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Investigation of parameters affecting the on-line combination of supercritical fluid extraction with capillary gas chromatography

Xianwen Lou, Hans-Gerd Janssen*, Carel A. Cramers

Eindhoven University of Technology, Laboratory of Instrumental Analysis, P.O. Box 513, 5600 MB Eindhoven, Netherlands

Abstract

Two different injectors, a split/splitless injector and a programmed temperature vaporizer (PTV) injector were investigated as the interface in on-line supercritical fluid extraction (SFE)–capillary gas chromatography (cGC). The parameters affecting the chromatographic peak shapes as well as the quantitative performance of the interfaces in on-line SFE–cGC were identified and studied. Particular attention was paid to the case where modified extraction fluids were used. Experiments were performed on two different samples. The first sample consisted of PAHs spiked on sand at different concentration levels. The other sample was a polymeric material.

Keywords: Supercritical fluid chromatography; Capillary gas chromatography; Interfaces; Programmed-temperature vaporizer; Injection methods; Polynuclear aromatic hydrocarbons; Polymeric samples

1. Introduction

Supercritical fluid extraction (SFE) is an attractive sample preparation method for chromatography. It is fast and enables the introduction of some selectivity in the extraction process. Moreover, the most commonly used fluid (CO_2) is inert, non-toxic and inexpensive. Furthermore, supercritical CO_2 is gaseous under ambient conditions. Therefore, the solute separation and concentration process is simplified and direct coupling of SFE to chromatographic techniques, especially to capillary gas chromatography (cGC), is greatly facilitated. The direct combination of SFE and cGC can, in many cases, be a straightforward procedure [1,2].

SFE can be combined with cGC either in the off-line or the on-line fashion. Off-line SFE–cGC is generally simpler to perform and allows the extracts to be analyzed at different cGC conditions or by any other appropriate technique. Therefore, off-line SFE–cGC should be the first choice during SFE method development [3]. To date, the majority of SFE applications is performed off-line. On the other hand, on-line SFE–cGC is more attractive in routine analysis since no sample handling steps are included between the SFE and cGC. On-line SFE–cGC operation basically involves three steps. First, the components are extracted by SFE. Next, the extracted components have to be transferred to the cGC column via a suitable interface. Finally, the components must be separated and detected by the cGC instrument. Each of the conditions in these three steps, i.e. SFE parameters, analyte transfer conditions, and the chromatographic separation parameters must be optimized carefully before the analysis can be completed successfully.

Optimization in SFE is rather complicated because many parameters affect the extraction kinetics. A number of research groups has investigated the parameters affecting the extraction process in SFE.

*Corresponding author.

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Langenfeld et al. [4] studied the influence of temperature and pressure on the SFE extraction of PCBs and PAHs from certified environmental reference materials using pure carbon dioxide and found that for achieving high extraction efficiencies temperature is more important than pressure. This is especially true if the interactions between the analytes and the matrices are strong. Similar results have been reported for the SFE extraction of polymeric samples. If pure CO_2 is used, high extraction recoveries can only be obtained at elevated temperatures [5,6]. Alternatively, higher yields can be obtained by the addition of a suitable modifier. Unfortunately, however, the effects of modifiers are highly matrix- and solute dependent. In the extraction of some environmental samples, for example, it was found that the modifier identity was more important than its concentration [7]. In contrast to this, both modifier identity and concentration were found to be important in the extraction of polymeric samples [8]. Summarizing, high SFE extraction efficiencies can be obtained either at high extraction temperature and pressure conditions or with the addition of a suitable modifier.

In a hyphenated method, the interface is the key to the technique. Several different interfaces have been described for on-line SFE–cGC. Among these are the split/splitless injector, the on-column injector and the programmed temperature vaporizer (PTV) injector [9–11]. Burford et al. [12,13] developed a simple and reliable on-line SFE–cGC system for the quantitative extraction and analysis of gasoline and diesel-range organics from environmental samples using a normal split/splitless injector as the interface. Hansen et al. [14] used coupled SFE–cGC with an on-column injector as the interface for the analysis of organic compounds in atmospheric aerosols. Houben et al. [11] showed applications of on-line SFE–cGC for atmospheric and cigarette smoke particles with a PTV injector as the interface. Levy et al. [15] reported the use of split SFE–GC in the analysis of a solid hydrocarbon waste with formic acid-modified CO_2. In all on-line SFE–cGC studies referred to above, only pure CO_2 or CO_2 admixed with small amounts of modifiers was used as the extractant. Little attention was paid to the quantitative performance of on-line SFE–cGC when modifiers were used. In this article, the quantitative aspects of the split/splitless and the PTV injector for on-line SFE–cGC with pure and modified CO_2 are studied and compared.

After selection of the interface, the cGC parameters, such as column temperature and split ratio (for the split/splitless injector), the stationary phase type and film thickness, column length and inner diameter should all be optimized. Compared to the optimization of the SFE process, the optimization of the cGC separation is relatively simple. Prior to starting the cGC separation, the GC column should be set at a low temperature to refocus the extracted components at the head of the column. In the ideal case, the optimum extraction conditions determined by off-line SFE can be used for on-line SFE–cGC without having to change or compromise.

The aim of this contribution is twofold. Firstly, the experimental parameters affecting the collection and chromatographic focusing of the extracted components in on-line SFE–cGC are investigated and optimized. Secondly, the quantitative aspects of on-line SFE–cGC with pure and modified CO_2 are studied and compared. Off-line SFE was used to optimize the SFE extraction conditions. Experiments were performed on two different samples. The first sample consists of PAHs spiked on clean sand at different concentration levels. This sample is representative for samples in which the components of interest are adsorbed onto the outer surface of the particles. The other sample is a polymeric material. Here the solutes are present in the particles to be extracted.

2. Experimental

SFE experiments were performed on a PrepMaster SFE instrument (Suprex, Pittsburgh, PA, USA). A 3 ml stainless steel extraction cell (Suprex) was fitted with hand-tight connectors (Suprex) for easy installation. Stainless steel frits (3 μm) were located at either end of the extraction cell. A fused silica capillary (50 cm×50 μm I.D.) was used as the restrictor. The carbon dioxide used in the experiments had a purity of 99.996% (Scott Specialty Gases, Breda, Netherlands).

In the off-line SFE experiments, the extracted material was collected by inserting the restrictor

outlet into a glass vial (10 cm×1 cm I.D.) containing 5 ml dichloromethane. After collection, dichloromethane was evaporated under a gentle flow of nitrogen and the extracted material was redissolved in a suitable amount of chloroform and analyzed using a gas chromatograph equipped with an on-column injector and a flame ionization detection (FID) system (GC 8000 series, Fisons Instruments, Milan, Italy). On-line SFE–cGC was carried out by inserting the restrictor directly into the injector of a gas chromatograph (GC-17A, Shimadzu Corporation, Kyoto, Japan) equipped with FID and a PTV injector (Optic, Ai Cambridge, Cambridge, UK). The PTV injector liner was packed with Dexsil 300 (12% coated on Chromsorb 750, 80~100 mesh) purchased from Chrompack (Middelburg, Netherlands). The split SFE–cGC experiments were also performed on the PTV injector. For these experiments the packed liner was replaced with an empty one. Prior to extraction, the GC oven and the PTV injector were brought to the desired temperatures. The PTV could be cooled using liquid CO_2. The carrier gas (helium) was shut off during extraction and turned on afterwards using a controlled event from the GC.

Six PAHs, e.g. naphthalene, acenaphthene, anthracene, pyrene, chrysene and benzo[*a*]pyrene, all from Supelco (Bellefonte, PA, USA) were selected as the test solutes for the analysis of PAHs in spiked sand. Two standard solutions (250 ppm and 25 ppm of each of the six PAHs) were prepared in hexane. For on-line SFE–split cGC and SFE–PTV-cGC, different amounts of PAHs (10 μl of 250 ppm and 1 μl of 25 ppm standard solutions, respectively) were spiked on approximately 3 g of sand which was then filled into the extraction cell. The extraction conditions for the spiked samples were 50°C and 300 bar, both for pure and modified CO_2. Three organic solvents, dichloromethane, chloroform and methanol were investigated as modifiers. 0.5 ml of these modifiers was spiked onto the sample prior to extraction.

The polymer samples used in this study, nylon-6 and poly (1,4-butylene terephthalate) (PBT) were purchased from Aldrich (Milwaukee, WI, USA). Approximately 0.05 g of the polymeric sample was weighed into the extraction cell. The rest of the extraction cell was filled with glass wool. The SFE extraction conditions used were previously determined to be optimum settings [8]. These conditions were: (1) 150°C and 300 bar for both nylon-6 and PBT with pure CO_2; (2) 50°C and 300 bar with modified CO_2. 0.5 ml methanol and 0.5 ml chloroform were used as the modifiers for nylon-6 and PBT, respectively.

The GC separations were started after the SFE extractions. Two fused-silica capillary columns coated with methyl silicone (both 25 m×0.32 mm I.D. with 0.52 μm and 0.18 μm film thickness, respectively) from Hewlett–Packard (Palo Alto, CA, USA) were used for the analysis of the PAHs. For SFE–cGC with the PTV injector, the PTV was cooled to the appropriate temperatures prior to commencing extraction. The column temperature was kept at 50°C during the extraction. After extraction, the PTV was heated to 320°C at 8°C/s. A splitless time of 4.5 min was used and the column temperature was programmed from 50°C (5 min) to 320°C at 10°C/min. For split SFE–cGC, the injection port was operated isothermally at 350°C and the column was kept at the appropriate low temperature. The column temperature was programmed to 320°C after extraction.

In on-line SFE–cGC of the polymeric samples, only the split injector was investigated as the interface, since the concentrations of the analytes in the polymer matrix are relatively high. Two Carbowax columns (both 25 m×0.32 mm I.D. with 1.2 μm and 0.18 μm film thickness, respectively) from Chrompack were used for the analysis of caprolactam in nylon-6. The injection port was operated at 260°C. The column was cooled to low temperatures during extraction and then programmed to 250°C at 10°C/min after extraction. For the analysis of the PBT sample, the column employed for the PAHs (cross-linked methyl silicone, 25 m×0.32 mm I.D., 0.5 μm film thickness) was used under identical temperature conditions as were used in the split SFE–cGC experiments of the PAHs.

3. Results and discussion

3.1. On-line SFE–cGC of environmental samples

As the aim of this contribution is to investigate the collection and focusing of the extracted components

and the quantitative aspects of the interfaces in on-line SFE–cGC, spiked samples were used as model samples. For samples spiked at relatively high levels of the target analytes, the split/splitless injector was used as the interface. On the other hand, for samples spiked with small amounts of analytes, the PTV injector was used.

3.1.1. On-line SFE–split cGC of spiked samples

The split injector has been widely used as a sample introduction system in cGC. It has also been found to be a simple, rugged and useful interface for on-line SFE–cGC using pure CO_2 [9]. Fig. 1 shows the comparison of the chromatographic peak shapes obtained by conventional split cGC and on-line SFE–cGC using the split injector as the interface. From this figure it can clearly be seen that excellent peak shapes can also be obtained with modified CO_2. The modifiers used have no adverse effects on the peak shapes under the experimental conditions tested. Except for naphthalene, all components are successfully trapped at the inlet of the cGC column. In Fig. 1, the initial temperature of the cGC column was 35°C, which is below the boiling points of all modifiers tested. Also at higher trapping temperatures of 50°C and 70°C, no adverse effect of the modifier on the peak shapes was observed. However, at a trapping temperature of 50°C the naphthalene peaks are seriously broadened, and at 70°C no naphthalene peaks could be detected.

The effects of a modifier on the peak shapes will depend on the amount of modifier transferred into the column. In split SFE–cGC only a small fraction of the modifier is actually transferred to the column. The vast majority is vented via the split line. In our experiments, the split ratio during extraction was

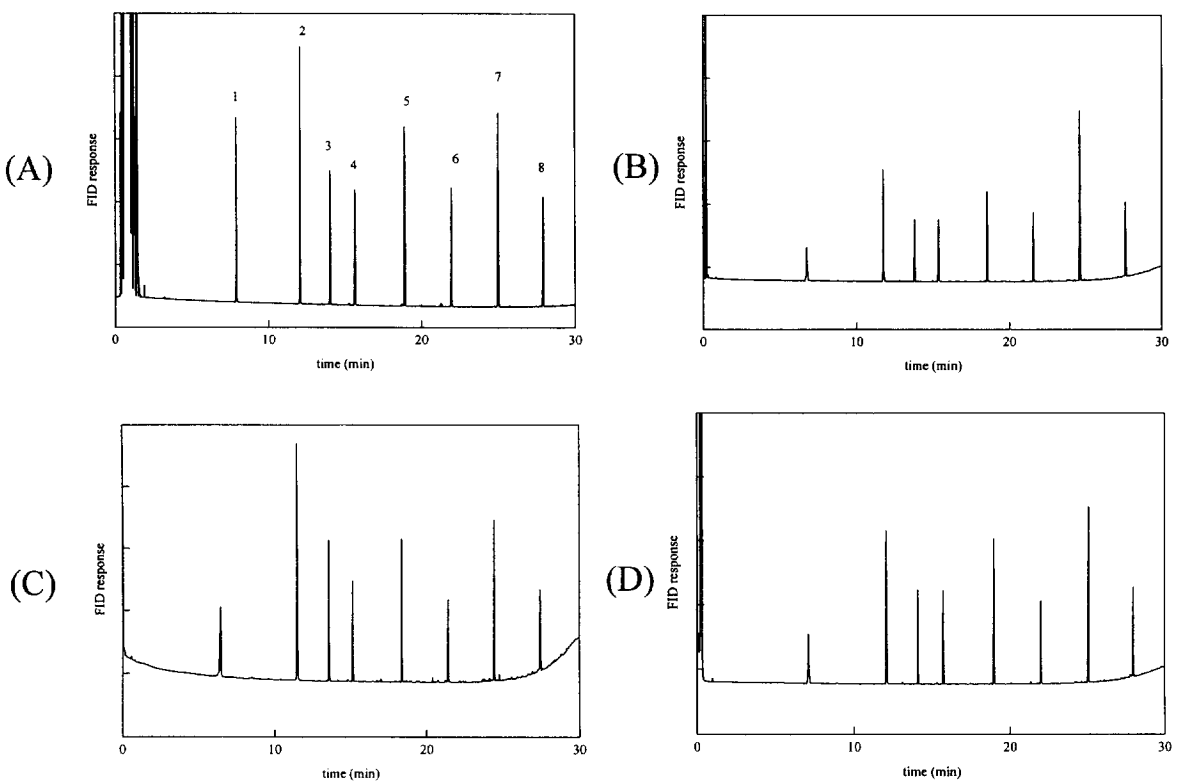

Fig. 1. Comparison of peak shapes obtained using conventional split injection with those obtained using on-line SFE–cGC. A standard solution was spiked onto clean sand and extracted on-line with modified CO_2. Extraction time: static 20 min+dynamic 30 min. Column: 25 m×0.32 mm I.D., 0.52 μm film. 1. Naphthalene, 2. Acenaphthene, 3. C_{16}, 4. Anthracene, 5. Pyrene, 6. Chrysene, 7. Benzo[*a*]pyrene, 8. C_{32}. (A) Split injection; (B) CO_2+CH_2Cl_2; (C) CO_2+CH_3OH; (D) CO_2+$CHCl_3$.

between 1:200~300 which means that only approximately 2–3 μl of modifier was transferred to the column. Therefore, the effect of the modifier on the peak shapes is limited. When looking to the influence of a modifier on band focusing in the GC column, two counteracting mechanisms can be distinguished. On the one hand modifiers can distort the trapping process by "washing" the trapped components along the cGC column. On the other hand, the uptake of a modifier by the stationary phase will facilitate focusing. The latter effect is called solvent trapping and is generally found to be more significant at trapping temperatures well below the boiling point of the solvent [16]. Moreover, at low temperatures the trapping efficiency of the stationary phase itself is higher. From the results and the discussion presented above, it can be concluded that in split SFE–cGC, low trapping temperatures are generally beneficial for collecting and focusing the extracted components at the inlet of the cGC column. This is especially true for the volatile components, irrespective whether modifiers are used or not. This makes the selection of trapping conditions in split SFE–cGC relatively easy. It is interesting to see that the conclusions reached here are in contrast to the observations in off-line SFE when employing solid-phase trapping. In the latter case, the optimum trapping temperatures should be selected above the boiling point of the modifier used, otherwise the liquified modifiers can rinse the target components from the trapping bed [17].

A second parameter that can affect the ability of the cGC column to focus the extracted analytes is the dynamic extraction time used in the extraction. Evidently, the shorter the dynamic extraction time, the easier is trapping. Fig. 2 shows the effects of the dynamic time on the peak shapes in split injection SFE–cGC at an initial column temperature of 35°C. At a dynamic time of 15 min all peak shapes, except that of naphthalene, compare favourably with the peak shapes obtained by conventional split cGC. For the SFE extraction of certain environmental samples, 15 min dynamic extraction can already be sufficient if the extraction conditions are suitably selected [2,3]. If longer dynamic times of 30 min and 60 min are employed, the peak shape of naphthalene gets significantly worse and also the acenaphthene peak starts to broaden. At a dynamic time of 60 min the naphthalene peak can no longer be detected, most likely because it is far too wide or already eluted from the column during the SFE process. Similar, but stronger, effects of the dynamic extraction time on the peak shapes were also observed at higher trapping temperatures. From these results it is evident that the components can be more easily trapped at shorter dynamic extraction times. Therefore, the extraction conditions in SFE should be carefully optimized to yield the shortest possible dynamic extraction times in order to facilitate focusing of the extracted solutes in the column inlet.

In the experiments described above the stationary phase film thickness of the capillary column used was 0.52 μm. In order to investigate the effect of film thickness on peak shapes, the column was replaced by a thinner film column (film thickness 0.18 μm). Also with this column, no significant effect of the modifiers on the peak shapes was observed. Compared to the 0.52 μm column, however, the 0.18 μm column was less capable of giving good peak shapes for the volatile components such as naphthalene.

In the previous paragraphs different parameters affecting the peak shapes in split SFE–cGC were discussed. In order to obtain good peak shapes, low trapping temperatures, columns with thick films as well as short dynamic extraction times are preferable. In addition to the peak shapes, another important point in on-line techniques is the quantitative performance of the interface. In conventional split injection discrimination is frequently observed, especially for samples covering a wide range of polarities and volatilities. It was reported previously that when pure CO_2 was used as the extraction fluid, discrimination-free operation could be obtained in on-line split SFE–cGC by operating the interface at sufficiently high temperatures [9]. Unfortunately, no evaluation of the quantitative aspects of the split/splitless interface is reported in literature for situations in which modifiers are used. A summary of the reproducibility and the quantitative performance of the split/splitless interface for on-line SFE–cGC using both pure and modified CO_2 is given in Table 1. As can be seen from this table, the reproducibility of split SFE–cGC is excellent. Only in the case where methanol is used as the modifier, the relative standard deviations (RSD%) of some peak areas are

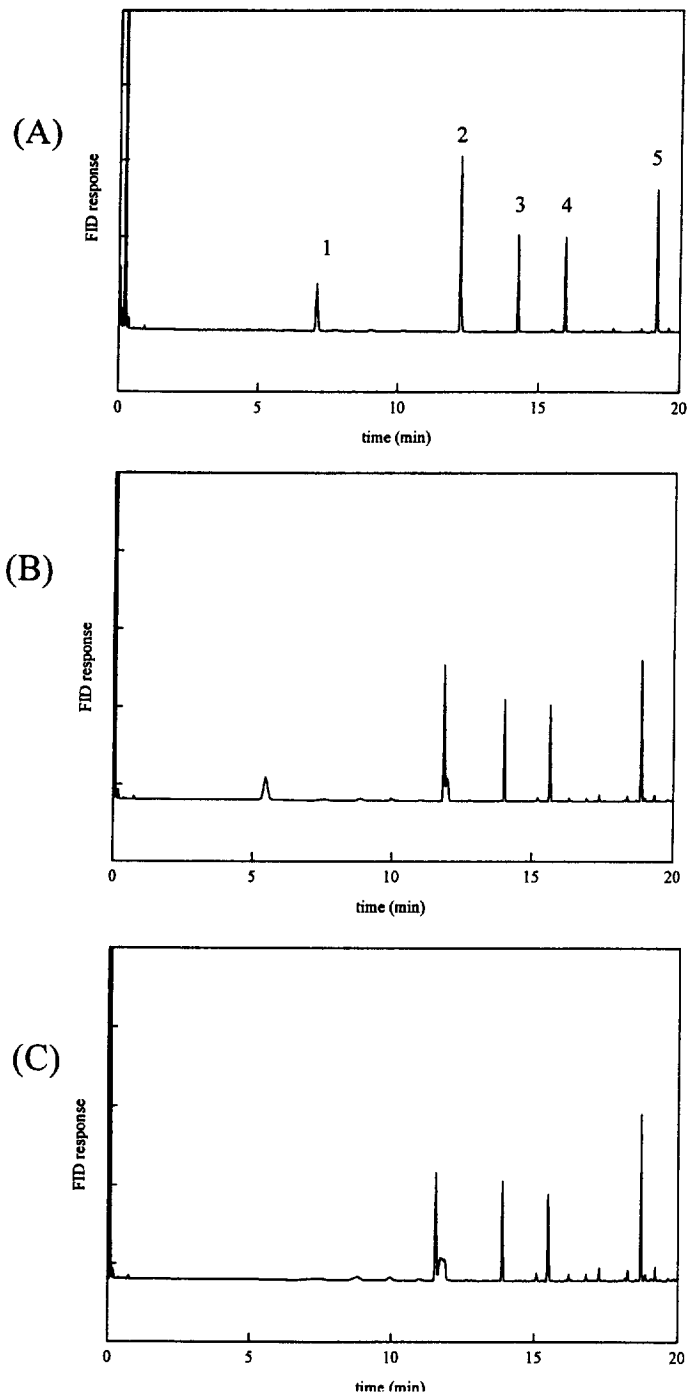

Fig. 2. Effect of dynamic extraction times on peak shapes in on-line split SFE–cGC. Chromatographic conditions and peak identification as in Fig. 1. Dynamic time (A) 15 min; (B) 30 min; (C) 60 min.

Table 1
Quantitative aspects of SFE–split cGC of PAHs from spiked sand using pure and modified CO_2 [a]

Component		Naphthalene	Acenaphthene	C_{16}	Anthracene	Pyrene	Chrysene	Benzo[*a*]pyrene
Pure CO_2	P.A.[b]	570142	912237	540121	545437	898845	658779	1442560
	(RSD%)[c]	(7.1)	(5.5)	(2.1)	(5.4)	(4.7)	(2.6)	(2.4)
	R[d]	1.094	0.998	Internal	1.059	1.079	1.070	1.072
	(RSD%)	(7.1)	(3.4)	standard	(3.2)	(2.6)	(2.4)	(1.9)
CO_2+	P.A.	600976	1043962	603702	583483	936719	632504	1556069
CH_2Cl_2	(RSD%)	(4.7)	(5.6)	(1.0)	(0.2)	(0.2)	(1.0)	(1.2)
	R	1.040	1.022	Internal	1.016	1.019	0.919	0.972
	(RSD%)	(5.2)	(4.8)	standard	(0.7)	(0.8)	(1.7)	(1.0)
CO_2+	P.A.	551701	937967	526600	519347	811894	579543	1317986
$CHCl_3$	(RSD%)	(1.9)	(8.4)	(2.1)	(2.4)	(2.7)	(4.0)	(3.2)
	R	1.095	1.053	Internal	1.036	1.012	0.966	1.005
	(RSD%)	(0.3)	(7.9)	standard	(0.4)	(0.8)	(4.1)	(2.7)
CO_2+	P.A.	1136573	2164132	1193804	978799	1367386	739941	1511771
CH_3OH	(RSD%)	(1.9)	(16.2)	(17.8)	(19.3)	(17.6)	(7.0)	(8.3)
	R	1.015	1.073	Internal	0.859	0.719	0.549	0.513
	(RSD%)	(17.2)	(2.0)	standard	(3.2)	(7.8)	(9.3)	(8.3)

[a] Trapping at 50°C.
[b] Peak area.
[c] Relative standard deviation, based on three experiments.
[d] Values relative to standard data.

slightly above 10%. The RSD of peak areas is better than 10% under all other conditions tested. In Table 1 the trapping temperature was 50°C. Similar results were also observed at 35°C and 70°C. Another interesting point that becomes evident from this table is that the quantitative aspects of the interface depend on which modifier is used. For the SFE extraction of PAHs, discrimination is absent if dichloromethane or chloroform is used as the modifier. If methanol is used, however, significant discrimination occurs. The reason for this is not yet completely clear. The discrimination observed for methanol might be due to the poor solubility of the PAHs in methanol, as discrimination-free operation can be obtained in the extraction of caprolactam from nylon-6 with methanol as the modifier as will be demonstrated below. Hence, by careful selection of the modifier, discrimination-free operation can be obtained in split SFE–cGC.

3.1.2. On-line SFE–PTV-cGC of spiked samples

The PTV injector has proven to be a useful and flexible injection system in GC. Apart from split and splitless injections, this device can also be used for large volume sample introduction in GC. In that mode the solvent can selectively be eliminated from the sample [16]. In on-line SFE–cGC using the PTV injector as the interface, the extracted components are first collected on the solid trapping material packed into the PTV liner. The extraction fluid, CO_2 and the modifier (if used), are vented through the split line. The trapped components are then transferred to the cGC column by heating the injector and sweeping the components in the splitless mode with carrier gas. With the PTV interface, all of the extracted components are transferred to the cGC column, resulting in a higher sensitivity compared to split SFE–cGC. Hence, on-line SFE–PTV-cGC is particularly attractive for trace analysis.

Fig. 3 shows the chromatogram of the PAHs obtained using on-line SFE–PTV-cGC. The quantitative performance of the PTV interface is shown in Table 2. In order to allow a direct comparison, identical amounts of the standard solution as in the spiking experiments were injected using a syringe. The peak areas obtained in on-line SFE–PTV-cGC were expressed relative to the peak areas found in the conventional PTV splitless injection. From this table, it can be seen that when pure CO_2 is used as the extraction fluid, higher trapping efficiencies for

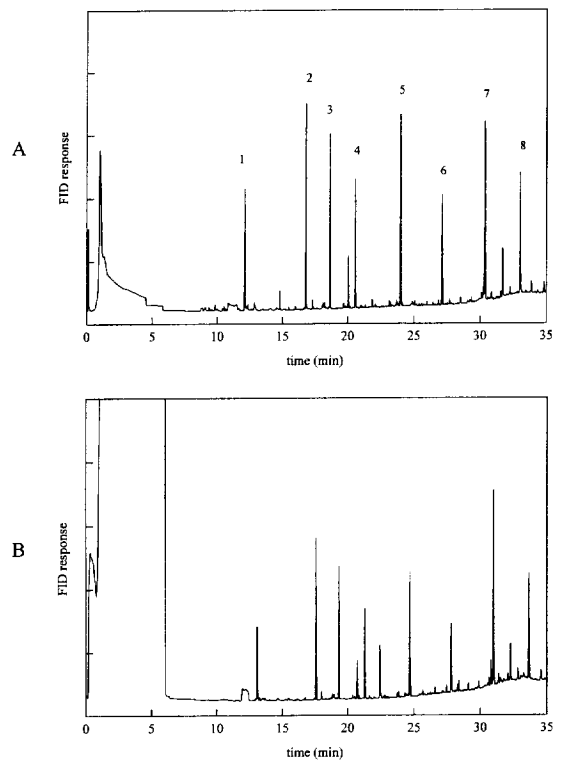

Fig. 3. Chromatograms of the spiked PAHs obtained using on-line SFE–PTV-cGC. A standard solution was spiked onto clean sand and extracted with on-line SFE–PTV-cGC. The PTV was kept at 0°C when pure CO_2 was used and at 45°C when dichloromethane was used as the modifier. Other chromatographic conditions and peak identification as in Fig. 1. (A) Pure CO_2; (B) $CO_2+CH_2Cl_2$.

Table 2
Recovery of spiked PAHs and alkanes in on-line SFE–PTV-cGC

	Extraction fluid			
	Pure CO_2			$CO_2+CH_2Cl_2$
Trapping temperature	0°C	45°C	70°C	45°C
Naphthalene	106[a]	85	3	59
Acenaphthene	105	100	85	88
C_{16}	106	103	90	91
Anthracene	107	108	96	94
Pyrene	120	120	107	98
Chrysene	104	112	97	100
Benzo[*a*]pyrene	95	102	95	109
C_{32}	104	120	106	109

[a] Recovery (%) expressed as peak areas in on-line SFE–PTV-cGC relative to the peak areas obtained in conventional PTV splitless injection.

the volatile components could be obtained by using lower trapping temperatures. For the less volatile components trapping is relatively easy and the trapping temperatures tested do not have a considerable effect on the trapping efficiency. When dichloromethane was used as the modifier, similar results were observed when the trapping temperature was above the boiling point of the modifier. When trapping was performed at a temperature below the boiling point of the modifier, however, a different situation occurred. No components could be trapped in the PTV at a trapping temperature of 0°C. This is easy to understand. At 0°C dichloromethane is liquified and rinses the extracted components from the PTV. From the results shown above it can be concluded that when pure CO_2 is used as the extraction fluid, the selection of trapping conditions is relatively straightforward. When modifiers are used, however, the selection of trapping conditions is more difficult. On the one hand, the trapping temperature should be selected above the boiling point of the modifier used, while on the other hand, the trapping temperature should be selected as low as possible for trapping the volatile components. Therefore, when a modifier is required in on-line SFE–cGC using a PTV interface, organic solvents with low boiling points, such as dichloromethane, should first be considered. Alternatively, a liner packed with a selective and strong adsorbent could be used.

3.2. On-line SFE–cGC of polymeric samples

Polymers are widely used materials nowadays. Their properties can be considerably affected by the presence of additives and/or oligomers. The increased diffusivity of supercritical fluids over liquids, the adjustable extraction temperature as well as the variable solvent strength, have made SFE attractive for polymer applications. Till now, most of the SFE applications to polymeric samples were carried out in the off-line mode. To our knowledge, there are no publications on directly coupled SFE–cGC analysis of polymeric samples.

In coupled SFE–cGC of polymeric samples, the split/splitless injector is the first choice for the interface. This mainly because the concentrations of the additives or oligomers are relatively high (from hundreds to thousands of ppm). The ability of on-line

split SFE–cGC to give good peak shapes at optimized SFE conditions is investigated by comparing the chromatograms from conventional split injections of the extracts obtained by off-line SFE with those from on-line SFE–cGC analyses. In the extraction of polymeric samples relatively long extraction times are frequently required. In order to investigate the effects of extraction time on the peak shapes, different extraction times were investigated experimentally. Fig. 4 shows the effects of the extraction time and stationary phase film thickness on the peak shapes generated by SFE–cGC of nylon-6. If nylon-6 was extracted for 50 min, very good peak shapes were observed for both the 0.18 μm and the 1.2 μm columns at all trapping temperatures tested. However, if the polymer was extracted for 80 min, considerably broadened peaks were observed with the 0.18 μm column at all trapping temperatures tested. In contrast to this, if the column with the thicker film (d_f=1.2 μm) was used at trapping temperatures below 60°C, good peak shapes were obtained. Nevertheless, the chromatographic peaks obtained with the thicker film column were also slightly broadened when trapped at 70°C. These observations support the conclusions reached in Section 3.1.1 that thick film columns and low trapping temperatures are profitable for obtaining good chromatographic peak shapes in on-line SFE–cGC.

A similar influence of trapping temperature and film thickness on the peak shapes was found when a modifier was used (see Fig. 5). If nylon-6 is extracted at 50°C and 300 bar with 0.5 ml methanol as the modifier, very good chromatographic peak shapes were observed for both the 0.18 μm and the 1.2 μm columns at the lowest trapping temperature

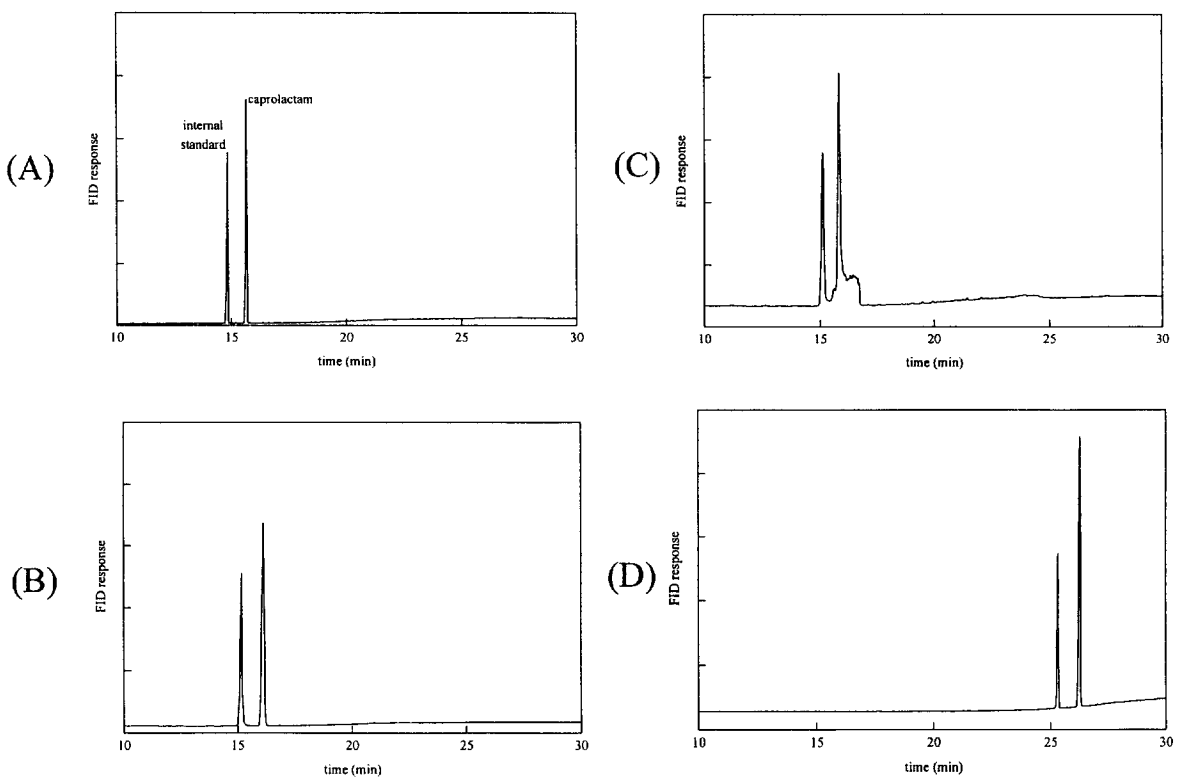

Fig. 4. Effects of extraction time and stationary phase film thickness on the chromatographic peak shapes of caprolactam in SFE–cGC with pure CO_2. Internal standard: Pentadecanoic acid methyl ester. (A) Split injection, 0.18 μm column; (B) SFE–cGC, static 20 min+dynamic 30 min, 0.18 μm column, trapping at 70°C; (C) SFE–cGC, static 20 min+dynamic 60 min, 0.18 μm column, trapping at 70°C. (D) SFE–cGC, static 20 min+dynamic 60 min, 1.2 μm column, trapping at 35°C.

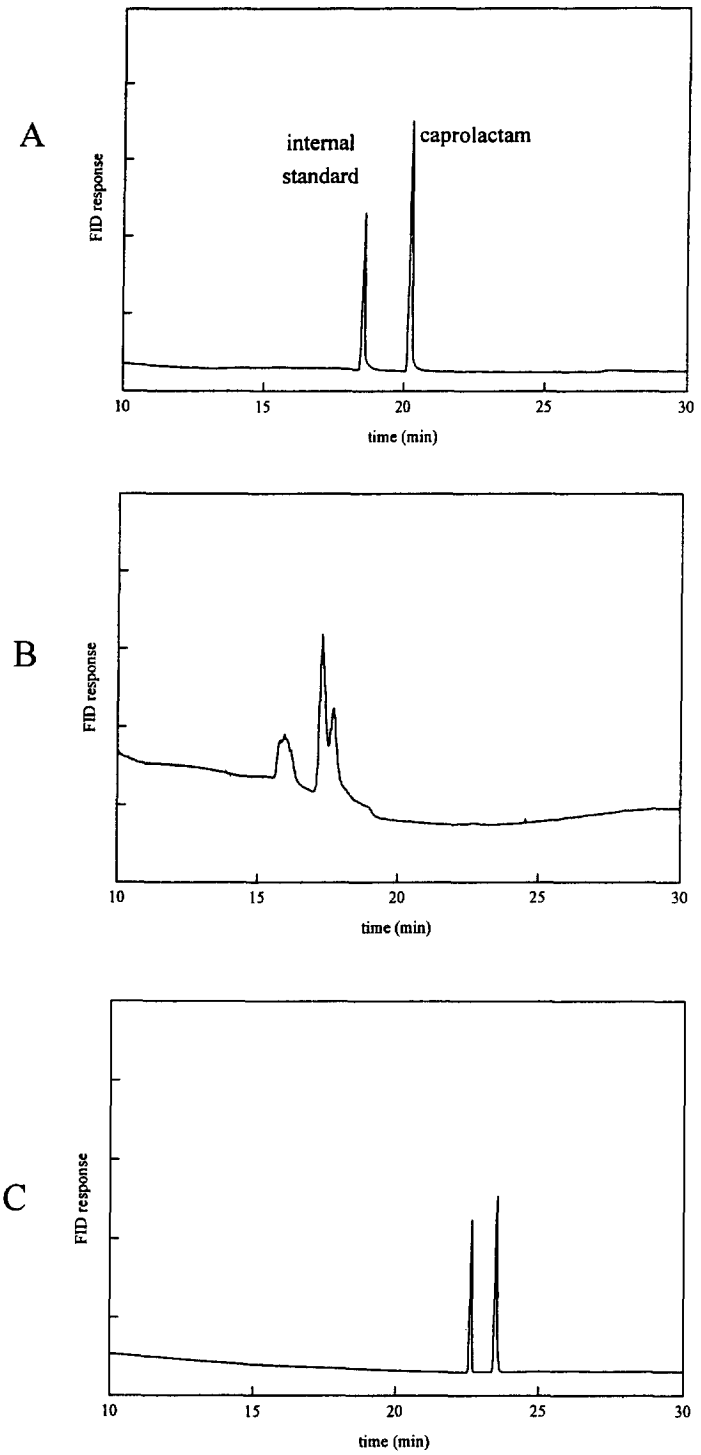

Fig. 5. Effects of trapping temperature and stationary phase film thickness on chromatographic peak shapes of caprolactam in on-line split SFE–cGC using modified CO_2. Internal standard: Pentadecanoic acid methyl ester. Extraction time: static 20 min+dynamic 30 min. (A) Trapping at 35°C, 0.18 μm column; (B) trapping at 60°C, 0.18 μm column; (C) trapping at 60°C, 1.2 μm column.

tested (35°C). However, for the 0.18 μm column the chromatographic peaks were seriously broadened and split at trapping temperatures higher than 60°C. For the 1.2 μm column very good peak shapes were obtained when trapping at 60°C. Only slight splitting of the peaks was observed at a trapping temperature of 70°C. It was shown in Fig. 4 that when nylon-6 was extracted with pure CO_2 for the same period of time, good peak shapes were obtained at all trapping temperatures tested on both columns. Therefore, the peak splitting must be due to the presence of the modifier. As discussed in Section 3.1.1, the effects of a modifier on the focusing of the extracted components at the head of the cGC column are twofold. The enhancement of retention power of the stationary phase by the up-take of modifier is more important for columns with thinner film thicknesses. For thick film columns this effect is less significant as the retention power of these columns is already relatively strong. From the results shown above, it is clear that when a modifier is necessary for the SFE extraction, it is better to select the trapping temperature well below the boiling point of the modifier. This is especially true when columns with thick films are not available or cannot be used because of the presence of high-molecular-mass components in the sample.

In order to investigate the quantitative performance of the coupled SFE–cGC analysis of nylon-6, the results obtained by on-line SFE–cGC were compared with those from off-line SFE–on-column injection cGC (Table 3). For both the on-line and the off-line mode, identical SFE conditions were used. It is obvious from Table 3 that the results obtained by on-line SFE–cGC agree very well with those obtained by off-line SFE–on-column injection GC.

On-line SFE–cGC was also applied to the analysis of the dimer and trimer in PBT. Also here very good peak shapes were observed at all the extraction conditions and trapping temperatures tested (Fig. 6). The boiling points of the dimer and trimer from PBT are much higher than that of caprolactam. It is therefore evident that it is much easier to trap these components.

Table 3
Quantitative aspects of on-line split SFE–cGC analysis of caprolactam in nylon-6

	Trapping temperature			
	35°C	50°C	70°C	On-column[a]
SFE conditions	ppm[d] (RSD%)[e]			
50°C and 300 bar[b]	2014 (5.9)	2051 (7.4)	2118 (8.0)	1852 (7.5)
150°C and 300 bar[c]	2244 (5.9)	2318 (7.9)	2300 (9.1)	2272 (3.6)

[a] Obtained with off-line SFE–cGC.
[b] 0.5 ml methanol as the modifier, extraction time: static 20 min and dynamic 30 min.
[c] Pure CO_2, extraction time, static 20 min and dynamic 60 min.
[d] Amount found relative to the mass of polymer weighed into the extraction cell.
[e] Based on three experiments.

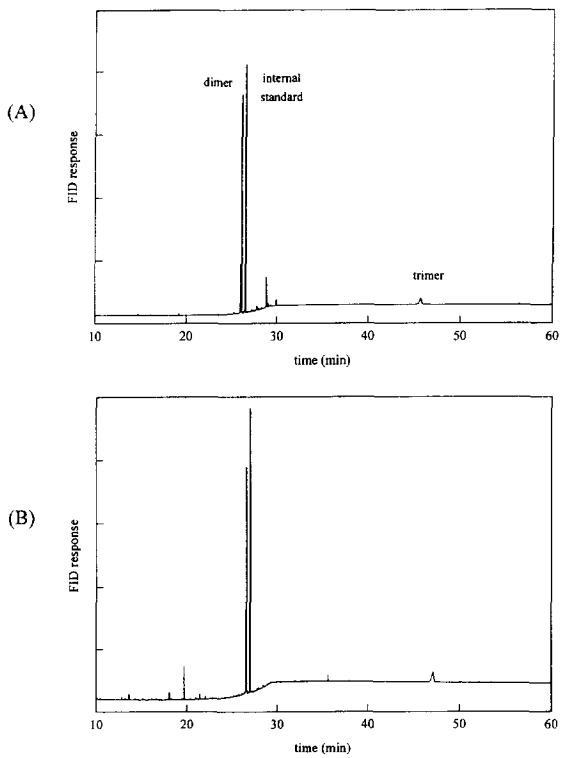

Fig. 6. Comparison of peak shapes obtained by conventional split injection with those by on-line split SFE–cGC analysis of the dimer and trimer in PBT. Internal standard: Irganox 1076 [octadecyl-3-(3,5-di-*tert.*-butyl-4-hydroxyphenyl) propionate, Ciba Geigy, Basle, Switzerland]. (A) split injection; (B) SFE–cGC, CO_2+$CHCl_3$ at 50°C and 300 bar, static 20 min+dynamic 30 min.

4. Conclusions

On-line SFE–cGC with a split interface was found to be suitable for samples that have high concentrations of extractable components. Under optimized conditions, modifiers have no adverse effects on the chromatographic peak shapes in split SFE–cGC. Discrimination-free operation could also be obtained in on-line split SFE–cGC when modified CO_2 was used as the extractant. Short dynamic extraction times, low trapping temperatures and columns with thick films were found to be beneficial for obtaining good peak shapes in split SFE–cGC. For on-line SFE–cGC with a PTV injector as the interface, the most important parameter to be optimized is the initial PTV trapping temperature. Low trapping temperatures will yield high trapping efficiencies when pure CO_2 is used. In contrast, when modified CO_2 is used, the trapping temperature should be selected above the boiling point of the modifier. On-line SFE–PTV-cGC is particularly attractive for trace analysis.

References

[1] T.L. Chester, J.D. Pinkston and D.E. Raynie, Anal. Chem., 66 (1994) 106R.
[2] S.B. Hawthorne, Anal. Chem., 62 (1990) 633A.
[3] M.L. Lee and K.E. Markides, Analytical Supercritical Fluid Chromatography and Extraction, Chromatography Conference, Provo, UT, 1990.
[4] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller and J. Pawliszyn, Anal. Chem., 65 (1993) 338.
[5] N.J. Cotton, K.D. Bartle, A.A. Clifford and C.J. Dowle, J. Chromatogr. Sci., 31 (1993) 157.
[6] X. Lou, H.-G. Janssen and C.A. Cramers, J. Microcolumn Separations, 7 (1995) 303.
[7] J.J. Langenfeld, S.B. Hawthorne, D.J. Miller and J. Pawliszyn, Anal. Chem., 66 (1994) 909.
[8] X. Lou, H.-G. Janssen and C.A. Cramers, J. Chromatogr. Sci., 34 (1996) 282.
[9] X. Lou, H.-G. Janssen and C.A. Cramers, J. High Resolut. Chromatogr., 16 (1993) 425.
[10] S.B. Hawthorne, D.J. Miller and M.S. Krieger, J. Chromatogr. Sci., 27 (1989) 347.
[11] R.J. Houben, H.-G.M. Janssen, P.A. Leclercq, J.A. Rijks and C.A. Cramers, J. High Resolut. Chromatogr., 13 (1990) 669.
[12] M.D. Burford, S.B. Hawthorne and D.J. Miller, J. Chromatogr. A, 685 (1994) 79.
[13] M.D. Burford, S.B. Hawthorne and D.J. Miller, J. Chromatogr. A, 685 (1994) 95.
[14] K.J. Hansen, B.N. Hansen, E. Cravens and R.E. Sievers, Anal. Chem., 67 (1995) 3541.
[15] J.M. Levy, R.A. Cavalier, T.N. Bosch, A.F. Rynaski and W.E. Huhak, J. Chromatogr. Sci., 27 (1989) 341.
[16] H.G.J. Mol, H.-G. Janssen, C.A. Cramers and U.A.Th. Brinkman, J. High Resolut. Chromatogr., 18 (1995) 19.
[17] M.N. Moore and L.T. Taylor, Anal. Chem., 67 (1995) 2030.