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Development of second-generation sample enrichment probe for improved sorptive analysis of volatile organic compounds

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ABSTRACT

The sample enrichment probe (SEP) has recently been introduced as a user-friendly and cost-effective method for the sorptive extraction of volatile organic analytes from gaseous and aqueous samples for GC and GC–MS analyses. In a further development of the SEP technique, thinner polydimethylsiloxane (PDMS) tubing on polyimide-coated fused silica, instead of stainless steel rods or stalks, were used to produce the second-generation SEPs. The new SEP does not require widening of the needle-guiding orifice of the septum cap and analytes are desorbed at a faster rate from the thinner sleeve, which reduces the risk of carry-over. The flowless period that was previously recommended for analyses of highly volatile analytes is made redundant by the faster desorption from the thinner sorptive medium. It was found that differences in the thermal histories of SEPs are not the cause of the high relative standard deviations (RSDs) reported in our first paper on the technique. Excellent reproducibility can be attained by careful handling and storing of loaded SEPs and by rigorously following a standardised analytical protocol.

1. Introduction

Several sorptive sampling methods using polydimethylsiloxane (PDMS) elastomer, commonly known and sold as silicone rubber, have been used for the analysis of volatile organic compounds (VOCs) in various matrices. This polymer is a popular choice of sorbent, owing to its ability to retain apolar and, to an acceptable extent, also polar organic analytes, as well as its thermal stability and the fact that only a limited number of well-characterised PDMS decomposition products are formed during thermal desorption of the trapped volatiles. The first use of PDMS as an absorbent in open tubular traps (OTTs) for the analysis of VOCs was reported by Burger and Munro [1], who utilised a thick lining of PDMS in a capillary column to trap organic compounds from a gaseous sample. Solid-phase microextraction (SPME), developed by Arthur and Pawliszyn [2], is a static sorptive sampling technique in which a thin fibre coated with PDMS is used. This technique has gained general acceptance by analysts, but unfortunately it has a relatively low sensitivity because of the small volume of polymer that is used as sorptive medium. The sensitivity problem can be circumvented using gum-phase extraction (GPE) in which volatiles are trapped in traps packed with PDMS particles [3]. However, stir bar sorptive extraction (SBSE), developed by Baltussen et al. [4], offers a more elegant solution to the sensitivity problem. In essence, this technique consists of the enrichment of the analytes from an aqueous solution in a sleeve of PDMS rubber on a glass-encapsulated magnetic stir bar. Although the technique was originally developed for the enrichment of analytes from aqueous media it can equally well be used for headspace analyses. Relatively expensive automated thermal desorption and cryotrapping equipment is required to ensure that the desorbed analytes are introduced into the gas chromatographic column as a sharply focussed band.

In 2006 a simple technique described as a high-capacity sample enrichment probe (SEP) was introduced for the enrichment of analytes from air and headspace samples [5]. In the SEP technique a relatively large volume of PDMS rubber is also used and in principle this technique is capable of producing results similar to those obtained by SBSE. In this technique the analytes are desorbed in the injector of the gas chromatograph (GC) and cryotrapping is circumvented. Since its introduction this technique has produced excellent qualitative results in many applications in our laboratory. In our opinion the value of the SEP technique lies in its simplicity and the extremely low cost at which qualitative applications, in particular, can be carried out. Unknown to us PDMS bars were developed specifically for headspace sorptive extraction (HSSE) by Bicchi et al. [6] and Tienpont et al. [7] already in 2000. In some respects HSSE is quite similar to the SEP technique.

Earlier attempts at using the SEP in quantitative work produced disappointingly low reproducibilities and it was hypothesised that the unsatisfactory quantitative results that were obtained in multiplicate analyses, using simultaneous enrichment with a plurality of SEPs, could probably be ascribed to the different thermal his-

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tories of the SEPs that were used [5]. In this communication we report on the further improvement and simplification of the SEP technique and on the development of protocols with which reproducible quantitative results can be obtained.

2. Experimental

2.1. Instrumentation

Analyses were carried out on Carlo Erba HRGC and HRGC 5300 GCs (Milan, Italy) and on a Thermo Electron Corporation Trace 2DGC (Milan, Italy) instrument fitted with split/splitless injectors and flame ionisation detectors operated at 230 °C and 280 °C, respectively. The injectors were used in the split mode. Standard 4-mm i.d. and 5-mm i.d. glass injector liners were used in the Carlo Erba and Trace instruments, respectively. The Trace GC was operated in the single-dimensional mode. A fused silica column (30 m × 0.25 mm i.d.) coated with PS-255 (DB-1 equivalent) at a film thickness of 1.2 μm, and made with a 5-m retention gap, was used for experiments on these instruments. The columns were programmed from 30 °C to 280 °C at 4 °C/min. Hydrogen was used as carrier gas at a linear flow velocity of 50 cm/s at 40 °C and the GCs were operated under constant pressure conditions. The data output of the Carlo Erba GCs was processed with Jasco-Borwin software, version 1.5 (Easton, MD), and Chrom-Card software, version 2.4.0, was used to process data on the Trace instrument.

2.2. Sample enrichment probes

Two SEP designs were used in the present investigation: Type 1, having fused silica stalks and Type 2 with shorter paramagnetic stainless steel stalks (Fig. 1).

Silastic® laboratory tubing (PDMS tubing) (0.64 mm i.d. × 1.19 mm o.d.) (Dow Corning, Midland, MI) was cut into lengths of exactly 30 mm (mass *ca.* 0.028 g). These sections of tubing (PDMS sleeves) were weighed to five decimal places, and groups having a mass variance of less than 0.14% were selected to manufacture SEP30s, i.e. SEPs with sleeves 30 mm in length. Fused silica tubing (0.7 mm o.d.) (Polymicro, Phoenix, AZ) was cut into lengths of about 130 mm and sealed off at both ends with an oxy-propane burner to produce stalks for Type 1 SEPs. Using ethanol as lubricating agent, each of these PDMS sleeves was gently slipped over the tip of a fused silica stalk and positioned with one end of the sleeve about 1 mm from the tip of the stalk. Care was taken not to stretch or compress the sleeves on their stalks. Type 2 SEP30s with shorter paramagnetic stainless steel stalks (100 mm × 0.66 mm) instead of fused silica stalks were made from guitar string (PL026, D'Addario, Farmingdale, NY). The Types 2 SEPs were made with sleeves positioned either 1 mm or 20 mm from the tips of the stalks. The completed SEPs were placed in a GC oven at 60 °C for 2 h to remove any residual ethanol and then conditioned overnight in a GC injector under hydrogen flow at 230 °C before use. A spherical NdFeB magnet (3 mm) glued to a stainless steel tube (2 mm o.d.) with epoxy glue was used to remove Type 2 SEPs from the GC's injector. Conditioned SEPs were stored individually or together in tubes (150 mm × 18 mm i.d.) with screw caps or B-14 ground-glass stoppers. Loaded SEPs were stored individually in storing tubes (140 mm × 2.0 mm i.d.) with B-5 ground glass stoppers or screw caps with 8-mm Teflon-faced septa, or were sealed off in an oxy-propane burner equipped with a small nozzle.

2.3. Sampling and analytical procedures

Single analyses of standard gas samples were carried out according to the basic procedure described by Burger et al. [5]. A centrally pierced septum was placed in a spare septum cap (cool) of the GC. Septa that have previously been used for conventional liquid injection are perfect for this purpose. The back end of the stalk of the SEP was inserted into the septum from its Teflon-faced side and the septum and cap were moved to a position on the stalk that would put the PDMS sleeve of the installed SEP halfway between the top and bottom of the GC's injector liner. This position was marked on the stalk. The resulting combination of SEP, septum and cap was used as a unit during conditioning, sampling and analysis [5]. To install the SEP in the injector, the carrier gas was turned off and the (hot) septum cap and septum were removed from the injector. Holding the previously described SEP-septum-cap assembly by the SEP's stalk, the SEP was lined up vertically with the orifice of the septum-supporting insert and without delay released to fall sharply into the injector, after which the septum cap was tightened, the carrier gas turned on and the analysis started. The SEP is left in the injector until the analysis has been completed and the oven has cooled down to the ambient temperature.

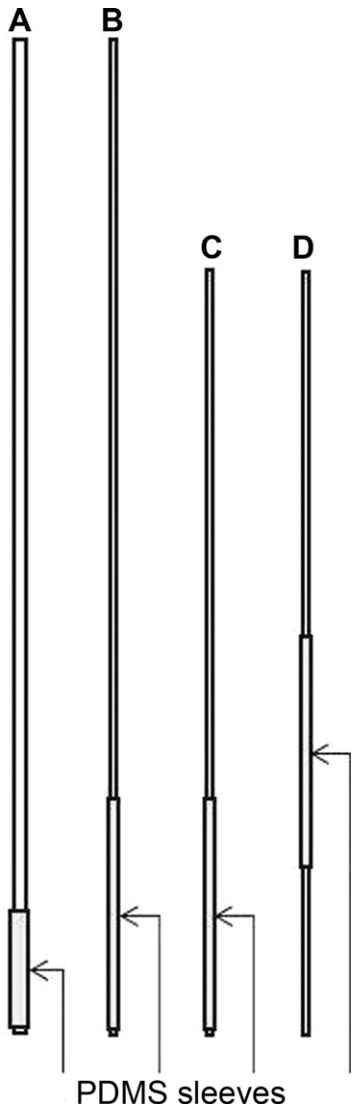

Fig. 1. Schematic illustration of various SEP designs. (A) SEP of the first generation (130 mm × 1.5 mm stainless steel stalk with 15 mm × 1.00 mm i.d. × 1.75 mm o.d. PDMS sleeve); (B) Type 1 SEP of the second generation (130 mm × 0.7 mm polyimide-coated fused silica stalk with 30 mm × 0.64 mm i.d. × 1.19 mm o.d. PDMS sleeve); (C) Type 2 SEP of the second generation (100 mm × 0.66 mm paramagnetic stainless steel stalk with 30 mm × 0.64 mm i.d. × 1.19 mm o.d. PDMS sleeve); and (D) Type 2 SEP of the second generation similar to C but with the sleeve positioned 20 mm from the tip of the stalk.