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Note

Supercritical fluid extraction of *s*-triazine herbicides from sediment[a]

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Supercritical fluid extraction (SFE) is a very useful technique for the isolation of organic compounds from a solid matrix. It has been used for the analysis of flavours and fragrances from natural products[1], toxic organics from resins[2], polycyclic compounds and polychlorinated biphenyls from environmental solids[3] and other compounds (ref. 4 and references cited therein).

Carbon dioxide is mostly used as a supercritical fluid because of its low critical temperature (32°C) and pressure (73 bar), which allows SFE to be performed at relatively low temperatures, avoiding thermal decomposition of analytes. Carbon dioxide is a non-explosive and relatively inert gas at normal temperature and pressure, which simplifies subsequent concentration of the compounds isolated by SFE. It is also possible to couple SFE with capillary gas chromatography (GC)[3,4]. Complete transfer of analytes from SFE directly into a capillary column is achieved by this on-line modification and lower detection limits may be reached.

The aim of this work was to measure the recovery of *s*-triazine herbicides from river sediment by SFE. The compounds used are listed in Table I.

TABLE I

s-TRIAZINE HERBICIDES STUDIED

Common name	*Systematic name*
Simazine	2-Chloro-4,6-bisethylamino-*s*-triazine
Atrazine	2-Chloro-4-ethylamino-6-isopropylamino-*s*-triazine
Propazine	2-Chloro-4,6-bisisopropylamino-*s*-triazine
Terbutylazine	2-Chloro-4-ethylamino-6-*tert.*-butylamino-*s*-triazine
Cyanazine	2-Chloro-4-ethylamino-6-(1-cyano)isopropylamino-*s*-triazine

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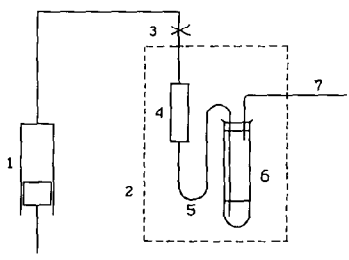
EXPERIMENTAL

Supercritical fluid extraction

All the SFEs were performed using a Varian 8500 syringe pump. The extractions were performed at a pressure of carbon dioxide of 230 bar and a temperature 48°C. The density of carbon dioxide under these conditions is about 0.80 g/ml[5]. The apparatus is shown schematically in Fig. 1. The cartridge for extraction of the sediment was constructed according to Fig. 2. The pressure of the supercritical carbon dioxide in the cartridge was maintained by means of a capillary fused-silica restrictor (30 cm × 25 μm I.D.). The time of SFE was 30 min and during this period approximately 18 ml of liquid carbon dioxide were pumped into the SFE system. The cartridge had an inner volume 0.57 ml and 500 mg of the sediment were extracted. The outlet of the restrictor was immersed in methanol in the test-tube to trap the isolated compounds. Although the test-tube was placed in the oven, losses of methanol during SFE were acceptable because it was cooled by carbon dioxide expansion from the restrictor (during SFE ice was precipitated on the outer wall of the test-tube from moisture in the oven). The volume of methanol in the test-tube was 1 ml at the beginning of the SFE and decreased to approximately 0.5 ml by stripping with gaseous carbon dioxide within the 30-min period. Venting of methanol vapour from the test-tube did not affect the recovery of *s*-triazines as they are relatively non-volatile and evaporation of a solvent is a common step, *e.g.*, for concentration of extracts from water[6]. The decrease in the methanol volume was corrected for by addition of an internal standard before chromatographic analysis.



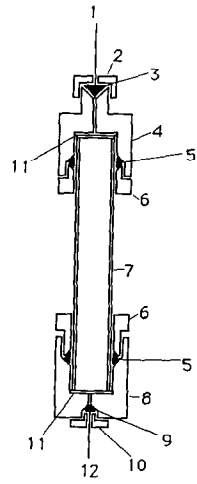


Fig. 1. Apparatus for SFE (not to scale). 1 = Pump for liquid carbon dioxide; 2 = oven; 3 = shut-off valve; 4 = cartridge with sample of sediment (for details see Fig. 2); 5 = restrictor; 6 = test-tube with methanol; 7 = fused-silica capillary (0.32 mm I.D.) for venting gaseous carbon dioxide.

Fig. 2. Extraction cartridge. 1 = Stainless-steel capillary; 2 = tubing union; 3 = metal ferrule; 4 = female nut; 5 = metal fitting; 6 = male nut; 7 = stainless-steel tubing; 8 = female nut; 9 = Vespel ferrule; 10 = male nut; 11 = stainless-steel frit; 12 = restrictor.

Capillary gas chromatography

For the GC analyses a Varian 3700 gas chromatograph equipped with a flame ionization detector and a laboratory-made cold on-column injector was used. The column was a fused-silica capillary (30 m × 0.3 mm I.D.) coated with Superox 20M. The temperature was programmed from 70 to 220°C at 20°C/min and then held at 220°C for 8 min. Hydrogen was used as the carrier gas (inlet pressure 0.95 bar). Volumes up to 2 μl were injected. No deterioration in peak shape was observed. Eicosane was used as an internal standard. Even very complex mixtures of *s*-triazines can be separated on poly(ethylene glycol)-based stationary phases[7].

High-performance liquid chromatography

For the separation of *s*-triazines, silica gel[8], amino- or cyano-bonded stationary phases[9,10] with a non-polar mobile phase or a reversed phase with methanol–water as the mobile phase[11,12] have been applied. Ultraviolet detection is very suitable as *s*-triazines exhibit strong absorbance at 220–240 nm[11]. An HP 1090 liquid chromatograph equipped with diode-array detector and a 25 cm × 0.46 cm I.D. column packed with reversed phase was used. The greatest absorbance was observed in the 220–225 nm region for all the compounds tested. For the measurements a wavelength of 225 nm was used. The flow-rate of the mobile phase [methanol–water (65:35, v/v)] was 1 ml/min. Volumes of 10–25 μl of the extract were injected. Thyophylline was used as an internal standard for high-performance liquid chromatographic (HPLC) experiments.

Recovery of s-triazines from sediment

The sediment was dried through lyophilization. A weighed amount (0.5 g) was spiked by a methanolic solution of *s*-triazines and the solvent was allowed to evaporate from the slurry overnight. The spiked sediment was then subjected to SFE. The extract after SFE was analysed by capillary GC or HPLC after addition of an internal standard. For the analyses of the lowest concentrations of *s*-triazines, methanol was evaporated by means of a mild stream of nitrogen to a final volume of 200 μl.

Simultaneously, a reference mixture representing 100% recovery was prepared by addition of the same amount of *s*-triazines and internal standard to methanol. Recoveries were calculated from the responses of a given compound corrected on the response of the internal standard obtained from analysis of the methanolic solution after SFE and of the "100% recovery" solution, respectively.

RESULTS AND DISCUSSION

Recoveries of SFE of *s*-triazines from the sediment by pure supercritical carbon dioxide are given in column B in Table II. It can be seen that recoveries are high, with the exception of simazine. The poor recovery of the latter might be explained by its low solubility in low-polarity solvents, including benzene. As the polarity of carbon dioxide is roughly similar to that of benzene, this explains why the recovery of simazine is low.

In the next experiment (column C in Table II), 20 μl of methanol were added directly into the SFE cartridge (into the inlet side of supercritical carbon dioxide) just before SFE. This simple modification of the supercritical carbon dioxide polarity

TABLE II

RECOVERY OF *s*-TRIAZINES BY SFE WITHOUT (B) AND WITH (C) METHANOL ADDITION

Compound	*Concentration in sediment (ppm)*	*Recovery (%)*	
		B	*C*
Propazine	60.8	96.4	96.4
Terbutylazine	40.2	82.4	91.8
Atrazine	60.2	86.2	91.0
Simazine	28.0	42.5	92.0
Cyanazine	81.2	92.4	90.2

increased the recovery of simazine considerably (see also Fig. 3). During all further experiments methanol was added to the cartridge before SFE.

For the analyses of the extracts given in Table II, flame ionization detection (FID) was used. Although the sensitivity of GC was sufficient for the analysis of lower concentration of triazines, the FID selectivity does not permit this, as interfering

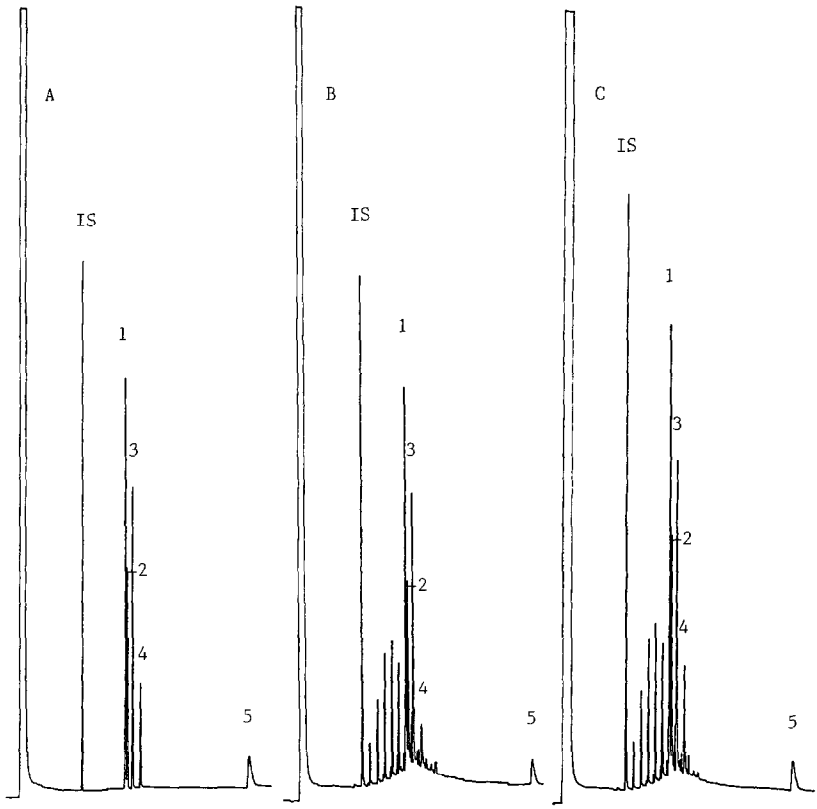


Fig. 3. GC analyses. (A) "100% recovery" solution; (B) SFE with pure carbon dioxide; (C) SFE with methanol addition. Peaks: IS = internal standard (retention time 4.10 min); 1 = propazine (6.62 min); 2 = terbutylazine (6.68 min); 3 = atrazine (6.96 min); 4 = simazine (7.44 min); 5 = cyanazine (13.67 min). Volume injected: 1.5 μl.

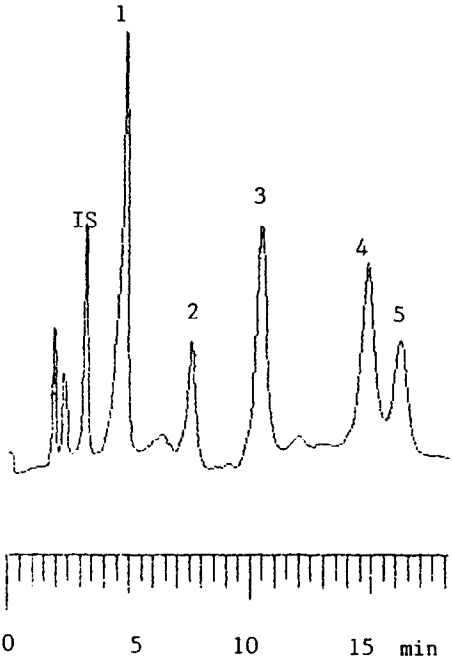


Fig. 4. HPLC analysis of *s*-triazines in sediment after SFE. Peaks: IS = internal standard; 1 = cyanazine; 2 = simazine; 3 = atrazine; 4 = propazine; 5 = terbutylazine. Volume injected: 10 μl.

compounds were co-extracted from the sediment by SFE. Interfering peaks overlap with *n*-alkanes (heneicosane and higher) which were originally present in the sediment. However, no particular attempt was made to identify these compounds unambiguously in this work. GC-selective ion monitoring can be applied to detect lower concentrations. In this work, however, the lower concentrations were measured by HPLC with diode-array detection (Fig. 4). Recoveries are summarized in Table III. Fig. 4 refers to concentrations given in the first column in Table III. HPLC showed a high selectivity even for the lowest concentrations tested, with the exception of propazine and terbutylazine, where interferences also occurred.

TABLE III

RECOVERY OF *s*-TRIAZINES FROM SEDIMENT (HPLC ANALYSES)

Compound	*Concentration (ppb)*	*Recovery (%)*	*Concentration (ppb)*	*Recovery (%)*	*Concentration (ppb)*	*Recovery (%)*
Cyanazine	4060	102.5	406.0	95.8	81.2	97.1
Simazine	1400	103.4	140.0	98.3	28.0	93.2
Atrazine	3010	95.8	301.0	102.0	60.2	91.8
Propazine	3040	103.5	304.0	94.1	60.8	ND[a]
Terbutylazine	2010	97.1	201.0	94.2	40.2	ND[a]

[a] Not detectable owing to interferences.

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