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Role of the retaining precolumn in large-volume on-column injections of volatiles to gas chromatography

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Abstract

In the present study the retaining precolumn, which is commonly used in a set-up for large-volume on-column injections, or when solid-phase extraction (SPE) or liquid chromatography is coupled to gas chromatography (GC), was removed after varying its length from the standard length of 3 m down to zero. A dramatic increase of the evaporation rate of the injected organic solvent was obtained from a typical value of 100 μl/min up to 300 μl/min. The increased evaporation rate allowed (i) injection of a larger volume in the same retention gap, (ii) faster injection/transfer of the organic solvent and (iii) reduction of the transfer temperature. As volatile compounds under partially concurrent solvent evaporation conditions are easily lost once the organic solvent has been removed via a solvent-vapour exit (SVE), the parameters for large-volume injection, i.e. the evaporation rate and injection speed, were optimised using accurate measurements of the real flow-rate of the carrier gas into the GC system. All these options have been evaluated over the last 4 years. In order to demonstrate that omitting the retaining precolumn had no effect on the application range of the on-column interface, analytes as volatile as benzene were injected into GC–MS using 50–200 μl of *n*-pentane solutions. Contaminants were extracted from river water and wastewater into *n*-pentane using in-vial liquid–liquid extraction. The detection limits for benzene, toluene, ethylbenzene and *m*-xylene were ~10 ng/l. To obtain optimum results the SVE had to be closed 1 s before the end of evaporation. Several brands of *n*-pentane were analysed to check for the presence of benzene. Most of them contained interfering compounds and benzene at the low μg/l level and therefore had to be cleaned by means of column chromatography. As another example C_8–C_{17} alkylphenones were extracted from wastewater with *n*-hexane. Detection limits were 10–40 ng/l.

Keywords: Large-volume injections; Water analysis; Evaporation rate; Retaining precolumn; On-column injector; Volatiles; Alkylphenones; BTEX

1. Introduction

When large volumes of organic solvents are introduced into a gas chromatograph in the on-column mode, as in the case of on-line coupled techniques such as LC–GC [1] and SPE–GC [2], the common GC set-up of injector–column–detector has to be modified [3,4]. In order to retain the large volume of liquid during injection/transfer and evaporation, a retention gap, a piece of deactivated fused silica, is inserted between the injector and the analytical column [5]. The solvent is injected into the retention gap which is often or usually connected to a retaining precolumn or, directly, to the analytical column. An early solvent-vapour exit (SVE) is

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generally inserted between the retaining precolumn and the analytical column to increase the evaporation rate and to protect the detector from excessive amounts of solvent vapour [6]. With a particular set-up of retention gap, retaining precolumn and analytical GC column, the evaporation rate is determined by the head pressure used and the lengths of the individual capillaries.

If a retaining precolumn is used, it serves only as a restriction to prevent too high a pressure drop over the retention gap [7]. A (retaining) precolumn, coated or uncoated, of 2–3 m is recommended in the literature [8,9]. Still, closure of the SVE remains critical [6]. For large-volume injection (LVI) of volatiles an on-column injector in combination with a retention gap is the preferred set-up and, in order to achieve a wide application range, partially concurrent solvent evaporation (PCSE) conditions are used. During on-column injection it is important to keep the injection rate higher than the evaporation rate. This guarantees the formation of a solvent film on the inner wall of the retention gap, which will trap the volatile analytes during solvent evaporation [10].

The introduction of an SVE controller [11] allows the determination of the accurate point in time at which the evaporation process ends. Although the SVE and the retaining precolumn were introduced more than 10 years ago [10,12], the role of the retaining precolumn has not been studied in detail until more recently [13]. In another study, the analyte losses in systems suited for on-column LVIs were investigated [9]. In both papers, it was shown that the retaining precolumn only acts as a restriction (cf. above). Therefore we prefer to call it a restricting precolumn. A length of 2 m of restricting precolumn connected to a 5-m retention gap [9] was sufficient to keep volatile compounds trapped in the solvent film when closing the SVE at the end of the evaporation process by using the SVE controller. It was also shown, when studying the fraction of the solvent evaporated during injection (expressed as $\vartheta =$ injection time/evaporation time) and the length of the solvent film in the retention gap (expressed as the fraction, f, of the total length of the retention gap that is wetted), that ϑ is the most critical parameter. When using a 2-m restricting precolumn, optimum injection conditions will be obtained if the degree of concurrent solvent evaporation is kept below 60%; that is, ϑ should be less than 0.6. During the optimisation it is recommended to select values for ϑ for which $f = 0.5–0.6$ [9,14].

In the present study the possibility of omitting the restricting precolumn was examined. Reducing the length of, or even omitting, the restricting precolumn will result in an increase of the carrier gas flow through the retention gap with the consequence of a higher evaporation rate. The effect on volatile analytes, i.e. compounds eluting directly after the solvent peak, was investigated. Two mixtures of volatile or relatively volatile test analytes were selected. Benzene, toluene, ethylbenzene and the three isomers of xylene (BTEX) are common industrial solvents and fuel components, which, because of their toxicity and possible carcinogenicity, have to be monitored at very low concentrations. As regards alkylphenones, acetophenone is used as a solvent in industrial processes, and several alkylphenones are used as fragrances in perfumes and flavours in foodstuffs and soft drinks. They are also well-known phenolic degradation products. Relevant applications have been developed in which LVI was combined with in-vial liquid–liquid extraction (LLE) [15].

2. Experimental

2.1. Chemicals and stock solutions

Several brands of *n*-pentane (J.T. Baker, Biosolve, Fischer, Fluka, Labscan, Merck, Rathburn and Riedel-de Haën) and *n*-hexane (J.T. Baker, Biosolve, Fischer, Fluka, Labscan, Merck, Prolabo, Rathburn, Riedel de Haën and Aldrich) were tested. For the BTEX applications, *n*-pentane from Rathburn (Walkerburn, Peebleshire, UK) was used after cleaning by means of column chromatography on a 30×2 cm I.D. silica (kieselgel, particle size: 60 mesh, 0.063–0.100 mm, Merck (Darmstadt, Germany) or alumina (Al_2O_3 90, particle size: 0.063–0.200 mm, Merck) column with a PTFE valve, to remove benzene and benzene derivatives.

A stock solution containing the C_8–C_{20} *n*-alkanes except for C_{16}, was prepared in *n*-hexane (Aldrich, Steinheim, Germany) and diluted to a concentration of 1 mg/l. The working solutions used for optimi-

sation of the parameters for LVI were prepared daily by diluting the stock solution in *n*-hexane or *n*-pentane.

Benzene, toluene, ethylbenzene and *m*-xylene (BTEX) were obtained from J.T. Baker (Deventer, The Netherlands) and chlorobenzene, used as an internal standard, from Merck. Acetophenone, *n*-decanophenone and *n*-undecanophenone were purchased from Acros (Geel, Belgium); propiophenone, butyrophenone, valerophenone and heptanophenone were all from Sigma-Aldrich (Steinheim, Germany). Valerophenone was used as internal standard. For this application, *n*-hexane from Aldrich was used.

Individual stock solutions of all test compounds were prepared at a concentration of 2 mg/ml in methanol (J.T. Baker). Mixtures were prepared by adding the proper volumes with subsequent 1000-fold dilution with methanol. Working solutions were prepared prior to use by further dilution in *n*-pentane or *n*-hexane. The stock solutions in methanol were also used for spiking purposes.

HPLC-grade water (J.T. Baker) was used for blank extractions. Samples and HPLC-grade water were spiked with the BTEX mixture to test the extraction method. Wastewater was obtained from the university wastewater control system. Water samples from the river Rhine and from the wastewater effluent at La Llagosta (Catalonia, Spain) were also analysed.

2.2. GC system for large-volume on-column injection

For method development, a Dualchrom HPLC–HRGC 3000 (Carlo Erba Strumentazione, Milan, Italy) equipped with an on-column injector, an FID-40 and an SVE valve was used [9]. A 5 m×0.53 mm I.D. piece of diphenyltetramethyldisilazane-deactivated retention gap (DPTMDS; BGB, Rothenfluh, Switzerland) was used for the introduction of large sample volumes under PCSE conditions. It was connected to a restricting precolumn and a 15 m analytical GC column (both 0.32 mm I.D. HP-101, $d_f = 0.30$ μm) via a glass press-fit and a Y-piece connector, respectively. The length of the restricting precolumn was varied between 3 m and zero. The SVE valve, which was actuated via a remote event of an SVE controller, was connected to the Y-piece via 0.2 m of 0.53 mm I.D. fused silica. The SVE was continuously purged through a 0.5-m×75 μm I.D. restriction. Helium 5.0 (Praxair, Oevel, Belgium) was used as carrier gas and the pressure was adjusted to generate a flow-rate of 2.0 ml/min through the GC system. With the purge of the SVE open, the flow-rate was 2.1 ml/min. The flow-rate was measured accurately with a mass flow meter (0–30 ml/min range; model F101D-HA; Bronkhorst Hi-Tech, Ruurlo, The Netherlands) at the inlet carrier gas line of the on-column injector with the SVE closed. Flows above 30 ml/min were measured with a soap film flow meter. When the restricting precolumn was removed, the head pressure had to be reduced so that the SVE controller could still control the closing of the SVE. This resulted in a flow of 1.65 ml/min with the SVE closed, and 29.4 ml/min with the SVE open.

A signal from an external trigger, e.g. the autosampler, was sent to the SVE controller at the start of an injection. After completion of the evaporation, when the flow-rate increased, the SVE controller actuated the closure of the SVE. A temperature programme from the boiling point of the solvent at 1 atm., 36 °C for *n*-pentane and 69 °C for *n*-hexane, to 280 °C at 10 °C/min was used; the final temperature was maintained for 2 min.

For injection a Harvard Apparatus 22 (SO. Natik, MA, USA) was used. The injection speed could be controlled between 1 and 1980 μl/min in steps of 1 μl/min. A 500- or 2500-μl syringe with a PTFE plunger tip was manually filled and, after mounting it in the Harvard Apparatus, the sample was transferred to the injector via the LC–GC transfer valve and a 50 cm×75 μm I.D. stainless steel capillary. Data were acquired by a Chromatography server and processed in the integration program xChrom (VG Data Systems, Altrincham, UK).

For the LLE–LVI–GC–MS analysis of aqueous samples, a Carlo Erba Series 8000 gas chromatograph equipped with the above large-volume injection set-up [11,14] with an on-column injector, an SVE and an MD 800 mass spectrometer (Carlo Erba Strumentazione) was used. The F101D-HA flow meter had a range of 0–200 ml/min. A retention gap (5 m×0.53 mm I.D.; DPTMDS-deactivated, BGB Analytik) and an analytical column (30 m×0.25 mm I.D., $d_f = 0.25$ μm; DB-XLB; J&W Scientific, Folsom, CA, USA) were used at a head pressure of 165

Table 1
Characteristic ions of the target analytes

Analyte	*m/z*	
	Base ion	Molecular ion
Benzene	77	78
Toluene	91	92
Chlorobenzene	112	114
Ethylbenzene	91	106
m-Xylene	91	106
Alkylphenones	105	120

kPa. No restricting precolumn was used. Experiments were done with 50–200 μl injections with injection speeds of up to 720 μl/min, using an AS 800 autosampler (Carlo Erba Strumentazione) with a 250-μl syringe. The temperature programme started at 35 °C (1 min), then at 5 °C/min to 70 °C and at 50 °C/min to 285 °C (2 min). For the determination of the alkylphenones a temperature programme starting at 69 °C (1 min), and then at 10 °C/min to 235 °C was used.

The mass spectrometer was operated in the electron ionisation mode (EI, 70 eV); the temperature of the transfer line was 300 °C. For identification purposes, the MS was operated in the TIC mode and for optimal analytical sensitivity in the SIM mode. The ions recorded in the SIM mode are listed in Table 1. During optimisation experiments the filament was turned on manually, 3 s after the pressure was restored to 10^{-5} Torr, to ensure that there was not too much solvent left to contaminate the source but that it was still possible to detect benzene.

2.3. Off-line and in-vial liquid–liquid extraction

In-vial LLE of the BTEX compounds or of the alkylphenones from water was performed by adding equal amounts of water and *n*-pentane or *n*-hexane to an autosampler vial [15]. The two-phase system was vigorously stirred for a few seconds by using a vortex mixer. The extraction yields were calculated by using direct injections of standard solutions as a reference.

In addition, to improve the detection limits a 50:1 (v/v) extraction of BTEX from water to *n*-pentane was performed in a 50-ml volumetric flask by adding 1 ml of pentane to 49 ml of sample and shaking [16].

3. Results and discussion

3.1. Evaporation rate

In order to create solvent effects to ensure the quantitative recovery and reconcentration of volatile analytes in GC, the injection speed has to be higher than the evaporation rate [17]. In this study the evaporation rate, which is different for each solvent and at each temperature as it is dependent on the boiling point of the solvent [8,18], was determined empirically for a number of solvents using the SVE controller [15] (Table 2). When an injection speed which caused the evaporation time to be at least 10% larger than the injection time, had been found, the evaporation rate of the solvent was determined at this

Table 2
Evaporation rates of some organic solvents analysed by GC–FID

Solvent	Flow-rate through column (ml/min)	T_{inject} (°C)	Injection speed[a] (μl/min)	Evaporation rate[b] (μl/min)	*n*	r^2	Standardised evaporation rate[c] (μl/min)
Pentane	2.1	36	300	271	9	0.9996	271
Methyl*tert*.-butyl ether	2.1	54	250	225	4	0.9998	225
Methyl acetate	1.6	55	225	149	4	0.9999	195
Methanol	2.1	64	150	86	4	0.9999	86
Hexane	2.2	69	350	316	10	0.9992	302
Ethyl acetate	2.3	77	250	186	3	0.9995	170
Acetonitrile	1.6	82	150	129	5	0.9996	168

[a] Giving an evaporation time which is at least 10% higher than the injection time.
[b] Average evaporation rate, calculated from reciprocal slopes.
[c] Corrected for the flow through the column to a flow-rate of 2.1 ml/min, i.e. $v_{evap\ std} = (v_{evap.}/\text{flow-rate}) \times 2.1$.

constant injection speed and with a stepwise increase of the injection time. The injection volume was plotted against the measured evaporation time and the average evaporation rate was calculated as the reciprocal value of the slope [9]. The evaporation rates of Table 2 were measured on the GC–FID at different carrier gas flow-rates. Therefore they were standardised to a flow-rate of 2.1 ml/min by dividing by the actual flow-rate and multiplying by 2.1. Pentane and hexane were the solvents which showed the fastest evaporation. Therefore, and also because of their high purity, these solvents were found to be the most favourable for LVI at a high injection speed. The other solvents can, however, be used if necessary, e.g. for LC–GC or SPE–GC coupling.

3.2. Restricting precolumn

3.2.1. Flow rate

During method development, the flow-rate through the GC system was set to 2.0 ml/min with all exits closed except the SVE purge. This was repeated for each new set-up, that is, when the length of the restricting precolumn was changed. As the flow-rate through the open SVE exceeded the 30 ml/min maximum of the flow meter when the restricting precolumn was omitted, the head pressure was decreased which resulted in a flow-rate of 1.65 ml/min with all exits closed and a flow-rate of 29.4 ml/min with the SVE open. The flow-rate through the open SVE could now be determined accurately by the digital read-out of the SVE controller. The repeatability in the read-out of the flow was excellent. The SVE valve was opened and closed five times and each time the flow through the open SVE and the flow through the GC system after closing the SVE were registered. The resulting values (ml/min) were 29.40 ± 0.02 and 1.65 ± 0.02, respectively.

3.2.2. Evaporation rate

The evaporation rate was increased by gradually reducing the length of the restricting precolumn. As a result, the injection volume could be increased. For each length of restricting precolumn, the evaporation rate was determined for *n*-hexane at 69 °C and the flow through the SVE was measured. When the length of the restricting precolumn was reduced from 3 m to zero, the volume injected into the 5-m retention gap over a period of 60 s could be increased from 150 to 365 μl. The evaporation rate determined with each set-up was plotted against the flow through the SVE and a strictly linear relationship was found; that is, the evaporation rate increased linearly with the flow-rate through the open SVE (Fig. 1). In the past few years we constructed many of these plots and always found a linear relationship between evaporation rate and flow-rate through the retention gap for the conditions chosen: boiling point of the solvent at 1 atm., and reducing the length of the restricting precolumn in order to increase the flow-rate through the retention gap; that is, the inlet pressure did not change dramatically since it was adjusted to cause a flow-rate of 2 ml/min through the column. With the CE 8000 series GC–MS, equipped with a flow meter with an upper limit of 200 ml/min and used for the analysis of the extracts, the injection volume could be further increased. The evaporation rates of *n*-pentane at 35 °C and *n*-hexane at 69 °C were now found to be 468 and 480 μl/min, respectively, when the flows through the open SVE surpassed the 200 ml/min upper limit of the flow meter.

For a 200-μl injection the fraction of the solvent evaporated during injection, ϑ, was 0.67 for *n*-pentane and 0.60 for *n*-hexane injections. This is the upper limit of, or even slightly above, what has been recommended in the literature [9]. The flooded zone of the system was not determined. Assuming that it was the same as in previous work [9], i.e. 4.2 cm/μl, f can be calculated to 0.56. This is within the values recommended, 0.5–0.6, as a starting point

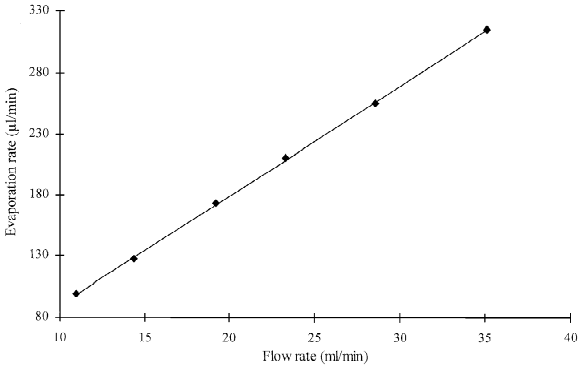

Fig. 1. Evaporation rate of hexane against flow-rate through the open SVE.

when optimising a system for large volume injection. Due to the high value of ϑ, the early eluting *n*-alkanes were however lost during solvent evaporation when the SVE was automatedly closed at the end of the evaporation, i.e. 25 s after starting the injection (Fig. 2). From the literature it is known that closing the SVE just before the last drops of liquid have evaporated, can prevent the loss of volatiles [6]. Indeed, when the SVE was closed 1 s earlier, i.e. 24 s after starting the injection, the performance was much better and the areas of C_{11}, C_{12} and C_{13} relative to C_{23} improved from 0.2, 0.3 and 0.5 to 0.9, 0.9 and 0.7, respectively. This is finally satisfactory.

3.2.3. Application range

During the experiments described in Section 3.2.2, a standard solution of the C_8–C_{20} alkanes in *n*-hexane was used to determine the application range for the various set-ups. There were no obvious differences, as can be seen in Fig. 3: C_8 could be analysed both with (0.3 or 3 m) and without a restricting precolumn.

The possibility to analyse very volatile compounds was tested with a standard solution of the BTEX mixture. These compounds have boiling points between 80.1 and 140 °C. When the SVE was closed by the SVE controller in an automated fashion at the end of the evaporation process, benzene and toluene were not recovered at all. However, when closing the SVE 1 s before the end of evaporation, as was discussed above, the most volatile analytes were recovered. This implied that 8 μl of solvent reached

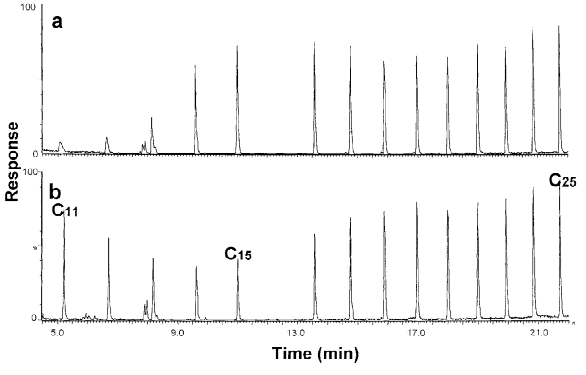

Fig. 2. GC–MS fragmentograms (m/z 57) of C_{11}–C_{25} *n*-alkanes, except C_{16}, with SVE being (a) automatedly closed by the SVE controller or (b) 1 s earlier.

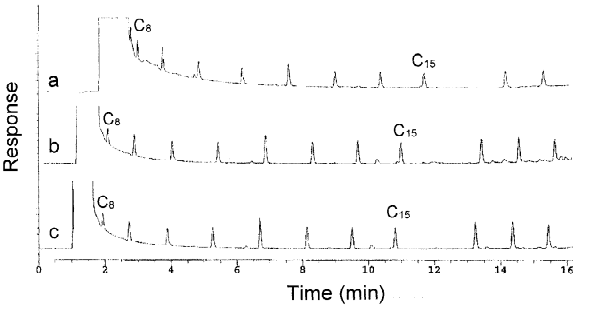

Fig. 3. GC–FID chromatograms of C_8–C_{20} *n*-alkanes, except C_{16}, showing the application range for set-ups with (a) 3 m, (b) 0.3 m and (c) no restricting precolumn.

the MS when the evaporation rate was 480 μl/min, or 8 μl/s. With this procedure, leaving 8 μl of solvent to trap the volatiles, high and repeatable recoveries were obtained for most of the volatile analytes. Admittedly, benzene, which elutes on the tail of the solvent peak still had a relative standard deviation (RSD) of 27% ($n=3$). The later eluting compounds showed better repeatabilities with RSD values of 15, 4.5 and 3.4% for toluene, ethylbenzene and *m*-xylene, respectively. As the SVE was closed before the evaporation was complete, the fact that ϑ was somewhat higher than is recommended (see Section 3.2.2) did not have an adverse effect on the recoveries.

When injecting alkylphenones in *n*-hexane and closing the SVE at the end of the evaporation process in the automated fashion there were considerable losses up to heptanophenone. However, closing the SVE 0.4 s before the end of the evaporation was enough to recover all the alkylphenones (Fig. 4). Acetophenone, the first eluting compound, has a boiling point of 201.7 °C. When comparing the peak areas relative to that of decanophenone, the peak areas of the first three eluting compounds increased from almost zero to 0.7, 0.9 and 0.9 when the SVE was closed 0.4 s before the end of evaporation. One could argue that it is a drawback of the procedure presented here that there is a greater variation in starting point and, consequently, in retention times of the chromatograms than under conventional conditions, due to slight variations in evaporation rate. However, here one should realise that using the sudden rise in helium flow-rate at the end of the solvent evaporation as the automated

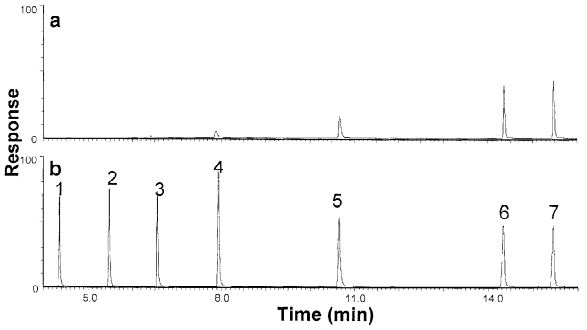

Fig. 4. GC–MS chromatograms (SIM) of alkylphenones, 200 μl of 100 μg/l solutions, recorded when closing the SVE (a) at the end of the evaporation or (b) 0.4 s earlier. Peak assignment: 1, acetophenone; 2, propiophenone; 3, butyrophenone; 4, valerophenone; 5, heptanophenone; 6, decanophenone; 7, undecanophenone.

trigger to start data acquisition, does indeed yield a more precise starting point but at the cost of the loss of most volatiles. Actually, in the present study no identification problems due to shifting retention times were observed.

All further experiments were performed, closing the SVE 1 s before the end of evaporation.

3.3. Practicality and performance data

3.3.1. Purity of solvent

A number of different brands of *n*-pentane were tested for their usefulness as solvents in ultra-trace-level detection in MS; unfortunately, all contained too high levels of the BTEX target compounds (Table 3). The *n*-pentane from Rathburn was found to be the least contaminated. Prior to use it was cleaned by means of gravity chromatography on a silica or, preferably, an alumina 30×2 cm I.D. column (both dried at 250 °C for 24 h before use), with a PTFE valve, to remove as much interferents as possible. Chromatographing on an alumina column proved to be superior considering the removal of the target analytes. However, silica did remove many of the other contaminants it contaminated the extract considering the target analytes. The *n*-pentane was collected as 15-ml fractions. The second and third fractions were found to be the cleanest, and were used for analysis. The background levels of the target compounds in *n*-pentane before and after the cleaning procedure can be read from Table 3. Other contaminants which were also present at similar or higher levels, before clean-up, were: 4-methyl-3-pentanoic acid, hexane, hexene, 2-methylpentane, cyclohexane, 2-ethylhexylester, 2,2,3-trimethylpentane, heptane, methyl-cyclohexane, 2-methyl-octane, 4-methyl-octane and heptanol. However, these contaminants did not interfere with the analysis.

Several different brands of *n*-hexane were also tested. It was found that *n*-hexane purchased from Aldrich could be used without any treatment. Except for some small peaks just above the noise level, it only contained two high-boiling phthalates eluting later than all target analytes.

Table 3
Background levels (ng/l), recorded by GC–MS (SIM), of the target compounds in *n*-pentane from Rathburn, before and after cleaning

Analyte	No clean-up	Silica	Alumina
Benzene	2190	2100	5
Toluene	480	680	25
Chlorobenzene	5	130	N.d.
Ethylbenzene	100	130	N.d.
m-Xylene	40	300	N.d.

N.d., below LOD.

3.3.2. Analytical data and applications

Calibration curves for benzene, toluene, ethylbenzene and *m*-xylene were linear over the complete range studied, 0.01–20 μg/l, when injecting 200 μl at 720 μl/min and using an evaporation rate of 468 μl/min. Due to the fact that benzene eluted on the tail of the solvent, its correlation coefficient was somewhat low, i.e. 0.955 (8 data points). The other analytes had much better correlation coefficients, i.e. 0.988–0.995. The calibration curves for the alkylphenones all gave excellent correlation coefficients, 0.999, when injecting 11 different concentrations between 0.01 and 100 μg/l.

As one example, the in-vial LLE of all target compounds, BTEX and alkylphenones, in water showed excellent recoveries and repeatability at the 20 and 100 μg/l level, respectively (Table 4). Analyte detectability, in the SIM mode, was also satisfactory, as is evident from the data included in the table. They represent results obtained after, in

Table 4
Percent recoveries of the LLE part of the procedure, and LODs of BTEX and alkylphenones for the complete LLE–GC–MS (SIM) procedure

Analyte	Recovery[a]		LOD[b] (ng/l)
	(%)	RSD (%)	
Benzene	102	3	35
Toluene	76	4	10
Chlorobenzene	102	4	5
Ethylbenzene	104	3	10
m-Xylene	102	4	10
Acetophenone	96	6	170
Propiophenone	100	7	10
Butyrophenone	100	5	10
Valerophenone	101	8	10
Heptanophenone	100	4	10
Decanophenone	96	2	70
Undecanophenone	98	3	10

[a] 1:1 extractions of HPLC-grade water spiked with BTEX at 20 μg/l or alkylphenones at 100 μg/l [organic solvent BTEX: *n*-pentane ($n=5$); alkylphenones: *n*-hexane ($n=2$)].

[b] 200 μl injection of 50:1 extract from HPLC water spiked with BTEX at 20 μg/l, 7-channel SIM mode, and 1:1 extract from La Llagosta wastewater spiked with alkylphenones at 200 ng/l, 2-channel SIM mode.

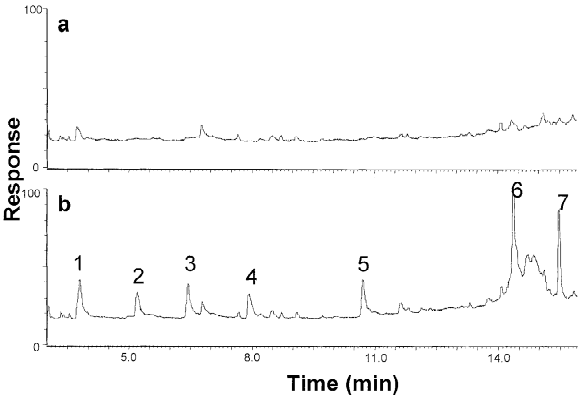

Fig. 5. GC–MS chromatograms (SIM) of La Llagosta wastewater after (a) 1:1 extraction into hexane and, (b) spiking at 200 ng/l and 1:1 extraction into hexane. For peak designation, see Fig. 4.

one instance, 50:1 HPLC-grade water–pentane extractions and, in the other, 1:1 wastewater–hexane extractions. With all analytes, the LODs quoted in Table 4 for LLE–GC–MS were, typically, less than 2-fold higher than those obtained by direct LVI–GC–MS. The exceptions were acetophenone and decanophenone with which the less than complete separation from matrix peaks adversely affected detectability (LODs for standards, 10–20 ng/l).

The LODs of the alkylphenones could be determined in the la Llagosta wastewater because these compounds were found to be absent from all waste- and river water samples tested (Fig. 5). In one case, viz. with a wastewater sample from a pumping unit located at the Free University campus, an unknown compound of some relevance was detected. As is shown in Fig. 6, an unknown peak appeared between toluene and ethylbenzene. Its mass spectrum was closely similar to that of toluene, and 1,3,5-cycloheptatriene which has a boiling point (116 °C) slightly higher than that of toluene (110 °C), was the only good match found in the library. Both toluene and the unknown were present at levels of about 20 μg/l.

4. Conclusions

In a large-volume on-column injection set-up, the evaporation rate can easily be increased by reducing the length of the restricting precolumn. As a consequence, larger sample volumes can be injected. The increase in evaporation rate is linearly dependent on the flow-rate through the open SVE measured at each length of restricting precolumn. As a result of removing the 3 m restricting precolumn, the time needed to evaporate the injected solvent decreased 3-fold.

The length of the restricting precolumn was not critical for the application range if the solvent vapour exit was closed 1 s earlier than when it is automatedly closed on a signal from the controller. To quote an example, C_8 *n*-alkane could be seen in all chromatograms recorded both with and without restricting precolumn and closing the SVE with the controller at the end of evaporation. However, when using the GC–MS with the 200 ml/min flow meter, the evaporation rate was too high to analyse volatiles when closing the SVE automatedly using the control-

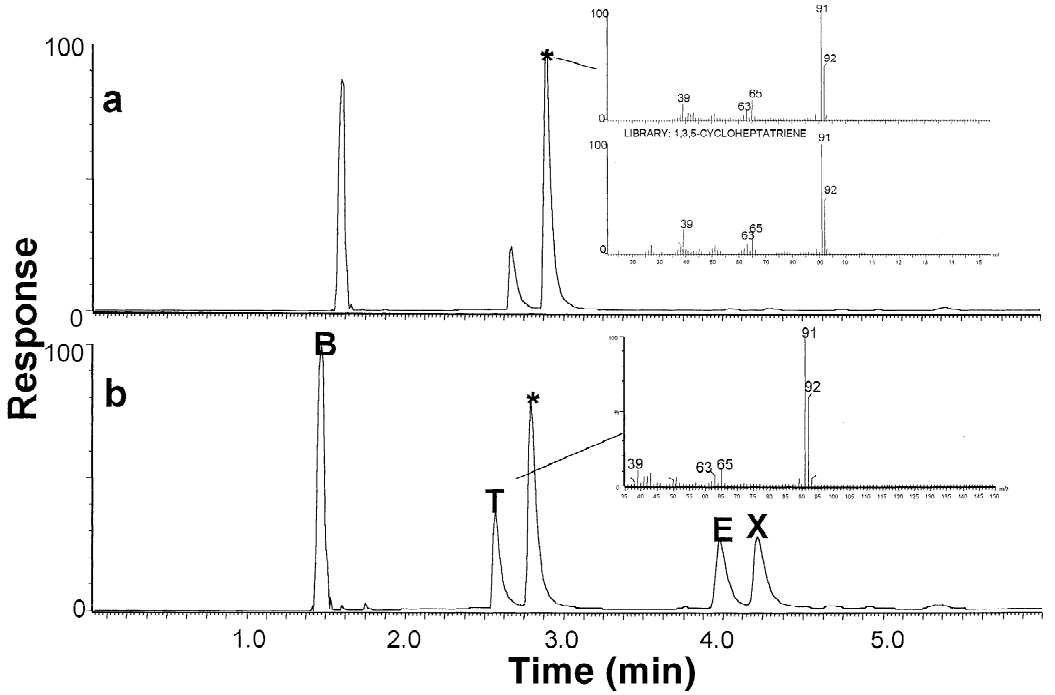

Fig. 6. GC–MS chromatograms (SIM) of 50:1 extracts of a university wastewater sample (a) without spiking, and (b) spiked with BTEX at 0.2 μg/l. The shift in retention time is due to slight variations in evaporation rate.

ler. When the SVE was closed 1 s earlier, even compounds as volatile as benzene could be determined quantitatively. Closing the SVE before the end of evaporation also made the analysis more robust and user friendly.

The in-vial liquid–liquid extraction of the target analytes, BTEX and alkylphenones, gave high recoveries and good repeatabilities. In combination with large-volume on-column injection, detection limits at the low ng/l level were reached. The complete procedure is robust and can be recommended for routine analysis.

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