposed methods exhibit adequately low detection limits, good precision, short derivatization time and low solvent, sample and reagent consumption.

1. Introduction

Phenols are important pollutants in water because of their wide use in many industrial processes, such as the manufacture of plastics, dyes, drugs, antioxidants and pesticides [1–3]. They are of great environmental concern owing to their high toxicity. For this reason, a number of phenolic compounds are listed in the US Environmental Protection Agency (EPA) list of priority pollutants [4].

Many analytical techniques have been used for the determination of phenols in aquatic environments. The sum of phenolic compounds is determined by various spectrophotometric methods [5–7] while high-performance liquid chromatography [8] and capillary electrophoresis [9,10] have been commonly used. Gas chromatography is often preferred, due to its inherent advantages of high resolution, rapid separation, low cost and ease of coupling with sensitive and selective detectors. The GC analysis of the polar phenols leads to broad, tailed peaks, decreasing the detection limits and the reliability of results. To alleviate this drawback, phenols are usually derivatized with a suitable derivatization reagent before injection into the GC. There are many derivatization methods including acetylation [11,12], benzylation [13], benzoylation [14], alkylation [15,16], silylation [17,18] and other means to convert phenols to less polar compounds associated with better chromatographic characteristics.

Extraction is a prerequisite to isolate and preconcentrate analytes prior to gas chromatographic analysis. Conventional extraction methods, such as liquid–liquid extraction [19] and solid-phase extraction [20] are the most commonly used techniques for the preconcentration and cleanup of phenols prior to GC determination. The prominent solid-phase microextraction (SPME) has already been successfully applied for the extraction of phenolic compounds for water analysis [21,22]. For the SPME gas chromatographic analysis of such polar compounds as phenols, derivatization can be performed in the aqueous sample [23] or on the SPME fiber after the preconcentration step [24–26]. The latter method is preferred when water-sensitive derivatization reagents, such as silyl donor compounds are employed. In recent years, single-drop microextraction (SDME) was developed as an alternative to SPME, affording analyte extraction in few microliters of organic solvents [27]. SDME circumvents problems such as sample carry-over and fiber degradation related to SPME and is fast and inexpensive. Analytical problems are readily addressed through the use of specific

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derivatization processes. Single droplet constitutes a convenient environment for derivatization reactions to take place.

Phase-transfer catalytic (PTC) derivatization has been valued as an analytical tool that promotes reactions between immiscible phases, achieving one-step extraction–preconcentration–derivatization [28]. PTC-assisted methylation of certain phenolic compounds has already been reported [29] exhibiting adequate sensitivity and selectivity whereas SDME of phenols from aqueous samples followed by in-syringe derivatization and GC–MS detection has also been published [30]. Recently, in the same context, endocrine disrupting phenolic compounds were analyzed after in-drop derivatization with ethyl chloroformate with the aid of ion-pairing agents [31]. In this process, the theoretical background was also established.

p-Toluenesulfonyl chloride (TSC) is an OH– and NH– group protective agent, almost exclusively used in organic synthesis and scarcely used for analytical purposes [32], mainly due to the fact that it is insoluble in water and thus, derivatization process needs an organic solvent. The tosylation of phenols preceded by the formation of an ion-pair, conceptually may result in a selective one-step preconcentration–derivatization procedure for the trace level analysis of phenolic moieties. In this research undertaking, two methods for the extraction–preconcentration–derivatization are developed and properly compared: a one-step classical PTC extraction–derivatization and a SDME–ion-pair transfer derivatization process leveraging the capability of TSC to react, under mild conditions, with hydroxyl groups. The tosylation, as a derivatization method is employed for the first time, for the determination of micropollutants by gas chromatography. Both the procedures are based on the transfer of 15 phenolates as ion-pairs in alkaline conditions, followed by tosylation in the organic phase. A thorough optimization of the procedures was carried out and a comparison of their analytical features was attempted.

2. Experimental

2.1. Reagents and chemicals

Riedel-de Haën (Seelze, Germany) supplied the GC grade solvents dichloromethane, chloroform, ethyl acetate, isooctane, toluene, *tert*-butyl methyl ether, diethyl ether and *n*-hexane. The ion-pairing agents tetrabutylammonium bromide (TBAB), tetrahexylammonium bromide (THAB), cetyltrimethylammonium bromide (CTAB), as well as *n*-pentadecane (internal standard), sodium chloride, sodium hydroxide, disodium hydrogen phosphate, TSC and the phenolic compounds used for the study were all obtained from Sigma–Aldrich Hellas (Athens, Greece). All the chemicals and solvents were of the highest grade available.

2.2. Solutions

Standard stock solutions of analytes (0.25–1.0 mg/ml) were prepared separately by weight, in methanol/water (30/70). The appropriate dilutions were made in double distilled water (DDW). Mixtures with the individual standard solutions were made aiming to prepare a working solution with the desired concentrations of each analyte. The extraction solvent (i.e. $CHCl_3$) contained *n*-pentadecane as the internal standard (I.S.) at a concentration of 0.1 mM and TSC at 0.05 M. Disodium hydrogenphosphate–NaOH buffer solution (0.5 M) was of pH 10.6 and the ion-pairing agents were prepared in this solution, at a concentration of 0.1 M. All the solutions were prepared weekly. The glassware used for the analyses was cleaned with AP-13 Extran alkaline soap (Merck, Darmstadt, Germany) for 24 h, washed with DDW and acetone and baked at 110 °C overnight while volumetric flasks were air-dried instead of baked. Single-drop experiments and injections were performed using a 10-μl microsyringe with angle-cut needle tip (0.6 mm glass barrel, I.D.; 0.11 mm needle I.D.).

2.3. Instrumentation–chromatographic analysis

The GC–MS analysis of the target compounds was performed on a Shimadzu (Kyoto, Japan) GC-17A gas chromatograph interfaced with a Shimadzu QP 5000 mass spectrometer, in the selective-ion monitoring (SIM) mode. Chromatography was conducted on a Supelco (Bellefonte, PA, USA) MDN-5 fused-silica capillary column (30 m × 0.25 mm I.D., 0.25 μm film thickness). Helium was used as the carrier gas and the flow rate was set at 1 ml/min. Samples were injected in the splitless mode with subsequent opening of vent valve after 1 min. The GC oven temperature was programmed as follows: 60 °C for 2 min, to 200 °C at 10 °C/min, held for 5 min, to 270 °C at 10 °C/min, held for 10 min. The total program run was 38 min. The injector and detector temperatures were set at 250 and 280 °C, respectively. The mass detector was operated in the electron impact (EI) mode at 70 eV and electron multiplier voltage of 1.30 kV. The mass fragments of the derivatives were obtained in the full scan mode in the scan range from m/z 50 to 500. A solvent delay time of 13.0 min was used to protect the ion multiplier of the MS instrument from saturation. System control and data acquisition were achieved with a personal computer using the CLASS-5000 Version 1.24 Chromatography Software (Shimadzu Chem. Lab. Analysis System and Software).

2.4. Analytical procedure

2.4.1. Classical PTC extraction–derivatization

In a typical procedure, a portion of 5 ml of aqueous solution, 0.5 ml of phosphate buffer 0.1 M (pH 10.6), 0.5 ml of TBAB solution 0.1 M and 0.3 ml of extraction solvent (i.e. $CHCl_3$, containing the I.S. and TSC 0.05 M) are successively added to a 10-ml tube bearing PTFE-lined screw-cap. The reaction tube is sealed and vigorously stirred for 40 min at room temperature so that the vortex formed is spread throughout the liquid volume. After phase separation, 1 μl of the organic layer is directly subjected to GC analysis.

2.4.2. SDME–ion-pair transfer derivatization

In a screw-capped vial of 10 ml sealed with PTFE-lined silicon septa are placed 5 ml of the sample, 0.5 ml of phosphate buffer solution 0.5 M (pH 10.6) and 0.5 ml ion-pairing agent solution 0.1 M. The sample solution is agitated at 230 rpm with a stir bar (10 mm × 3 mm) for 2 min. A microsyringe is rinsed with the organic solvent (i.e. $CHCl_3$, containing the I.S. and the TSC) several times and then 3 μl are drawn into the syringe. With the needle tip out of the solution, the plunger is depressed by 1 μl. The needle is then immersed in the sample and is fixed with a stand and clamps. The plunger is pushed down exposing 1.8 μl of organic drop to the stirred aqueous solution, for 20 min. After extraction–derivatization, the drop is retracted into the microsyringe, which in turn is removed from the sample vial and the organic solvent drop is injected into the GC system for analysis.

An analytical set for the construction of the appropriate calibration curves consisted of triplicate six analytical standards of various concentrations. The derivatives were quantified by the height ratios relative to the I.S. Recalibration was taking place for checking the stability of the system and chromatographic column performance.

2.4.3. Sample treatment

Surface waters were collected from Lake Pamvotis (Ioannina), Acheron and Kalamas rivers, from the region of Epirus as well as