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Short communication

Solute trapping in off-line supercritical fluid extraction using controlled modifier condensation

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Abstract

A new approach to solvent trapping, based on controlled modifier condensation, is presented. The trapping system consists of a fused-silica capillary (30 cm × 500 μm I.D.) equipped with a cryofocusing device. As a trapping mechanism, nebulization of expanding supercritical mixture with condensing modifier, followed by analyte trapping into moving liquid layer is assumed. In spiking experiments a urea-based herbicide, flufenoxuron, was extracted with 10% methanol-modified CO_2 and recoveries of over 90% were found. The resulting solvent volumes needed for quantitative trapping are much lower (ca. 0.3 ml) than in the case of direct bubbling through bulk liquid.

1. Introduction

In previous work [1] a new off-line trapping method for analytical supercritical fluid extraction (SFE) was proposed. A solute precipitating from an expanding supercritical phase was trapped on the surface of the inner wall of a piece of fused-silica tubing. It was found that a relatively small volume of liquid solvent (50–100 μl) was required to rinse the precipitated solute efficiently from the trapping capillary. The resulting solutions were of higher solute concentration when compared to solutions obtained by direct trapping into liquid solvents. An added advantage was that the solution obtained by this method could be analysed directly without further concentration.

The described method was successfully tested with model fluoranthene solutions spiked onto inert glass beads. Recoveries around 96% were found up to linear flow velocities of 2 m s^{-1} (measured at ambient conditions) of expanding CO_2 in the trapping capillary. As proposed, the method can be used with pure extracting fluid. When pure CO_2 or N_2O are used, however, their solubilizing power is often insufficient for efficient extraction of polar analytes. Then the extracting power can be enhanced by adding of polar modifiers such as methanol or other organic solvents. The object of the present work was to investigate whether the described method could be used when the extracting fluid is modified and whether the modifier could be exploited in the trapping process.

When a relatively volatile modifier is present at low concentration, the modifier evaporates

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almost completely following decompression of the extracting fluid and the proposed trapping procedure described previously can be applied as in the case of a pure fluid. At higher modifier concentrations a proportion of the total modifier remains in the gaseous state following depressurization of the fluid at a given capillary temperature. The remaining modifier liquifies and forms a film on the inner wall of the capillary. The precipitated analytes are trapped in the liquid film rather than on the capillary wall. The analytes are thereafter swept out the capillary as the liquid modifier moves down the trapping capillary and are collected as a solution in liquid modifier in a vial. The aim of this paper is to verify the assumed trapping mechanism quantitatively when modifier condensation is controlled by a cryofocusing device. A urea-based herbicide, flufenoxuron, is used as a model solute for the investigation.

2. Experimental

All extractions were performed on a laboratory-built system consisting of a Varian 8500 syringe pump with a cooled head and a heated extraction cell linked to a specially designed and constructed trapping device. The pressure in the cell was maintained using 15 cm length of fused-silica capillary tubing with an internal diameter of either 20 or 25 μm as a linear flow restrictor. The end of the restrictor was located in a ceramic heating device which was programmed to a desired temperature to prevent restrictor plugging. The tip of the restrictor was located inside a 30 cm × 500 μm I.D. fused-silica capillary. The extraction system and trapping device is shown schematically in Fig. 1. The extracting fluid employed was CO_2 modified with 10% of methanol by volume (ECM Speciality Gases, Stoke on Trent, UK). The trapping system was equipped with a cryogenic cooling device which operated on an 8 cm length of the 500 μm I.D. capillary. The cooling device was located immediately after the ceramic restrictor heater. The cooling was provided by expanding carbon dioxide supplied from another source and controlled

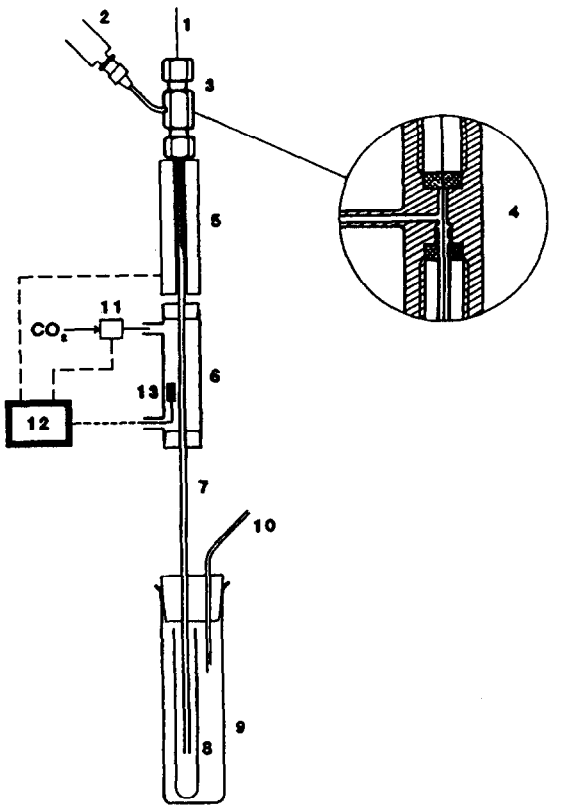

Fig. 1. Schematic representation of the trapping system. 1 = Restrictor; 2 = syringe; 3 = connecting union; 4 = detailed inner configuration of the connecting union; 5 = heater; 6 = trapping capillary; 7 = cryofocuser; 8, 9 = vials; 10 = output of CO_2; 11 = solenoid valve; 12 = control unit; 13 = thermistor.

by a solenoid valve and a temperature controller, which also regulated the extraction cell and restrictor heater temperature. A 30-μl sample of a 0.8 mg ml^{-1} flufenoxuron standard in 1,4-dioxane was spiked onto glass beads in an extraction cell of internal volume 0.6 ml. The solvent was allowed to evaporate prior to extraction. A series of extractions were carried out for various experimental conditions. Each extraction was performed at 40 MPa and 60°C; the other extraction conditions and parameters are summarized in Tables 1 and 2.

The flow-rate of gaseous CO_2–methanol was measured using a bubble flow meter coupled to the collection microvial. The volume of methanol collected from the 500-μm capillary was

Table 1
Flufenoxuron recovery (spike experiments)

Experiment No.	Recovery (%) in		Total recovery (%)
	Condensed modfier	Rinsing solvent	
1	75.6	19.8	95.4
2	92.2	3.5	95.7
3	87.6	2.9	90.5
4	85.6	3.8	89.4
5	76.2	10.2	86.4
6	80.2	15.9	96.1
Mean	82.9	9.4	92.3
R.S.D. (%)	7.3		4.0

Flow-rate of CO_2 100 ml min^{-1} (at ambient conditions), cryofocusing temperature −30°C.

determined by mass and density calculations. After each extraction the trapping capillary was rinsed with 100 μl of methanol (HPLC grade, Fisons Chemicals, Loughborough, UK). An additional rinse with methanol was carried out to determine whether any analytes are retained in the trapping capillary after the initial wash.

The collected methanol and methanol-rinse fractions were analysed by reversed-phase HPLC. The HPLC system consisted of a Merck–Hitachi L6000 reciprocating pump, a Rheodyne 6-port injection valve with a 10-μl sample loop, a 25 cm × 4.5 mm I.D. S10 ODS2 packed column (Spherisorb), a Merck–Hitachi L4000 UV detector and a Hewlett-Packard 3395 integrator. The mobile phase was acetonitrile–water–propan-2-ol (60:35:5, v/v/v). Analyte recoveries were calculated by absolute calibration. A calibration curve was prepared by analysis of a set of standard flufenoxuron solutions.

Table 2
Flufenoxuron recovery (spike experiments)

Experiment No.	Recovery (%) in		Total recovery (%)
	Condensed modifier	Rinsing solvent	
1	75.6	14.5	90.1
2	73.8	7.7	81.5
3	79.2	7.5	86.7
4	81.0	7.0	88.0
5	73.1	10.7	83.8
6	72.9	11.0	83.9
Mean	75.9	9.7	85.7
R.S.D. (%)	4.1		3.4

Flow-rate of CO_2 180 ml min^{-1} (at ambient conditions), cryofocusing temperature −30°C.

3. Results and discussion

Flufenoxuron has been quantitatively recovered from spiked soil samples in previous studies [2]. Extraction was found to be quantitative after 20 min at 60°C and 40 MPa with carbon dioxide modified with 10% of methanol. The aim of this study was not to examine the extraction efficiency, but to evaluate the trapping procedure.

An extraction time of 15 min was found to be sufficient for quantitative extraction at flow-rates of approximately 100 ml min^{-1} (flow of CO_2 at ambient conditions) with the 20-μm restrictor. After an initial extraction a repeated extraction gave no further flufenoxuron recovery. Glass beads were found to be a good inert support for flufenoxuron and allowed efficient and fast extraction. Since the vapour pressure of pure methanol under ambient conditions is ca. 88 mmHg (1 mmHg = 133.322 Pa), only a very small amount of methanol condenses in the capillary when the system is operated without cooling. Because of restrictor heating methanol is not condensed, but swept out in gaseous state from the trapping capillary in a stream of carbon dioxide. For the cooling operation, a cryofocusing device was located immediately after the restrictor heater. At constant measured flow-rate of expanding CO_2 the total amount of collected condensed methanol during 15 min was determined for different temperatures of the cryofocusing device.

It can be seen from Fig. 2 that practically linear dependence of collected methanol volume on the cryofocusing temperature was obtained at temperature interval from −30°C to 25°C. The experimental work was split into two sections to

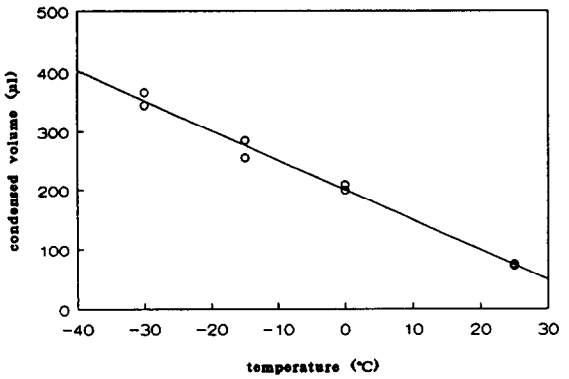

Fig. 2. Dependence of volume of condensed methanol on cryofocusing temperature for 10% methanol-modified CO_2. Pressure 40 MPa, restrictor 20 μm I.D., flow-rate of CO_2 100 ml min^{-1} at ambient conditions.

evaluate the effect of flow-rate of expanding carbon dioxide.

All experiments were performed at a cryofocusing temperature of −30°C to obtain approximately 300 μl of liquid phase for repeated analysis by liquid chromatography. The results are summarized in Tables 1 and 2. Flufenoxuron has a high solubility in methanol and therefore only a small amount of methanol is required to dissolve the flufenoxuron extracted. The flow-rates of CO_2 measured at ambient conditions were 90–110 ml min^{-1} for a restrictor of 20 μm I.D. and 170–190 ml min^{-1} for one of 25 μm I.D.

In both cases an average analyte recovery around 10% in methanol wash was obtained as a result of analyte precipitation on the part of capillary wall between the restrictor tip and the point of appearance of methanol condensation. The analyte recovery in the methanol collected with the 25-μm restrictor was lower than for a 20-μm restrictor, 75 and 83%, respectively. The value of total flufenoxuron recovery also reflects this fact.

Higher flow-rates produced larger amounts of condensed methanol by virtue of a larger amount of methanol being passed through the system but reduced recovery of analyte in the methanol fraction condensed. Lower R.S.D. values for total flufenoxuron recovery provide evidence of better reproducibility of the overall trapping process than of individual steps. A more rigorous investigation of the analyte recovery in the collected methanol versus the amount of methanol collected would be to extract an analyte that is less soluble in methanol than flufenoxuron. A more definite relationship between amount of extracted analyte in the collected modifier and the amount of collected modifier could be established.

4. Conclusions

A new approach to trapping into liquid solvent for off-line SFE with a modified extracting fluid was investigated. The flufenoxuron recovery from an idealised matrix was found to be quantitative and reproducible. Recoveries for the trapping device, when operated with cooling were 85.7% (R.S.D. 3.4%) for the 25-μm restrictor and 92.3% (R.S.D. 4.0%) for the 20-μm restrictor. The trapping efficiencies obtained with this device appear dependent on the flow-rate of expanding CO_2 through the trapping capillary: the higher the flow-rate the lower the analyte recovery. An analyte with a lower solubility in methanol than flufenoxuron could be used to verify the relationship between the amount of collected methanol and the trapping efficiency.

Acknowledgement

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References

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