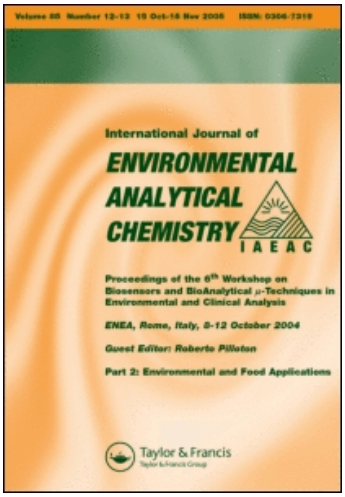

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Louter, A. J. H. , Rinkema, F. D. , Ghijsen, R. T. and Brinkman, U. A. Th.(1994) 'Rapid Identification of Benzothiazole in River Water With On-Line Solid-Phase Extraction-Gas Chromatography-Mass Selective Detection', International Journal of Environmental Analytical Chemistry, 56: 1, 49 — 56
To link to this Article: DOI: 10.1080/03067319408044416
URL: http://dx.doi.org/10.1080/03067319408044416

Intern. J. Environ. Anal. Chem., Vol. 56, pp. 49-56
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RAPID IDENTIFICATION OF BENZOTHIAZOLE IN RIVER WATER WITH ON-LINE SOLID-PHASE EXTRACTION-GAS CHROMATOGRAPHY-MASS SELECTIVE DETECTION

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(Received, 16 August 1993; in final form, 20 August 1993)

Solid-phase extraction coupled on-line with gas chromatography-mass spectometry and off-line with gas chromatography-atomic emission detection is shown to be a rapid technique for the trace-level determination and provisional identification of (an) organic pollutant(s) in surface water.

KEY WORDS: SPE-GC, water samples, solid phase extraction, GC-MS, GC-AED, confirmation, benzothiazole.

INTRODUCTION

The identification of unknown pollutants in river water samples requires the use of sophisticated analytical techniques which can provide adequate structural information. Especially if early warning is the primary goal of the analysis, provisional identification should be carried out rapidly. In our experience, on-line liquid chromatography-capillary gas chromatography (LC-GC) can efficiently be used to achieve this aim. In such a situation, the LC part of the system essentially consists of a small pre-column (typically dimensions: (2–10) mm × (2–4.6) mm I.D.) packed with a hydrophobic stationary phase, which is used for analyte trace enrichment and sample clean-up. In other words, this system actually is an on-line solid-phase extraction-GC (SPE-GC) water analyser. The set-up and automation of the analyser have been reported in a recent paper[1]. Its practical usefulness and robustness are, however, still a matter of some debate. In order to demonstrate the potential of SPE-GC with mass selective detection (SPE-GC-MSD) in trace-level analysis, we therefore report a recent real-life application in the present short communication.

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EXPERIMENTAL

Chemicals

Ethyl acetate, methanol and HPLC-grade water were purchased from J. T. Baker (Deventer, the Netherlands). The river water sample was filtered through a 0.45 μm membrane filter (Schleider & Schuell, Dassel, Germany) prior to preconcentration. A stock solution of benzothiazole (Riedel de Haen, Seelze, Germany) was prepared in methanol. Spiked solutions were prepared by adding an aliquot of the stock solution to water samples.

The river water sample was taken on March 15, 1993 from the river Meuse at Keizersveer, the Netherlands and analysed on March 24, 1993.

The SPE system

Trace enrichment was performed on a PROSPEKT sample preparation system of Spark Holland (Emmen, the Netherlands). The PROSPEKT system (see Figure 1) consists of three pneumatic Rheodyne six-port valves, an automated cartridge exchanger and a solvent delivery unit (SDU) equipped with a six-port solvent delivery valve and a single piston LC pump. Timed events such as valve switching, solvent selection and switching auxiliary channels on/off could be programmed via software on the PROSPEKT controller unit.

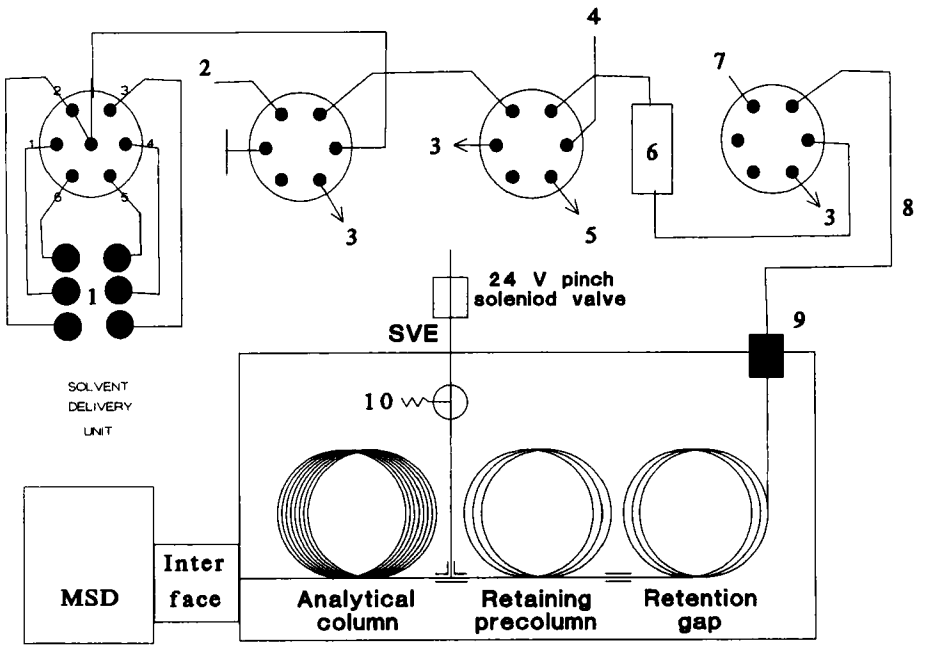


Figure 1 Set-up of system for automated on-line SPE-GC with MSD detection. 1, solvents; 2, nitrogen gas; 3, waste; 4, ethyl acetate pump; 5, prepressurizing restriction; 6, PLRP-S precolumn; 7, restriction; 8, interfacing capillary; 9, on-column injector; 10, SVE restriction.

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 metering pump from Milton Roy (Riviera Beach, FL, U.S.A.) was used for delivering the desorption solvent ethyl acetate.

A 0.60 m × 100 µm PEEK capillary coupled to a 0.15 m × 110 µm I.D. stainless-steel capillary was used for interfacing the PROSPEKT module with the GC on-column injector.

GC System

GC-MSD. A Hewlett-Packard (Palo Alto, CA, USA) Model 5890 Series II gas chromatograph equipped with a pressure-programmable on-column injector and a Model 5971A mass selective detector was used for GC analysis. The injector was connected to a 5 m × 0.32 mm I.D. retention gap deactivated with diphenyltetramethyldisilazane (DPTMDS) (BGB Analytik, Zürich, Switzerland), a 3 m × 0.20 mm I.D. retaining precolumn and a 46 m × 0.20 mm I.D. capillary GC column, both containing BGB-5 (5% diphenyl-polysiloxane and 95% dimethyl siloxane (BGB Analytik)) with a film thickness of 0.12 µm. Helium was the carrier gas at an inlet pressure of 200 kPa. Connections were made with conventional glass press-frits, a glass press-frit Y-piece (BGB Analytik) and a Swagelock T-piece which was connected to a solvent vapour exit.

GC-AED. A Hewlett-Packard Model 5890 Series II gas chromatograph equipped with a Model 5921A Atomic Emission Detector was used for GC-AED. The GC was equipped with a loop-type interface[2] with a 100 µl loop, connected to a 9 m × 0.53 mm I.D. retention gap, a 3 m × 0.32 mm I.D. DB-17 (J & W, Folsom, CA, U.S.A.) retaining precolumn and a 25 m × 0.32 mm DB-17 analytical column with a film thickness of 0.25 µm.

The relevant parameters for GC-MSD and GC-AED operation are presented in Table 1.

Table 1 Relevant parameters in GC-MSD and GC-AED analysis.

Parameter	*GC-MSD*	*GC-AED*
Temperature programming		
Initial temperature (°C)	85	100
Initial hold time (min)	7	6
Rate (°C/min)	10	20
Final temperature	280	270
Final hold time (min)	10	5
Carrier gas	He	He
SVE open time (min)	2.2	1.2
Column head pressure	200	140
Interface temperature (°C)	290	
Mass range (amu)	35–450	
Scans/sec	1.7	
Threshold	500	
Element wavelength (nm)		
C		193.031
S		181.379
N		174.261
Scavenger gas		O_2/H_2
Make-up flow (ml/min)		75

On-line SPE-GC-MSD

Trace enrichment of the water samples was performed using the PROSPEKT according to a previously described method[1], which essentially consists of preconcentration of 10 ml of sample (1 ml/min), clean-up with 1 ml of HPLC-grade water and purging with nitrogen gas for 30 min (at ambient temperature). Desorption was carried out with 90 µl of ethyl acetate which was introduced into the GC using partially concurrent solvent evaporation (85 µl/min) at a temperature of 85°C. The actual transfer started when 0.75 min time had elapsed and lasted 1.05 min. At the same time the SVE was opened and the inlet pressure of the GC was raised from 200 to 290 kPa for 2.1 min. The observed solvent evaporation rate was 63 µl/min. The SVE was closed after 2.2 min, i.e. just before complete evaporation of the solvent; next, the inlet pressure was decreased to 200 kPa.

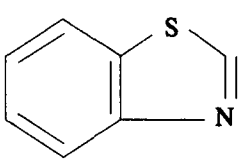
After desorption, the PLRP-S cartridge was flushed with an additional 85 µl of ethyl acetate as clean-up step prior to reconditioning and re-use.

Off-line SPE with GC-AED

Sample preparation was the same as with the on-line procedure except for the desorption volume, which now was 500 µl of ethyl acetate. From this volume, 100 µl were injected on the GC-AED by means of a loop-type interface[2].

RESULTS AND DISCUSSION

GC-MSD. A sample suspected to contain a relatively high concentration of benzothiazole was subjected to SPE-GC-MSD using the procedure described above. The sample volume analysed was only 10 ml. In the chromatogram, shown in Figure 2, trace A, a rather large peak (denoted as 1) appeared at a retention time of 14.8 min. Recording of the mass spectrum showed the base peak to be at m/z = 135, with the peak at m/z = 137 probably being a sulphur isotope peak (M + 2, one S atom), since its intensity is too high for a C14 isotope peak of such a relatively small molecule. The molecular weight of 135 indicated the presence of at least one nitrogen atom, and the intensity at m/z=136 (M+1) suggested the presence of 7–8 carbon atoms. The combined data indeed indicate the presence of benzothiazole, as was further confirmed by the good match of the mass spectrum with that in the NBS library (see Figures 3A and B).



Structure of benzothiazole

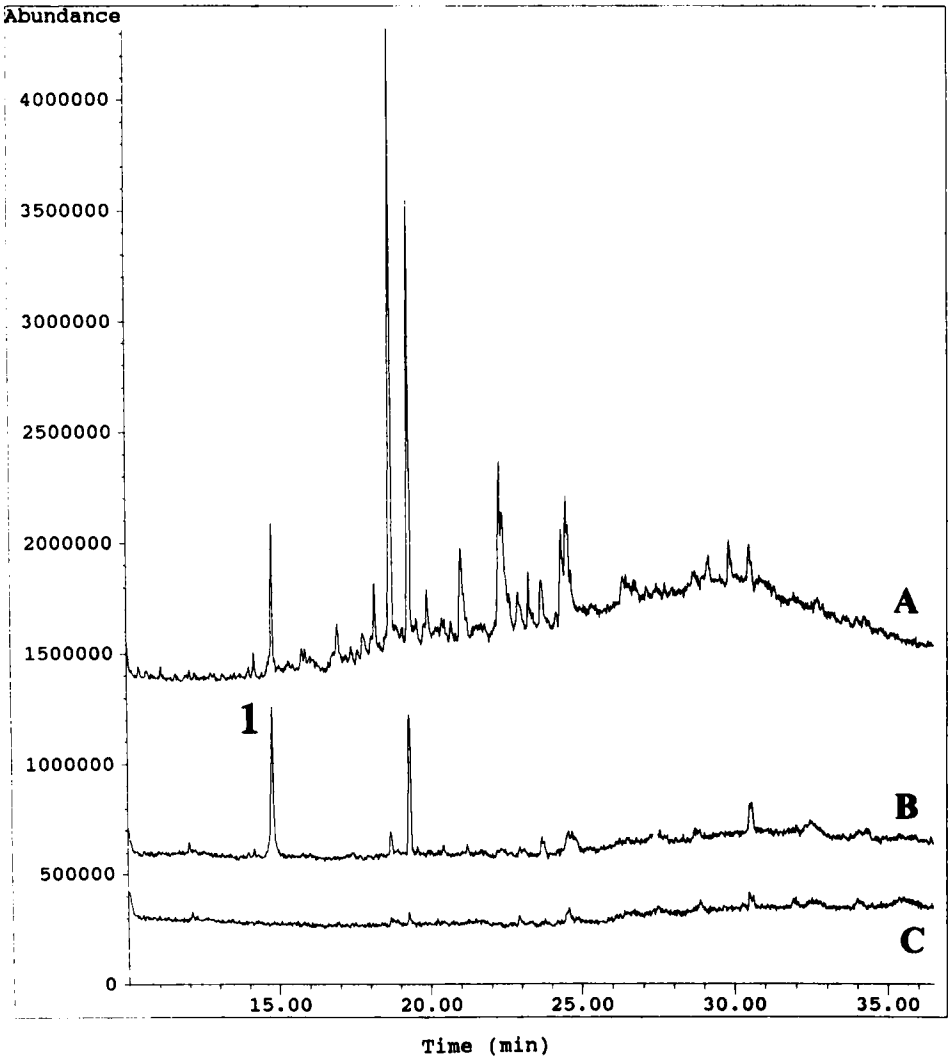


Figure 2 SPE-GC-MSD chromatograms obtained after trace enrichment of **(A)** 10 ml of river Meuse water sampled at Keizersveer on March 15, 1993, **(B)** 10 ml of HPLC-grade water spiked with 1 μg/l of benzothiazole, and (C) system blank (conditioning, clean-up and desorption). Peak 1 designates benzothiazole.

As the next sample, 10 ml of HPLC-grade water spiked with 1 μg/l of benzothiazole were analysed (Figure 2, trace B). With identical retention time and mass spectrum (not shown), this one-point calibration showed the suspected pollutant to be present at a level of 1 ± 0.1 μg/l; actually, 1 μg/l is the so-called European Community alert level for pesticides in surface water. As a further verification of the analytical integrity of the total procedure, a sample blank—i.e. the SPE-GC procedure (conditioning plus clean-up) excluding the sample load-

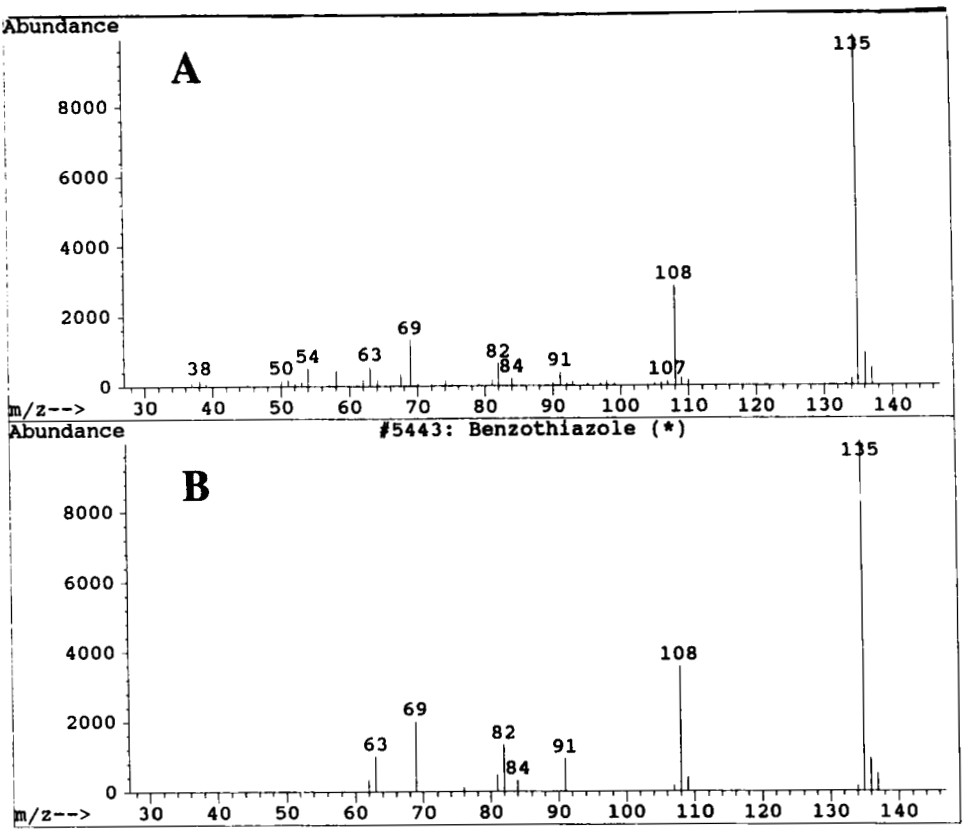


Figure 3 Mass spectra of (**A**) observed compound at 14.8 min, and (**B**) benzothiazole from NBS library.

ing—was run to demonstrate the absence of any interferences and/or carry-over effects (Figure 2, trace C). The recovery of benzothiazole with SPE-GC-MSD was 80 ± 12 % (n=3) at a level of 1 µg/l. The whole procedure of confirmation and quantification took less than three hours, showing that on-line SPE-GC-MSD can indeed provide rapid information.

GC-AED. In recent studies, we have explored the use of large-volume injections in GC-AED, and shown that up to at least 100 µl of sample solutions in ethyl acetate can be injected without any flame-out or maintenance problems[2]. In order to illustrate the usefulness of this technique for the confirmation of analyte identity, off-line SPE on a PLRP-S-containing cartridge was carried out, 100 µl (or 20 %) of the 500 µl of organic eluate being directly injected on the GC-AED system. Relevant data are shown in Figure 4 which combines the results found for the river water sample discussed above, and a standard solution of benzothiazole (20 ng/ml) using the C, S and N channels. Since the GC conditions were different from those in GC-MSD, the analyte peak shows up at 8.8 min rather than at 14.8 min. The relative intensities of the C, S and N signals of benzothiazole and the surface

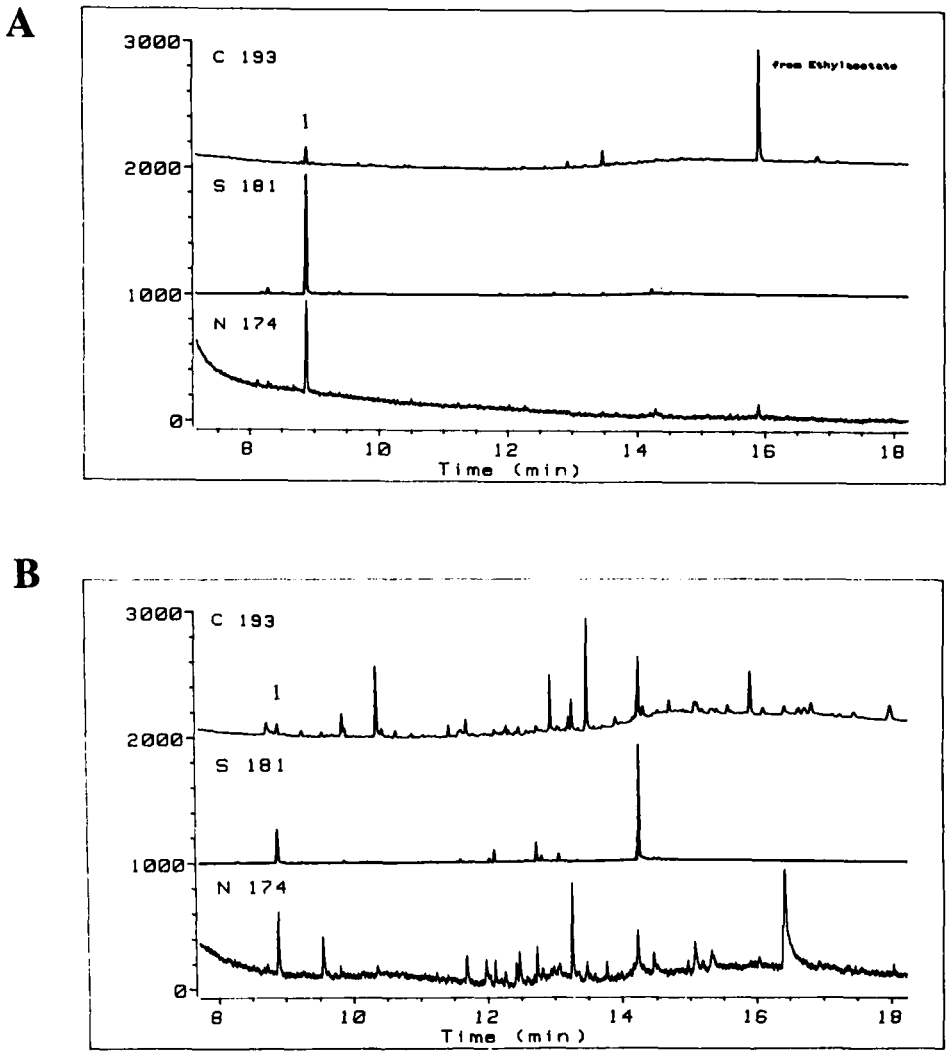


Figure 4 GC-AED chromatograms of large-volume injections of **(A)** trace enrichment of 10 ml of river Meuse water (same sample as in Figure 2) and **(B)** benzothiazole standard (20 ng/ml) in ethyl acetate. C, carbon channel; S, sulphur channel; N, nitrogen channel.

water pollutant agreed nicely (Table 2), the slight deviation observed for the ratios involving nitrogen probably being caused by the fact that this signal was rather close to the detection limit. On the basis of the combined GC-AED information, there is no doubt, however, that the unknown peak may be assigned to benzothiazole.

Table 2 Relative C, S and N intensities of benzothiazole and peak 1 of Figure 4A.

Compound	*C : S ratio*	*C : N ratio*	*N : S ratio*
Benzothiazole	1 : 8.2	26.5 : 1	1 : 218
Peak 1	1 : 8.2	25.1 : 1	1 : 206

CONCLUSIONS

The present study shows that on-line, and fully automated, SPE-GC-MSD is well suited for the rapid screening of surface water samples to achieve preliminary verification and quantification of environmental pollutants at the trace level, using small sample volumes (ca. 10 ml) and very little organic solvent (50–100 µl!). Such an approach is especially useful when accidental spills or discharges require rapid action. In other words, further attention should be devoted to designing an automated SAMOS GC water analyser that can be considered the counterpart of the recently reported, and commercialised, on-line SPE-LC-UV or SAMOS LC system[3,4] the acronym indicating a System for the Automated Monitoring of Organic substances in Surface water. The complementary information provided by GC-AED strongly suggests that it will be worthwhile to pursue the topic of large-volume injections or, in other words, the design of an on-line SPE-GC-AED system.

Acknowledgements

We thank the Rhine Basin Program (Amsterdam/Waldbronn) for financial support and Mr. R. Soniassy (Hewlett-Packard, Waldbronn, Germany) for the use of the GC-AED system.

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