

# In-tube solid-phase microextraction sampler for long-term storage

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## Abstract

Capillary extractors are proposed as samplers-preconcentrators to overcome losses of volatile organic compounds found using “classical” solid-phase microextraction fiber-holder samplers. A set of equal-size extractors was used to extract in-tube an aqueous solution of benzene, toluene, ethylbenzene and xylenes (BTEX) at 146 ppb. After storage for 6–30 days at 0–4 °C (or –15 °C) GC analyses were carried out to study BTEX recovery. Results demonstrated that sample preservation was very good: recovery was higher than 98% after 6 days, and more than 95% after 30 days. Capillary extractors, due to their high performance in preserving sample integrity, represent a real breakthrough for on-site sampling of volatile compounds by solid-phase pre-concentration techniques.

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## 1. Introduction

### *1.1. Externally coated solid-phase microextraction (SPME) fibers: the problem of volatile organic compound (VOC) losses*

In recent years SPME has been widely used as a valuable technique devoted to sampling and pre-concentration of organic compounds from water and other matrices [1–5]. The great interest in this technique derives from its several advantages, namely its solventless nature, the ease of use and low detection limits, and the commercial availability of fibers, fiber-holders and automated ancillary devices (e.g. autosamplers) specially devoted to SPME. The picture is quite favourable as a whole, but some unresolved problems still remain, notwithstanding efforts to solve them. One problematic aspect con-

cerns the accuracy of VOC determinations after SPME on-site sampling. By using standard (externally coated) SPME fibers, losses of VOCs are unavoidable when GC injection is delayed following SPME sampling. Efforts have been made to reduce these evaporative losses by designing SPME fiber-holders specific for on-site sampling [6], but the results obtained using these devices have not been encouraging. Low VOC recovery seems to be due to the physical state of the extracting phase (a coating *external* to the fiber core), because mass exchanges with atmosphere are very difficult to avoid with the “external coating” design.

### *1.2. Capillary extraction and storage by capillary extractors*

Recently the author has studied a different approach to solid-phase microextraction, which uses open tubular traps with embedded press-fits [7–10].

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These “capillary extractors” are made by using pieces of common apolar open-tubular capillary columns. In this way the extracting phase is totally shielded from external cross-contamination by the glass (or fused silica) support; VOCs sampled by capillary extractors might be lost by slow diffusion through the thin holes of extractor ends. So, long-term storage of VOCs within capillary extractors capped with press-fit caps seems to have very good potential to solve several problems linked to on-site sampling by standard SPME.

### *1.3. The choice of benzene, toluene, ethylbenzene and xylenes (BTEX)*

Since the BTEX system is especially important from an environmental point of view [11], BTEX was the VOC system selected to test the after-sampling long-term storage effectiveness of in-tube extractors.

## **2. Materials and methods**

### *2.1. Capillary extractor preparation*

Preparation of capillary extractors consisted of: (i) preparing glass high-resolution (HR) GC columns [12]; (ii) cutting them into 15-cm-long pieces; and (iii) giving rise to press-fits into their ends [13]. Glass was the preferred support material to make in-tube SPME extractors since the author makes his own borosilicate glass HRGC columns. Extractive results are expected to be the same if fused-silica support replaces capillary glass.

#### *2.1.1. Drawing of raw glass capillaries and their coating*

Coiled borosilicate glass capillaries were drawn from 8-mm O.D. Duran glass rods by means of a laboratory-made glass-drawing machine. The drawing-coiling process gave capillaries of outer and inner diameters equal to 0.1 times those of the original Duran rods, and also produced turns of 0.50 m/coil. Various capillaries including some with 0.16 mm I.D. were prepared. They were leached, rinsed, dehydrated, persilylated overnight at a temperature of ~400 °C with hexamethyldisilazane–di-

phenyltetramethyldisilazane (1:1, v/v), and then statically coated with PS255, a Petrarch Systems polydimethylsiloxane gum with ~1% vinyl groups (Fluka, Italy). PS255 was dissolved in pentane–dichloromethane (1:1, v/v) in the amount required to form a film thickness of 0.5 µm [14] by the static coating procedure.

Freshly coated capillaries were put under inert gas, ends were closed by glass fusion, and the coated polymer was immobilized by heating from 170 to 200 °C (rate 0.3 °C/min). Dicumylperoxide (2%, w/w, with respect to the PS255 phase) was the stationary phase crosslinker. Coated and crosslinked capillaries were conditioned under normal helium flow by heating from 60 to 320 °C (rate 10 °C/min) for not less than 40 min. Conditioning profiles (bleed curves) were recorded as proof of sound static coatings.

Detailed procedures of the above treatments are described in Ref. [12].

#### *2.1.2. Press-fit realization*

Press-fits on glass extractors were made with a thin, sharpened tungsten tool [13] with the aid of an alcohol flame. The method is both rapid (~1 min/glass extractor) and very effective, giving rise to smooth leak-proof conical seats. In practice, the internally coated glass capillary was held ~3–4 cm from one end, keeping it between the index finger and thumb of the left hand. The tungsten tool, held with the correspondent fingers of the right hand, was inserted carefully into the thin hole of the glass capillary, and this assembly was put into the boundary of the alcohol flame. As soon as glass softened, the tungsten tool was continuously rotated with a smooth and rapid finger action, clockwise and anti-clockwise. Just a few seconds were required to soften and mould the borosilicate glass like a lightly and precisely tapered seat (i.e. a press-fit) which made possible leak-proof connections with the usual fused-silica capillaries.

#### *2.1.3. Press-fit caps*

Fused-silica caps were made from 2-cm pieces of deactivated fused-silica capillary of 0.32 mm I.D. One end of every piece was closed by fusion on a butane–oxygen micro-flame. After in-tube samplings, performed with several capillary extractors,

press-fit caps were applied finger-tight to the ends of the extractors, which were stored as such (full of liquid and capped) for the required time.

## 2.2. BTEX sample preparation

### 2.2.1. Pure BTEX mix

Benzene (Rudi Pont, purity >99.5%), toluene (redistilled, high purity, single peak by GC analysis), ethylbenzene (Fluka, >99%), and *ortho*-, *meta*-, and *para*-xylenes (from Aldrich, purities >99%) were used as primary substances. A BTEX stock standard mixture (six compounds) was prepared by mixing 2.00 ml of each component, and was stored at room temperature in a screw-closed glass bottle.

### 2.2.2. Aqueous BTEX standards

The BTEX solution was prepared by adding 1  $\mu$ l of the above BTEX stock mix to 1.14 l of Milli-Q water matrix subjected to moderate magnetic stirring. The resulting concentration of each aromatic compound was 146 ppb (v/v).

## 2.3. In-tube SPME sampling of aqueous BTEX

Every capillary extractor was charged with BTEX by fast-squeeze extraction [10] using 1.00 ml of the aqueous sample. A fused-silica transfer-line [10] allowed comfortable delivery of 1 ml of aqueous sample per extractor by a 10-ml Valco syringe equipped with a PTFE-tip plunger. Extractions were fast, and carried out at ambient temperature with a sampling time of  $10 \pm 2$  s. A set of 17 identical extractors was used, so that the sampling syringe had to be refilled once for all required samples. Details of the squeeze mode of sampling are described in Ref. [10].

## 2.4. After-sampling storage conditions

The 17 BTEX-charged extractors (Section 2.3) were plugged with fused-silica caps so that their hold-up volumes remained full of liquid. Three extractors were immediately analyzed, seven extractors were refrigerated at  $-15$  °C and the those remaining were stored at  $0$ – $4$  °C. During storage, sets of three extractors were taken from the refrigerator at selected times (after 6 and 30 days,

respectively) and analysed to ascertain BTEX recovery [10].

## 2.5. GC instrumentation, injection and elution steps

GC analyses were performed with a Perkin-Elmer 8500 gas chromatograph equipped with a flame ionization detection (FID) system set at  $200$  °C and a programmed temperature vaporizer (PTV) injector that remained unheated (hot injectors are not required with capillary extraction). A single GC method was used to perform all measurements. Care was taken to adjust the FID sensitivity to the reference value obtained at storage-time “0”, which was reproduced by careful regulation of FID-flame gases. The separation medium was a PS255,  $3 \text{ m} \times 0.16 \text{ mm}$  I.D.,  $0.5 \mu\text{m}$  capillary column laboratory made from Duran borosilicate glass as described in Section 2.1.1. Carrier was helium at 10 p.s.i.g. with pressure regulation (1 p.s.i.g. = 6894.77 Pa above atmospheric pressure). Oven isothermal temperature was  $40$  °C. Borwin software from Jasco (Italy) at a sampling frequency of 25 Hz was employed to acquire raw GC data and to store chromatograms. GC injections were performed following the recommendation described in Ref. [10] plus an intermediate cryofocussing step. The cryofocusser was a cheap laboratory-made device [15] which used liquid nitrogen to focus analytes and was able to re-inject them quickly by a temperature gradient of  $\sim 450$  °C/s applied at the focusing zone.

## 3. Results and discussion

Capillary extraction is an SPME technique that has several inherent advantages [7–10] in comparison with standard SPME: (i) it is very fast (the sampling step of VOC compounds requires only a few seconds); (ii) headspace influence is nil (during extraction the capillary extractor is always filled with liquid); (iii) heated injectors are not required (the extractor itself realizes GC injection by assuming the role of precolumn injector liner); (iv) band-broadening during the GC injection process is nil [10], while band-broadening in space is under control or can be made negligible [10,15]; (v) injection yield is maxi-

mized (capillary extractors inject 100% of the extracted amount); (vi) peak shapes are inherently symmetric; (vii) capillary extractors are remarkably inert (similar to persilylated apolar columns) and quite reusable (hundreds of times with clean water samples) because the extracting phase is immobilized and can be cleaned without danger using either high temperature or organic solvents; and (viii) since manual capillary extraction is extremely simple to perform, the technique should not be difficult to automate.

The list is not exhaustive, because two major advantages, very important for VOC sampling and for sample storage, must be cited: (i) the possibility of cross-contamination from the surrounding environment is extremely low, and (ii) capillary extractor can be easily *leak-proof* capped with (finger-tight fused-silica) caps.

Indeed the present work aimed at experimentally verifying these two major points. So, a set of several

extractors of equal size and film thickness were used to extract “in-tube” the BTEX sample described in Section 2.2.2. To record the FID response corresponding to 100% BTEX recovery, some extractors were analyzed at once just after capillary extraction; the others were refrigerated within two compartments of the laboratory refrigerator. Two sets of three extractors each were withdrawn from the refrigerator after specified times (storage at 0–4 and –15 °C, respectively) and analyzed for BTEX recovery.

Storage was extended to 30 days. Qualitatively, BTEX chromatograms from extractors stored for 1 month were indistinguishable from those from extractors freshly charged with BTEX (Fig. 1), thus demonstrating the remarkable level of stability provided by capillary extraction. Incidentally, it was noted that a few extractors became uncapped during storage at –15 °C; these extractors showed the presence of numerous new peaks coming from the

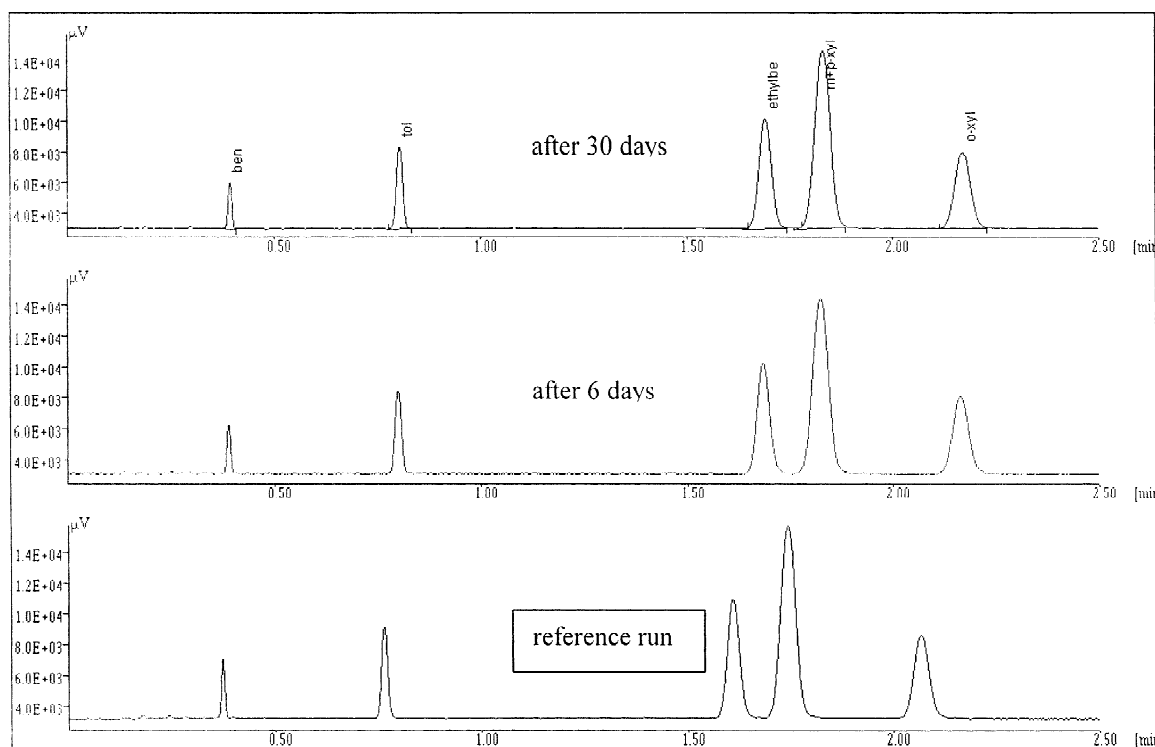


Fig. 1. BTEX analyses performed by capillary extraction–HRGC during the 0–4 °C long-term storage assay. FID sensitivity was kept rigorously unchanged throughout the time span of measurements (1 month). Note that reference run was obtained with a slightly higher carrier velocity.

Table 1  
BTEX recovery (%) after 6 days of storage at 0–4 and –15 °C<sup>a</sup>

Storage temperature	Benzene		Toluene		Ethylbenzene		<i>m</i> + <i>p</i> -Xylenes		<i>o</i> -Xylene		Average value±%RSD ( <i>n</i> =5)	
	A <sup>b</sup>	H <sup>c</sup>	A	H	A	H	A	H	A	H	A	H
0–4 °C	99		100.6		99.9		99.3		98.7		99.5±0.76%	
		97.4		98.3		97.6		97.3		98.1		97.7±0.45%
–15 °C	92.7		97		96.8		97		98.6		97.9±1.5%	
		89.4		94.6		95.5		94.6		96		95±0.73%

Areas and heights values are shown for each analyte.

<sup>a</sup> Recovery (%) = 100 · (response at time *t*) / (response at time 0); each number is the averaged amount recovered from three extractors.

<sup>b</sup> By area response.

<sup>c</sup> By height response.

Table 2  
BTEX recovery (%) after 30 days of storage at 0–4 and –15 °C

Storage temperature	Benzene		Toluene		Ethylbenzene		<i>m</i> + <i>p</i> -Xylenes		<i>o</i> -Xylene		Average value±%RSD ( <i>n</i> =5)	
	A <sup>b</sup>	H <sup>c</sup>	A	H	A	H	A	H	A	H	A	H
0–4 °C	93.3		99.7		98.1		97.8		99.4		97.7±2.6%	
		90.1		96.6		96.2		95.6		96.9		95.1±3.0%
–15 °C	78		99.1 <sup>a</sup>		87		87		90.4		85.6±6.2%	
		77		97.9		86		85		88		84±5.8%

Areas and heights values are shown for each analyte.

<sup>a</sup> Data were rejected, because a toluene uptake from the freezer atmosphere was probable.

<sup>b</sup> By area response.

<sup>c</sup> By height response.

freezer atmosphere, thus providing counterevidence of the effectiveness of the press-fit caps. Repeatabilities of capillary extractions (*n*=3) measured on freshly-charged extractors (i.e. just before storage) were 17% for benzene (excluding a possible outlier, this value is much lower), 2.0% for toluene and ethylbenzene, and 1.3% for the xylenes. However, for subsequent analyses repeatability values for all BTEX compounds were less than 4.5% RSD (*n*=3).

Final results are summarized in Tables 1 and 2.

#### 4. Conclusions

This brief study has shown that recovery of BTEX volatiles sampled by capillary extractors is remarkably high because glass or fused-silica wall-coated extractors are highly inert and can easily be leak-proof capped.

The supposed assumption that capillary extractors do not lose VOC substances when stored capped by

fused-silica press-fits is confirmed. The results show that the recovery rate for BTEX was better than 98% of the initial amount after 6 day of storage at 0–4 °C, while it was not less than 95% after 1 month.

It is also confirmed that a refrigeration temperature below the the freezing point of water is unfavourable, because diffusion out of the extractors is enhanced if residual sample filling the hold-up volume is frozen.

Results have shown that capillary extractors are suitable for *on-site* sampling, or whenever chromatographic analyses of VOCs cannot be carried immediately after SPME sampling.

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