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Citation for published version (APA):

Houben, R. J., Janssen, J. G. M., Leclercq, P. A., Rijks, J. A., & Cramers, C. A. M. G. (1990). Supercritical fluid extraction-capillary gas chromatography: on-line coupling with a programmed temperature vaporizer. *Journal of High Resolution Chromatography*, 13(10), 669-673. <https://doi.org/10.1002/jhrc.1240131003>

DOI:

[10.1002/jhrc.1240131003](https://doi.org/10.1002/jhrc.1240131003)

Document status and date:

Published: 01/01/1990

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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Supercritical Fluid Extraction-Capillary Gas Chromatography: On-Line Coupling with a Programmed Temperature Vaporizer

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Key Words:

Supercritical fluid extraction (SFE)

On-line SFE-GC

Programmed temperature vaporizer (PTV)

Summary

A simple and versatile system is described for the on-line coupling of SFE to capillary GC. The interfacing consists of a programmed temperature vaporizer (PTV) injector. With this injector it is possible to combine solute trapping, elimination of a high flow of extraction fluid, and quantitative transfer of solutes to the separation column. The problems caused by impurities in the extraction fluid in on-line SFE-GC are discussed. Simple methods are described for the purification of commercially available carbon dioxide. The trapping efficiency of the PTV injector is studied. Applications of the SFE-PTV-GC system are given for the analysis of polymer anti-degradants, polar compounds, and samples with environmental relevance.

1 Introduction

Many samples in analytical chemistry consist of trace components in a complex and interfering matrix. For the identification and quantification of these components, isolation from the matrix is often necessary. Sample pretreatment can be a difficult and time-consuming step that might lead to erroneous results. Supercritical fluid extraction (SFE) is a technique which offers several advantages over conventional liquid (e.g. Soxhlet) extractions. Supercritical fluids generally have solvent strengths comparable with liquids, while having lower viscosities and higher solute diffusivities [1]. SF extractions can, therefore, result in recoveries comparable with those obtained using conventional techniques, but in shorter extraction times. Carbon dioxide is an inexpensive and non-toxic extraction fluid with mild critical parameters. This enables the application of low extraction temperatures, thereby reducing the risk of analyte degradation during the extraction. The possibility of adjusting the solvating power of the solvent, simply by adjusting instrumental parameters, adds to the attractiveness of supercritical fluids for sample pretreatment.

By comparison with off-line extractions and analysis, on-line combination favors faster analysis, requiring a lower quantity of sample. The on-line coupling of SFE and supercritical fluid chromatography (SFC) can be realized by depositing the

extracted solutes in the loop of a switching valve [2, 3]. On-line coupling to high performance liquid chromatography is comparable [4].

As supercritical fluids decompress into gases under typical GC conditions, the on-line coupling of SFE and GC is relatively simple and several interfaces based on standard GC injectors have been described in literature. Most of the work performed on directly coupled SFE-GC employs an on-column injection port. In this way the eluate from the flow restrictor, connected to the extraction cartridge, is transferred directly into the column. This method was described by Hawthorne *et al.* [5, 6], Wright *et al.* [7], and Schmidt *et al.* [8].

The on-column approach has some disadvantages, however [6]. The internal diameter of the separation column often prohibits the handling of a high flow of extraction fluid, the components transferred to the column can contaminate it, and column overloading can occur. It has been found, furthermore [6], that the formation of a frozen plug of carbon dioxide inside the column can result in a decrease in the amount of solutes transferred into it. Levy *et al.* [9] described the use of a hot split-splitless injector for on-line SFE-GC. Nielsen *et al.* [10] studied the use of a thermodesorption-cold trap injection system. With this system it is possible to trap the extracted solutes, while venting the extraction fluid.

In GC, the programmed temperature vaporizer (PTV) injector has proven to be an easy to use and flexible injection system [11]. Besides split and splitless injections, this device is capable of on-line sample preconcentration by selective elimination of the solvent [12, 13]. In this work, we describe the coupling of SFE to GC employing a PTV injector. Some preliminary results are given regarding the optimization of the trapping efficiency. The PTV injector is capable of handling high flow rates, thus reducing the extraction time necessary. The transfer of solutes to the column which takes place on heating the injector, can be complete for solutes up to C_{50} [14].

One of the problems associated with on-line SFE-GC is caused by the impurities present in the extraction fluid. It is shown that commercially available carbon dioxide can be further purified by means of simple methods.

Finally, the applicability of the SFE-PTV-GC system is demonstrated for "real world" samples.

2 Experimental

2.1 Instrumentation

A Schematic Diagram of the equipment for on-line SFE-GC is shown in **Figure 1**. The experimental set-up for the supercritical fluid extractions consisted of a high pressure syringe pump, a thermostatted extraction vessel and a tapered restrictor. A Varian 8500 syringe pump (Varian Associates, Wallnutt Creek, CA, USA), modified to enable constant pressure operation, was used for fluid delivery. The pump cylinder was cooled to facilitate filling of the pump. The extraction vessel was a standard LC cartridge column (Knauer GmbH, Berlin, GFR) with a length of 10 cm and an inner diameter of 4 mm. The extraction cartridge was placed in a GC oven to maintain a constant temperature, above the critical temperature of the extraction fluid. A preheating coil was incorporated between the pump and the extraction cartridge to heat the fluid to the desired temperature prior to its entering the extractor. High pressure conditions were maintained within the extraction cartridge by using a stainless steel tapered restrictor as the outlet. The restrictor was prepared by pinching the end of a stainless steel capillary (111 μm i.d.) with a pair of pliers to give the desired flow rate.

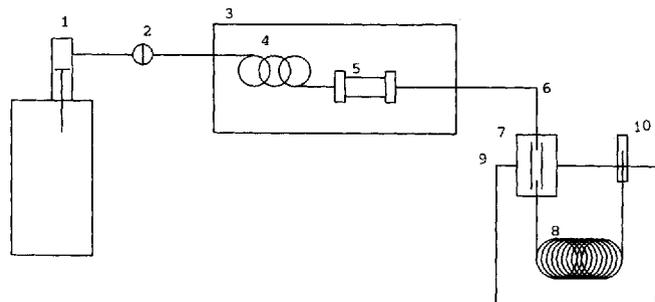


Figure 1

Schematic diagram of the equipment for on-line SFE-GC. 1 = high pressure pump; 2 = open/close valve; 3 = oven; 4 = fluid-preheating coil; 5 = extraction vessel; 6 = restrictor; 7 = PTV injector; 8 = GC column; 9 = GC; 10 = FID Detector.

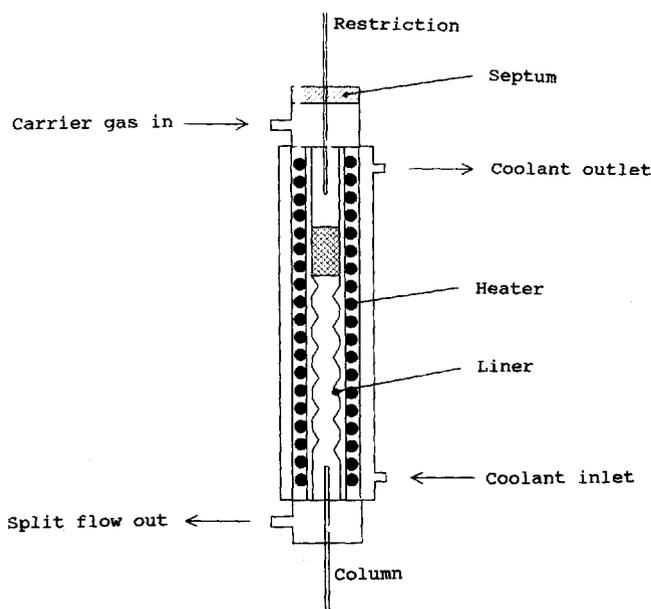


Figure 2

Detailed schematic diagram of the SFE-GC-PTV interface.

On-line coupling of SFE to capillary GC was established using a commercially available PTV injector (Gerstel GmbH, Mülheim, GFR) mounted on top of an HP 5890 GC (Hewlett Packard, Avondale, CA, USA). No modifications were made to the PTV injector. The restrictor coming from the extraction cell was inserted directly into the cooled liner of the PTV injector. A more detailed schematic diagram of the PTV injector is given in **Figure 2**.

The heart of the PTV injector is a low thermal mass, baffled glass liner packed with a small plug of silanized glass wool. A packed liner was used to prevent solute breakthrough [12]. The heating system of the injector enables heating rates up to $12^\circ/\text{s}$. The maximum temperature of the injector is 450°C . The split vent of the injector can be closed by a relay switch, hence the system can be used for split and splitless injections. Carbon dioxide with a purity of 99.996% (Intermar BV, Breda, The Netherlands) or a custom-made carbon dioxide-ethanol mixture (1.6 mol% ethanol) was used as extraction fluid. The gas chromatographic column was a $20\text{ m} \times 250\ \mu\text{m}$ i.d. column coated with a $0.2\ \mu\text{m}$ film of OV-1 stationary phase (Chrompack, Middelburg, The Netherlands).

2.2 Procedures

2.2.1 Quantification of Impurities in Carbon Dioxide

For the determination of the impurities present in the carbon dioxide, 10 ml of liquid CO_2 (measured at 200 bar and 23°C) was decompressed through a $30\text{ cm} \times 30\ \mu\text{m}$ i.d. linear restrictor. The outlet of the restrictor was placed in a cooled conical tube. The impurities in the expanding gas flow were trapped in the tube, which was kept at a temperature of approximately -20°C by means of an ice/salt bath. The components deposited in the tube were dissolved in hexane ($50\ \mu\text{l}$). This sample was analyzed off-line by high temperature GC in which $1\ \mu\text{l}$ of the sample was injected on-column onto a $10\text{ m} \times 320\ \mu\text{m}$ i.d. column with a $0.1\ \mu\text{m}$ film of HT-5 stationary phase (SGE, Ringwood, Victoria, Australia). The temperature program started at 40°C . The heating rate and final temperature were $15^\circ/\text{min}$ and 340°C , respectively.

2.2.2 Optimization of the Extraction Efficiency

Off-line SFE was used to optimize the extraction efficiency for the polymer additive Irganox 1010 in polyethylene. The extracted solutes were collected as described in Section 2.2.1. The high molecular weight of Irganox 1010 precluded the use of GC analysis for quantitation; the samples were, therefore, analyzed by capillary SFC. The SFC experiments were performed on a Carlo Erba SFC 3000 instrument (Carlo Erba Instruments, Milan, Italy). The extracted solutes were collected in fractions of 10 min each to examine the extraction time necessary. A solution of Irganox PS802 was added to the sample as the internal standard for quantitative analysis.

2.2.3 On-Line SFE-GC

At the start of an on-line SFE-GC analysis the sample was charged into the SFE cell and the injector cooled to sub-ambient temperatures. Typically, a temperature of -20°C was used. By employing liquid CO_2 cooling, temperatures down to approximately -70°C could be obtained. After stabilization of the injector temperature, the restrictor was inserted in the liner. The open/close valve between the pump and the extraction cell was subsequently opened, thereby allowing preheated CO_2 to enter the cell. The extracted components were deposited in the cooled

PTV injector and the gaseous CO₂ flow was vented through the split vent. At the end of the extraction cycle the restrictor was withdrawn from the injector. After a 5 s delay to allow the solid CO₂ to vaporize, the split vent was closed and the temperature program of the injector started. The temperature program of the injector comprised an initial hold of 10 s at the cryogenic temperature, a heating rate of 12°/s and a final temperature of 300 °C. The injector was held at 300 °C for 10 min. For concentrated samples, split injection was used to avoid overloading the chromatographic column.

3 Results and Discussion

3.1 Purification of the Extraction Fluid

The purity of the extraction solvent is a large problem in chromatographic analysis at trace levels. The low concentrations of the components of interest necessitate a preconcentration step during sample pretreatment. This implies, however, that impurities in the extraction solvent are also preconcentrated. Normal liquid solvents can readily be purified *in situ* by distillation. Distillation of liquid carbon dioxide is, on the contrary, not possible with standard laboratory equipment.

A single plate distillation of liquid CO₂ is, however, easy to obtain. Normally the CO₂ used to fill the pump is taken from a cylinder filled with liquified CO₂ and equipped with a diptube. Because the impurities generally have much higher boiling points than the CO₂, the impurities are almost exclusively contained in the liquid phase. Hence, the purity of the gaseous CO₂ phase is expected to be higher than that of the liquid phase. **Figures 3A** and **3B** represent gas chromatograms of the impurities contained in an equal mass of CO₂ taken from the liquid and the gaseous phases, respectively. These traces clearly demonstrate that a significant gain in CO₂ purity can be obtained by filling the pump from the gaseous phase instead of the liquid phase.

An alternative method of purification is the use of an activated carbon-black adsorption trap. **Figure 3C** shows the gas chromatogram of CO₂ from the liquid phase after passing through an active carbon adsorption trap installed between the CO₂ bottle and the pump. Figure 3C shows a considerable reduction of the amount of impurities relative to Figure 3A.

3.2 Optimization of the Extraction Efficiency

SFE is suitable for the analysis of antidegradants in polymers [15]. The recovery of the UV-stabilizer Irganox 1010 in polypropylene was optimized by off-line SFE. Important factors are the temperature, the pressure and the time of extraction. The temperature and pressure applied during extraction influence the properties of both the extraction fluid and the polymer matrix. Increased temperatures lead to higher diffusion coefficients and more polymer swelling, both favoring mass transport (**Figure 4**). Increasing the pressure, and hence the density of the fluid, increases the component solubility. The highest recovery was found at a temperature of 55 °C and a pressure of 300 bar, where the resistance to mass transfer, both in the polymer matrix and in the extraction fluid, was at its minimum. This implies that the extraction time can be relatively short; under these conditions, the extraction was complete after 10 min.

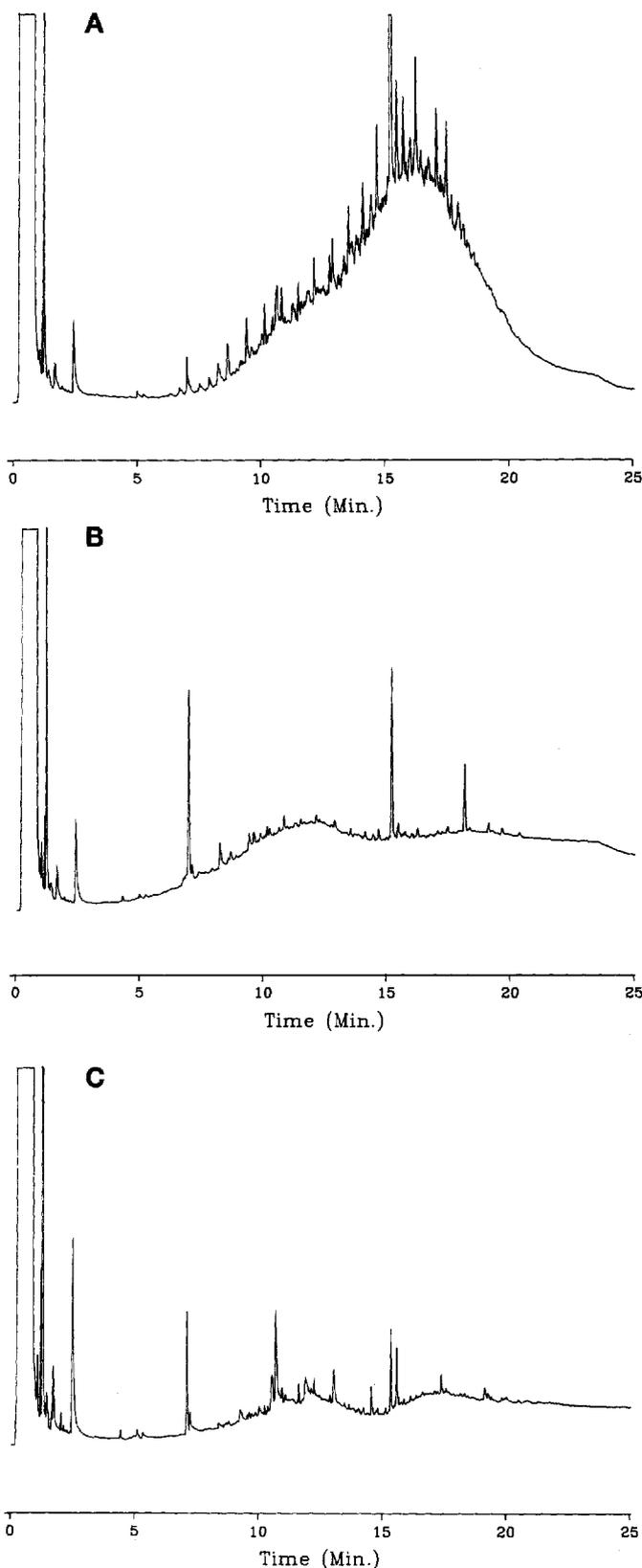


Figure 3

Purification of the extraction fluid by simple fluid handling techniques. A = analysis of CO₂ taken from the liquid phase without filter; B = CO₂ from the gaseous phase without filter; C = liquid phase with filter.

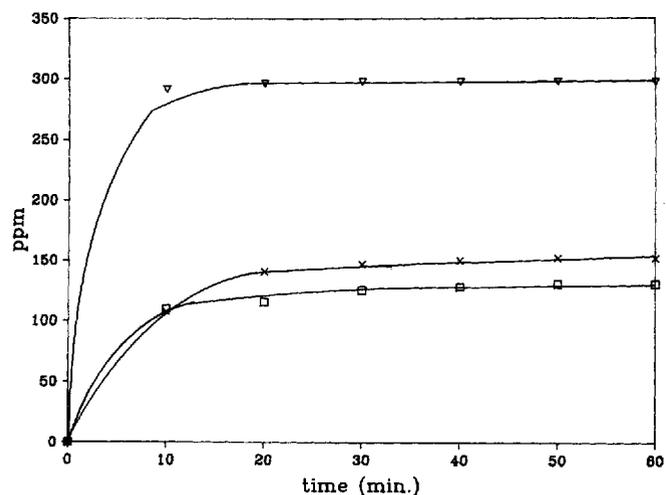


Figure 4

Extraction recovery of Irganox 1010 from polypropylene, related to the amount of polymer (parts per million). Conditions: \square = 45 °C, 300 bar, t = 55 °C, 200 bar, r = 55 °C, 300 bar

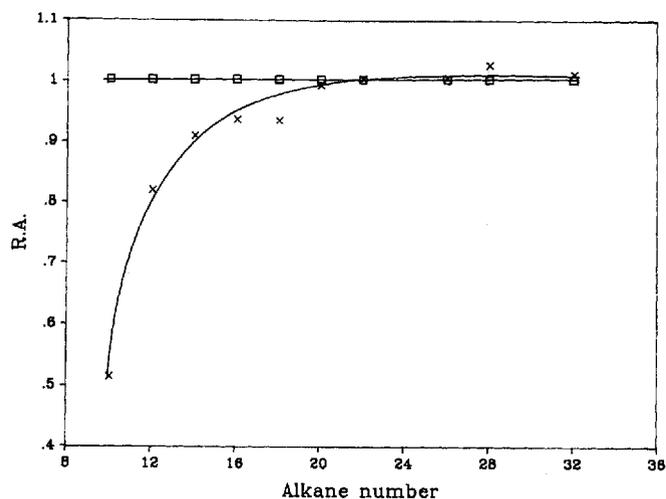


Figure 5

Trapping efficiency of the PTV injector. \square = splitless injection, \times = solvent vent/splitless injection. PTV conditions: initial temperature = -20 °C; initial hold = 0 min in the splitless mode and 12 min in the solvent vent mode; heating rate = 12°/s; final temp. = 300 °C; total gas flow through the injector = 400 ml/min.

3.3 Trapping Efficiency of the PTV Injector

Figure 5 depicts the trapping efficiency of the PTV injector for the normal alkanes C_{10} to C_{32} in the splitless and the solvent-vent modes [13]. The areas of the alkane peaks in the solvent-vent mode were related to the corresponding areas in the splitless mode (relative areas-RA). The results are illustrative of the possibility of trapping and holding extracted components in the cooled PTV injector. Solute trapping is complete for alkanes with a boiling point more than 250 °C above the trapping temperature.

3.4 Modified Extraction Fluids

The extraction of polar solutes from complex, highly retentive matrices with pure supercritical CO_2 as the extractant is often extremely difficult. A considerable reduction of the required extraction time can be obtained by using CO_2 mixed with a low concentration of a polar modifier (e.g. an alcohol) [16]. To demonstrate the compatibility of the present on-line SFE-PTV-GC system with a CO_2 /ethanol mixture (1.6 mol%), extractions with pure CO_2 and with modified CO_2 are compared in Figures 6A and 6B.

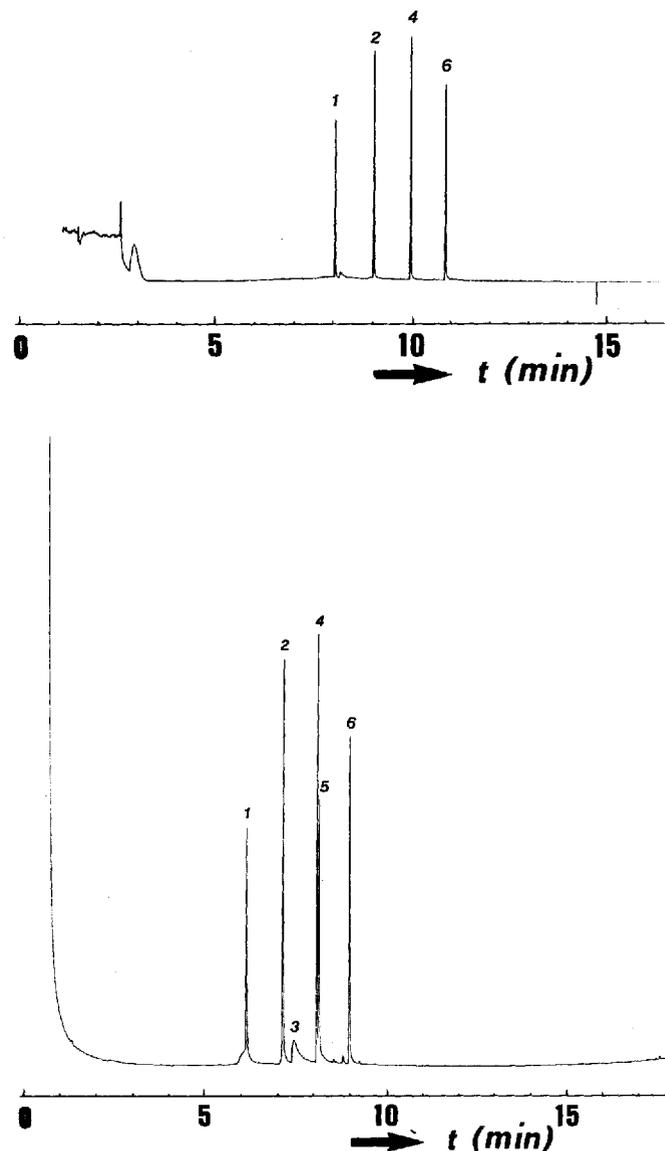


Figure 6

On-line SFE-PTV-GC with modified extraction fluids. Peak identification: 1 = $n-C_{11}$, 2 = $n-C_{12}$, 3 = nicotine, 4 = $n-C_{13}$, 5 = DCHA, 6 = $n-C_{14}$. SFE conditions: P = 250 bar, T = 45 °C, extraction time = 10 min. PTV conditions: isothermal at -20 °C (10 min); heating rate = 12°/s; final temperature = 300 °C (10 min). GC conditions: isothermal at 40 °C (11 min); rate = 15°/min; final temperature = 320 °C; injection = splitless (delay time = 1.5 min).

A model system consisting of an octadecyl-modified silica as the matrix, spiked with test solutes with different polarities, was extracted with pure CO₂ and with the CO₂/ethanol mixture. The extraction was performed at a temperature of 45 °C and a pressure of 250 bar. The test mixture spiked on the octadecyl silica included the normal alkanes C₁₁ through C₁₄ and the polar solutes nicotine and dicyclohexylamine (DCHA), dissolved in cyclohexane. The concentration of the solutes was 10 ng/μl. Figure 6A shows the result of the extraction and subsequent GC analysis of the spiked octadecyl silica with pure carbon dioxide; in this case only the non-polar normal alkanes are extracted, the polar solutes remaining adsorbed on the matrix. Extraction of these solutes with pure CO₂ is impossible or would require extremely long extraction times. Figure 6B shows the chromatogram after extraction with the modified fluid. As can be seen in this figure, two additional peaks appear for nicotine and DCHA. Very good peak shapes are observed for the alkanes and DCHA. The extraction recovery for these compounds was higher than 80 %. The poor peak shape for nicotine is most probably caused by the activity of the GC column and does not arise from the extraction process.

3.5 Applications

The performance of the on-line SFE-GC system is illustrated by the representative chromatograms shown in **Figures 7** and **8**. The application of on-line extraction-gas chromatography for sample pretreatment and analysis of chimney particulate matter is illustrated in Figure 7. The chromatogram was obtained by extraction of a filter used to collect particulates in the chimney of a wood stove. The filter was folded and put as such in the extraction cartridge. Extraction at 250 bar and 50 °C removed all of the extractable material within 20 min. The conditions for the extraction and the GC analysis are given in the figure caption. The chromatogram in Figure 8 shows the analysis of the supercritical CO₂ extract from cigarette tobacco.

Flame ionization detection was used for all the applications described above. Obviously, the on-line combination of SFE with GC-MS will benefit most from the PTV technique described.

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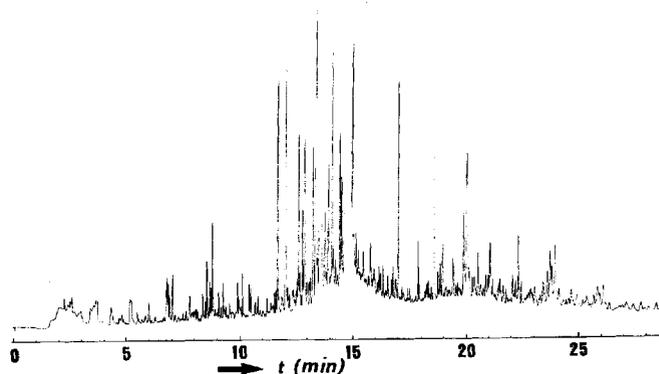


Figure 7

Chromatogram obtained after on-line extraction of a carbon black filter. Extraction conditions: $P = 250$ bar, $T = 50$ °C, extraction time = 10 min. Further conditions as in Figure 6.

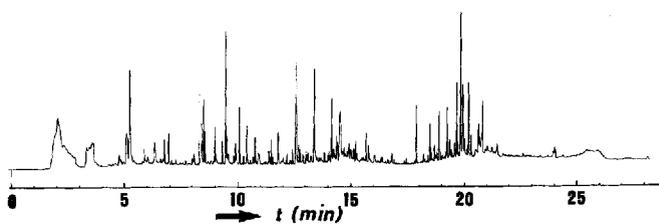


Figure 8

Chromatogram of an extract of cigarette tobacco. Extraction conditions: $P = 275$ bar, $T = 35$ °C, extraction time = 10 min. For PTV and GC conditions, see Figure 6.

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Ms received: May 17, 1990

Accepted: July 27, 1990