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Journal of Chromatography A, 1121 (2006) 259–267

JOURNAL OF CHROMATOGRAPHY A

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Simplified analysis of organic compounds in headspace and aqueous samples by high-capacity sample enrichment probe

Ben V. Burger*, Brenda Marx, Maritha le Roux, Wina J.G. Burger

Department of Chemistry and Polymer Science, Stellenbosch University, Private Bag, Stellenbosch 7600, South Africa

Received 21 September 2005; received in revised form 5 April 2006; accepted 10 April 2006

Abstract

A sample enrichment probe (SEP) consisting of a thin rod of an inert material and provided at one end with a short sleeve of polydimethylsilicone rubber was used for the high-capacity sample enrichment of analytes from gaseous and aqueous samples for analysis by gas chromatography (GC) and its hyphenated techniques. The silicone rubber was exposed to the analytical sample, after which the end of the rod carrying the silicone rubber was introduced into the injector and the analytes thermally desorbed and analysed by GC. This technique is similar to, but differs from, solid-phase microextraction (SPME) in that a much larger volume of the sorptive phase is employed, the sorptive phase is not introduced into the inlet of the GC via a needle and the injector is opened to the atmosphere for the introduction and removal of the SEP. In the determination of volatile and semi-volatile organic compounds in gaseous and aqueous media, the SEP technique gave results comparable with those obtained by the stir-bar-sorptive extraction (SBSE) and high-capacity sorption probe (HCSP) techniques. Implementation of the SEP technique requires only minor adaptations to the gas chromatograph and does not require any auxiliary thermal desorption and cryotrapping equipment.

Keywords: Headspace analysis; Environmental analysis; Water analysis; Sorptive sample enrichment; Silicone rubber; Sample enrichment probe (SEP)

1. Introduction

Despite the ability of gas chromatography (GC) and its hyphenated techniques to detect picogram quantities of analyte, the selective enrichment of sample analytes has to be employed in order for these techniques to reach the limits of detection (LOD) and quantification (LOQ) required for biological and environmental analyses. The LOD can be reduced by large-volume injection [1], but only within limits. Solvent extraction of the analytes and concentration of the extract can also reduce LOD but it is time consuming, it is difficult to concentrate extracts without selectively losing the more volatile analytes, and solvents are expensive to dispose of. Using adsorbents or absorbents to selectively extract analytes from samples is an attractive alternative to solvent extraction, and various systems have been developed for this purpose [2,3]. One of the most popular is solid-phase microextraction (SPME) [4], which has gained wide acceptance because it is simple to use and its non-automated version does not require adaptation of the gas chromatograph or additional expensive instrumentation. However, the enrichment that can be achieved with SPME is low because of the unfavourable partition between the microlitre volumes of sorbent on the fibre and large sample volumes. To increase the sensitivity of headspace analyses, Baltussen et al. [5] developed stir-bar-sorptive extraction (SBSE) [5] in which the analytes are enriched in a sorptive sleeve of rubber on a magnetic follower or stir-bar. This technique can be applied to both liquid and gas samples. Because a much larger volume of the sorptive stationary phase is used in this technique, the sensitivity of this method is much higher than that of SPME. Pettersson et al. [6] developed the high-capacity sorption probe (HCSP) in which a similarly large volume of the sorptive stationary phase is employed. These methods are flexible in as far as the volume of the sorptive medium is concerned, and they can therefore be adapted to a variety of applications. Solid-phase aroma-concentrate extraction (SPACE) [7], in which volatiles are enriched in an absorbent consisting mainly of graphite–carbon coated on a stainless-steel rod, is another recently introduced sample enrichment method.

Because a very small volume of sorptive phase is used in SPME, thermal desorption of the enriched material takes place

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* Corresponding author. Tel.: +27 21 808 3328; fax: +27 21 808 3360.
E-mail address: lecus@sun.ac.za (B.V. Burger).

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doi:10.1016/j.chroma.2006.04.007

almost instantaneously and the volatiles desorbed from the fibre need not be cryofocused on the column. The large volumes of sorptive material employed in SBSE, HCSP and SPACE preclude instantaneous desorption of the volatiles, which therefore have to be cryofocused on the column. This complicates implementation of these techniques and creates a niche for a simple method that can be used for analytical troubleshooting and for applications that do not require high-throughput, automated instrumentation.

When possibilities of simplifying high-capacity sorptive sampling in trace gas chromatographic analysis are considered, it is important to realise that employing injector temperatures far below the boiling point of a high-boiling analyte does not necessarily have an adverse effect on the peak width with which the analyte is eluted from a column under otherwise normal conditions, provided the injector liner is clean and not packed with an adsorbent. Despite the slow vapourisation of such a compound at injector temperatures below its boiling point, it is quantitatively transferred to the column as long as the sample does not run down the liner to the bottom of the injector before it is completely vapourised. If in a temperature-programmed analysis, this process is completed before the elution temperature of the compound is reached, a high-boiling compound will elute with a peak shape similar to that obtained by injecting the sample at an injector temperature above its boiling point. This principle is also applicable to the slow thermal desorption of heavy analytes from a large volume of sorptive phase. The critical problem in simplifying this type of analysis is thus not so much obtaining acceptable peak shapes for high-boiling compounds but rather obtaining sharp peaks for volatile compounds that are not efficiently cold-trapped on the column. In this paper we report on the development of a simple sample enrichment probe (SEP) and a protocol for the analysis of volatiles from solid and aqueous samples without having to employ cryofocusing.

2. Experimental

2.1. Instrumentation

The standard-sized needle-guiding channels through the septum cap and septum-supporting insert of the split/splitless injector of a Carlo Erba HRGC 5300 gas chromatograph were enlarged using a 2.4-mm drill bit. The instrument was equipped with an FID. Data were acquired at a sampling rate of 25 Hz and were processed using Jasco-Borwin software, version 1.5. The following columns were used: glass open-tubular column A (40 m × 0.3 mm I.D.), coated with 0.25 μm PS-089 (5% Ph-substituted polydimethylsiloxane); fused silica open-tubular (FSOT) column B (33 m × 0.32 mm I.D.), coated with 1.2 μm PS-255 (100% polydimethylsiloxane); glass open-tubular column C (40 m × 0.3 mm I.D.), coated with 2.5 μm PS-255. All analyses were carried out with hydrogen as carrier gas at a linear flow velocity of 50 cm/s, measured at an oven temperature of 40 °C.

Low-resolution EI mass spectrometry (LR-EIMS) was performed on a Carlo Erba QMD 1000 GC-MS instrument using column A and helium as carrier gas at a linear velocity of 32.25 cm/s at 40 °C. The temperatures of the line-of-sight interface and ion-source were set at 250 and 180 °C, respectively. Mass spectra were recorded at 70 eV.

2.2. SEP preparation

SEPs were made according to the schematic drawing in Fig. 1A using stainless-steel rods (130 mm × 1.5 mm), with one rounded end and a sharp point at the other. A section (15-mm length), about 3 mm from the rounded end, was machined to a diameter of 1.4 mm. Laboratory-grade PDMS rubber tubing (1.00 mm I.D. × 1.75 mm O.D.) (Müller Labor Betrieb, Heidelberg) was cut into lengths of exactly 15.0 mm using a sharp blade. These sections of PDMS rubber tubing (PDMS sleeves)

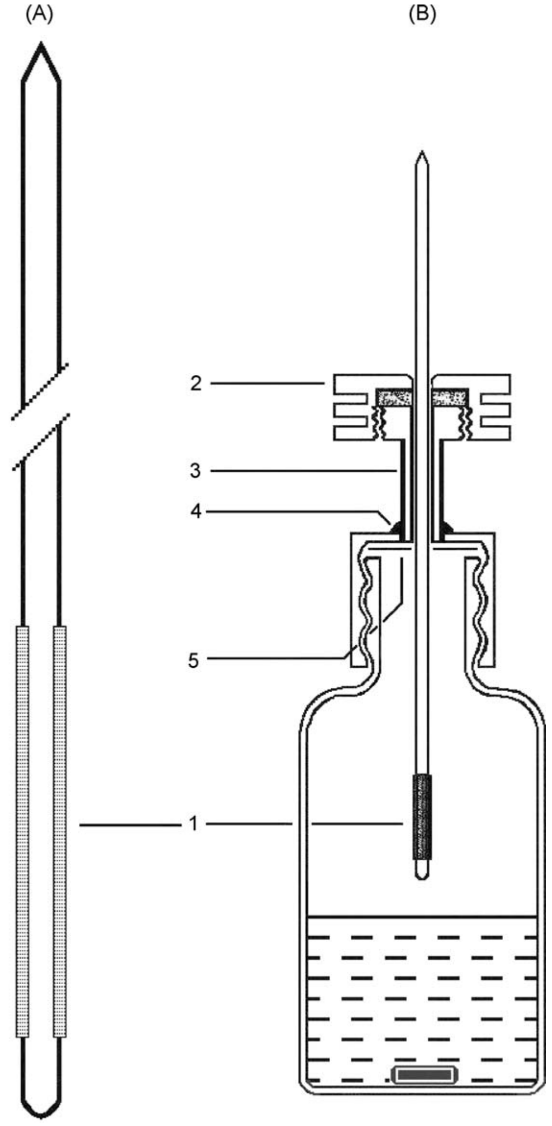

Fig. 1. (A) Sample enrichment probe (SEP) made from stainless steel with (1) a 15-mm sleeve of PDMS rubber; (B) sample bottle with a SEP installed for enrichment of headspace volatiles from an aqueous solution; (2) standard septum cap of the GC with its central hole enlarged to 2.4 mm; (3) stainless-steel insert in the phenolic cap of a standard reagent bottle; (4) epoxy glue applied to the outside surface of the cap around the insert; (5) Teflon gasket.