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Note

Automated on-line trace enrichment and determination of organic compounds in ground and tap water by high-performance liquid chromatography

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There is great need for analytical methods suitable for determining concentrations in water of less than 0.1 μg/l of trace constituents, which is the EEC maximum allowed concentration of pesticides[1].

Sample loading for high-performance liquid chromatographic (HPLC) trace enrichment is effected on-line by changing the bottle containing the sample by the operator[2–5] or by filling an adequately dimensioned loop with a syringe[6], or off-line after preconcentration of the sample to a few millilitres and subsequent injection with a commercial liquid sampler.

An automated system to feed the enrichment column with the necessary large sample volume is described. The instrument setup allows the selection of the sample volume to be concentrated and the unattended processing of up to 32 water samples.

EXPERIMENTAL

Materials

All six port valves are pneumatically activated Valco type AC6W (Valco, Houston, TX, U.S.A.). The 16-port sampling valves are also pneumatically activated models (Valco type ASD16P), one of which is equipped with a binary encoder to indicate the position of the valve, corresponding to the sample number. The second valve is connected in parallel. The data system decodes the sample number from the injection sequence and activates the selection valve to direct the sample on to the concentration column. A magnetic micro gear pump (P1 in Fig. 1) is used to flush and fill the connecting tubes (Micropump Series Paragon P-11-361-500, 0–24 V d.c., flow range 0–6 ml/min; Micropump, Concord, CA, U.S.A.). The enrichment pump P2 is a constant-flow pump (Model LC 410; Kontron, Zürich, Switzerland) with remote flow-rate control. The eluent pump (P3) of the separation column is a constant-flow pump (Model A 300 CS; Gynkotek, Munich, F.R.G.). The timed switching events are delivered by the laboratory data system (Model 3357 LAS; Hewlett-Packard, Avondale, PA, U.S.A.)[7] It is equipped with electronic control modules (ECM Model 18653 B) and analogue-to-digital converters (A/D Model 18652 A) for data aquisition. The ECM provides a binary input of the sampling valve position and seven 110-V a.c. power outputs used to control the solenoid valves. These outputs are switched on and off independently by the system software (the chromatographic integration software)

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or by post-analytical user programs initiated by the chromatographic integration system software.

The binary encoder of the sampling valve (V-1) allows random access of the samples and is used to access the bottle of the calibration standards several times within an analytical sequence by the laboratory data system.

A programmable sequence timer with eight times exits of 110 V a.c. (Alpha Electronics, Stutensee, F.R.G.) can also be used to control the switching times without restriction of the overall chromatographic behaviour of the system if no adequate data system is available. Each solenoid valve may be electrically connected in parallel with 110 V a.c. relays to control external devices or functions. The programmable electronic timer restricts the use of the system to only 16 samples without random sample access.

A UV detector Model LC 786 (Kratos, Westwood, NJ, U.S.A.) was used.

Chromatographic conditions

The chromatographic columns (stainless steel, 4–12 cm × 4.6 mm I.D.) are packed with Nucleosil 100 C_{18}, particle size 5 or 10 μm (Macherey, Nagel & Co., Düren, F.R.G.). The eluents are mixtures of acetonitrile (E. Merck, Darmstadt, F.R.G.) and water containing 15–50% of the modifier at a flow-rate of 1 ml/min. The detector wavelength is set at 220 μm.

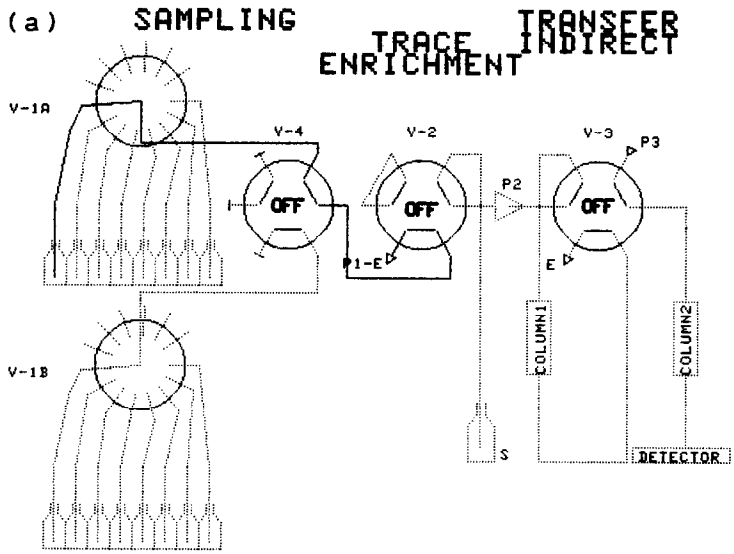
Procedure

The exits of the 16-port sampling valves (V-1A and V-1B) are connected through valve V-4 to the enrichment valve (V-2) (Fig. 1a and b).

The micro gear pump (P1-E) at the exit of the enrichment valve (V-2) sucks the sample through the 16-port valve directly from the bottle to waste and flushes the connecting tubes (Fig. 1b). After rotating the enrichment valve (V-2) into the ON position (Fig. 1c), the sample stream is directed through a constant-flow low-dead-volume pump (P2) and the switching valve (V-3) on to the enrichment column (column 1). During the enrichment step the flow of the pump P2 is set to a higher rate which reduces the sampling and overall analysis time. After the enrichment step, the valve V-2 is rotated back into the OFF position and the enrichment column is rinsed for a preset time period with a rinsing solvent(s) (Fig. 1d). The polarity of the rinsing solvent is selected so as not to elute the analytes from column 1. After rotating the transfer valve V-3 (ON position) the flow (P3) of the separation column 2 is directed on to the enrichment column 1 for a short transfer period (Fig. 1e). The analytes are transferred on to column 2. Finally, the analytes are eluted and detected after rotating the transfer valve (V-3) back into the OFF position (Fig. 1f). Fig. 1 illustrates the arrangement in the indirect transfer technique[8].

Standard preparation. Water completely free from organic substances in detectable amounts (Nanopure HPLC water purifier; Barnstead, subsidiary of Sybron, Newton, MA, U.S.A.) is used to prepare the standard solutions. Stock solutions of the compounds are first prepared at concentrations of 1 mg/ml in ethanol and thereafter diluted with water to the concentration range 0.05–1 ng/ml (0.05–1 ppb).

Sample analyses. Samples of ground and tap waters are analysed without any pretreatment. The sample containers are directly connected to the sampling valve by immersing 1/8-in. PTFE tubing. An immersible filter is connected to the PTFE tube if the samples are contaminated with particulates.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V-1B
V-4
V-2
V-3
P3
P2
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E
OFF
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OFF
COLUMN1
COLUMN2
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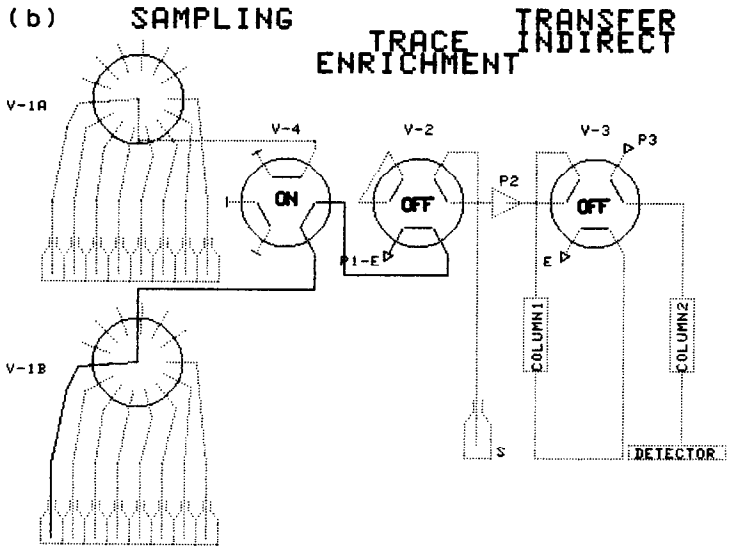
DETECTOR


(b)
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TRACE ENRICHMENT
TRANSFER
INDIRECT
V-1A
V-1B
V-4
V-2
V-3
P3
P2
P1-E
E
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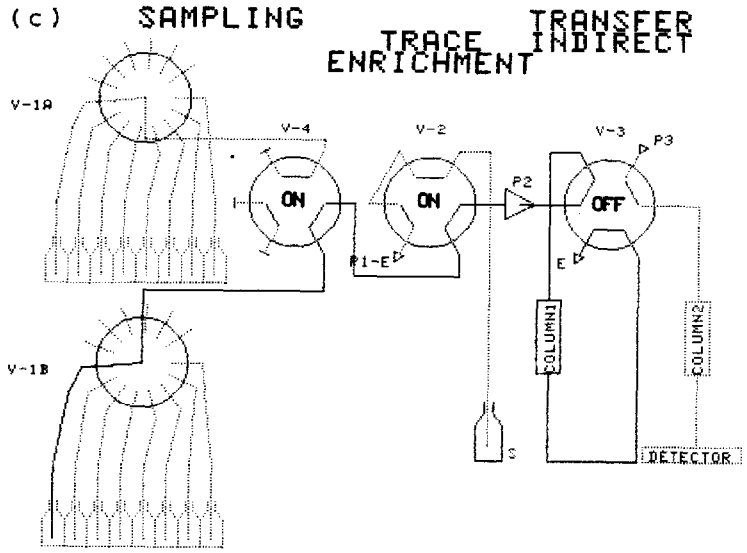
DETECTOR

Fig. 1.



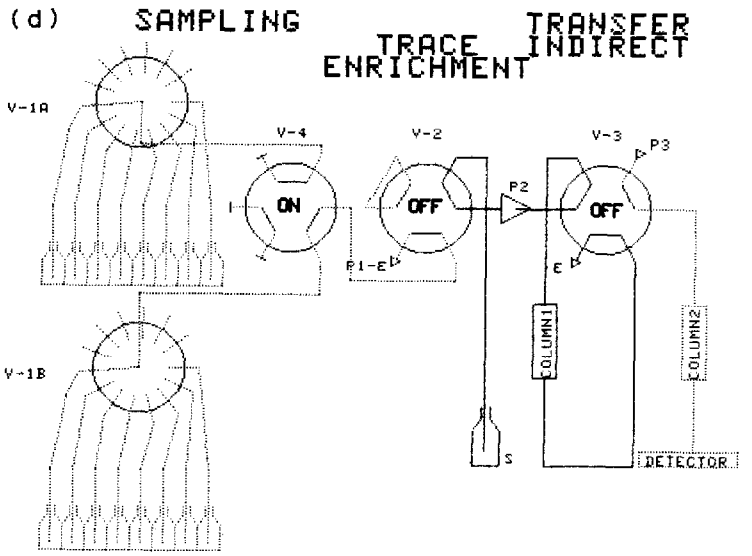


Fig. 1.

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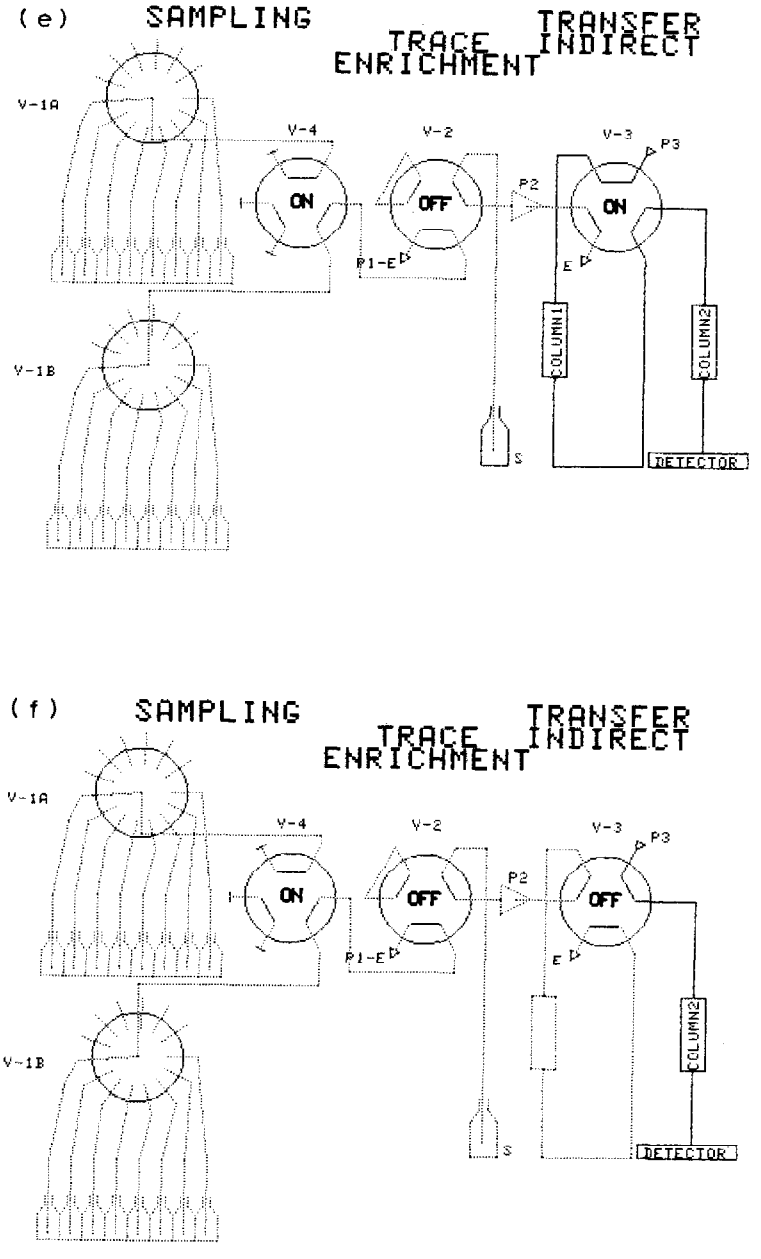


Fig. 1. Flow diagram of the automated enrichment and separation network designed to handle up to 32 samples. Dotted lines are standby positions; solid lines show the actual sample flow. V-1 to V-4, pneumatically actuated high-pressure valves; OFF = standby positions, ON = transfer positions. Valve V-4 is used to switch the flow from the sampling valves V-1A or V1B. (a), (b) Standby position, sample container connected to the rinsing pump (P1-E); (c) injection pump (P2) in-line with the sample container and the enrichment column; (d) injection valve (V-2) in standby position, enrichment column and pump (P2) are flushed with rinsing solvent; (e) transfer indirect with the mobile phase of the analytical column directed to the enrichment column and the analytical column; (f) elution of the analytical column.

Calibration. The chromatographic system is calibrated by enriching a preselected volume of the aqueous standard solutions. The resulting peak heights are used to calculate a linear regression curve.

RESULTS

Table I shows the structure of the compounds used to evaluate the performance of the enrichment and the chromatographic separation system. All these compounds are used as herbicides or are degradation products thereof.

The relative standard deviations (R.S.D.) of the measured peak heights from the calculated linear calibration graphs are given in Table II, and range from 1.5 to 19.8%. Four values from 39 calibration graphs show R.S.D. values higher than 10%. About 30 min per sample are required for the enrichment and subsequent on-line chromatographic determination.

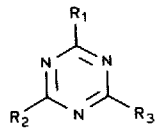
The linear calibration graphs were calculated from four concentrations in the range 1–20 ng in 20 ml of water. Each standard solution was measured at least twice. Metolachlor calibration graphs were calculated from standard concentrations of 2.5–50 ng in 50 ml of water.

DISCUSSION

Cross-contamination of the system is minimized as the sample feeding lines are flushed with the sample itself by the pump (P1-E) at the valve V-3 before directing the flow to the enrichment column. The enrichment pump and all connecting lines which are flushed with the sample are washed with the rinsing solvent (see also Fig. 1d).

TABLE I

COMPOUNDS EXAMINED



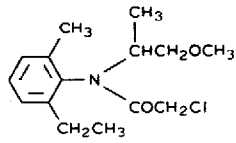
Compound	R_1	R_2	R_3
Atrazine	Cl	$NHCH_2CH_3$	$NHCH(CH_3)_2$
Simazine	Cl	$NHCH_2CH_3$	$NHCH_2CH_3$
Terbutylazine	Cl	$NHCH_2CH_3$	$NHC(CH_3)_3$
Terbutryn	SCH_3	$NHCH_2CH_3$	$NHC(CH_3)_3$
GS 26379	Cl	NH_2	$NHC(CH_3)_3$
G 28279	Cl	NH_2	$NHCH_2CH_3$
G 30033	Cl	NH_2	$NHCH(CH_3)_2$
Metolachlor			

TABLE II

CALIBRATION EXPERIMENTS

Compound	*Range of R.S.D. (%)*	*n*
Atrazine	1.9– 6.7	9
Simazine	1.5–10.8	5
Terbutylazine	4.5– 7.6	4
Terburyn	5.2– 5.6	2
GS 26379	1.7– 6.4	5
G 28279	2.8–14.2	5
G 30033	4.8–19.8	5
Metolachlor	3.6–12.5	4

Adsorption of the components to be analysed in the PTFE tubes or other components of the system was not detected. Standard and sample analyses were run under identical conditions (concentration and enrichment).

Depending on the separation problems, additional switching functions may be included in the chromatographic network to improve the separation[8].

CONCLUSION

This automated on-line enrichment and desorption technique maintains reproducible chromatographic adsorption conditions, as the same enrichment column is used throughout the analyses and reconditioning of this column is standardized.

To achieve the same sensitivity with on-line as with off-line enrichment techniques, a smaller volume of water sample had to be treated and the time required for concentration can therefore be proportionately reduced.

Calibration samples and analytical samples are run under identical conditions. The linearity of the calibration graph shows the integrity of the overall system, including the adsorption, desorption and final chromatographic separation. As demonstrated, the relative standard deviations of the calibration curves are in an acceptable range for trace analysis.

The method of on-line enrichment with an automated sampling device is obviously advantageous from the viewpoint of sensitivity, rapid sample handling and costs when large monitoring programmes are to be performed. About 600 samples of potable water of different origins were analysed, and demonstrated the superiority of this automated on-line procedure over the previously used labour-intensive off-line techniques with prepacked cartridges for sample enrichment.

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