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Note

Rapid micro extraction procedure for analyses of trace amounts of organic compounds in water by gas chromatography and comparisons with macro extraction methods

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Analysis of trace amounts of organic compounds in water usually requires recovery into a small volume of solvent before determination by gas chromatography (GC). This may be by solvent extraction[1–3] or by sorption on macroreticular resin[4,5], polyurethane foam[6], carbon[7], or other materials[8–10] before solvent extraction. In most methods the solvent phase requires further concentration which may cause serious losses of compounds[5]. Thus, methods of analyses which avoid the solvent concentration step are preferable for the recovery of trace organics in water.

Described below is a rapid procedure with relatively simple equipment which gives acceptable yields for the analysis of several compounds at low levels.

EXPERIMENTAL

Micro method

An extraction flask was developed (Fig. 1) similar to the rapid liquid extraction used by Grob *et al.*[11]. The flask which contained 980 ml of water and 200 μl of hexane, was shaken manually for 2 min. By tilting the extraction flask and carefully adding water through the side arm, the solvent layer was held in the centre portion and finally

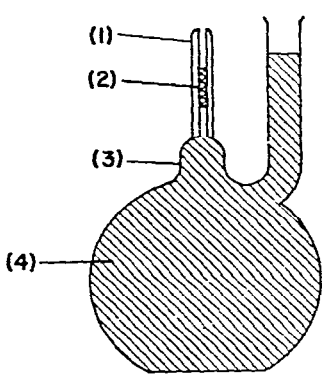

Fig. 1. Micro extraction flask. 1 = Capillary tube. 2 = solvent layer; 3 = modified 1-l volumetric flask; 4 = water sample.

displaced into the capillary tube. About 50 μl were recovered and were suitable for direct analysis by GC.

Macro methods

A steam distillation–solvent extraction head similar in design to No. 6555, manufactured by Ace Glass Co. (as used by Veith and Kiwus[12]) was made with a reduced solvent capacity of 10 ml. Each 10-l water sample was passed through this system (Fig. 2) in about 8 h. The hexane layer was removed and analysed by GC.

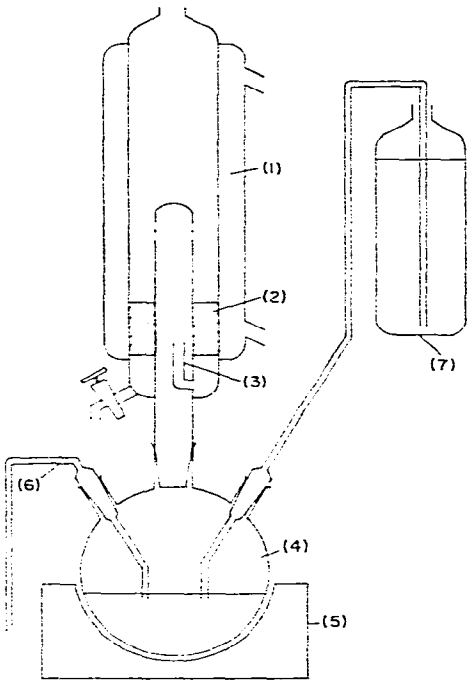

Fig. 2. Continuous steam distillation and extraction apparatus (modified Nielsen-Kryger). 1 = Condenser; 2 = solvent layer; 3 = water overflow; 4 = boiling flask; 5 = heating mantle; 6 = overflow; 7 = sample reservoir.

A continuous-extraction apparatus was developed (Fig. 3) which consisted of three inverted 250-ml volumetric flasks clamped to a retort stand, from which a bar was connected to a vibratory mixer. This was adjusted to give a vigorous shaking of all three flasks. Each 10-l sample was siphoned through the apparatus in about 4 h and extracted with a total solvent volume of 10 ml. The hexane was recovered in a separatory funnel for analysis by GC.

Quantitative analyses in all cases was based on the use of internal standards and integration of peak areas. Glass-distilled hexane was used throughout.

Gas chromatographic conditions

A Hewlett-Packard 5750 gas chromatograph was used with an Infotronics C.R.S. 208 integrator for quantitative analysis. A 2 m $\times$ 6 mm O.D. glass column was packed with 10% Dexsil 400 coated on Chromosorb W AW, 80–100 mesh.

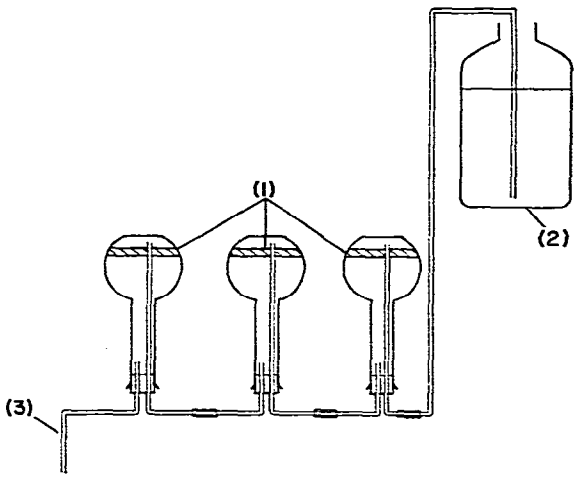

Fig. 3. Continuous solvent extraction apparatus. 1 = Solvent layer (hexane); 2 = sample reservoir; 3 = overflow.

Temperatures: electron-capture detector 260°, flame ionization detector 230°, injector 220°; column 235° or 50–200° (programmed at 20°/min); pulse interval: 50 μsec; flow-rates: helium 25 ml/min, hydrogen 30 ml/min, air 250 ml/min, argon 50 ml/min.

RESULTS AND DISCUSSION

In order to measure evaporative losses, hexane was spiked with 1 mg/l concentrations of three separate groups of organic compounds, concentrated from 10 ml to 1 ml using a micro Snyder column at 90° and a rotary evaporator at 50° and analysed by GC. Recovery of hydrocarbons with boiling points up to 250° was low (from 8–61 %) with both the micro Snyder column and the rotary evaporator. The recovery of phthalate esters and pesticides using the rotary evaporator was slightly better than the micro Snyder column but both techniques showed losses of 10% or more for pesticides (Table I).

A comparison of the micro extraction procedure was made with the extracts from two macro methods (Fig. 4). In both the tap and the distilled water extracts the micro extract gave as good a recovery if not better than the macro methods. Since the micro method was so rapid while the macro methods require several hours preparation, further work was concentrated on the micro extraction procedure.

Tap water samples spiked with ng/l concentrations of selected pesticides and μg/l concentrations of hydrocarbons (C_{10}, C_{12}, C_{14} and C_{16}) were extracted successively with 200 μl of hexane and analysed by GC using electron-capture and flame ionization detectors, respectively. There was a mean recovery of 58.3% in the first 200-μl extract and 94.3% in three 200-μl extracts. The standard deviations (calculated from 16 values, four analyses of four extracts) for the first extract range from 2.9 to 10.3% with the higher values at the ng/l level (Fig. 5, Table II). Distilled water was extracted in a similar way and analysed for phthalate esters using a flame ionization detector and showed comparable results (Table II). The identity of these phthalate esters was confirmed by GC–mass spectrometry. The typical *m/e* peak at 149 showed the presence

TABLE I

RECOVERIES ON CONCENTRATING FROM 10 ml TO 1 ml IN HEXANE

Substance	*Boiling point (°C)*	*Recovery (%)*	
		Micro Snyder column (90°)	*Rotary evaporator (50°)*
Lindane	—	81	92
Aldrin	—	77	84
Heptachlor epoxide	—	78	90
α-cis-Chlordane	—	78	87
Dieldrin	—	79	85
n-Octane	126	37	8
n-Decane	174	57	25
n-Dodecane	216	59	39
n-Tetradecane	254	61	49
Dipropyl phthalate	305	81	100
Diisobutyl phthalate	298	82	96
Dibutyl phthalate	340	82	100
Butyl glycolyl butyl phthalate	219 at 5 mmHg	84	100

of the phthalate residue and the M + 1 peaks at 279 and 337 using the chemical ionization mode, identified the parent compounds.

Water from a local river was analysed with a single 200-μl extraction using an electron-capture detector and several peaks in the pesticide group as well as phthalate esters were found (Fig. 5).

When 1 l of water was extracted with 200 μl of solvent, only about 50 μl were recovered because of losses due to solubility and evaporation. Thus, a concentration factor of $\times$20,000 was achieved. But since the extraction efficiency was only about 50% in the first extract (Table II) the true concentration factor was $\times$10,000.

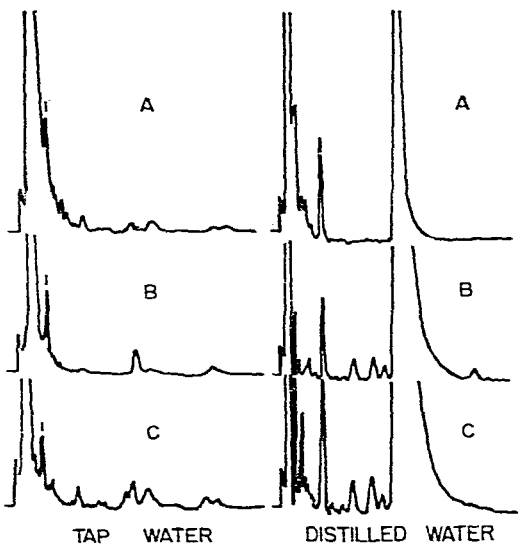

Fig. 4. Gas chromatograms of continuous steam distillation (A), continuous solvent extraction (B) and micro extraction (C) of tap and distilled waters.

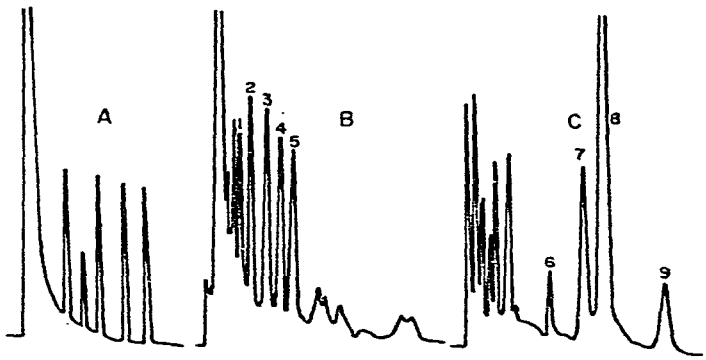

Fig. 5. Micro extraction chromatograms. A, Tap water + 50 μg/l hydrocarbons; flame ionization detection; temperature program; peaks: C_{10}, C_{11}, C_{12}, C_{14} and C_{16} hydrocarbons. B, Tap water + 10 ng/l pesticides; electron-capture detection; isothermal (235°); peaks: 1 = lindane, 2 = aldrin, 3 = heptachlor epoxide, 4 = α-*cis*-chlordane, 5 = dieldrin. C, Red River water; conditions as in B; peaks: 6 = dibutyl phthalate, 7 = butyl glycolyl butyl phthalate, 8 and 9 = phthalate esters.

TABLE II

RECOVERIES FROM TAP WATER USING MICRO EXTRACTION PROCEDURE

Substance	*Concentration*	*Recovery in 1st extract (%)*	*Rel. stand. dev. (%)**	*Total recovery in 3 extractions (%)*
Aldrin	10 ng/l	47.9	5.6	89.4
Heptachlor epoxide		58.5	8.2	91.3
α-*cis*-Chlordane		59.2	10.2	92.0
Dieldrin		62.2	10.0	92.6
n-Decane	50 μg/l	69.3	3.7	98.6
n-Dodecane		60.3	3.3	97.3
n-Tetradecane		56.0	3.9	96.7
n-Hexadecane		52.9	2.9	96.4
Dibutyl phthalate	2.5 μg/l	65.5	5.9	96.6
Butyl glycolyl butyl phthalate	25 μg/l	43.6	4.0	89.7

* 4 analyses of 4 extracts.

When 10 l of water were extracted with 10 ml of solvent, losses due to solubility and evaporation are proportionally less significant than with the micro-procedure and about 8 ml of solvent were recovered. Thus the concentration factor was about × 1250. The extraction efficiency will be higher than with the micro procedure but the concentration factor cannot exceed × 1250 without using a solvent concentration step.

The superior concentration factor of the micro method, the absence of a concentration step and speed of analysis are advantages in routine quantitative analyses of water samples.

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