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## Note

# On-line system for supercritical fluid extraction and capillary gas chromatography with electron-capture detection

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Supercritical fluids have been succesfully used for industrial extractions for many years[1] because of their strong solvating power, low viscosity and high solute diffusivities, yielding good mass transfer during extraction. More recently, analytical chemists have studied the potential of supercritical fluid extraction (SFE) as an alternative to time-consuming classical methods such as Soxhlet extraction and steam distillation. Off-line SFE of different adsorbents spiked with polycyclic aromatic hydrocarbons and other pollutants was described by Raymer and co-workers[2,3] and Wright *et al.*[4] Sugiyama and Saito[5] described a simple (off-line) micro-scale SFE system and its application to gas chromatography–mass spectrometry of lemon peel oil. McNally and Wheeler[6] studied the efficiency of SFE from complex matrices via retention characteristics in packed supercritical fluid chromatography (SFC). Engelhardt and Gross[7] combined the benefits of SFE with packed SFC in an on-line system.

In environmental trace analysis, one often deals with components that have a relatively good thermal stability (*e.g.*, polycyclic and polychlorinated aromatic hydrocarbons) and can be easily determined by capillary gas chromatography (GC). The gaseous effluent that is obtained in SFE after decompression is in principle compatible with GC. An on-line SFE–GC system allows the entire extract, rather than an aliquot, to be concentrated and analysed. As the final aim of our present project (the short-term sampling of air) usually yields only a few picograms of relevant analytes, improvement of the detection limit of the method is essential. Introduction of the entire extract into a chromatographic system, via on-line SFE–GC, might achieve this.

Hawthorne and co. workers[8–10] designed an on-line SFE–GC interface consisting of a linear fused-silica restrictor which is inserted in the on-column injector of a capillary gas chromatograph. However, the restrictor becomes fragile after a few extractions and is therefore replaced after each extraction. Wright *et al.*[11] described a

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similar method. Another interface for on-line SFE–GC was reported by Levy *et al.*[12], who proposed decompression via a stainless-steel restrictor which is inserted, through a septum, into a hot split–splitless GC injector.

Both interfaces can be succesfully used for the extraction and determination of particular components in (environmental) solids, adsorbents and other materials at the ppm level. However, both approaches suffer from several disadvantages. Stainless-steel restrictors are not inert and may interfere with trace-level analysis. In addition, the introduction of the entire gaseous effluent, *e.g.*, carbon dioxide or dinitrogen oxide, into the capillary GC column restricts the flow of SFE and consequently increases the extraction time and/or the allowable inner diameter of the GC column. Also, the stability of, *e.g.*, an electron-capture detector, might be negatively influenced; in fact, this detector cannot be used with dinitrogen oxide. Finally, the frequent replacement of fused-silica restrictors is disadvantagous for routine analysis. Therefore, the aim of this study was the design of an on-line SFE–GC system that can be utilized for the analysis of environmental samples at the picogram level, without the drawbacks mentioned above.

## EXPERIMENTAL

### *Apparatus*

The on-line SFE–GC system is shown in Fig. 1 and consists of (1) a cylinder with carbon dioxide (Rommenhöller, Rotterdam, The Netherlands) having a dip tube; (2) a stainless-steel frit (2 μm); (3) a Carlo Erba (Milan, Italy) Phoenix 20 syringe pump, equipped with a control unit for pressure programming and (4) a coolant supply set at 5°C; (5) a thermostated water-bath, set at 42°C; (6) a heat exchanger; (7) the extraction vessel, which was made from an empty 5.0 cm × 2.0 mm I.D. high-performance liquid chromatographic column; (8) a Rheodyne (Cotati, CA, U.S.A.) Model 7335 stainless-steel 0.5-μm filter; (9) a Valco (Houston, TX, U.S.A.) Model C6W switching valve; (10) a Whitey (Highland Heights, OH, U.S.A.) Model SS-43S4 shut-off valve; (11) an LDC/Milton Roy (Ivyland, PA, U.S.A.) Critical Ex-

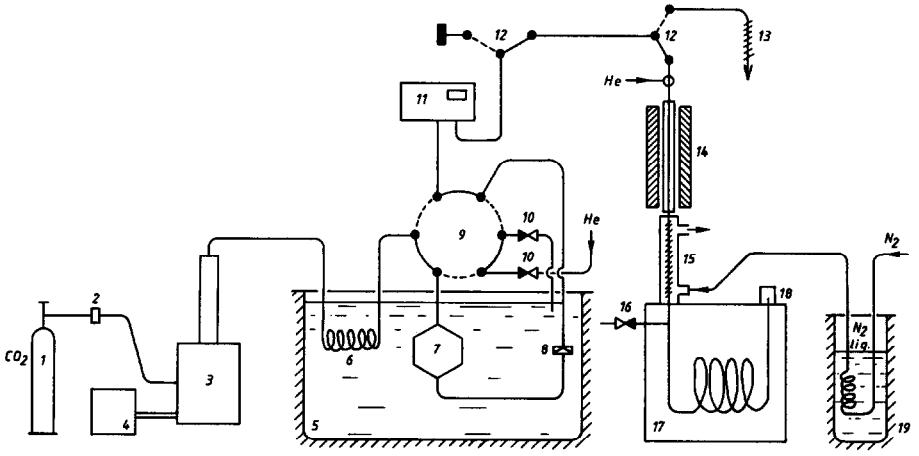


Fig. 1. Design of the on-line SFE–GC system. For explanation, see text.

traction Monitor, set at 210 nm; (12) a Valco Model C3W switching valve; (13) a laboratory-made electrically heated linear fused-silica restrictor with a collection tube for off-line sampling; (14 and 15) a thermodesorption/cold trap injection system[13] which contains a 20 cm × 25 μm I.D. fused-silica restrictor (Chrompack, Middelburg, The Netherlands); (16) a vent; (17) a Carlo Erba Model 5300 Mega high-resolution gas chromatograph, equipped with (18) an electron-capture detector and a 60 m × 0.22 mm I.D. DB-1 column (J&W Scientific, Folsom, CA, U.S.A.), with helium at a pressure of 220 kPa as carrier gas; and (19) a Dewar vessel filled with liquid nitrogen.

*Chemicals*

Stock solutions and dilutions of hexachlorobenzene (HCB), PCB 101, PCB 153 and PCB 180 were prepared in Nanograde acetone (Promochem, Wesel, F.R.G.).

*Procedure*

The extraction vessel is filled with 100 mg of Tenax GC (Chrompack) and cleaned for 16 h with a flow of purified helium in an oven at 250°C. The Tenax is spiked via injection of 10 μl of an acetone solution containing 1500 pg of HCB and 300 pg each of PCB 101, PCB 153 and PCB 180. Then the extraction vessel is closed and mounted in the SFE–GC system. Starting with the situation as shown in Fig. 1, the two valves 10 are opened and valve 9 is switched, so that the contents of the extraction vessel can be dried on-line with purified helium at 120 ml/min. After 5 min, valves 10 and 9 are switched to their original positions. Next, valve 12 is switched to the capped position and the extraction vessel is pressurized to 20 MPa at a water-bath temperature of 42°C (these conditions have been reported[2,3] to provide adequate extraction of PCBs from Tenax using supercritical carbon dioxide). Then the vent 16 is opened and the capillary cold trap, 15 is cooled to 5 ± 2°C, while the restrictor is heated to 300°C in the oven (14). When these conditions have been reached, valve 12 is switched to its original position and the extraction proceeds. The extracted components are deposited in the cold-trap (15), while the gaseous carbon dioxide leaves the system via the vent. The extraction is stopped, by switching valve 12 to the capped position, when 11.5 ml of carbon dioxide, measured at the pump, have passed through the sample. After a 1-min delay, the vent is closed, the cold-trap flash-heated to 300°C and the released components are transferred to the capillary GC column. The extraction requires less than 35 min. The extraction vessel can be decompressed during the GC separation by switching valve 9 and opening valve 10. The next extraction vessel can then be mounted in the SFE–GC system.

## RESULTS AND DISCUSSION

*Design of the on-line SFE–GC system*

The proposed SFE–GC system is basically an elution system, and does not suffer from the drawbacks of a recycling system[14], in which the extract may be contaminated by, or lost in, the recycle pump and where usually only a fraction of the extract is transferred to the chromatographic system. Another important feature is the restrictor, which is shown in Fig. 2. The fused-silica restrictor is inserted in an 18 cm × 0.6 mm I.D. glass tube which fits in a conventional thermodesorption/cold-trap

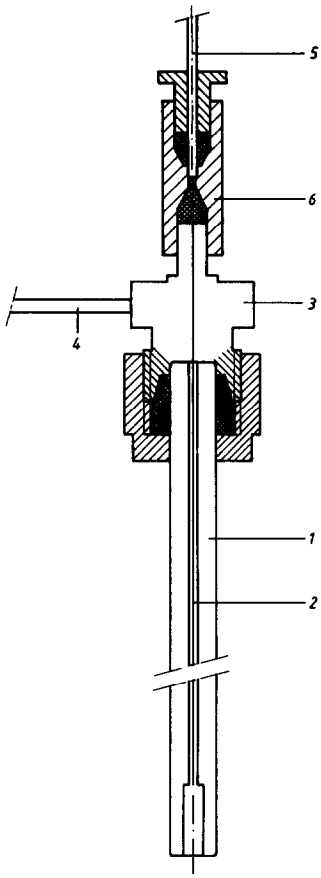


Fig. 2. Design of the restrictor. 1 = Glass tube (18 cm × 0.6 mm I.D.); 2 = 20 cm × 25 μm I.D. fused-silica capillary; 3 = 1/4-in. T-piece; 4 = helium carrier line; 5 = supercritical fluid; 6 = 1/16–1/32-in. reducing union.

injector. The restrictor is protected in this way and is re-usable; in practice, we have used the same restrictor for several weeks. In addition, the desorption oven is used as a restrictor oven and prevents condensation or precipitation of the extracted components during decompression in the restrictor.

The co-axial addition of helium carrier gas to the restrictor effluent allows pressure-controlled operation and prevents backflushing of supercritical carbon dioxide into the helium carrier line. The use of a vent is very practical, because now the carbon dioxide flow-rate is not restricted by the inner diameter of the capillary GC column, and no backflushing of gaseous carbon dioxide into the helium carrier line will occur.

Cryogenic operation of the entire gas chromatograph is unnecessary. Refocusing of the analytes occurs in the cold-trap of the injection system, which can be cooled to −50°C if required.

The on-line SFE–GC system is equipped with an UV absorbance monitor and a

second heated restrictor for detection and (off-line) collection of components which are present in relatively high concentrations. The system also allows on-line density-programmed SFE–GC. The influence of the addition of modifiers to the supercritical carbon dioxide on the refocusing efficiency in the cold-trap has not yet been investigated.

*Purity of supercritical carbon dioxide*

One of the most serious problems associated with on-line SFE–GC is the purity of the supercritical fluid, *e.g.*, carbon dioxide. In SFC, impurities will cause a background signal which may interfere with trace analyses when programmed-density SFC is applied. In on-line SFE–GC, the impurities in the supercritical fluid are, as a rule, preconcentrated in the cold-trap and subsequently injected into the capillary gas chromatograph. This results in a high background, which seriously limits trace analysis. We have compared carbon dioxide obtained from several manufactures. Unfortunately, none of these turned out to be really suitable for trace-level analyses. Even research-grade purity (99.999%) carbon dioxide still contains a few ppm of water and "total hydrocarbons". The water content limits the temperature range of the cold-trap to values above 0°C, and the hydrocarbons often show typical oil patterns in a flame ionization detector; occasionally the detector flame was even extinguished (!). Both phenomena will have an impact on the recovery: too high a temperature of the cold-trap causes breakthrough of the more volatile solutes. Oil residues will create a film in the cold-trap which may act as a stationary phase, thereby reducing the desorption efficiency and introducing a memory effect. So far, the best results were obtained with "food-grade" carbon dioxide obtained from Rommenhöller.

*Application to the determination of polychlorinated aromatic hydrocarbons*

The GC–electron capture detection (ECD) system was calibrated by direct injection of the sample into a plug of quartz-wool that had been inserted into a glass thermodesorption tube. After evaporation of the solvent, the tube was placed in the thermodesorption/cold-trap injector and analysed under similar time and temperature conditions as for SFE–GC. The spiked 100-mg Tenax samples were analysed as described under Experimental. The recovery was calculated relative to the results obtained in calibration experiments. The reproducibility was determined by performing three experiments on different days. The memory effect was determined by a second SFE–GC run on each sample. The results are given in Table I.

TABLE I

RESULTS OF THE ANALYSIS OF SPIKED TENAX SAMPLES

| *Component* | *Amount added* | | *Recovery (%)* | *Reproducibility (%)* | *Memory (%)* |
|---|---|---|---|---|---|
| | *pg* | *ppb*[a] | | | |
| HCB | 1500 | 15.0 | 52 | 12 | 2 |
| PCB-101 | 300 | 3.0 | 58 | 12 | 7 |
| PCB-153 | 300 | 3.0 | 59 | 10 | 9 |
| PCB-180 | 300 | 3.0 | 63 | 9 | 13 |

[a] The American billion ($10^9$) is meant throughout.

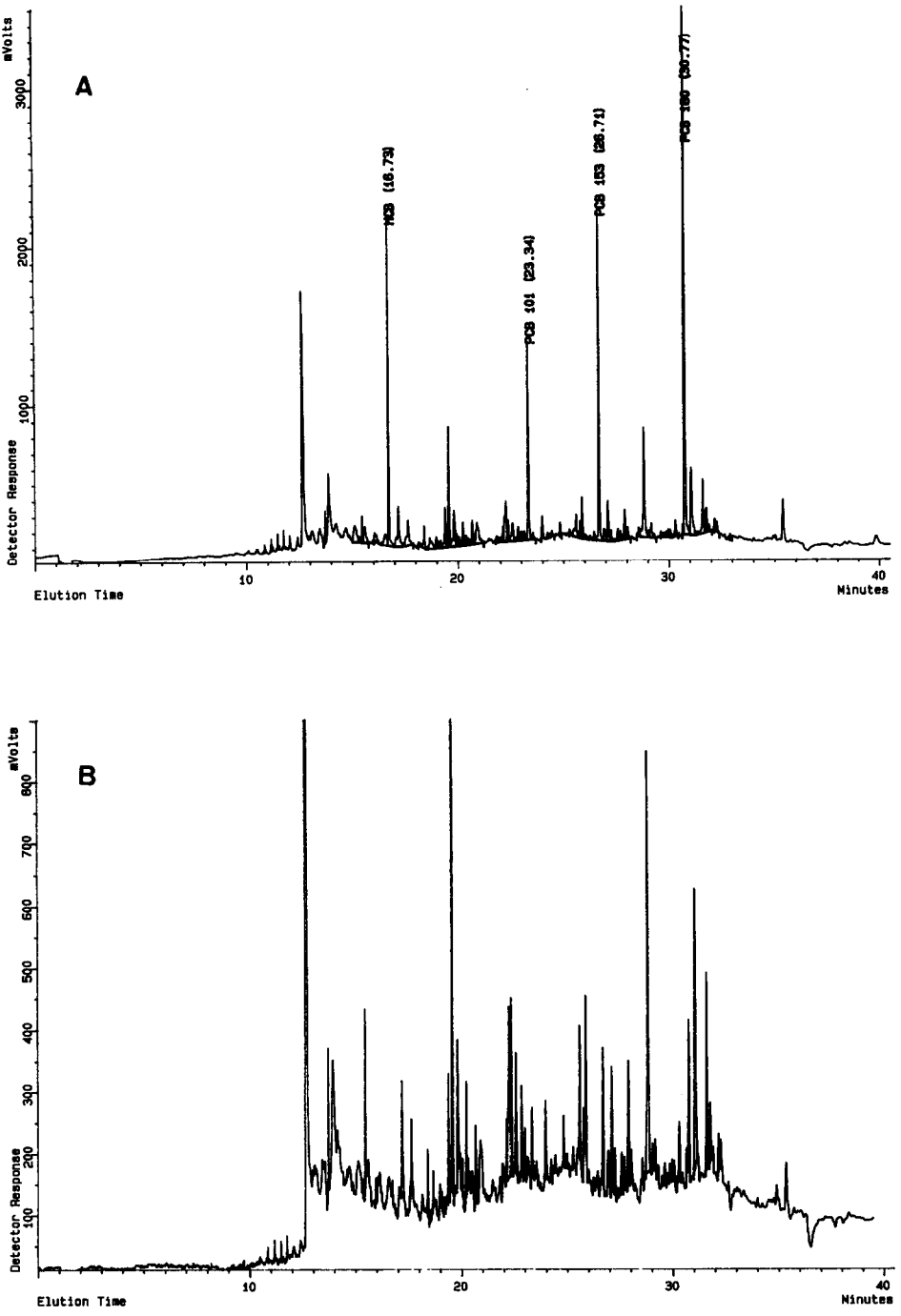


Fig. 3. Chromatograms of (A) Tenax, spiked with 1500 pg of HCB and 300 pg of the PCB 101, 153 and 180, and extracted using 11.5 ml of supercritical carbon dioxide; and (B) 11.5 ml of supercritical carbon dioxide (note the difference in the detector response scale).

The recoveries are of the order of 50–65%. A second extraction with a further 11.5 ml or a single extraction with double the volume of supercritical carbon dioxide increases the recovery by only 2–13%, as indicated by the memory effect. An explanation for the incomplete recovery might be the reduced sensitivity of ECD for the components of interest during co-elution with the oil residues. Note that the oil contamination was absent when the GC–ECD system was calibrated, resulting in a calibration error and an apparent loss of components. In addition, the most volatile component, HCB, may be partly lost by breakthrough in the cold-trap (it should be noted that the flow-rate through the cold-trap is increased during SFE compared with the calibration of the GC–ECD system); moreover, fogging may occur in the cold-trap, which can cause a partial loss of the components.

The memory effect is not caused by incomplete desorption from the cold-trap, as was indicated by a second thermodesorption between the first and second extractions. Obviously, incomplete extraction and/or retention in the system are responsible for the memory effect.

Despite the incomplete recoveries, the system was found to be fairly stable, as indicated by the reproducibility of 9–12%. With the present procedure, the attainable detection limit is about 30 pg (0.3 ppb) for the individual PCBs. A typical chromatogram is shown in Fig. 3A. The spiked components are seen to be superimposed on the impurities present in the supercritical fluid itself, as demonstrated by comparison with Fig. 3B.

## CONCLUSIONS

The on-line SFE–GC system shows several advantages over the systems described in the literature. The system is robust and compatible with existing thermodesorption/cold-trap equipment, it does not restrict the choice of GC columns or detectors and has potential for environmental trace analyses, as was demonstrated by the analysis of Tenax spiked with polychlorinated aromatic hydrocarbons at the picogram level. The recovery of these analytes is satisfactory.

The detection limit for the individual PCBs is 30 pg, which appears to be a significant improvement over results such as reported in, *e.g.*, refs. 9 and 15. For a further decrease in the detection limit to 1–5 pg (which is no problem for ordinary capillary GC–ECD and will be sufficient for our air-sampling project), the availability of carbon dioxide of higher purity is required. Should it become available, then the recovery of more volatile components will also increase, because the temperature of the cold-trap can be lowered.

Efficient purification of carbon dioxide, further optimization of the recovery of the analytes and application of the on-line SFE–GC system for the analysis of air samples are currently being investigated.

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