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Lab-In-Syringe automation of stirring-assisted room-temperature headspace extraction coupled online to gas chromatography with flame ionization detection for determination of benzene, toluene, ethylbenzene, and xylenes in surface waters

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ABSTRACT

Online coupling of Lab-In-Syringe automated headspace extraction to gas chromatography has been studied. The developed methodology was successfully applied to surface water analysis using benzene, toluene, ethylbenzene, and xylenes as model analytes. The extraction system consisted of an automatic syringe pump with a 5 mL syringe into which all solutions and air for headspace formation were aspirated. The syringe piston featured a longitudinal channel, which allowed connecting the syringe void directly to a gas chromatograph with flame ionization detector via a transfer capillary. Gas injection was achieved via opening a computer-controlled pinch valve and compressing the headspace, upon which separation was initialized. Extractions were performed at room temperature; yet sensitivity comparable to previous work was obtained by high headspace to sample ratio V_{HS}/V_{Sample} of 1.6:1 and injection of about 77% of the headspace. Assistance by in-syringe magnetic stirring yielded an about threefold increase in extraction efficiency. Interferences were compensated by using chlorobenzene as an internal standard. Syringe cleaning and extraction lasting over 10 min was carried out in parallel to the chromatographic run enabling a time of analysis of <19 min. Excellent peak area repeatabilities with RSD of <4% when omitting and <2% RSD when using internal standard corrections on 100 $\mu g\,L^{-1}$ level were achieved. An average recovery of 97.7% and limit of detection of 1–2 $\mu g\,L^{-1}$ were obtained in analyses of surface water.

1. Introduction

Gas chromatography (GC) remains the major instrumental technique for the analysis of volatile compounds of low molecular weight with a stronghold in the determination of environmental pollutants. While GC is a relatively robust technique with operation and maintenance being straightforward, it often requires sample preparation to achieve analyte enrichment, for matrix removal or to obtain volatile and thermostable species by derivatization reactions.

Headspace (HS) sampling techniques [1], taking advantage of analytes volatility, are preferably used for this task as they can be applied both to liquid and solid samples. They are environmentally-friendly while being easily implemented and automated [2–4].

A classification can be made to direct headspace extraction (HS-E) and techniques based on simultaneous analyte trapping either in a solvent drop (e.g. supported on the injection needle) or a sorbent (coating a supporting fiber). Related techniques are single-drop microextraction (HS-SDME) and solid-phase microextraction (HS-SPME).

The solvent drop or SPME fiber act as a sink for the analyte, i.e. the concentration gradient between HS and sample remains. Thus, more analyte can be extracted and eventually transferred. However, these approaches require consumables (costly SPME fiber) or solvents and imply additional challenges (drop formation, stabilization, and transfer) while typical drawbacks of floating or immersed SDME [5] and SPME [6] such as drop recovery [7] or surface deterioration are avoided. Studies [8,9] conclude that apart from matrix removal, HS methodologies can enhance time- and extraction efficiency. Due to the extent of related developments, the reader is referred to comprehensive reviews [2,3,10].

Direct HS-E can be carried out either in static or dynamic mode. In static mode, analyte evaporation is completed inside a sealed

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vial and promoted by sample heating and stirring and less often by pressure decrease [11]. Aiming at high reproducibility and phase equilibrium, a fraction of the HS gas is aspirated after a selected extraction time into a gas-tight syringe, and injected in GC. In dynamic mode, the sample is purged by an inert gas with downstream analyte retention e.g. on a cold-trap and then thermally desorbed. Advantages involve the possibility of exhaustive and efficient extraction from large sample volumes leading to a better sensitivity. However, removal of moisture originating from the sample can require an additional drying step and the instrumental complexity is significantly increased by required extractor, trap, flow regulators, and valves. Moreover, extraction vial and injection syringe (batch-wise) or transfer line (online coupling) need generally to be heated to promote volatilization and to avoid loss of analyte [9]. Two thorough surveys are recommended reading [1,4].

Secondary analyte concentration by HS-SPME, HS-SDME, and in particular by sample purging and downstream cold-trap require manual work or sophisticated instrumentation for the automation of these procedures [12]. For example, use of needle traps combined with in-syringe HS-E required manual trap insertion into the GC injector and yielded low reproducibility and throughput [13].

Flow techniques (FT) are versatile tools for the automation of sample pretreatment. However, to the best of our knowledge, they have not been used for HS-E for GC. This gap appears to be related to features of FT that are not compatible with the HS-E concept. Typically, FT operate with sub-milliliter sample volumes and procedural steps are performed in flow within a tubing manifold so that interfacial areas are small. On the other hand, hybrid FTs exist that are based on batch operations and mixing chambers [14,15]. Among these, the technique Lab-In-Syringe (LIS) [16,17] appears particularly promising for the automation of HS-E. It has already proven its potential for the automation of HS-SDME [18,19] and liquid-liquid microextraction coupled to GC [20].

BTEX present pollutants of high environmental mobility. They are derived from petro-chemical industry and used as gasoline components, solvents, and for synthesis. Sources of contamination include imperfect combustions and leakages from landfills, waste sides, storage tanks, and pipelines [21]. They have high impact on human health with chronic damage to liver and nervous system, and potential carcinogenic activity proven at least for benzene. Due to oil spills and depositions, BTEX can be found in surface and ground water at trace levels. Despite extensive developments of methodologies for their determination, the interest in simplified and sensitive analytical methods remains as BTEX count to the group of priority pollutants [22].

HS-E, SDME (immersed/floating/HS), and SPME (immersed/HS) linked to GC are the most frequently used methodologies for BTEX analysis. Specific shortcomings such as instrumental complexity and need for manual handling can deteriorate their repeatability and robustness. Predominantly static HS-E, being the simplest of the former methodologies, is limited by using only a small part of the entire HS even if coupled online to GC [23].

In this report, we propose LIS automated static HS-E coupled online to GC using BTEX as model analytes, where the void of a computer-controlled syringe pump acted as an airtight-sealed yet size-adaptable and stirred extraction chamber [24,25].

2. Experimental section

2.1. Chemicals and solutions

Purified water was from a MilliPore system (Merck, Prague, Czech Republic). Methanol (ChromaSolv, ≥99.9%, Honeywell Riedel-de-Haën) was used for system cleaning and standard preparation. Further chemicals were of analytical reagent grade and purchased from Sigma Aldrich (Prague, Czech Republic). Stock solutions of benzene (B), toluene (T), ethylbenzene (E), chlorobenzene (Cl-B), ortho-, meta-, and para-xylene (o-X, m-X, p-X) in methanol were prepared by weighing the required amounts in 10 mL volumetric flasks. Aqueous standards were prepared by subsequent dilutions. Stock solutions of NaCl (300 g/L), 1-pentanol, H_2SO_4 (1 mol/L), NaOH (2 mol/L), Na_2CO_3 (1 mol/L), Triton X-100 (0.1 mmol/L), and SDS (0.1 mmol/L) were tested as modifiers or interferences, respectively.

Cl-B was used as internal standard since its suitability was reported previously [23,26]. It exhibited characteristics comparable with the analytes including peak characteristics, solubility, and volatility.

Three surface water samples were obtained from local pond and two rivers in Hradec Králové, Czech Republic. Samples were stored before analysis in glass bottles at 4 °C in the dark. A snow sample was taken 3 days after precipitation from the upper 5 cm and about 2 m away from a highly-frequented road and about 50 m from a gasoline station. All samples were decanted to remove sediments. Elimination of fine sediments through a filter paper was required only for one sample.

2.2. Lab-In-Syringe extraction system

The developed extraction system including operation is depicted in Fig. 1. An image of the system is given as Fig. A1 (in the Supplementary materials). Extractions were carried out inside the void of a 5 mL glass syringe on a CavroXP3000 syringe pump (Tecan, Switzerland). The pump featured a 3-position head valve and was connected at port IN via a 28 cm long loading tube (PEEK, 0.8 mm ID) to the central port of a low-pressure 6-port selection valve from Vici Valco (Schenkon, Switzerland). All solutions and air for HS formation were aspirated from the valve into the syringe void. Head valve port OUT was used for waste disposal while the port MIDDLE was permanently closed.

As a special characteristic, a 1.5 mm diameter hole was drilled through the syringe piston into which a piece of PEEK tubing (7.5 cm, 0.5 mm ID) was glued with silicone. This permitted a secondary access in the syringe void circumventing the head valve. The syringe pump was used upside-down so that the HS would be between the sample and the piston and could be expulsed via this "piston-channel".

Two 17 cm and 40 cm long pieces of untreated fused silica capillary (0.4 mm od, 0.25 mm ID) were joined by a 3 cm long sleeve of silicone rubber tubing (3 mm od, 0.3 mm ID) and used for transfer of the HS gas from the syringe to the GC. The shorter capillary was inserted and sealed to the PEEK tube inside the syringe piston. The longer capillary was connected to a stainless steel injection needle (7 cm, 0.4 mm ID), which was permanently positioned in the GC injection port. The silicone rubber tube allowed closure of the transfer capillary by a "normally-closed" pinch-valve (P/N075P2NC12-10SM, BioChem Fluidics, Boonton, NJ).

For homogenous mixing and promotion of HS enrichment, a magnetic stirring bar (1.4 mm length, 4 mm diameter) was placed inside the syringe. Due to the upside-down orientation of the syringe, the stirring bar remained down at the head valve inlet. Bar rotation was induced by a closely positioned DC motor made from a PC ventilator with mounted neodymium magnets. The motor was powered by a simple regulation circuit, activated via one of three auxiliary outputs of the syringe pump. The second and third outputs were used to operate the pinch valve, i.e. for opening of the transfer line, and to trigger the GC and data acquisition via a relay contact, respectively. The entire system was controlled by open-source software Cocosoft 4.4 (FI-Trace Group, University of the Balearic Islands, Spain) [27].

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