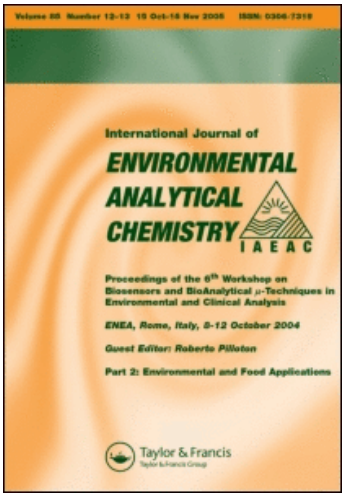

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Solid-Phase Extraction and Capillary Gas Chromatographic Determination of Triazine Herbicides in Water†

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A facile and efficient method is described for the determination of trace quantities of triazine herbicides, terbutryn, prometryn and ametryn in water. The procedure involved preconcentration of water samples by sorption on chromatographic grade silica gel particles with chemically modified surface, being covalently bonded with a nonofunctional C_8H_{17} group. This was followed by solvent desorption with 2-propanol. The determinative step was achieved by capillary gas chromatography on Supelcowax-10 fused silica column using a nitrogen-phosphorus detector. The limit of detection was 0.1 μg–10 μgL^{-1}.

KEY WORDS: Ametryn, prometryn terbutryn, chromatography, water.

INTRODUCTION

Pollution of groundwater, streams and wells by synthetic organic chemicals has been recognized as an important environmental problem within the last few years. It is increasingly apparent that water is being contaminated by various waste disposal activities such as landfills, municipal and waste water discharges, and deep well

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disposal. In addition, contamination can result from accidental spills or direct spraying operation or agricultural run-off or leaching associated with widespread use of herbicides and other agrichemicals.

Many derivatives of *s*-triazine constitute economically important herbicides for effective control of many broadleaf and grassy weeds in a variety of crops grown worldwide.[1] The *s*-triazines are mutagenic and sometimes pathogenic to living organisms.[2] The persistence of triazines in soil[3,4] interferes with the use of the land for growth of certain crops. Because of these detrimental properties, the fate and water pollution potential of the triazine herbicides need to be studied and monitored for proper use in agricultural practices. Several methods[5–13] are known for triazine residue determination in water. It is desirable to adapt and/or modify existing analytical methods and/or develop new ones to determine these chemicals in natural and municipal waters. This, in turn, will aid environmental impact assessment and regulatory decision with respect to the introduction of these chemicals into hydrologic environment.

Recently, there are several projects investigated by IR-4 (a US National Agricultural Program for clearance of animal drugs, microbials and biochemicals, and pesticides for minor or special uses) concerning triazine herbicides terbutryn, ametryn and prometryn to increase the production of a number of economically important minor crops like cassava, taniers, yams, sorghum and parsley grown in southern US, Puerto Rico and elsewhere in the United States. A need exists to determine these chemicals in various run-off and natural waters to assess their water polluting potential. This results in the development of a procedure involving solid-phase extraction and capillary gas chromatographic determination of terbutryn, prometryn and ametryn in water.

EXPERIMENTAL

Reagents

All organic solvents were of pesticide-grade or HPLC grade. The standards, terbutryn, 99.7% purity, prometryn, 99% purity and ametryn, 99.5% purity, were obtained from the Environmental Protection Agency, USA.

Standard stock solutions were made as follows: 5.3 mg terbutryn in 10 ml ethyl alcohol; 7.2 mg prometryn in 25 ml ethyl alcohol and 4.5 mg ametryn in 10 ml ethyl alcohol. For working solutions, appropriate dilutions were made and mixed together as needed in 2-propanol.

Instrumentation

The gas chromatograph used was a Hewlett Packard 5880 A equipped with a Nitrogen-Phosphorus detector, and a split-splitless capillary inlet system operating in the split mode. The detector was operated at a temperature of 300°C. The chromatographic column was a 15 m × 0.25 mm I.D. fused-silica capillary with Supelcowax 10 stationary phase of film thickness 0.25 μm. The column carrier gas was nitrogen with a flow rate of 1.0 ml min^{-1}.

The injection temperature was 200°C and the column temperature was isothermal at 60°C for 0.5 min followed by temperature programming to 240°C at 10°C min^{-1}, the final temperature being maintained for 15 min.

Splitless injection was used, opening the splitter 0.80 min after injection. Additional "make-up" gas (nitrogen) was added to the capillary effluent at a flow rate of 30 ml min^{-1}. Air and hydrogen gas flows through the detector were 60 ml min^{-1} and 3 ml min^{-1} respectively. The septum purge was 1.0 ml min^{-1} with nitrogen and the splitter valve flow rate was 50 ml min^{-1}, also with nitrogen.

Samples and fortification procedure

Water samples collected from Lake Alice, an ecologically preserved, man-made lake near the University of Florida, were shown not to contain interferences or residues of chemicals studied. Representative 200 ml samples brought to pH 6.0 were fortified with known amounts of working standard solutions to give 0.1–10 $\mu g L^{-1}$ concentration of the chemicals. The fortified samples were mechanically shaken and allowed to stand 1 h before extraction. The entire contents were extracted without any subsampling.

Solid-phase extraction of samples

1 mL or 2.8 mL prepacked C_8 cartridges (Bond Elut disposable solid-

phase extraction column of Analytichem International, CA, USA) were used. The column was washed first with 2–3 mL HPLC-grade methanol followed by 5 mL HPLC-grade water. The system was assembled under aspirator vacuum. A 200 mL volume of water, pH 6.0 was passed through the column at a flow rate of 5–10 mL min^{-1}, followed by washing with 10–20 mL HPLC-grade water. Entrapped water was removed by suction under full aspirator vacuum for ca 10 min. The column was next placed inside a 15 mL graduated centrifuge tube, and eluted with 2 mL 2-propanol. The eluate was analyzed by gas chromatography. In most cases, eluates were analyzed without any reduction in volume. However, for detecting triazines below 1 $\mu g L^{-1}$ they were concentrated to suitable volumes under a gentle stream of nitrogen at 50°C.

RESULTS AND DISCUSSION

Several kinds of liquid phases, viz. OV-101, DEGS-PS, carbowax 20M etc. were used by different workers[6,14,15] for the gas chromatographic analysis of the triazines employing packed columns. The chemically-bonded Ultrabond® packings were reported[6] to be superior to conventional materials for these compounds. Use of fused silica capillary columns of OV-1, DB-1701, DB-5 and DX-4 were also reported.[9] In the present study, the polarity, inertness and high thermal stability of bonded fused silica Supelcowax-10 column were found to be very well-suited to the water-based triazines. Well-defined capillary peak and resolution were found consistently reliable for quantitative measurements. Reproducibility of retention time with standard chemicals in the presence of 2-propanol or methanol and water over several months remained consistently within ± 0.01 min.

Most of the methods known in the literature comprise an extraction step employing classical liquid-liquid partition followed by column clean-up and a subsequent operation to reduce the volume by concentration prior to the determinative step. More recently, novel methods[6,7] involving solid phase extraction in Separon SE 50/50 column or C_8 column were reported. The procedure presented herein used Bond Elut disposable solid-phase extraction column C_8 (octyl), with packings 500 mg/2.8 mL or 100 mg/1.0 mL. The material

consisted of 40 μm. 60 Ångstrom porosity, end-capped irregular silica gel particles covalently bonded with a monofunctional C_8H_{17} group. The sorbent was held in place by two 20 μm porous polyethylene frits. When water samples were passed through these cartridges and eluted with water, the triazines remain on the sorbent. After removing the water entrapped in the sorbent, desorption of the triazines was achieved by 2-propanol or methanol. It is important to remove the water trapped in the column prior to desorption operation. Otherwise, loss of triazines are likely to occur due to incomplete desorption.

Figure 1 shows a representative chromatogram of 3 triazine standards, prometryn, terbutryn and ametryn. Figure 2 and Figure 3 show the typical chromatograms of a control and a fortified sample of water, respectively.

Quantitatively reliable measurement of response was determined by reproducible recovery of the triazines from control samples of water fortified with the chemicals. Recoveries renged from 70–90% at fortification levels of 1 $\mu g\,L^{-1}$. The data are presented in Table I. The minimum amount possible to determine with reproducible recovery and giving a signal to noise ratio of 3:1 or higher was considered as the limit of detection. The limit of detection was 0.1 $\mu g\,L^{-1}$.

TABLE I
Recovery of prometryn, terbutryn and ametryn from fortified samples of water.

Compound	[a]Recovery % at each fortification level (μgL^{-1})			
	1.0	2.0	5.0	10.0
Prometryn	70±4.1	87±5.0	89±2.3	89±6.0
Terbutryn	90±3.8	86±4.7	83±3.7	88±2.9
Ametryn	84±5.1	90±6.0	81±4.2	90±5.8

[a]Average of 3 replicate determinations with standard deviations.

Because of the nature and immediate objective of the IR-4 projects, mentioned earlier, the present communication is confined only to 3 triazine herbicides, prometryn, terbutryn and ametryn in

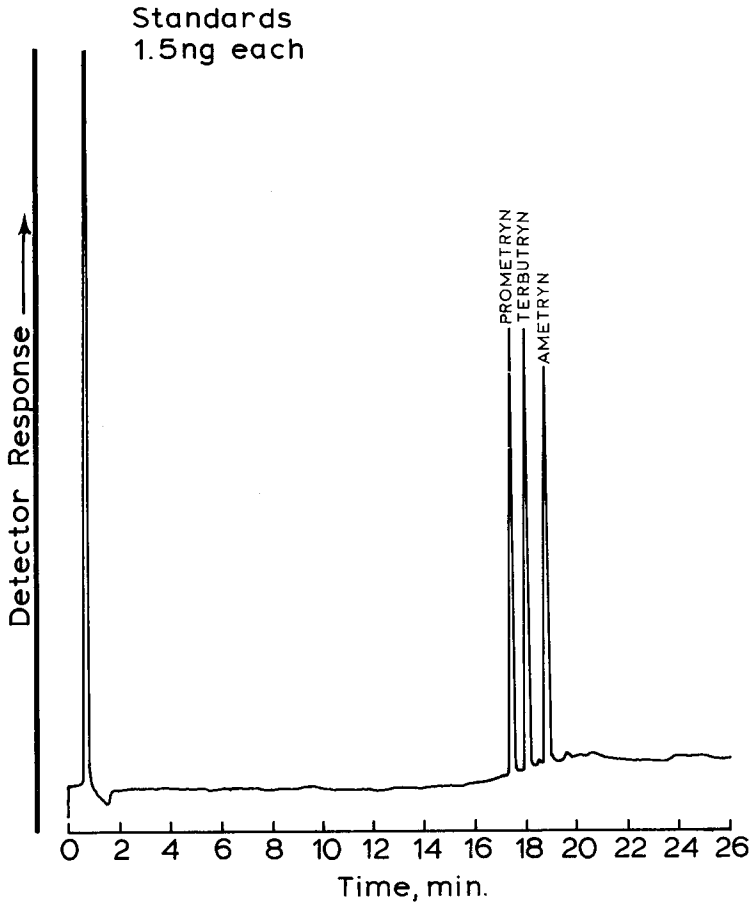

FIGURE 1 Chromatogram of a mixture of standards, 1.5 ng each.

water. However, preliminary investigation showed that the procedure can be extended as well to most of the triazine herbicides, viz., prometon, propazine, atrazine, simazine, simatryn and atraton, etc. In-depth studies concerning their recovery and capillary gas chromatographic separations are in progress, and will be reported in a future communication.

An efficient and reliable method for determining environmental contaminants in a substrate should not only be facile but also

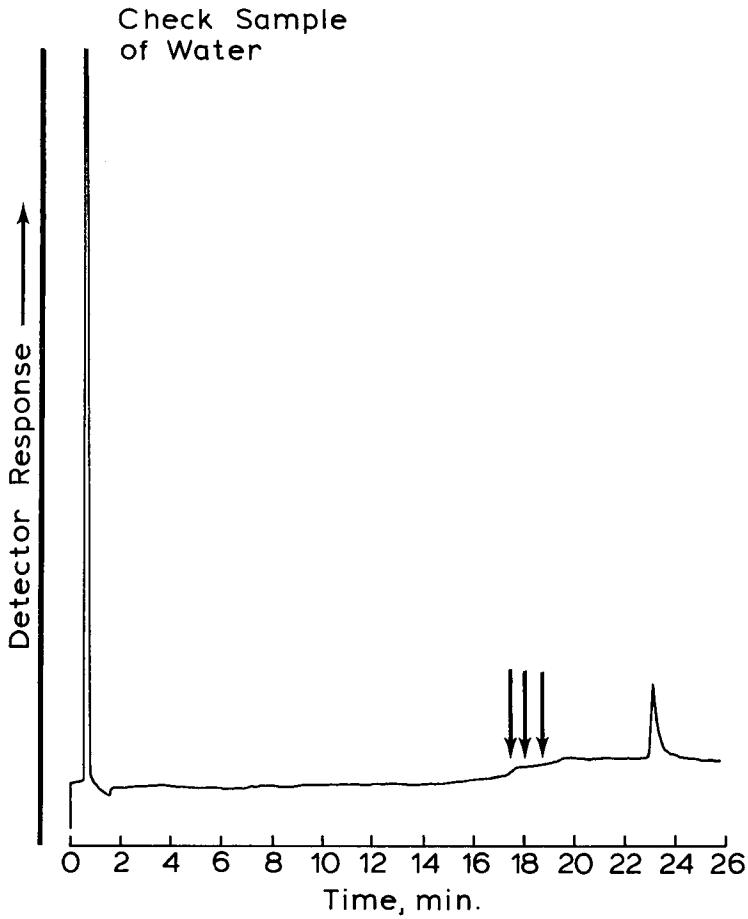

FIGURE 2 Chromatogram of a control sample of water. 1 μl injection representing 100 μl original sample.

capable of being handled by any operator with minimal training and experience. Most importantly, given the right facilities, the procedure should be easily adaptable to laboratory robotic operation and/or laboratory automation with minimum complexity, whenever necessary, for allowing unattended processing, analysis and data reporting of a very large number of samples. In view of the utmost simplicity in operation it is believed that the method communicated herein has all the potentialities for such needs.

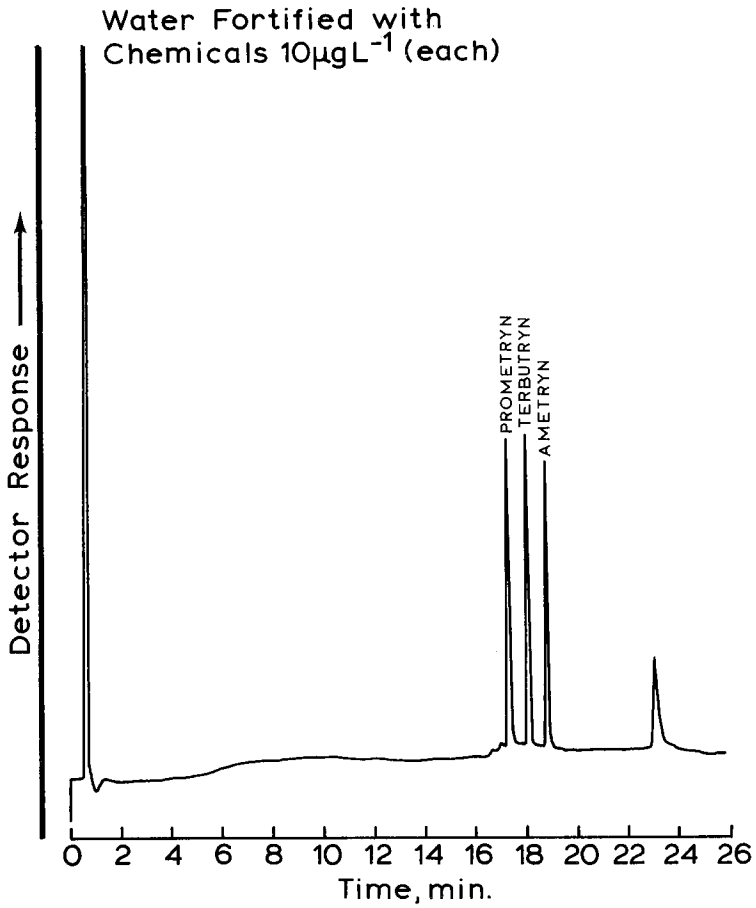

FIGURE 3 Chromatogram of a control sample of water fortified with $10\,\mu gL^{-1}$ each of prometryn, terbutryn and ametryn. $1\,\mu l$ injection representing 100 ul original sample.

CONCLUSION

An efficient method is developed for determination of triazines in water with a detection limit of $0.1\,\mu gL^{-1}$. The extraction step consists in sorption of the triazines on a C_8 column followed by desorption with 2-propanol. The determinative step involves capillary gas chromatography using a fused silica Supelcowax-10 column and an N-P detector.

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