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# Guidelines for capillary extraction–capillary gas chromatography: preparation of extractors and analysis of aromatic compounds in water

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**Abstract**

The benzene, toluene, ethylbenzene and xylenes system (BTEX) in clean water is studied to verify the performance of *capillary extraction* as an extraction-preconcentration technique well hyphenated with GC. The approach uses pieces of coated capillaries usually 5−30 cm long, trimmed from customary high-resolution GC columns but carrying glass press-fits at their ends. The preparation of these 'capillary extractors' is explained, and their performance is discussed providing guidelines for use. Injection by capillary extraction is such that (i) band broadening in time is null, and (ii) band broadening in space cannot be higher than the extractor length. Speed, cleanliness and operative simplicity of the capillary extraction approach are remarkable, pros and cons are complementary to those of solid phase microextraction (SPME) or stir bar sorptive extraction (SBSE). Capillary extraction–capillary GC analysis of aqueous BTEX samples, in a clean water matrix, allows low part-per-billion detection limits, and does *not* require heated injectors or cryofocusing devices.


*Keywords:* Capillary extraction; Extraction methods; Instrumentation; Water analysis; Benzene; Toluene; Ethylbenzene; Xylenes

## 1. Introduction

To detect target analytes at ppm-ppt levels in aqueous samples, solid phase microextraction (SPME) [1,2] uses 1 cm extractive fibers externally coated with polymeric sorbents [3]. During extraction, the fiber remains immersed in the aqueous sample for a known amount of time, after which it is desorbed into a *heated* GC injector or into an HPLC solvent desorption interface [4,5]. Stir bar sorptive extraction (SBSE) [6] can further extend detection limits to ppq ($1/10^{12}$) exploiting the extractive properties of 50−200 μl of methylsilicone (PDMS) rubber, but requires a dedicated hot injector and suffers from unavoidable disadvantages such as high bleed of stir-bar extractors, injection artifacts, and carryover.

Looking for the simplest way to perform SPME, the author realized recently that heated GC injectors were unnecessary if SPME fibers or stir-bars were replaced with tracts of routine apolar high resolution (HR) GC columns which had embedded *press-fits*

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at their ends [7–9]. These devices, named 'capillary extractors', are a form of the open tubular traps which were pioneered by Kaiser and Rieder [10], Grob and co-workers [11–13], Roerraade and Blomberg [14–16], and studied by many others, particularly for headspace analysis [17–20].

The absorptive action of apolar capillary extractors (immobilized (PDMS)) is based on the common partition law. We define the following: $K_d$, distribution constant; $C_s$, concentration of analyte in the extracting phase (at equilibrium); $C_w$, analyte concentration in the aqueous phase (at equilibrium); $n_s$, moles extracted at equilibrium into the sorptive phase; $C_0$, initial concentration into aqueous phase; $V_s$, volume of extractant; and $V_l$, volume of aqueous phase.

The partition law at equilibrium (in absence of headspace) may be written as follows [21]:

$$n_s = \frac{K_d V_s C_0}{1 + K_d(V_s/V_l)} \quad (1)$$

This study shows the details of capillary extractors preparation and their profitable use as suggested by Eq. (1). Of remarkable interest for pollution studies [22,23], the benzene, toluene, ethylbenzene and xylenes (BTEX) are chosen to represent the aromatic compounds.

## 2. Experimental

### 2.1. Pure BTEX mix

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

### 2.2. Aqueous BTEX standards

Diluted BTEX solutions were made by adding microliter amounts of the undiluted BTEX mixture to 270−1160 ml of water obtained from a Milli-Q purification system (Millipore, Bedford, MA, USA). Solubility limits were never exceeded (an exception is addressed below) since cloudiness due to heterogeneous mixing appeared at no time except the very instant of BTEX addition.

### 2.3. Preparation of BTEX samples to check linearity

A primary BTEX solution was prepared at 0.15 ppm per analyte by adding 1 μl BTEX pure-mix to 1100 g of Milli-Q water. Samples of various concentrations were salted with NaCl and then subjected to capillary extraction by the fast 'squeeze' method (4 s/ml, see below) using a 9 cm × 0.25 mm i.d., 0.3 μm PS255 (dimethylsilicone) glass capillary extractor. Extractions were carried out in duplicate. To construct the linear graph, the 0.15 ppm standard was used both neat and diluted by 2, 5, 10, and 20 times, and two more concentrated aqueous standards were also prepared by adding 1 and 10 μl, respectively, of BTEX pure-mixture into 56 ml of Milli-Q water. Nominal concentrations were 2.98 and 29.8 ppm, however the most concentrated standard had a cloudy appearance, suggesting solubility shortcomings.

### 2.4. Extractors preparation

Preparation of capillary extractors consisted of (a) preparing glass or fused-silica (FS) HRGC columns [24], (b) trimming them into pieces of suitable length, and (c) moulding their ends as press-fits.

The author preferred *glass* to make extractors due to the transparency as well as the low cost of this support material. Additionally, to set extractors as a GC precolumn (see Fig. 2 of [8]) a glass extractor with embedded press-fits needs just two FS ↔ glass junctions (supposing the use of a FS analytical column) whereas four junctions (two commercial press-fits) are required using a FS extractor so doubling the risk of leaks.

#### 2.4.1. Drawing of raw glass capillaries and their coating

Coiled borosilicate glass capillaries were drawn from 8 mm outlet diameter Duran glass tubes by means of a laboratory-made glass-drawing machine. The drawing–coiling process, which produced turns of 0.50 m/coil, gave capillaries of outer and inner diameters equal to 0.1 times those of the original rods. Freshly coiled capillaries (0.21 and 0.25 mm

i.d., among others) were leached, rinsed, dehydrated, and persilylated overnight with hexamethyldisilazane (pure, or mixed 1:1 (v/v) with diphenyltetramethyldisilazane) at temperatures near 400 °C. Then they were statical coated with PS255 (a Petrarch Systems polydimethylsiloxane gum with ∼1% vinyl groups, purchased from Fluka, Milan, Italy). To static-coat the glass capillaries, suitable amounts of PS255 were dissolved into pentane-dichloromethane (1:1 (v/v)) to furnish a film thickness of 0.3 μm. Freshly coated capillaries were put under inert gas, ends were closed by glass fusion, then the PS255 phase was immobilized by oven-programmed heating from 170 to 200 °C (rate 0.3 °C/min). Dicumylperoxide (0.2–2% (w/w) with respect to the PS255 phase) was the stationary phase cross-linker. Coated and cross-linked 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 recipes of the above treatments are described in [24].

*2.4.2. Press-fit realization*

Press-fits were made onto glass extractors by a thin, sharpened tungsten tool [25] and an alcohol flame, as shown in Fig. 1. This method is both rapid (about 1 min/glass extractor) and effective, giving rise to smooth conical seats. In practice, the internally coated glass capillary was held at about 3–4 cm from one end, keeping it between index and thumb fingers of the left hand. The tungsten tool was held with the same fingers of the right hand. The tool was in axe while it was inserted with delicacy in the thin glass hole of one capillary end. Then the glass end and the metal tool were put as a whole into the boundary of an alcohol flame exactly as shown in the photograph. As soon as the softened glass appeared red in color, the tungsten tool was pushed deeper into the capillary end while continuously rotating clockwise and counter-clockwise. A few seconds were required to soften and mould the borosilicate glass into a lightly and precisely tapered seat (press-fit) which allows for fast and (mostly) leak-proof connections with FS capillaries. Optionally an air supply admitting tens to hundreds ml/min of gas through the capillary

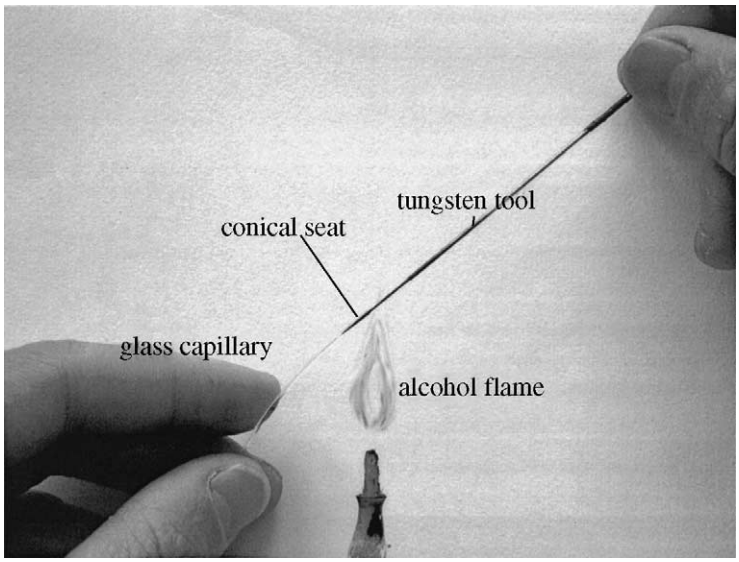


Fig. 1. Press-fit fashioning of the glass ends of a capillary extractor. This photo shows the relative position of hands, the tungsten tool, and the capillary end with respect to the alcohol flame. It is important to tilt the capillary butt at about 40°–60° from horizontal, and to heat it with the boundary of the flame point. This assures a homogeneous softening of glass while heating. It is also fundamental to rotate the metal tool as consistently and precisely as possible.

outlet made the glassblowing action easier by lowering the glass temperature enough to finely control the heat-modeling process. Air effectively cleans the softened glass end from carbonized stationary phases and silanization coatings. With very adsorptive or basic analytes an inert gas must replace air to best retain inertness at the capillary ends.

### 2.5. The sampling FS 'transfer-line'

Samples were transferred onto capillary extractors using a Teflon-tipped glass syringe which was connected to a transfer-line ending with a 0.32 mm i.d. FS tube. Fig. 2 shows the items used by the author. Fig. 3 shows the details of the transfer-line.

### 2.6. Sampling mode

Aqueous samples (1 ml) were usually taken up with the PTFE-tipped syringe (Fig. 2) and subjected to squeeze-extraction. A larger syringe (5 ml Series A-2, from Valco) was preferred during reproducibility experiments without headspaces. In practice, all capillary extractions were carried out at ambient temperature (22–25 °C) with sampling time of $4 \pm 1$ s (occasionally of ~10 s). Squeeze extractions performed with salting used 3.5 ml aliquots of sample.

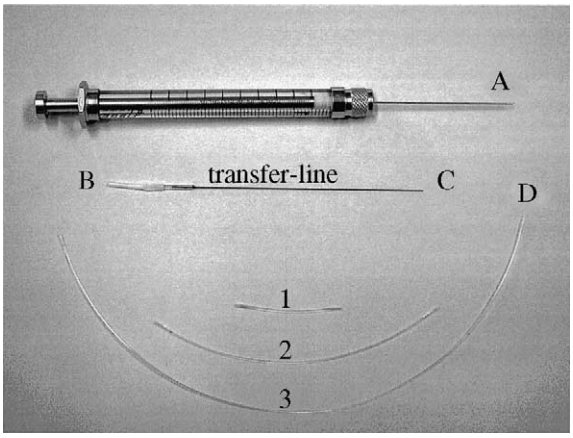


Fig. 2. Capillary extraction tools: the 1 ml leak-proof sampling syringe, the sampling transfer-line ending with a 0.32 mm i.d. fused silica capillary, and some capillary extractors (items 1–3). The sample is charged in the syringe and needle A is connected with side B of the transfer-line making a leak-proof seal with the Teflon tube. The FS capillary side (C) is then joined with the press-fit end (D) of the capillary extractor. Finally, sample may be "in-tube squeezed" for a few seconds. The extract can be analyzed immediately or stored in its extractor for months with negligible losses [31].

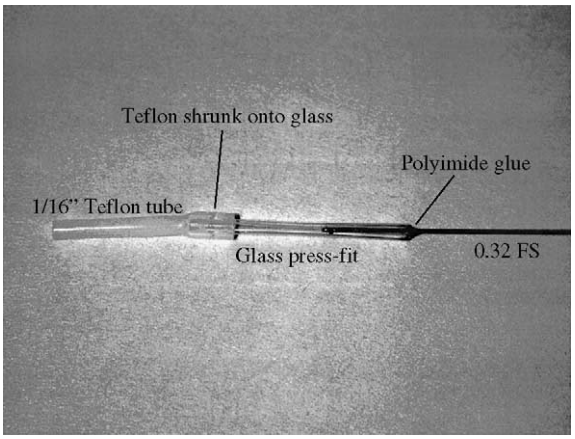


Fig. 3. Particulars of the sampling transfer-line: a short piece of 1/16 in. o.d. × ~0.3 mm i.d. PTFE tube (1 in. = 2.54 cm), made shrinkable ([24], p. 85) on one end, was fitted onto one side of a glass press-fit suitable for 0.32 mm i.d. FS capillaries. After the attachment of the 10–20 cm piece of a FS capillary, a drop of polyimide glue reinforced the connection. The i.d. of the PTFE tube was selected to achieve a leak-proof and easy connection with the syringe.

### 2.7. Salting-out recipe

1.15 g of NaCl (purity > 99.5%, Farmitalia Carlo Erba, Milan. Italy) was weighed into a 4 ml screw-capped glass vial. A PTFE stir-bar (1.5 mm × 10 mm) was added together with 3.50 ml of BTEX aqueous sample (headspace resulted about 0.5 ml). Moderate magnetic stirring was applied until salt dissolution. Sample was sucked into the sampling syringe by piercing the vial liner (polyethylene/aluminum/cardboard multilayer), with the cap slightly unscrewed to avoid vacuum. Three 1 ml samplings were allowed per salted sample. Since sample headspace increased if multiple samples were taken from the same 3.5 ml sample, the "no headspace" approach was performed when headspaces were unwanted.

### 2.8. 'No headspace' multi-sampling

BTEX samples were salted as usual and taken up with a 5 ml leak-proof PTFE-tipped Valco syringe

(Series A-2, Code 050035). The syringe was filled entirely with liquid. Discharging 1 ml of sample at a time, a series of five squeeze-samplings was allowed, without headspace interference. The method was used to check the reproducibility of capillary extraction (see Section 3).

### 2.9. GC instrumentation and elution modality

GC analyses were performed with a Perkin-Elmer 8500 gaschromatograph equipped with a flame ionization detection (FID) system (set at 200 °C), and a programmed temperature vaporizes (PTV) injector that remained unused (the injection process used here was independent from the PTV). The laboratory-made analytical column was a PS255 polydimethylsiloxane, 10 m × 0.21 mm i.d., 0.3 μm (film thickness). It was made using static coating recipes [24]. Carrier gas was hydrogen at 10 psi, with pressure regulation. Borwin software from Jasco (Como, Italy) was employed for acquisition of raw GC data and storage of chromatographic data (1 psi = 6894.76 Pa).

#### 2.9.1. Extractor assembly and extract elution

BTEX analyses were carried out with the GC oven at room temperature (24±3 °C). Carrier gas was taken from the PTV injector nut (a suitable source of carrier gas). Of course pressure was set to have the required linear velocity.

The analytical column inlet was disconnected (press-fit joint) temporarily. Within 0.5 to 1 min residual carrier pressure inside the column subsided and stabilized to atmospheric value. In the meanwhile the sample was in-tube extracted and the capillary extractor hold-up volume was emptied from residual aqueous sample by reversing the syringe action or connecting the full extractor to a peristaltic pump moving very slowly (breakthrough of air into the extractor must be kept to a minimum to avoid loss of BTEX volatiles). The analytical column inlet was connected with one end of the ‘charged’ capillary extractor and, finally, the press-fit connection of the FS carrier line with the second extractor end started gas-chromatography.

## 3. Results and discussion

Short capillaries trimmed from (apolar) GC glass capillary columns cannot be considered capillary extractors until they incorporate their press-fits [25,36], whereupon the squeeze-extraction step is very easily performed (Fig. 2). Detection of extracted analytes can be done using isothermal or temperature programmed GC [7,8]. Interestingly, hundreds of capillary extractors may be prepared from a single 20 m HRGC column. Moreover, apolar capillary extractors are reusable and their sensitivity can be enhanced or the selectivity varied by contacting them with solvents vapors [26].

### 3.1. The partition law

Eq. (1) indicates that if $K_d V_s/V_l$ is negligible with respect to unity, the ratio $n_s/V_s$ takes its maximum possible value, equal to ($K_d C_0$). This happens easily using capillary extraction. Using this technique $V_s$ is normally about $10^{-1}$ to $10^{-3}$ μl [38] but extractors with $V_s \sim 1$ μl or more might be prepared [27] though their use might require a cryofocalizer [28].

When $K_d V_s$ is much higher than $V_l$, (1) becomes $n_s = (V_l C_0)$ and the analyte is actually depleted from the aqueous sample. SPME and SBSE have obviously a complementary character towards analyte depletion in comparison with capillary extraction, because they generally use much more extractant.

Remarkably, in this study $V_l/V_s$ ratios were about $10^5$, so analytes wound up in an extremely small amount of extractant [29]. Due to this and to the following reasons, extracted analytes are injected into the GC flow-path with outstanding performance:

(1) Extractant layers are so thin (usually <0.5 μm) that kinetics of mass-transfer [30] are much faster than those concerning SPME fibers or SBSE stir-bars.
(2) The low amount of extracting phase enhances baseline stability and overall quality of chromatographic data (no system peaks due to extractant are visible in practice).
(3) The GC injection process is an extremely gentle ‘on-column’ injection, that injects the *entire* sampled amount into the GC column *without* thermal stress (a solventless, cold, on-column injection). Neither SPME nor SBSE could operate so mildly.

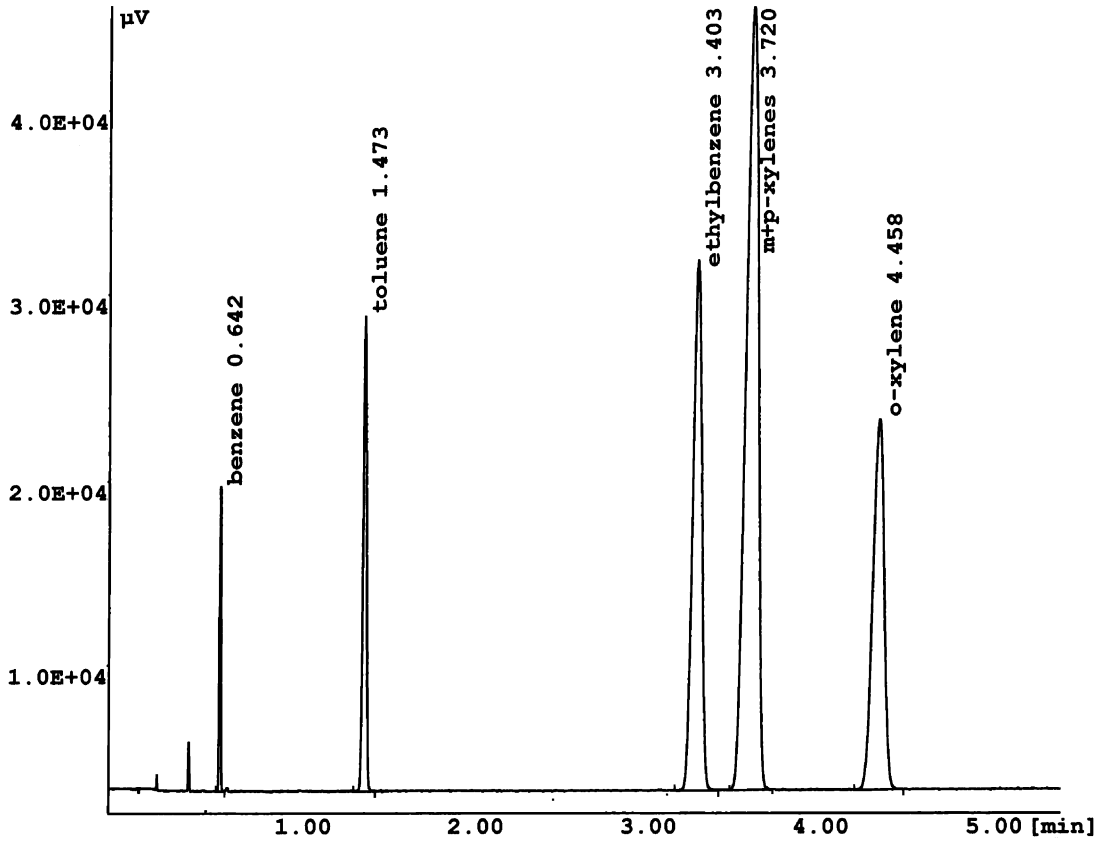


Fig. 4. In-tube extraction of a 1.2 ppm BTEX sample: sample volume was 1 ml, sampled by a 4 s squeeze extraction through a 10 cm × 0.25 mm i.d., 0.3 μm PS255 glass capillary extractor. The couple of impurities at 0.28 min and 0.47 min are dichloromethane and *n*-hexane, respectively.

(4) With capillary extraction, 'band broadening in time' concerning GC injection band is always *null*, while 'band broadening in space' will be linked only to extractor length [8]. This explains why capillary extraction does not need cryofocusing.

In practice, peak quality of BTEX analysis by capillary extraction is impressively good. Fig. 4 shows a 4 s squeezed capillary extraction–HRGC analyses carried out on a 1.2 ppm BTEX sample. One should note the chromatogram cleanliness, as well as the symmetry of all peaks, including the almost unretained organics coming from the water matrix (dichloromethane (0.28 min) and *n*-hexane (0.47 min)).

Capillary extraction also has its 'critical' aspects, that users should be aware of when using the technique. Most important is the possibility of analyte loss (breakthrough) during extractors manipulation, a risk easily avoided by trained operators.

### 3.2. The breakthrough problem

After extraction, it is necessary to empty the capillary extractor of several μl of sample excess which fill up the extractor void-volume. This operation might be delayed for months (with negligible losses of BTEX and without cross-contamination) if extractors are capped with press-fit caps [31]. However, when extractors are uncapped, manipulation must be accurate enough to avoid extract losses.

Though the sampling syringe itself would be suited for drying, in this study a peristaltic pump was applied with excellent results. The operator should be careful

with either device: air/water meniscus should not move back faster than ∼2 cm/s, because the suction action must be stopped in time to avoid any breakthrough of air (plus volatile organic compounds).

To quantitate breakthrough effects, a set of experiments was performed in which a certain amount of air (from 10 to 250 μl, dispensed by a gas tight (250 μl) syringe) was allowed to breakthrough into a 10 cm × 0.21 mm i.d., 0.3 μm (film thickness) PS255 extractor (4 μl hold-up volume) just after the usual capillary extraction sampling. Results indicated that even at room temperatures benzene was lost within the first 10 μl of excess air, toluene within 40 μl, while 120 μl of air completely cleaned the extractor of all BTEX compounds.

The system must be looked at in closer detail to avoid a second possible source of 'breakthrough' losses. The analytical column should be disconnected from the inlet carrier gas supply about 0.5–1 min before the capillary extractor is connected with the column, to avoid any backflushing action due to residual carrier overpressure [8]. Breakthrough is not a serious concern for semivolatiles, while the connection between extractor and carrier line is uncritical, independently of analyte volatility.

### 3.3. Influence of extractor length on BTEX peaks

#### 3.3.1. Effect on peak width

Several extractors of 0.25 mm i.d. × 0.3 μm, with lengths varying from 1.2 to 35 cm were used to study the effects of extractor length on peak width. One ml of BTEX solution at 1.2 ppm was driven (syringe) into each of them and extract was analyzed by GC. Data are plotted in Fig. 5 showing peak width at half height ($W_h$) versus extractor length. The curve trends were further confirmed by acquiring more data points (not shown) in the 0−11 cm range, which allowed for extrapolation of the BTEX $W_h$ values obtained using an extractor of negligible length (Table 1). $W_h$ for benzene was just 0.5 s and all peaks were quite symmetric. The flat baseline with a high-frequency noise better than 110 μV allowed $2\sigma$ detection limits between 14 and 8 ppb. Longer extractors induced an increase on $W_h$ which was very small for extractor length ≤10 cm, with the last value corresponding to 1% of the analytical column length $L$. So, as a rule of thumb valid for extractors which have i.d. and $d_f$ comparable with those of the GC column, $L$/100 appears as the capillary extractor length that assures a negligible injection variance *even without cryo- or retention power-focusing*.

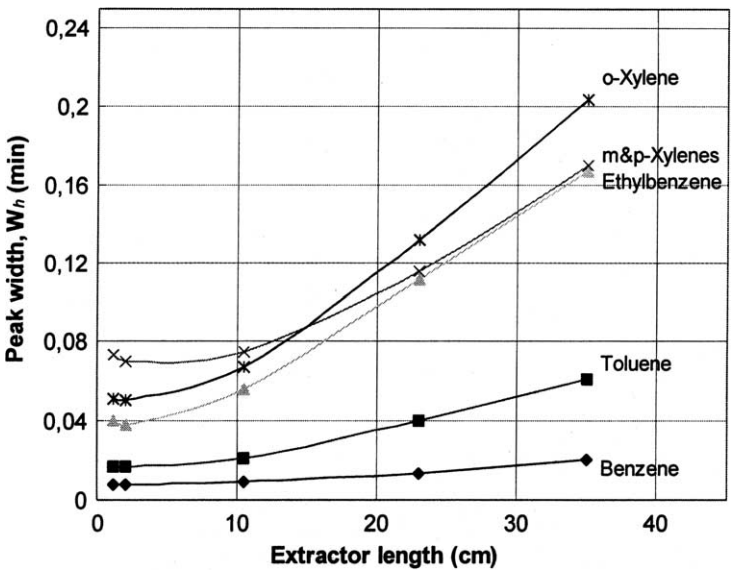


Fig. 5. BTEX peak widths at half height $W_h$ vs. extractor length: data for the unresolved *m*- and *p*-xylene pair (labeled '×' on the data points) appear with a somewhat different trend owing to a chromatographic resolution effect (resolution between *m*- and *p*-xylene is higher with shorter extractors).

Table 1
Peak broadening and detection limits of BTEX components

| | Benzene | Toluene | Ethylbenzene | (*m* + *p*)-Xylenes | *o*-Xylene |
|---|---|---|---|---|---|
| $W_h$ (s) | 0.5 | 1.1 | 2.5 | 4.7[a] | 3.3 |
| $DL_{2\sigma}$ (ppb) | 14 | 9 | 8 | 11 | 12 |

Peak-widths at half height ($W_h$) are extrapolated values which refer to a capillary extractor of negligible length ($\sigma^2_{inj} = 0$).
[a] The value, higher than expected, discloses some separation within the pair.

### 3.3.2. Effect on peak area and peak height

It was also verified (data not shown) a linear relationship ($r^2 \geq 0.998$ for all BTEX compounds) between analyte peak areas and extractor length. Peak heights, however, reached a flat plateau after an initial linear increase of peak height versus extractor length (Fig. 6). This trend is logical, as concentration of an analyte in a sample-equilibrated extractor is constant if the analyte concentration in the sample $C_0$ does not vary; since any extractor becomes the injector device during the HRGC, it will *transfer its concentration profiles* onto the GC column as a squared-plug pulse of analyte. Whenever injection variance [32] is negligible in comparison to total peak variance (extractor length less than 0.3–0.5% of column length) both peak areas and heights increase linearly with extractor length. When injection variance is the predominant term contributing to peak broadening the final peak height resulting on the chromatogram remains constant, fixed by the extractor injection profile.

### 3.4. Effect of sample volume on peak height

One ml of sample was enough to equilibrate a typical capillary extractor (10 cm × 0.25 mm i.d., 0.3 μm) for all BTEX analytes except for *m*- and *p*-xylenes (which required a volume of 1.5–2 ml) as demonstrated by the data summarized in Fig. 7. Note that the benzene curve slightly descends from 0.2 ml onward. A similar effect is visible for toluene between 1 and 4 ml of sampled volume, but also acts from ∼0.3 ml onward. Competitive absorption of more lipophilic BTEX components towards analytes with lower $K_d$ (benzene, but also toluene) very likely influences overall composition of the stationary coating and consequently $K_d$ varies as the extraction proceeds.

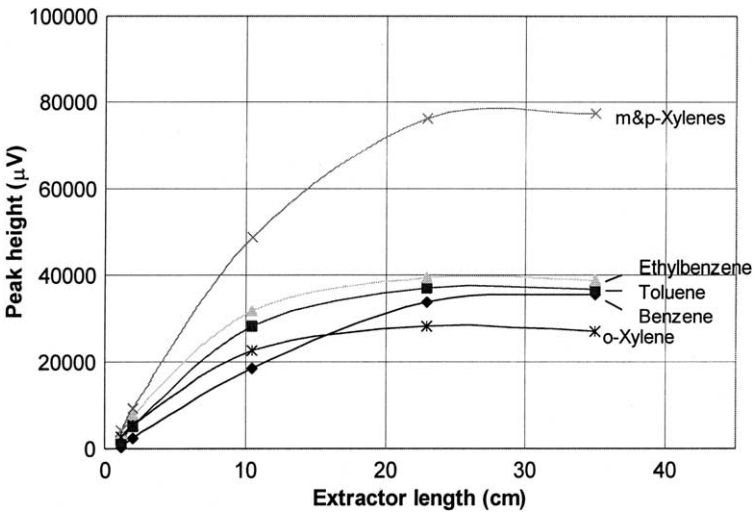


Fig. 6. Effect of extractor length on peak height of BTEX compounds extracted by in-tube SPME: extractors are 0.25 mm i.d., 0.3 μm PS255. Sample volume is 1 ml per extraction.

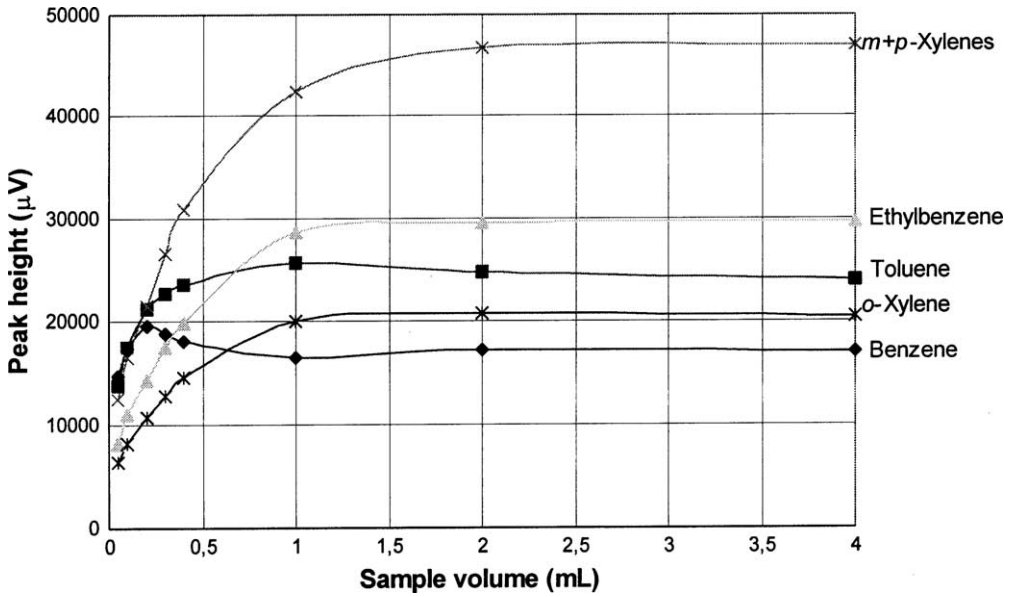


Fig. 7. Effect of squeeze volume on BTEX peak response by height: sample volumes between 50 and 4000 μl were fast squeezed through a single capillary extractor, 10 cm × 0.25 mm i.d., 0.3 μm PS255. BTEX concentration was 1.2 ppm per analyte. Sampling flow rate (manual operation) was about 0.25 ml/s.

### *3.5. Strategies to enhance capillary extraction sensitivity*

Capillary extraction of hydrophobic analytes may well reach low ppb detection limits [7–9]. BTEX analysis is not an exception in spite of the very minute volumes of extracting phase coated inside usual capillary extractors (about 0.1–0.005 μl). To make the best use of such tiny amounts the user may:

(1) Use a short analytical column and, if possible, hydrogen as the carrier gas (analyte peaks are narrowed, FID detectability is enhanced).
(2) Use higher carrier velocities than optimum.
(3) Salt aqueous sample before extraction to increase $K_d$.
(4) Phase-soak extractant with suitable compounds (swelling with a volatile solvent *reversibly* increases the total mass of 'extractant').
(5) Perform extraction at a different temperature (specifically, a temperature that will increase $K_d$).

Several of the above approaches have been used throughout this work. The selected analytical column, for example, was rather short (10 m) and might have been trimmed even shorter (∼3 m) considering excess resolution among BTEX components. Moreover, carrier gas was hydrogen, at high velocity (60 cm/s). Feasibility of the phase-soaking approach and salting (see below) were also confirmed to be useful approaches.

#### *3.5.1. Effect of phase-soaking on detectability*

Light alkanes and dichloromethane were selected to scout phase-soaking [26] of a typical PS255 coated extractor. To avoid unwanted defocusing effects [33] only rather volatile, very water-insoluble solvents were studied. Solubility in water [34] of methylene chloride (1.30% (w/w), 25 °C) and cyclohexane (0.006%, 25 °C) should explain why these solvents are less effective than *n*-hexane (0.00123%, 25 °C) or *n*-pentane (0.0038% (w/w), 25 °C). *Vapor-phase* soaking gave better reproducibility than swelling by corresponding liquid. In the last case, the capillary extractor excess amount of the water-immiscible soaker was quite difficult to reproduce.

In practice, vapor-phase soaking simply required a preventive squeezing of 1 ml pentane vapors into the PS255 capillary extractor, followed immediately by the capillary extraction–HRGC. Using *n*-pentane

Table 2
BTEX responses, expressed as peak heights (μV) for *neat* and for vapor-phase *soaked* capillary extraction

| Extractor[a] pre-treatment | Benzene | Toluene | Ethylbenzene | (*m* + *p*)-Xylenes | *o*-Xylene |
|---|---|---|---|---|---|
| *n*-C5 soaking[b] | 251746 | 159776 | 61245 | 100733 | 54526 |
| No one (neat extraction) | 20712 | 26711 | 26317 | 46136 | 19873 |
| Ratio soak/neat | 12.2 | 6.0 | 2.2 | 2.2 | 2.7 |

[a] Capillary extractor: 10 cm × 0.25 mm i.d., 0.3 μm PS255.
[b] Soaking by 1 ml of *n*-pentane vapor (at ambient temperature).

Table 3
Reproducibility of BTEX analysis at 1.2 ppm per component. Replicate in-tube extractions ($n = 8$) carried out with *n*-C5 vapor-phase soaking

| | Benzene | Toluene | Ethylbenzene | (*m* + *p*)-Xylenes | *o*-Xylene |
|---|---|---|---|---|---|
| By peak area | 21 | 11 | 5.9 | 5.6 | 6.5 |
| By peak height | 24 | 14 | 6.7 | 5.3 | 7.0 |

Values are in R.S.D. (%) units.

vapor-soaking (Table 2) repeatability of area counts resulted better than 3.0% R.S.D. ($n = 5$). Table 3 reports percent R.S.D. values of a set of BTEX capillary extractions performed with a *n*-pentane soaked extractor. Vapor-soaking gave better reproducibility for less volatile compounds. With *n*-pentane soaking the response gain was notable, particularly for benzene and toluene. Chromatograms revealed that peak widths at half height on the swelled in-tube extractors are *smaller* than those obtained using neat extractors. The focusing effect termed 'phase-soaking' by Grob [33] was probably the reason for $W_h$ decrease.

### 3.5.2. Effect of salting

Salting-out the aqueous BTEX sample with sodium chloride (33% (w/v (volume of unsalted sample))) or 43% (w/v) of sodium sulfate, increased capillary extraction of all BTEX components; neatly for benzene and toluene, slightly for the other BTEX aromatics. The two salts were equally effective. Table 4 summarizes the results of two replicate in-tube extractions performed taking advantage of salting-out effects; $2\sigma$ detection limits are also included. It was confirmed that capillary extraction–HRGC achieves low ppb detectability even with 4 s extractions.

### 3.6. Effect of extractor size and geometry

Phase ratio $\beta$ of an extractor is the ratio of its internal gas volume, $V_g$, versus $V_{PDMS}$, thus:

$$V_{PDMS} = \frac{l(\pi D^2/4)}{\beta} = l\left(\frac{\pi D^2}{4}\right)\left(\frac{C_{coat.\,sol}}{100}\right) \qquad (2)$$

Table 4
Effect of salting by NaCl on BTEX extraction

| | Benzene | | Toluene | | Ethylbenzene | | (*m* + *p*)-Xylenes | | *o*-Xylene | |
|---|---|---|---|---|---|---|---|---|---|---|
| | A[a] | H | A | H | A | H | A | H | A | H |
| Salted/unsalted response ratio | 4.8 | 4.9 | 2.7 | 2.8 | 1.04 | 1.03 | 1.01 | 1.02 | 1.22 | 1.27 |
| R.S.D. (%) ($n = 2$) | 2.0 | 0.6 | 2.8 | 1.5 | 2.5 | 0.4 | 2.5 | 1.2 | 2.4 | 1.8 |
| $DL_{(2\sigma)}$[b] with NaCl (ppb) | 1.4 | | 1.9 | | 5.3 | | 3.1 | | 6.1 | |
| $DL_{(2\sigma)}$ without NaCl (ppb) | 6.7 | | 5.2 | | 5.5 | | 3.2 | | 7.6 | |

Concentration is 1.2 ppm (v/v) per component.
[a] A: by peak area; H: by peak height.
[b] $2\sigma$ detection limit.

Table 5
Retention times of BTEX components obtained by different injection modalities

| Retention time (s) | Unretained peak (methane) | Benzene | Toluene | Ethylbenzene | (*m* + *p*)-Xylenes | *o*-Xylene |
|---|---|---|---|---|---|---|
| By septum injection | 16 | 44 | 96 | 217 | 238 | 284 |
| By capillary extraction[a] | 11 | 39 | 90 | 208 | 226 | 272 |
| Absolute difference | −5 | −5 | −6 | −9 | −12 | −12 |
| Difference (%) | −31 | −11 | −6.3 | −4.1 | −5.0 | −4.2 |

[a] Press-fit assembly performed following guidelines reported in Section 2.

where $l$ is the extractor length, $D$ its internal diameter, and $C_{\text{coat.sol}}$ is the concentration (by % v/v) of the static coating solution used to prepare the capillary extractors (i.e. $C_{\text{coat.sol}}$ = (ml of stationary phase per ml of coating solution) × 100 ≅ $100/\beta$).

Eq. (2) shows that if capillary extractors of different sizes have identical $V_{\text{PDMS}}$ values, then they will also have the same value of the product:

$$lD^2C_{\text{coat. sol}} \quad \left(\text{or, equivalently, } \frac{lD^2}{\beta}\right) \tag{3}$$

In practice, term (3) allows for calculation of the length of extractors that have the same volume of extracting phase. Comparison among extractive abilities of such extractors gave the following results:

(1) Analytes with high $K_d$ values are much better extracted on thinner but longer extractors; detection limits of few ppts were demonstrated [9] on analytes with $K_d$ on the order of $10^5$–$10^6$.
(2) Extraction of analytes that diffuse very fast, or with low $K_d$, are almost independent from the geometrical feature of the extractor, the major variable of concern being $V_{\text{PDMS}}$.
(3) Very thin (thus rather long) extractors, require longer sampling times than usual, and the pushing action even by hands could dissipate enough energy within the extractor to modify its temperature. Moreover, swelling effects might also modify the partitioning characteristic of the extracting phase (with cross-displacement effects [37]).

### 3.7. Retention time variation induced by the injection modality

This study was conducted by manually mounting the extractors in the GC oven. Of course users may prefer to put the extractors into the carrier flow-path by using rotating injection valves, possibly with automatic control. In practice, differences exist as far as retention times are concerned. All retention times obtained using septum injection (PTV body unheated; in-tube extractor mounted and under steady conditions in the GC oven before syringe injection of BTEX vapors) are slightly increased in comparison to the capillary extraction–HRGC injection set-up as described above. In particular, it was observed (Table 5) that retention times ($t_R$) of more highly retained compounds

Table 6
Reproducibility of BTEX analysis (raw data included) by capillary extraction–HRGC

| Replicate number | Height (μV) | | | | |
|---|---|---|---|---|---|
| | Benzene | Toluene | Ethylbenzene | (*m* + *p*)-Xylenes | *o*-Xylene |
| 1 | 13003 | 12272 | 4972 | 7707 | 3977 |
| 2 | 12598 | 10907 | 4829 | 7416 | 3829 |
| 3 | 12908 | 11080 | 5002 | 7474 | 3902 |
| 4 | 12480 | 10747 | 4633 | 7167 | 3787 |
| 5 | 12240 | 9643 | 4082 | 5992 | 3368 |
| Average | 12646 | 10930 | 4704 | 7151 | 3773 |
| Standard deviation | 313 | 937 | 377 | 676 | 237 |
| R.S.D. (%) | 2.5 | 8.6 | 8.0 | 9.5 | 6.3 |

Concentration is 150 ppb per component, with salting by NaCl (33 g/110 ml of sample).

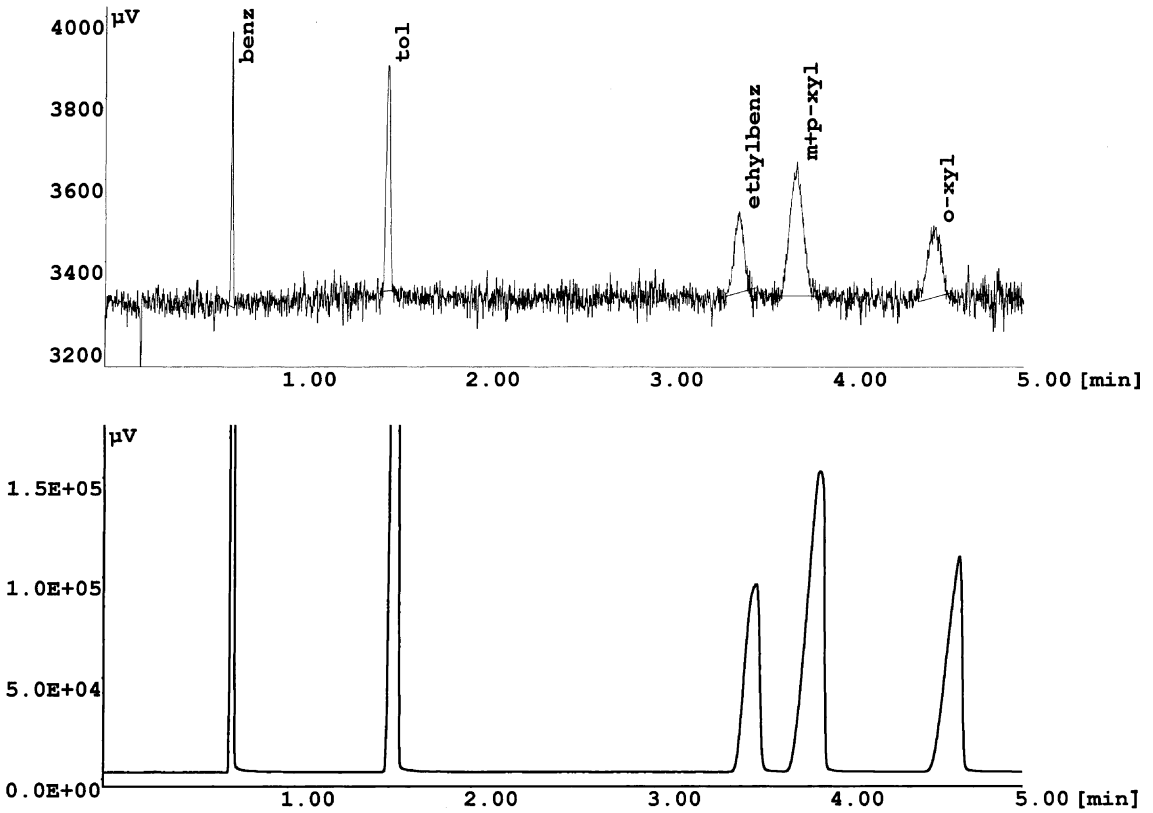


Fig. 8. Comparison between the 7.5 and the 29,800 ppb BTEX samples taken from the linearity assay of capillary extraction. The diluted sample is shown in the upper half. Extractor: 9 cm × 0.25 mm i.d., 0.3 μm PS255. Samples were salted-out with NaCl.

Table 7
Data about capillary extractions performed with aqueous BTEX samples in the concentration range 7.5–29,800 ppb

| Sample concentration (ppb, v/v) | R.S.D. (%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Benzene | | Toluene | | Ethylbenzene | | (*m* + *p*)-Xylenes | | *o*-Xylene | |
| | A[a] | H | A | H | A | H | A | H | A | H |
| 7.5 | 11 | **2.0** | 15 | **3.0** | 30 | **11** | 13 | **7.2** | 24 | **11** |
| 15 | 1.8 | **0.84** | 4.1 | **4.3** | 3.4 | **6.7** | 4.3 | **2.3** | 1.3 | **1.7** |
| 30 | 9.4 | **5.8** | 6.8 | **1.3** | 4.6 | **2.3** | 2.8 | **2.5** | 2.4 | **6.2** |
| 75 | 8.0 | **5.8** | 1.4 | **1.3** | 2.0 | **3.9** | 0.26 | **2.7** | 2.4 | **3.6** |
| 150 | 1.0 | **0.51** | 2.0 | **1.1** | 2.7 | **3.2** | 1.5 | **3.5** | 1.9 | **5.1** |
| 2980 | 1.2 | **4.1** | 0.8 | **0.11** | 1.7 | **2.4** | 1.9 | **0.62** | 2.0 | **0.86** |
| 29800[b] | 6.3 | **3.7** | 7.9 | **4.9** | 11 | **8.6** | 11 | **8.2** | 10 | **6.8** |

Glass extractor: 9 cm × 0.25 mm i.d., 0.3 μm PS255; $n = 2$ for every concentration level.

[a] A: by peak area response; H: by peak height response (bold numbers).

[b] This sample was visibly 'cloudy'.

are effected to a lesser degree than those of less retained compounds, while the absolute differences are in reversed order. The last results were unexpected, but seem logical. During GC elution from the manually connected in-tube extractor, the analytical column is put initially at atmospheric pressure, then it is subjected to an inrush of carrier gas with higher carrier velocity than with septum injection, as confirmed by a lower unretained retention time. Higher carrier gas velocity also means a reduction of the number of interactions between analyte molecules and the retaining column coating. Thus analytes were eluted earlier, and the absolute difference rose with interaction level, i.e. with $t_R$.

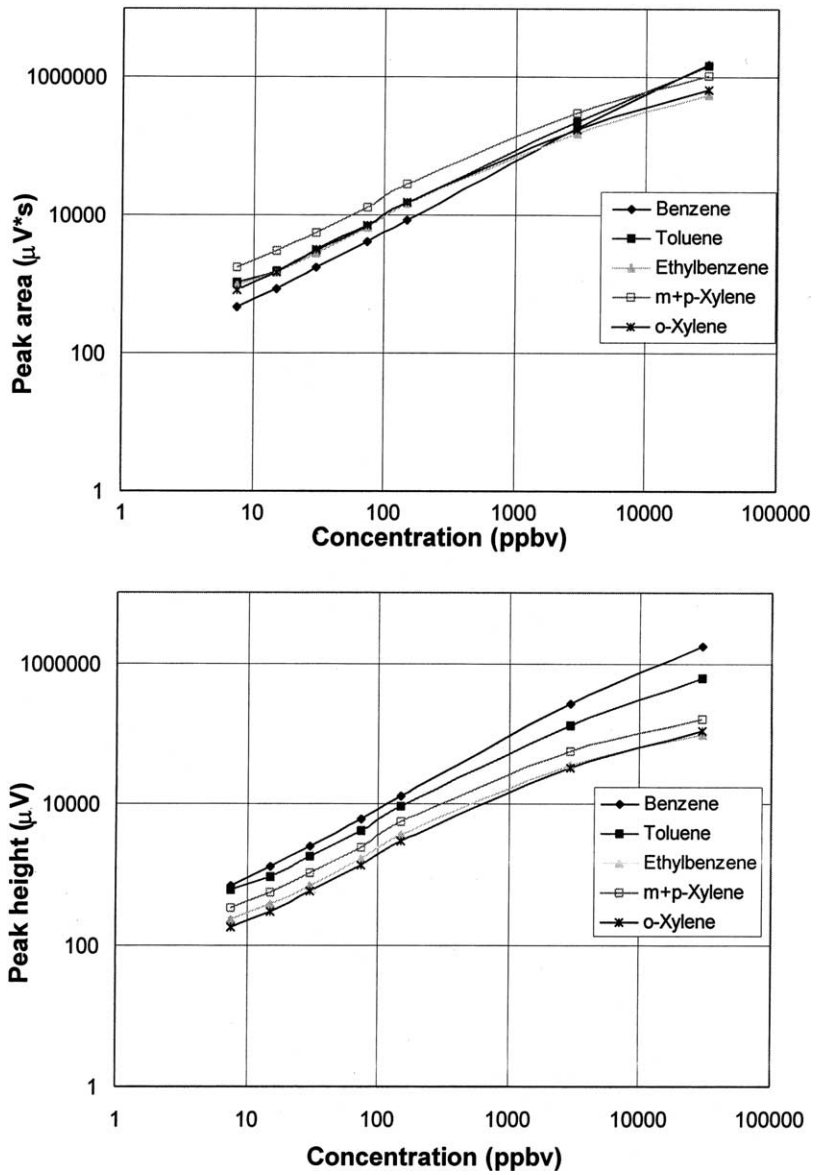


Fig. 9. Quantitative calibration data of capillary extraction in the BTEX concentration range 7.5–29,800 ppb using an extractor 9 cm × 0.25 mm i.d., 0.3 μm. Upper graph results from peak area quantitation; lower one is generated from height calculation.

As a result, $t_R$ calibrations should always be done consistently.

### 3.8. Reproducibility of squeezed in-tube extractions

Precision of capillary extraction is of obvious interest. Some values were already reported discussing soaking and salting-out effects. Those reproducibility figures were usually obtained from 1 ml squeezed samples, sampled from ∼4 ml of liquid, a situation in which headspace volumes increased systematically after each sampling action.

Since it is known from SPME theory that headspace takes an active role in the extraction of volatile compounds, the following reproducible results were obtained using the 'no-headspace' in-tube sampling technique described in Section 2. Extractions were performed by salting with NaCl, using a capillary extractor 9 cm × 0.25 mm i.d., 0.3 μm PS255; 1 ml sample at 150 ppb was rapidly squeezed at 0.1 ml/s while using standard care (Table 6).

Precision of the technique was found to be acceptable considering the high extraction speed. Benzene, the most volatile analyte, was detected with better precision than other BTEX compounds, and that might not be the case with SPME and SBSE.

### 3.9. Capillary extraction linearity

Data devoted to studying the linearity of capillary extraction–HRGC was acquired in the range of 7.5–29,800 ppb per component. Extractions were performed in duplicate on 1 ml samples, according to the squeeze method. Fig. 8 shows a chromatogram of the most diluted BTEX sample and one of the most concentrated one. Fig. 8 confirms the accuracy of the calculated detection limits reported in Table 4 with reference to salted extractions. It also shows that with manual mounting of extractors in the GC oven, there may be some variability of retention times as a result of $t_R$ dependability on the operator's sense of timing. A rotating injection valve would eliminate this variability effect, but during analyses of real samples performed with manual operation it is advisable to use relative retention times to offset these effects.

Fig. 8 also shows that even with very concentrated samples capillary extraction does not lose its inherent good peak shape, baseline quality, or peak resolution, even though 30 ppm BTEX samples heavily overload the GC column.

Table 7 summarizes the data obtained with corresponding graphs in Fig. 9 (reference to both area and height calibration). Trends through the rather wide calibration range appear linear at lower concentrations. Linear regression equations using the nominal values through the axes origin all gave $r^2$ values higher than 0.996 for area counts from 0 to 150 ppb (0–3000 ppb for height quantitation). At the highest concentration, the slight deviation from linearity depends on the fact that preparation of the 29,800 ppb BTEX standard resulted in a cloudy aqueous solution (some components exceeding their solubility limits) giving rise to a heterogeneous system.

## 4. Conclusion

This study has shown that aqueous BTEX samples at ppm to ppb levels can be extracted within a few seconds (mostly with negligible depletion [38]) and ruggedly analyzed using capillary extraction coupled to GC-FID. Chromatographic peak shapes and baseline stability is superior when compared with SPME [22] and SBSE. It would be impossible for routine SPME or SBSE to perform equilibrium or near-equilibrium extractions within 3–5 s with perfectly symmetrical chromatographic peaks without the use of cryfocusing techniques and heated injectors (a clear advantage for portable GC applications). The absence of any 'system' peaks is a major feature of the proposed approach.

Soaking and salting-out effects have been investigated and show the capacity to increase extraction performance. Capillary extraction for BTEX analyses in clean water is reproducible within about 10% R.S.D. and suitable for on-site sampling [35]. The extractors themselves act as both effective microextractors and cold *on-column* injector liners. The BTEX storage within capillary extractors (capped with press-fit caps) has been demonstrated to be excellent [31] also because these extractors are persilylated devices. For the quantitative extraction/preconcentration/GC analysis of thermally unstable compounds capillary extraction may provide very high accuracy. The complementary nature of capillary extraction as a whole

towards SPME and SBSE is evident. Among several ‘microextraction’ techniques capillary extraction has the charming feature to require simple items and the simplest capillary GC instrumentation.

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