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Short Communication

Sensitivity enhancement in dynamic "off-line" supercritical fluid extraction

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ABSTRACT

A method for analytical supercritical fluid extraction in "off-line" mode was developed with the aim of obtaining maximum sensitivity, *i.e.* maximally concentrated solute solutions after extraction without further concentration steps. Dry deposition on the inner capillary wall was used, followed by rinsing of the trapped solutes using a minimum volume of the solvent. For the case of an inert support (glass beads) spiked with fluoranthene, the reproducible minimal volume of the solvent was determined and the influence of flow velocity in the trapping capillary was studied.

INTRODUCTION

At present, supercritical fluid extraction (SFE) is one of the fastest developing analytical sample preparation techniques [1,2]. Among the problems encountered in SFE, efficient trapping of analytes from the depressurized supercritical fluid is still difficult to achieve. Two modes of SFE, "on-line" and "off-line", are practised. When comparing these methods, the overall higher sensitivity of the "on-line" mode and the reproducibility of sampling in "off-line" mode have been emphasized. One way to increase the sensitivity in "off-line" SFE is to decrease the solvent volume in which extracted analytes are dissolved, so as to avoid further concentration steps, during which serious losses of solutes can occur. At the same time the high trapping efficiency must be maintained. This paper reports a new approach to trapping in SFE.

Analyte trapping into a liquid solvent [3–7] is one of three commonly used collection methods. The end of the restrictor is immersed in a vial filled with liquid solvent, in which the analytes are to be trapped, and the decompressed fluid bubbles through the liquid and vents to the atmosphere. The liquid solvent (usually methylene chloride, methanol or hexane) must be compatible with the analytes of interest and the flow of the decompressed fluid maintained below a certain limit, at which violent bubbling of the liquid solvent can lead to analyte loss. The vial is often cooled to decrease solvent evaporation.

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The solvent volumes used in this method are usually larger than 1 ml.

Collection on solid sorbents [8–12] may involve three trapping mechanisms —cryogenic trapping, adsorption and absorption. Chromatographic solid supports are mainly used as packing material. The recoveries of analytes depend on the combination of trapping and rinsing efficiencies. The solvent volumes in this case are also rarely less than 1 ml.

Trapping on solid surfaces is the best way to decrease the solvent volume and obtain more concentrated solutions in dynamic SFE, without further concentration steps. The reason why this collection method is not used more widely follows from the character of the expanding solute–fluid mixture, in which the formation of solute particles [13] and aerosols has been confirmed. Inefficient trapping in an open glass bulb [14] of 100 ml volume is hardly surprising.

On the other hand, this collection system is successfully used in "on-line" SFE–GC, in which analytes are cryogenically focused on the wall of metal or fused-silica capillaries. The question thus arises as to why this method is not also used in "off-line" dynamic SFE. The aim of this work is to verify this approach, in which flash heating after cryogenic focusing is replaced by solvent rinsing of analytes from capillary walls into a glass microvial.

EXPERIMENTAL

The device used in the work is schematically shown in Fig. 1. A personal computer-based syringe pump HP 5001 (Laboratory Devices, Prague, Czech Republic) is connected through an on–off valve to the extraction vessel, which is inserted into a thermostatically controlled aluminium tube. The temperature was maintained at 50°C in all experiments. The internal volume of the extraction vessel was approximately 2.5 ml, but in all cases a replaceable cartridge of internal volume 0.6 ml was used. The cartridge was packed with glass beads (∅ *ca.* 0.2 mm) held in place by glass wool plugs. The glass beads were spiked with standard solutions of fluoranthene in tetrachloromethane. The absolute amounts of fluoranthene were in the range 5–20 μg.

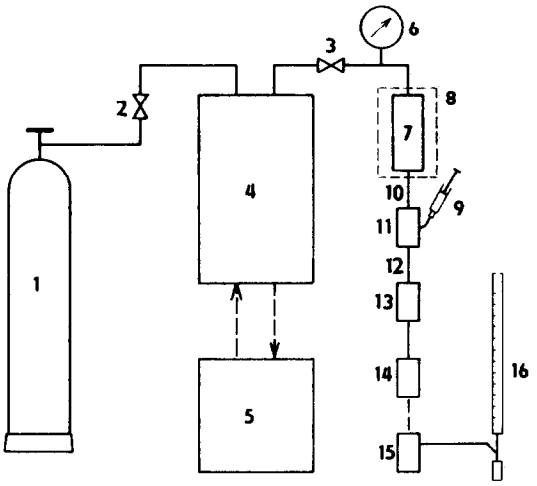

Fig. 1. Schematic diagram of SFE device. 1 = Tank of CO_2; 2,3 = "on–off" valves; 4 = syringe pump; 5 = personal computer; 6 = pressure gauge; 7 = extraction cell; 8 = metal (aluminium) oven; 9 = syringe; 10 = restrictor; 11 = connecting union; 12 = trapping capillary; 13 = heater; 14 = cryofocuser; 15 = vials, 16 = bubble flowmeter.

Supercritical pressures were maintained inside the extraction cartridge by using capillary restrictor–fused-silica tubing (I.D. 17 μm, lengths from 10 to 25 cm).

The sample trap (see Fig. 2) consisted of fused-silica tubing (30 cm × 500 μm I.D.) into which the capillary restrictor was inserted through the connection union. This allowed injection of an arbitrary amount of a suitable solvent to wash out the trapped analytes into a glass microvial. The flow-rate of CO_2 was measured by a bubble flowmeter at ambient conditions. All GC–flame ionization detection (FID) analyses were performed by using a CHROM-5 gas chromatograph (Laboratory Devices) on a packed SE-30 column.

RESULTS AND DISCUSSION

The proposed analyte collection method for "off-line" SFE consists of two steps: the trapping of the analytes onto an inner surface of the capillary (*ca.* 500 μm I.D.) and their subsequent washing from the capillary inner surface by a

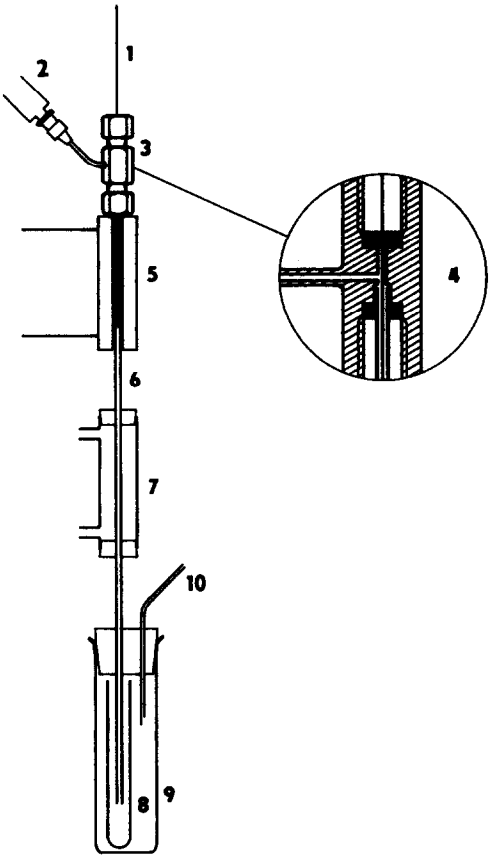

Fig. 2. Schematic representation of the trapping system. 1 = Restrictor; 2 = syringe; 3 = connecting union; 4 = detailed inner configuration of the connecting union; 5 = heater; 6 = trapping capillary; 7 = cryofocuser; 8,9 = vials; 10 = output of CO_2.

small volume of solvent into a glass microvial. There are several experimental parameters on which the efficiency of the entire process could depend and which can be summarized as follows:

(a) Parameters related to the trapping step: (1) type of sample and its matrix concentration; (2) extraction conditions (type of extracting fluid, pressure, temperature); (3) type of restrictor used; (4) linear velocity of gas in the trapping capillary; (5) length and diameter of the trapping capillary; (6) surface properties and temperature.

(b) Parameters related to the rinsing step: (7) type of solvent; (8) volume of solvent used for rinsing; (9) timing of rinsing process.

The two steps cannot be studied separately, and only the efficiency of the entire process can be determined. In this preliminary work, the influence of the linear velocity of the expanding gas in the trapping capillary on the percentage recovery of fluoranthene has been studied.

TABLE I

DEPENDENCE OF PERCENTAGE RECOVERIES ON LINEAR VELOCITIES IN THE TRAPPING CAPILLARY AT DIFFERENT PRESSURES

Restrictor length 30 cm, spiked amount 5 μg.

Pressure (MPa)	Linear velocity (cm/s)	Extraction time (min)	Recovery (%)
13.8	102	40	99
16.6	136	20	97
19.4	157	15	101
22.0	201	10	95
24.6	212	10	94

The percentage recoveries in Tables I and II are averages of two extractions, and the concentration of fluoranthene in each extracted sample was determined as an average of three subsequent analyses. Different linear velocities were obtained through different extraction pressures (Table I) or by the use of restrictors of different length (Table II). In both cases up to linear velocities of *ca.* 2 m/s, fluoranthene was practically quantitatively trapped. The spiked amount of fluoranthene was 5 μg (Table I) and was

TABLE II

DEPENDENCE OF PERCENTAGE RECOVERIES ON LINEAR VELOCITIES IN THE TRAPPING CAPILLARY AT DIFFERENT RESTRICTOR LENGTHS

Pressure 22.0 MPa, spiked amount of fluoranthene 20 μg.

Restrictor length (cm)	Linear velocity (cm/s)	Extraction time (min)	Recovery (%)
25	113	20	98
20	126	15	100
15	151	15	96
10	253	10	97

increased to 20 μg (Table II) with no effect on resulting recoveries. The rinsing solvent volume was 100 μl.

The reproducibility of this collection mode was determined by ten repeated extractions, keeping all parameters at constant values (linear velocity ≈ 1 m/s, spiked amount 20 μg). When 100 μl of tetrachloromethane were used, an average percentage recovery 96% with R.S.D. 3.4% was obtained.

The same series of experiments were performed with a washing volume of 50 μl with effectively the same results. This value is the practical limiting volume when a capillary of *ca.* 500 μm I.D. is used, and repeated analyses must be carried out.

CONCLUSIONS

A new method of analyte collection after off-line SFE is proposed. A fused-silica capillary (*ca.* 500 μm I.D.) was used as the trap, followed by analyte rinsing with a small volume of appropriate solvent (*ca.* 100 μl). The method proved to be efficient for the quantitative trapping of a test substance (fluoranthene) (*ca.* 95%). Quantitative rinsing of fluoranthene with a smaller volume of tetrachloromethane (50 μl) from the trapping capillary resulted in an increase in the concentration within the solution.

Future work will involve the application of this technique to samples of varying volatilities. The influence of a number parameters, discussed above, must also be tested.

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