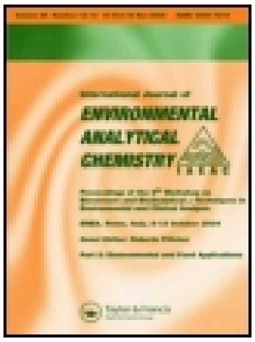

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DETERMINATION OF ENVIRONMENTALLY SIGNIFICANT PESTICIDES BY GAS CHROMATOGRAPHY

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The present work describes the use of glass capillary column gas chromatography in analysing trace amounts of a mixture of diazinon, parathion, malathion, β-endosulfan and cyanazine in natural water. Sample preparation for capillary GC is discussed. In certain cases special techniques have been used for clean-up. The techniques used for detection were flame ionization and electron capture detection. GC-MS was used as a confirmatory method. An approach to determination and confirmation of unknown degradation products of pesticides in the samples is discussed.

KEY WORDS: Pesticides, organophosphorus, s-triazine, carbamates, gas chromatography, photolysis.

INTRODUCTION

The steadily increasing number of environmental significant pesticides requires the development of residue-analytical techniques which allow the detection of as many compounds as possible with only a few clean-up and detection steps. This is true not only of organochlorine and organophosphorous insecticides but also of carbamate- and triazine-herbicides. Various chromatographic techniques are used for the investigation of these substance classes.[1–5] They serve for the concentration and separation of the substances under investigation from the complex material as well as for the quantitative separation and determination of the individual components.[6,7]

For the analysis of organochlorine and organophosphorus pesticides the method of choice is in most cases capillary gas chromatography with ECD, FID, FPD or MS-detection. Also many triazine-herbicides, e.g. cyanazine, can be analysed with

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gas chromatography. This technique, however, requires thermal stability and a certain degree of volatility of the compounds to be analysed. If the compounds are thermally labile (e.g. carbamate-herbicides) they decompose during gas chromatography[8] and only non-reproducible peaks of the fragments appear in the gas chromatogram. The determination of these pesticides must be carried out with liquid chromatography. In the cases in which direct gas chromatographic analysis is prevented due to a lack of volatility, the problems can be solved by derivatization (e.g. phenylurea herbicides and phenoxyalkyl acids can be converted into volatile derivates).

Our contribution deals with the analysis of selected compounds in several environmental compartments, such as water and soil with gas chromatography. Further we analysed some photodegradation products of the pesticides carbetamide, diazinon and phenmedipham using GS-MS combination.

The analytical improvements made in our institute included chemical aspects, viz. the pre-separation and main separation of interfering substances on suitable adsorbents as well as technical aspects, viz. the conditions for separation and programming the chromatograph.

MATERIALS AND METHODS

1. Instrumentation

Carlo Erba Fractovap 4130, 3200, 4200 S Fractovap and Hewlett-Packard 5890 A gas chromatographs equipped with ^{63}Ni-electron capture; flame ionization detectors (FID) were used with 2 m × 2 mm i.d. glass columns containing 1.5% SP-2250/1.95% SP-2401 on 100/200 mesh supelcoport and another column packed with 1.5% OV-17/1.95% QF on 100/200 mesh supelcoport. The operating conditions when using the FID were: injection port 220 °C, column temperature 218 °C, carrier gas flow rate 40 ml N_2/min, purge flow rate 48 ml N_2/min. Capillary gas chromatography with ECD and FID has been used for identification of dichlorvos, diazinon, parathion, malathion, gardona and β-endosulfan by comparing the retention times of these compounds with internal standards at a higher concentration and with GC-MS combinations. The response of FID and ECD was stable and linear over a wide range and it was possible to use this response to study the drift of the ECD detector as often occurs after the injection of dirty samples. The limit of detection under the stated conditions was in the 350–400 ng range but there was obviously a variation in response depending on the molecular structure and molecular weight of the organic compounds.

2. Analysis and Identification

For analysis of the pesticide mixture after extraction from soils we employed a glass column (2 m × 0.16 mm i.d.) containing 1.5%/V-17/1.95% QF on 100/200 mesh and Carlo Erba Fractovap 4200 series equipped with FID. The analysis of s-triazine was performed on 30 m × 0.25 mm i.d. capillary glass columns DB-5 and with ECD detector. The operation conditions were: temperature program 10 °C for 1.5 min, then 12 °C/min to 190 °C for 15 min; carrier gas flow was 20–25 ml/min, hydrogen 5 ml/min and air 50 ml/min. Three metabolites of atrazine, four metabolites of cynazine and five metabolites of carbetamide were identified by comparison of major fragments in the GC-MS combination.[9]

3. *Sampling and Extraction*

All solutions were prepared with double distilled, deionized water. All chemicals and organic solvents used were of analytical reagent grade. The organophosphorus compounds were commercially available by Riedel de Haen (Seelze-Hannover, FRG). Gardona was obtained from Shell (Shell-Sittingbourne Research Centre, Kent, UK). The extraction has not been studied systematically but a two-step extraction with n-hexane and dichloromethane has been used. Our own experience demonstrated that refluxing with dichloromethane or extraction with 30 ml dichloromethane/n-hexane in small centrifuge tubes leads to recoveries with comparable and reproducible results of ±8%.

4. *Irradiation Conditions*

The irradiation apparatus used for this study was similar to that described previously. It consisted of a high pressure mercury lamp (Philips HPK 125 W) having a maximum emission at 340 nm, with a quartz or pyrex filter and a cooling jacket. About 95% of the lamp dipped into the reaction mixture cooled to 20–25 °C. Samples were taken at different times of irradiation and immediately analysed (Figures 1–3).

Preparation of standard solutions: The guideline for the preparation of standards was obtained from the Manual of Chemical Methods for Pesticides and Devices EPA. Each substance (approx. 0.1–0.2 mg/25 ml) was prepared by dissolving in 2–3 ml acetone and diluting to 25 ml with isooctane. The stock solutions of each substance was further diluted with the solvent to be tested. All injections were made with solutions containing a single compound.

5. *Determination of Diazinon and Parathion-Methyl in Soil*

After extraction with 150 ml dichloromethane/n-hexane and filtration through quarz wool the residue was again extracted with 80 ml dichloromethane for 30 minutes. The united extracts were concentrated to approx. 10 ml at 30 °C using a rotary evaporator. For clean-up we used column chromatography with alumina as stationary phase and dichloromethane as mobile phase to purify the extracts. After drying with Na_2SO_4 and concentration at 30 °C the residues were redisolved in 5 ml n-hexane. The final analysis was done by gas chromatography (Figures 4–6).

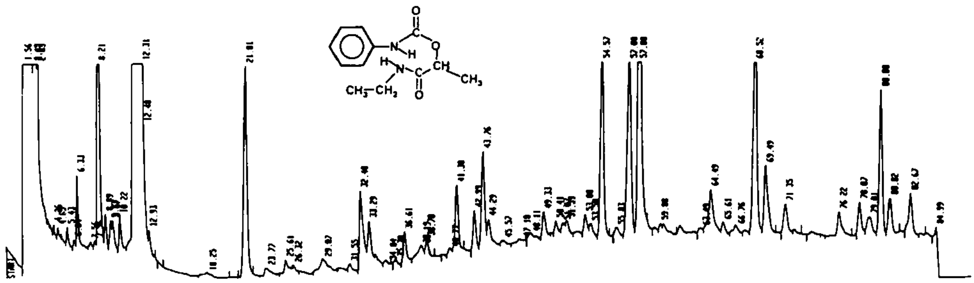

Figure 1 Glass capillary gas chromatogram of carbetamide (10^{-4}M) in chloroform by UV-light ($\lambda \leq 290$ nm) after extraction with n-hexane:ethylacetate 20:80. Gas chromatographic conditions are described in the text.

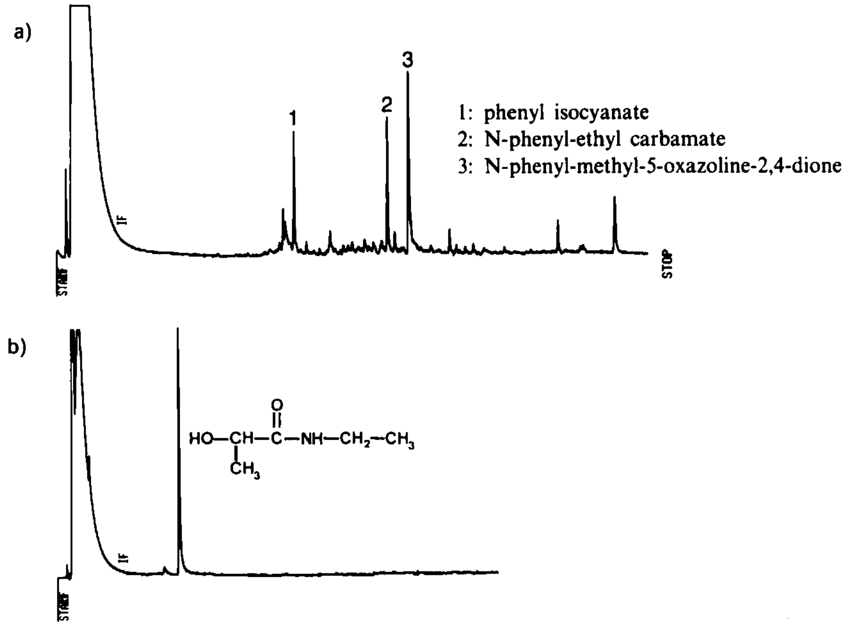

Figure 2 Gas chromatogram of photoproducts (a) and (b) on glass capillary columns after clean-up and elution.

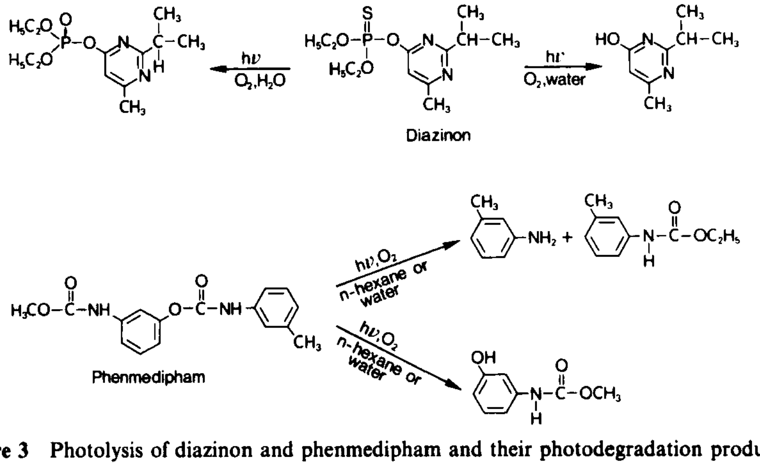

Figure 3 Photolysis of diazinon and phenmedipham and their photodegradation products.

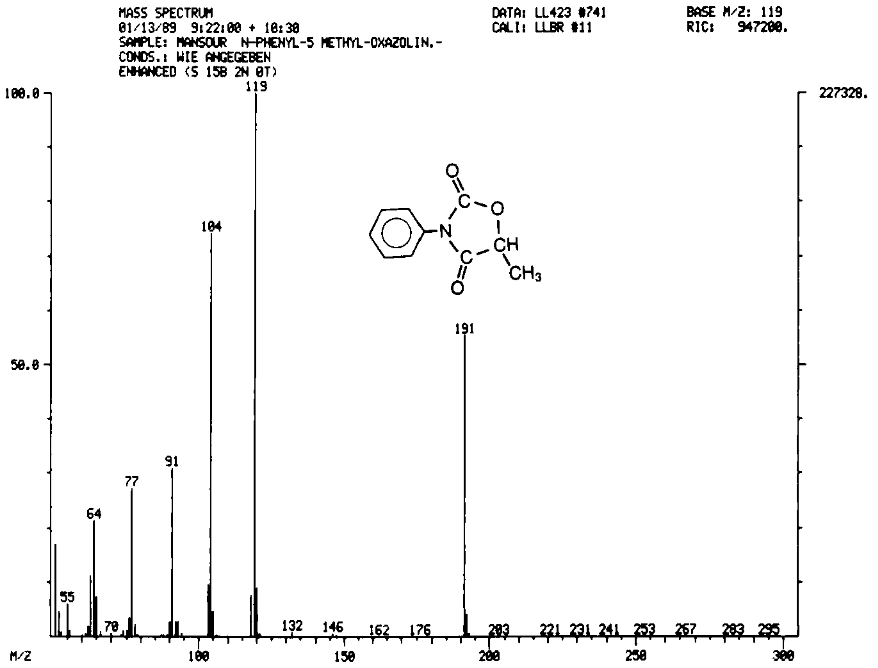

Figure 4 GC-MS of photoproduct N-phenyl-5-methyl-oxazolidine-2,4-dione.

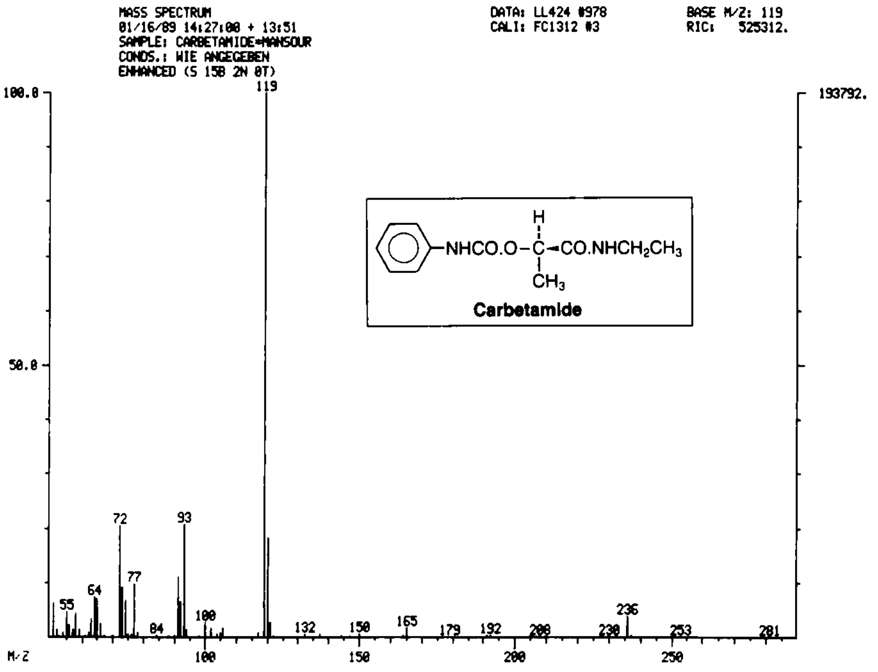

Figure 5 GC-MS electron ionization mass spectrum (70 eV) of carbetamide.

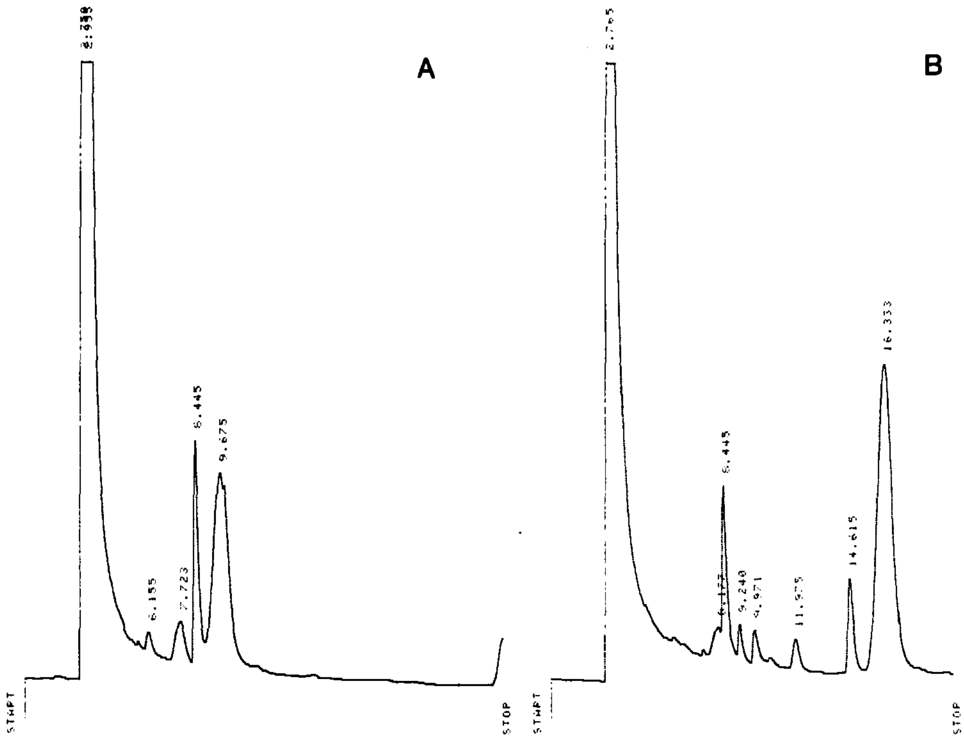

Figure 6 Capillary analysis using flame ionization detection of diazinon (A) and parathion-methyl (B) in water and soil solutions under sunlight conditions. Diazinon $t_R = 9.67$, parathion-methyl $t_R = 16.33$.

6. *Analysis of S-Triazine in Water*

a) Extraction 250 ml of the water sample were extracted in vacuum volumetric flasks (Supelco Inc.) equipped with Supelclean solid phase extraction tubes (RP-18 adsorption tubes of Baker Co., SPE disponible tubes C-18 on silica gel). The adsorbens was preconditioned by washing with several ml n-hexane, acetone and distilled water. To prevent during elution the development of a second phase in the reservoir by the remaining water in the extraction column which could cause a distribution of s-triazine between n-hexane and acetone/water and therefore falsify the analytical results, the SPE tubes from the samples were dried overnight in an exsiccator over silica gel in vacuum flasks. The elution was also done in SPE vacuum manifold flasks.

b) Gas chromatographic measurement We used a Hewlett-Packard 5890-A instrument equipped with Ni-ECD and 30 m DB-5 capillary column with 0.32 mm i.d. × 0.26 μm film thickness. The analysis had the following conditions: column flow of nitrogen carrier at 50 °C: 10 ml/min. Temperature programme: from initially 50 °C in steps of 7 °C/min to finally 290 °C for 10 min. Injection: 1.6–1.8 μl sample (Figure 7). The quantitative determination was done by calibration with an external standard. Parallel to each analytical run aqueous s-triazine solutions

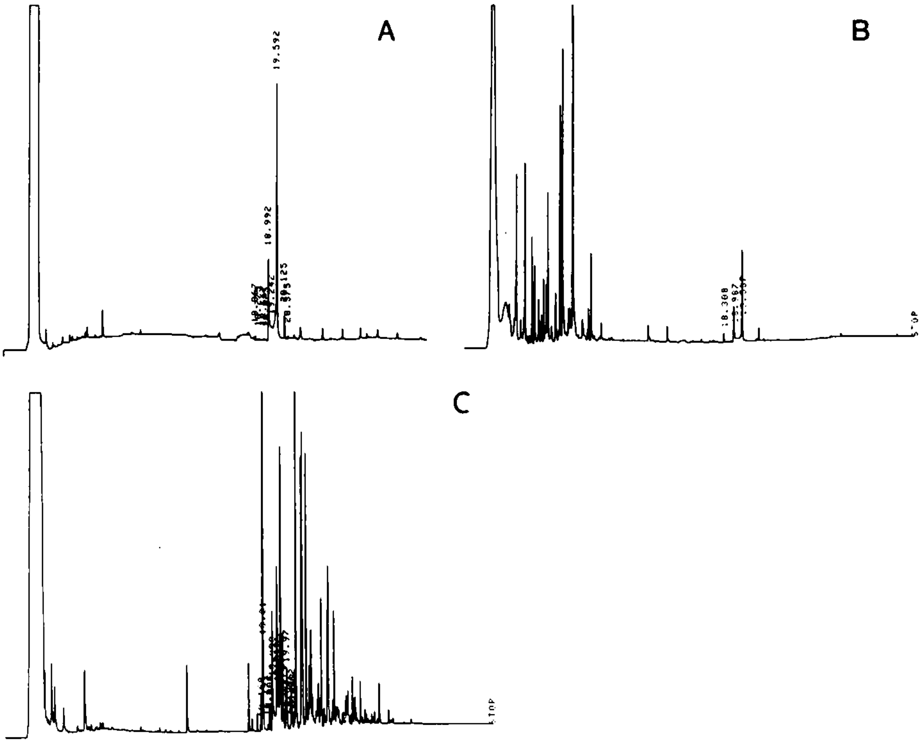

Figure 7 Gas chromatographic analysis of cyanazine. A: Standard solution (6 μg/ml), injection 1.6 μl ($t_R = 19.59$). B: Phototransformation of cyanazine in water in presence of humic acid ($\lambda \geq 300$ nm), $t_R = 19.55$. C: Quantification of cyanazine ($t_R = 19.97$) in river water after extraction.

(1 μg/100 ml) were extracted and in the same way treated like the samples. The results are mean values from mostly three sample preparations. The single results differ partly for more than 5%.

CONCLUSIONS

The methods and techniques used for the detection of several organophosphorus, carbamates and s-triazine in soil and water at the ppm-level are simple and fast. Our aim was to consider the relevant factors for the analysis of the compounds but we did not intend to obtain an overview of the gas chromatographic determination of pesticides in various matrices. Identification of compounds was achieved by use of columns of different polarity in connection with FID and ECD. The degradation products of carbetamides were analysed with an efficient column described in this article. For the determination of organophosphorus in soil a good extraction is essential, and the analysis of samples shows that the method yields accurate results. In our work recoveries were satisfactory and standard deviations varied from 10–15%. The reproducibility of the method can still be enhanced by optimization of all the relevant parameters.

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