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Large-volume injections in gas chromatography–atomic emission detection: an approach for trace-level detection in water analysis

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Abstract

The ruggedness and analytical performance of on-line capillary gas chromatography–atomic emission detection (GC–AED) have been studied using 100-μl injections of sample solutions in ethyl acetate, via a loop-type interface. A series of organophosphorus compounds were selected as test analytes; they were monitored using the carbon, sulphur, nitrogen, chlorine, bromine and phosphorus channels. The system showed no flame-outs or other maintenance problems even after 300 large-volume injections. The analytical potential of the system, expressed in terms of repeatability, linearity and minimum detectable amount, was not affected and a 100-fold increase in analyte detectability, in terms of concentration units, compared with a conventional 1-μl injection was observed.

As an application, GC–AED was combined off-line with solid-phase extraction. Several environmental contaminants were preconcentrated from river and tap water samples, and 20% (100 μl) of the ethyl acetate eluent were directly analysed. With a sample volume of only 10 ml, the detection limits of the organophosphorus pesticides typically were ca. 0.1 μg/l.

1. Introduction

Atomic emission detection (AED) is a selective detection method specifically designed for capillary gas chromatography (GC) which is, in principle, capable of detecting any element except helium [1]. Although the minimum detectable amounts vary greatly per element [2] and, for several elements, are distinctly higher than are found with other selective detection systems such as nitrogen–phosphorus (NPD) or electron-capture (ECD) detection [3], the multi-element detection capability makes AED highly interesting for, e.g., rapid screening and surveying studies. The information so obtained will often be complementary to that collected by means of GC with mass spectrometric (MS) detection. In order to improve the analyte detectability of GC–AED and, also, to explore the potential of an on-line coupling of column liquid chromatography (LC) or LC-type solid-phase extraction (SPE) approaches, i.e. SPE–GC–AED (cf. Refs. [4–6]), the use of large-volume injections of, typically, 100 μl has been studied in this paper. Compared with the 1-μl injections conventionally used in capillary GC, such large-volume injections should improve analyte detectability (in concentration units) by about two

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orders of magnitude and, consequently, should make GC–AED highly suitable for trace-level environmental analysis. In the present project, from among the interfaces commonly used to enable large-volume injections [7], the loop-type interface was selected because it is the least complicated to operate and, actually, allows injection volumes up to several millilitres.

In work on on-line SPE–GC, ethyl acetate is often used as a desorption solvent [8–10]. Since SPE–GC–AED is one of the goals we have in mind (see above), ethyl acetate was also used in this study. The several approaches to large-volume injection GC and on-line SPE–GC have been discussed in the recent past [4–6]. Although there are apparently no real problems with such techniques irrespective of the detector selected, this will probably not be true for rather vulnerable detection devices such as a Fourier transform infrared detector or an AED system. The primary goal of the present study was therefore to test, and improve, the ruggedness of the GC–AED system. Eleven organophosphorus pesticides (OPPs) were selected as model compounds. They contain several hetero atoms (Cl, Br, S, P, N, O) which for the present study has the advantage that several AED channels can be tested. Finally, since OPPs can be extracted rather easily from water on C_{18}-bonded silica or polymer sorbents [11], the off-line combination of SPE and GC–AED was briefly studied as a first attempt to assess the practicality of on-line SPE–GC–AED.

2. Experimental

2.1. Chemicals

Benzothiazole, bromophos-ethyl, coumaphos, diazinon, ethion, fenchlorphos, mevinphos, parathion-ethyl, pyrazophos, sulphotep, tetrachlorvinphos, triazophos and triphenylphosphine oxide were obtained from Riedel-de Haën (Seelze, Germany). The structures of the analytes are shown in Fig. 1. Ethyl acetate and HPLC-grade water were purchased from J.T. Baker (Deventer, Netherlands) and methanol from Rathburn (Walkerburn, UK). High-purity helium gas (5.0 purity grade) was obtained from Union Carbide (Westerlo, Belgium). Stock solutions of the analytes were prepared in methanol and ethyl acetate. Spiked solutions were prepared by spiking water samples with an aliquot of the stock solution.

All river water samples were filtered over 0.45-μm membrane filters (Schleicher & Schuell, Dassel, Germany), Amsterdam tap water was directly used for preconcentration without any pretreatment.

2.2. GC equipment

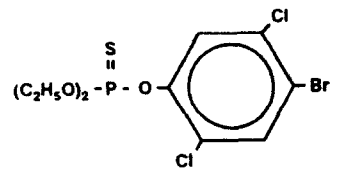
A Hewlett-Packard (Avondale, CA, USA) Model 5890 Series II gas chromatograph with a Hewlett-Packard Model 5921 A atomic emission detector and a Hewlett-Packard Model 7673 autosampler were used for GC–AED.

The GC–AED large-volume injection system is shown in Fig. 2. It consists of a loop-type interface with a 100-μl stainless-steel loop, a 9 m × 0.53 mm I.D. diphenyltetramethyldisilazane-deactivated retention gap (BGB Analytik, Zurich, Switzerland), a 3 m × 0.32 mm I.D. DB-17 (J & W, Folsom, CA, USA) retaining precolumn with a film thickness of 0.25 μm and a 25 m × 0.32 mm I.D. DB-17 analytical column with a film thickness of 0.25 μm. Connections were made with press-frit connectors (Chrompack, Middelburg, Netherlands). The early solvent vapour exit (SVE) was opened and closed with a 24 V pinch solenoid valve (Type S 104; Sirai, Milan, Italy) which clamped a piece of 2 mm O.D. silicone tubing. Helium was used as carrier gas.

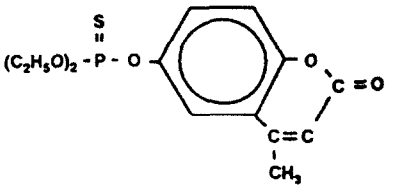
Large-volume injections with the loop-type interface were made at a head pressure of 200 kPa and a temperature of 100°C (6 min hold time), followed by temperature programming to 270°C (final hold time, 5 min) at a rate of 20°C /min. The SVE open time was 90 s. Relevant AED parameters are recorded in Table 1.

2.3. SPE system

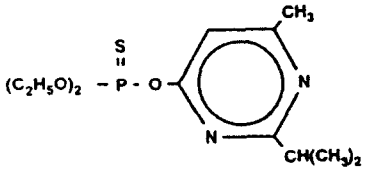
Trace enrichment of the OPPs from water samples was performed on a Prospekt sample preparation system of Spark Holland (Emmen,



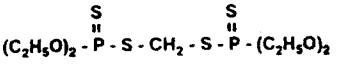
Bromophos-ethyl



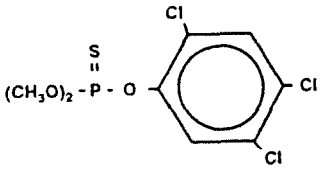
Coumaphos



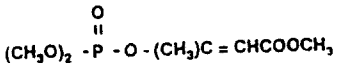
Diazinon



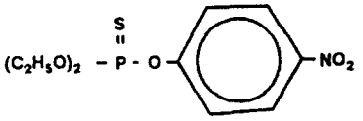
Ethion



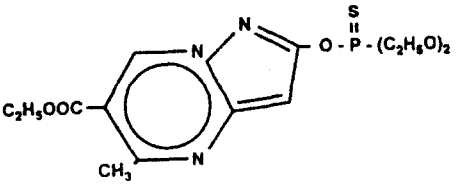
Fenchlorphos



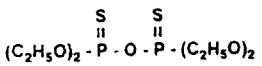
Mevinphos



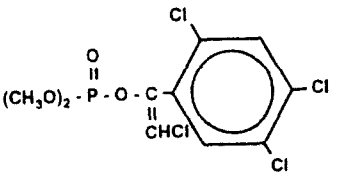
Parathion-ethyl



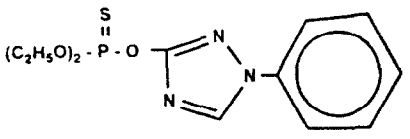
Pyrazophos



Sulphotep



Tetrachlorvinphos



Triazophos

Fig. 1. Structural formulae of the organophosphorus pesticides used as test analytes.

Netherlands) [12]. The Prospekt system contains three pneumatic Rheodyne six-port valves, an automated cartridge exchanger and a solvent delivery unit equipped with a six-port solvent delivery valve and single-piston LC pump. Timed events such as valve switching, solvent

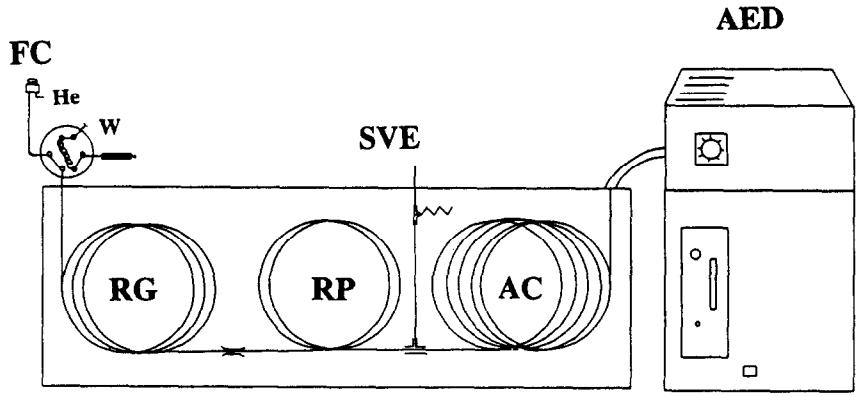


Fig. 2. Instrument configuration of large-volume injection GC–AED. AC = Analytical column; FC = flow controller; RG = retention gap; RP = retaining precolumn; SVE = solvent vapour exit; W = waste.

selection and on/off switching of auxiliary channels could be programmed via software on the Prospekt controller unit.

Water samples were preconcentrated on 10 mm × 1.5 mm I.D. precolumns packed with PLRP-S (15–25 μm) styrene–divinylbenzene copolymer (Spark Holland). A MicroMetric pump from Milton Roy (Riviera Beach, FL, USA) was used for delivering the desorption solvent ethyl acetate, which was collected in a GC autosampler vial (Chrompack). Prior to use the cartridges were conditioned with 500 μl of ethyl acetate and 2.5 ml of HPLC-grade water. A 10- or 50-ml water sample was preconcentrated at a flow-rate of 5 ml/min, and, next, clean-up was carried out with 1 ml of HPLC-grade water. The cartridge was dried by 30 min of nitrogen gas purging at 3 bar. Finally desorption was carried out with 500 μl of ethyl acetate at a flow-rate of 100 μl/min.

Table 1
AED parameters used for GC–AED

Element	Wavelength (nm)	Scavenger gas	Make-up flow (He, ml/min)
C	193.0	H_2, O_2	40
S	181.4	H_2, O_2	40
N	174.2	H_2, O_2	40
P	185.9	H_2	80
Cl	480.2	O_2	40
Br	478.6	O_2	40

Spectrometer purge rate: 2 l/min of nitrogen; transferline temperature: 300°C; cavity temperature: 300°C; window purge flow-rate: 40 ml/min; solvent vent time: 7 min; waterbath temperature: 65°C.

3. Results and discussion

3.1. Large-volume injections: system ruggedness and performance

The first aim of the study was to test the robustness and analytical performance of the GC–AED system or, rather, of the AED system as a detector when using large-volume injections. As regards the latter aspect, studying element responses in terms of linearity, repeatability and analyte detectability appeared to be good criteria. The injection volume selected was 100 μl, because this is a typical volume for both LC–GC heart-cut and SPE–GC desorption operations. Besides, the two-order magnitude difference with 1-μl injections should create sufficient trace-enrichment potential.

Preliminary experiments using the original set-up —i.e. without an early solvent vapour exit— showed that the injection of 100-μl samples in ethyl acetate did not cause any flame-outs [13]. However, the evaporation rate through the AED solvent vent was rather low. Consequently, too much time was required to evaporate the solvent and early-eluting compounds were lost in the

solvent peak. However, if a second, so-called early solvent vapour exit (SVE, cf. Fig. 2) was inserted between the retention gap and the retaining precolumn, the solvent evaporation rate became sufficiently high to prevent such problems. At an oven temperature of 100°C, the evaporation of 100 μl of ethyl acetate now took 78 s. The SVE was closed after 90 s.

With the complete set-up of Fig. 2, the ruggedness of the GC–AED set-up under large-volume-injection conditions turned out to be excellent. No plasma flame-outs occurred even after 300 injections. The combined chromatograms obtained after three injections (the C, S and N channels can be monitored simultaneously, as can the Cl and Br channels; the P channel had to be monitored separately) of 100 μl of a standard solution of the eleven OPPs (100 pg/μl in ethyl acetate or 10 ng injected per compound) is shown in Fig. 3. The six traces shown are all of good quality. As regards the analytes, bromophos-ethyl is the most interesting compound because it shows up in five out of the six traces. The repeatability obtained for these injections was comparable with the repeatability obtained with 1-μl injections (see Table 2). Actually, the R.S.D. values themselves are quite satisfactory for all but the N channel. This may well be due to the fact that the injected amounts were rather close to the detection limit with this relatively insensitive channel (10 ng corresponds to S/N ratios of 3–10; see Table 3 below). We have no explanation for the poor repeatability observed for tetrachlorvenphos with 100-μl, but *not* 1-μl, injections on all three relevant channels.

The linearity of the AED response was tested in the 0.5–50-ng range both for 100-μl and 1-μl injections for all six elements monitored (six data points; $n = 2$). For the C, S and N channels, the regression coefficients, R^2, were equal to or better than 0.992, 0.9981 and 0.9968, respectively. There was one exception only, viz. pyrazophos (N channel) with $R^2 = 0.9647$ for 1-μl as against, fortunately, $R^2 = 0.9996$ for 100-μl injections. The R^2 values for the Cl, Br and P channels were at least 0.9984, 0.9998 and 0.9974, respectively. Actually, the results for the 100-μl injections were slightly better than those for the 1-μl studies.

In Table 3 the absolute detection limits (S/N = 3) of all OPPs for 100-μl injections are given, both per compound and per element. It is evident, as is also known from literature [1,14], that from among the six channels tested, the S and P channels display the best sensitivity. With analyte detection limits of below 100 pg (S) and 50–300 pg (P), respectively, for most of the OPPs tested, GC–AED with 100-μl injections

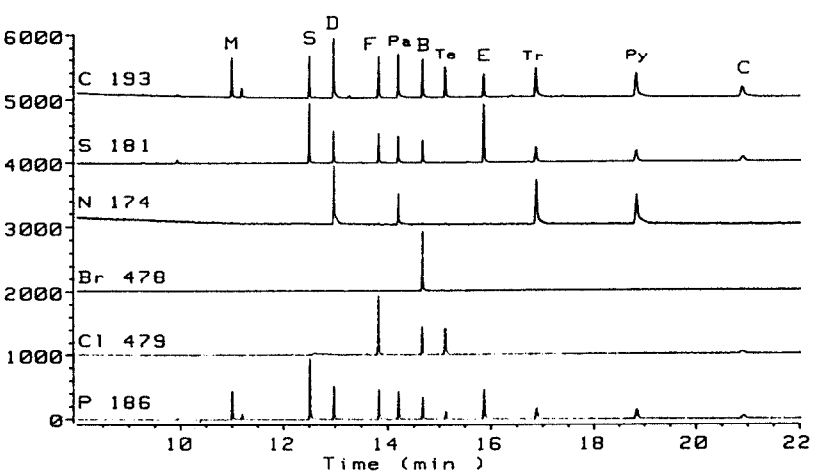


Fig. 3. GC–AED chromatogram (recording of the C, S, N, Cl, Br and P traces) obtained after 100-μl injections of OPPs in ethyl acetate (100 pg/μl). Peaks; M = mevinphos; S = sulphotep; D = diazinon; F = fenchlorphos; Pa = parathion-ethyl; B = bromophos-ethyl; Te = tetrachlorvinphos; E = ethion; Tr = triazophos; Py = pyrazophos; C = coumaphos.

Table 2
Relative standard deviations (R.S.D.s; $n = 8$) of 100-μl/1-μl injections of OPP mixture in ethyl acetate

Compound	R.S.D. (%) for channel:					
	C	S	N	Cl	Br	P
Mevinphos	2.2/1.6	–	–	–	–	3.7/3.2
Sulphotep	1.8/0.9	2.0/1.9	–	–	–	3.9/2.7
Diazinon	1.9/1.0	2.7/1.9	12/6.6	–	–	5.1/3.1
Fenchlorphos	3.1/2.1	2.7/3.2	–	2.4/1.6	–	4.1/3.2
Parathion-ethyl	2.8/5.0	2.9/2.1	10/13	–	–	5.2/3.7
Bromophos-ethyl	2.6/3.7	2.6/2.9	–	2.9/2.3	1.4/3.2	3.7/5.0
Tetrachlorvinphos	9.9/3.7	–	–	14/4.2	–	21/5.7
Ethion	2.9/1.9	2.9/2.8	–	–	–	3.7/3.6
Triazophos	3.6/3.5	5.0/4.2	17/13	–	–	7.0/6.7
Pyrazophos	3.0/5.1	4.3/7.4	26/13	–	–	4.8/8.0
Coumaphos	3.6/4.9	4.8/5.8	–	6.8/17	–	5.5/6.1

Analyte concentrations 100 pg/μl and 10 ng/μl for 100- and 1-μl injections, respectively; i.e., injected amount, 10 ng.

obviously becomes attractive for (selective) trace-level environmental analysis. Further it should be noted that the relatively high detection limits observed for the late-eluting pyrazophos and coumaphos are caused by their larger peak width rather than due to a lower element response.

Finally, a direct comparison of the conventional 1-μl and large-volume 100-μl approach was made by injecting all OPPs in standard solutions containing 10 ng/μl and 100 pg/μl of analyte, respectively. That is, the injected amount of the analytes was the same, i.e. 10 ng, in both series. The results showed that the AED response for the 1- and 100-μl injections was the same within 10–20% for all channels and all analytes tested. In other words, the expected 100-fold increase in analyte detectability (in terms of concentration units) was indeed found.

3.2. Off-line SPE–GC–AED

In order to demonstrate the usefulness of 100-μl injection GC–AED and to provisionally explore the potential of on-line SPE–GC–AED, large-volume GC–AED was combined off-line with SPE, using spiked surface and tapwater as real-life samples. As a first test, the analyte

Table 3
Detections limits (pg; $S/N = 3$) per compound (element) for 100-μl injections of OPPs in ethyl acetate

Compound	Detection limit (pg) for channel					
	C	S	N	Cl	Br	P
Mevinphos	575 (220)	–	–	–	–	250 (35)
Sulphotep	300 (90)	20 (4.0)	–	–	–	40 (8)
Diazinon	225 (100)	40 (4.0)	975 (90)	–	–	80 (9)
Fenchlorphos	175 (50)	40 (4.0)	–	240 (80)	–	80 (7)
Parathion-ethyl	325 (140)	40 (4.5)	2000 (100)	–	–	110 (12)
Bromophos-ethyl	375 (110)	60 (4.5)	–	330 (60)	560 (110)	120 (10)
Tetrachlorvinphos	1250 (410)	–	–	860 (330)	–	370 (30)
Ethion	500 (140)	20 (6.0)	–	–	–	75 (12)
Triazophos	1100 (510)	90 (9.0)	1650 (220)	–	–	360 (35)
Pyrazophos	850 (380)	140 (12)	3000 (330)	–	–	450 (35)
Coumaphos	1550 (730)	240 (21)	–	3900 (380)	–	900 (75)

Table 4
Recoveries (and R.S.D.s; $n = 5$) of eleven OPPs in off-line SPE–GC–AED

Compound	Recovery (%)	R.S.D. (%)
Mevinphos	87	7
Sulphotep	95	6
Diazinon	110	9
Fenchlorphos	85	4
Parathion-ethyl	95	10
Bromophos-ethyl	42	22
Tetrachlorvinphos	86	9
Ethion	72	11
Triazophos	104	5
Pyrazophos	96	4
Coumaphos	102	18

For experimental details, see text.

recoveries and the repeatability of the procedure were determined by spiking HPLC-grade water with 1 μg/l of all eleven OPPs and preconcentrating 10 ml of the spiked sample on a SPE cartridge. For desorption, 500 μl of ethyl acetate proved to be sufficient. From the eluate, 100 μl (or 20%) were injected into the GC–AED system. The results which were determined using the P 186 channel and which are reported in Table 4 show that good recoveries (85–110%) were obtained for all but two test analytes (ethion and bromophos), while the R.S.D. values are satisfactory for such trace-level work. Since demonstration of the general usefulness of the procedure rather than a dedicated application was the primary aim of the study, no attempt was made to improve the recoveries of ethion and bromophos.

As a real-life application, the off-line SPE–GC–AED chromatograms recorded for 10 ml of river Rhine water without and with a 1-μg/l OPP spike are shown in Fig. 4. It is obvious that the detection limits are in the order of 0.1–0.5 μg/l for all compounds; that is, they are below the alert and alarm levels for pesticides in surface water, which are 1 and 3 μg/l, respectively. It is also clear that none of the selected OPPs is present in the surface water sample at such levels.

As another example, 50 ml of tap water were preconcentrated using the same procedure as before, the only difference being that 340 μl of ethyl acetate were now used for desorption. Chromatograms of blank tap water, and tap water spiked with 0.1 μg/l of triphenylphosphine oxide (TPPO) are shown in Fig. 5. The obvious presence of TPPO at a concentration of 0.05 μg/l was confirmed by means of on-line SPE–

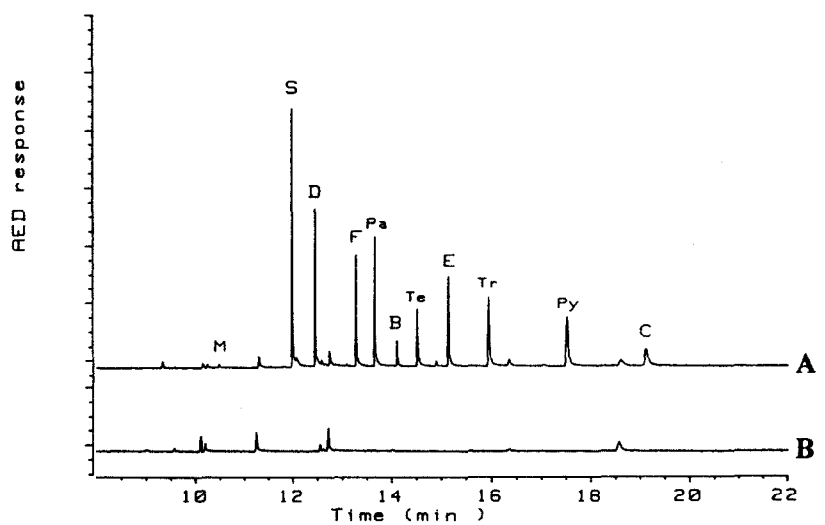


Fig. 4. GC–AED chromatograms (P trace) obtained after injection of a 100-μl aliquot (20%) of the ethyl acetate extract, resulting from preconcentration by means of SPE, of 10 ml of river Rhine water: (A) spiked with 1 μg/l of OPPs (for peak assignment, see Fig. 3), (B) blank.

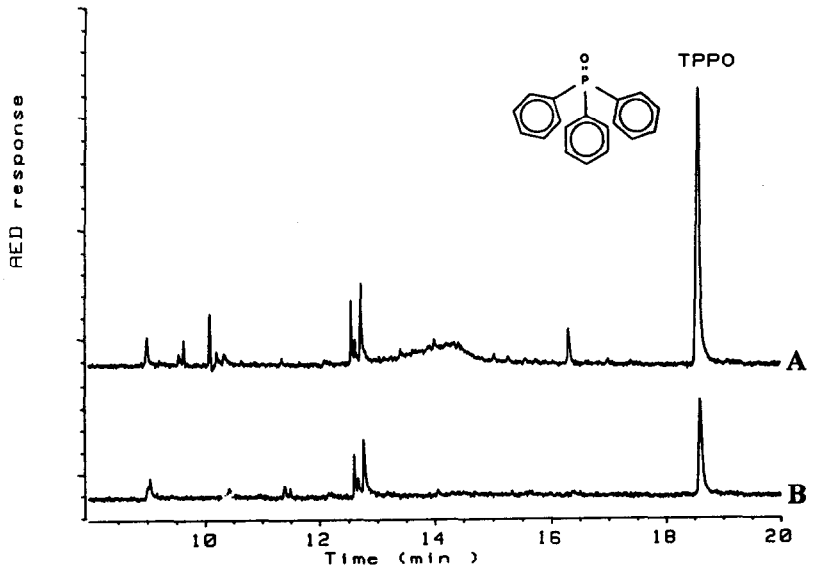


Fig. 5. GC–AED chromatograms (P trace) obtained after injection of a 100-μl aliquot (30%) of the ethyl acetate extract, resulting from preconcentration by means of SPE, of 50 ml Amsterdam tap water: (A) spiked with 0.1 μg/l of TPPO, (B) blank.

GC–MS (data not shown). From Fig. 5B one can calculate that the detection limit under the experimental conditions used (30% analyte transfer from SPE to GC–AED) is ca. 0.02 μg/l.

A final example deals with the analysis of a sample from the river Meuse in which benzothiazole (for structure, see Fig. 6) was suspected to be present [15]. 10 ml of river Meuse water were preconcentrated on a cartridge and after desorption with ethyl acetate, a 20% aliquot was injected and analysed by monitoring the C, N and S channels of the GC–AED system. The traces of Fig. 6A–C nicely illustrate the identification power of the present procedure in real-life samples, and the quantification potential even at around the 1 μg/l level (Fig 6D). Of course, the additional advantage that the three element channels can be covered in one run, will not be encountered in every study!

4. Conclusions

Contrary to what is often suggested, large-volume injections of up to 100 μl can be used in GC–AED to enhance analyte detectability without any experimental (flame-out) or maintenance problems. Linearity and repeatability are according to expectations. Two real-life applications (dealing with surface water) illustrate that environmental pollutants such as organophosphorus pesticides and benzothiazole can be identified at, typically, the 0.1–0.5 μg/l level when using 10-ml samples. In tapwater TPPO could be identified at the 0.05 μg/l level when using 50-ml samples.

The present preliminary studies on SPE combined off-line with GC–AED, with an analyte transfer of typically some 20%, strongly suggest that on-line SPE–GC–AED using 10–50-ml water samples will be a useful addition to the list of sophisticated procedures for the trace-level analysis of organic pollutants in water samples. Current research is aimed at setting up such a system.

Acknowledgement

The present work was carried out within the framework of the Rhine Basin Program (Amsterdam/Waldbronn). The authors thank Hew-

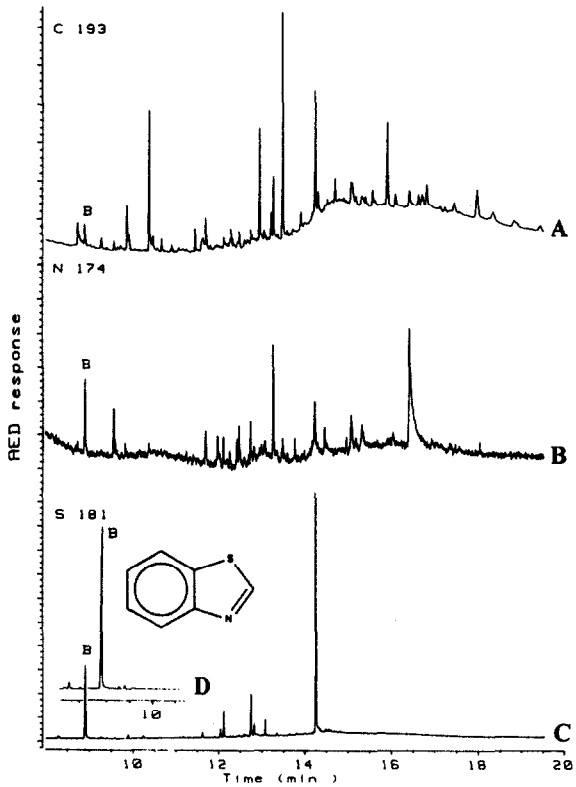


Fig. 6. GC–AED chromatograms (P trace) obtained after injection of a 100-μl aliquot (20%) of the ethyl acetate extract, resulting from preconcentration by means of SPE, of 10 ml of river Meuse water; (A) C trace, (B) N trace, (C) S trace; (D) S trace of the chromatogram obtained after injection of 100 μl of benzothiazole in ethyl acetate (20 pg/l).

lett-Packard for putting the GC–AED combination at their disposal.

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