

INVESTIGATION OF CONDITIONS FOR THE DETERMINATION OF PESTICIDES IN WATER USING SOLID PHASE EXTRACTION

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Received January 14, 1992

Accepted March 23, 1992

The conditions for the preconcentration of carbamate, phenylurea and triazine pesticides from water samples were investigated, and optimized methods were developed for the determination of the pesticide groups. Bakerbond spe C18 cartridges were used for the preconcentration. The preconcentrated carbamate and phenylurea pesticides were eluted from the cartridges with acetone, whereas the triazine herbicides were eluted with chloroform. After additional concentration by evaporation, the eluates were analyzed by RC-HPLC on an AQUAPORE RP-300 column using a methanol-water mixture as the mobile phase.

The extensive use of pesticides in agriculture is hazardous to sources of drinking water. In this connection, rapid yet efficient methods for their determination are sought. The pesticide concentrations in waters are usually too low to enable the water samples to be analyzed directly; preconcentration must be largely resorted to. Solvent extraction is being replaced with solid phase extraction (SPE), a rapid method where several samples can be analyzed simultaneously and the consumption of organic solvents is minimal. The preconcentration process can be partly or fully automated. With the use of a suitably chosen sorbent the preconcentration is combined with purification. The hazard of formation of emulsions, which is an adverse factor in solvent extraction, is avoided in SPE.

Sorbents that have been employed for the preconcentration of nitrogen pesticides include, e.g., Tenax GC (ref.¹), microporous organic adsorbents such as XAD resins² or Separon³, and in exceptional cases also graphitized charcoal⁴. Tatar and Popl⁵ examined the applicability of various kinds of sorbents to the preconcentration of pesticides from water. Most frequently used is silica gel modified with octadecyl (C18) groups⁶⁻¹⁰. The eluting solvents are chosen with respect to the type of analyte. Medium polar solvents such as ethyl acetate¹¹, acetonitrile¹², acetone¹³ and methanol^{14,15} are usually applied to the elution of carbamate, phenylurea and triazine pesticides.

The aim of the present work was to examine factors affecting the results of determination of pesticides in water using the SPE method. We selected a suitable sorbent for the preconcentration of the analytes from water and paid attention to the choice of the kind and volume of eluting solvent, conditions of the sorption process and conditions of

HPLC analysis of the eluate. The results were used to develop simple and rapid, yet efficient procedures for the determination of carbamate, phenylurea and triazine pesticides in waters.

EXPERIMENTAL

Chemicals and Apparatus

The following standards of pesticides, obtained from the Central Agricultural Testing and Certification Institute in Brno, were used: metoxuron, bendiocarb, carbaryl, propham, propoxur, desmedipham, phenmedipham, linuron, hexazinone, simazine, terbutryn, prometryn, terbuthylazine, atrazine and metoprotryn. Solvents included methanol and acetone of UV spectral grade, chloroform, ethyl acetate and diethyl ether of reagent grade purity (further purified in the laboratory), and distilled water for chromatography (purified in the laboratory on a Separon SGX- C18 column 5 μm , 150 \times 3.3 mm i.d., manufactured by Tessek, Prague).

The pesticides were preconcentrated on a mult extractor manufactured by the Military Repair Enterprise No. 084, combined with an analytical pump of Zeiss (Germany). Chromatographic analyses were performed on a PU 4002 liquid chromatograph equipped with a variable-wavelength UV detector (Pye-Unicam, U.K.). The chromatographic column was AQUAPORE RP-300 (7 μm , 250 \times 4.6 mm i.d.; Pye-Unicam, U.K.), the sorption cartridges were Bakerbond spe C18 (3 ml, 500 mg, and 6 ml, 1 000 mg).

Procedure

Prior to preconcentration, the pH of the water sample was adjusted with 0.1M NaOH or 0.1M HCl to pH 6.5 – 7.5 for the analysis of triazine pesticides, and to pH 5.5 – 6.5 for the analysis of carbamate and phenylurea pesticides. The sorption column was conditioned with 5 ml of acetone, 2 \times 3 ml of chloroform, 1 ml of acetone and 2 \times 3 ml of water for the triazine pesticides, and with 2 \times 5 ml of acetone and 2 \times 3 ml of water for the carbamate and phenylurea pesticides.

The water samples were fed onto the sorption columns through a Teflon tube at a suction rate of 5 ml min^{-1} . After sucking the sample through, the reservoir was washed with 3 ml of distilled water, and the water was sucked through the sorbent. Thereafter, 1 ml of distilled water was sucked through the sorbent. Residual water was removed from the sorbent by applying an underpressure of 88 kPa for 5 min.

The carbamate and phenylurea pesticides were eluted with 1.2 ml of acetone, the triazine pesticides, with 2.0 ml of chloroform. The solvent was evaporated in an air stream at a temperature lower than 40 $^{\circ}\text{C}$. The walls of the vessels used to work up the eluate were rinsed with 2 \times 50 μl of acetone; the solvent was evaporated to dryness and the residue was taken up in 50 μl of methanol. A 20 μl aliquot was injected on the liquid chromatographic column.

The pesticides were separated using methanol–water mobile phases at volume ratios of 49 : 51 for the carbamate and phenylurea pesticides, and 57 : 43 for the triazine herbicides; the flow rate was 1.00 ml min^{-1} in either case, detection wavelength was 230 nm.

RESULTS AND DISCUSSION

Based on previous investigations^{17,18}, silica gel modified with octadecyl (C18) groups was chosen for the preconcentration. This is a nonpolar sorbent exhibiting very good properties for the preconcentration of medium polar substances from polar matrices.

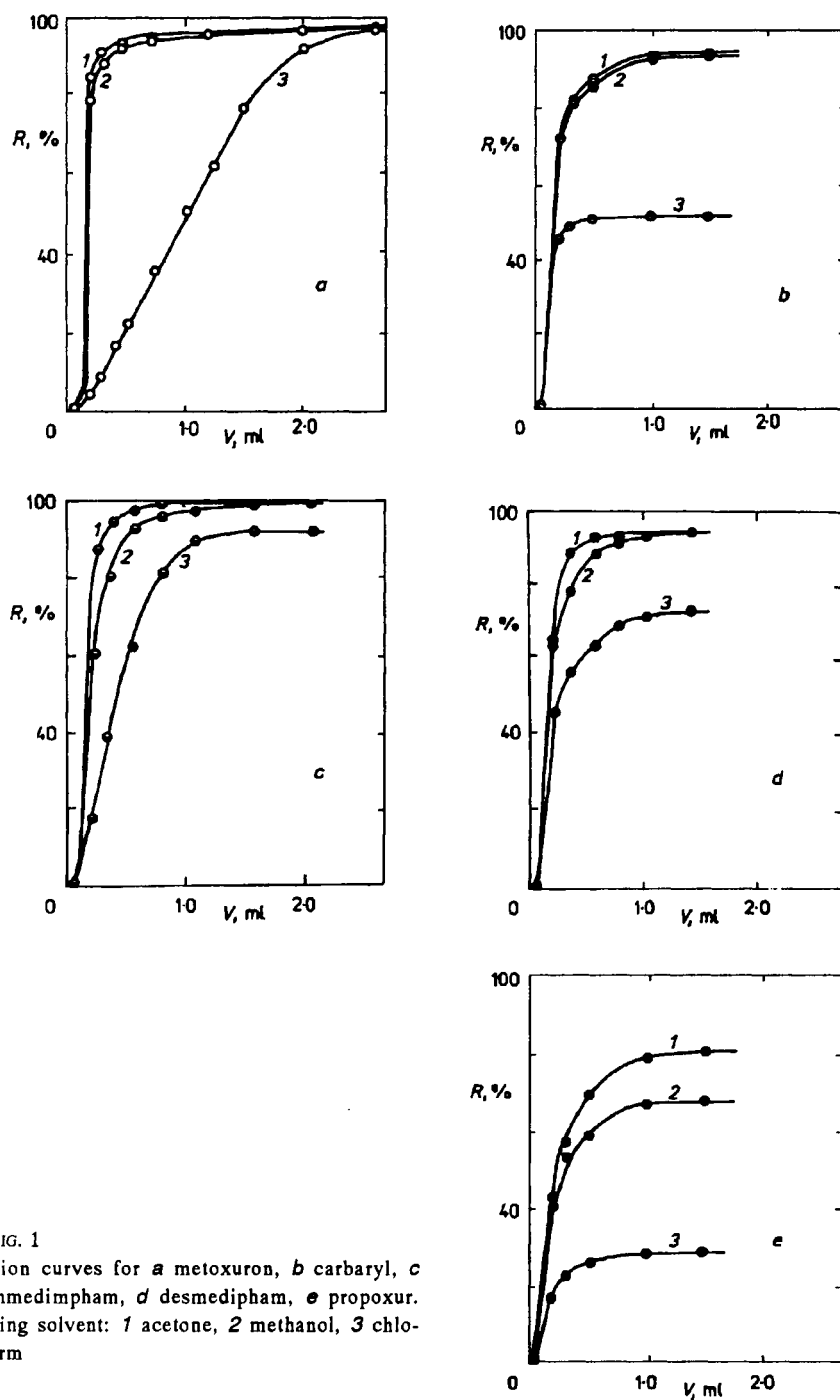


FIG. 1
Elution curves for *a* metoxuron, *b* carbaryl, *c* phenmedimpham, *d* desmedipham, *e* propoxur.
Eluting solvent: 1 acetone, 2 methanol, 3 chloroform

The eluents were low-boiling medium polar solvents (polarity indices ranging from 2.9 to 6.6) possessing high solvation ability for the pesticides under study.

The shape of the elution curves was examined to establish the minimum volume of solvent necessary for a quantitative elution. For the elution of the carbamate and phenylurea pesticides (Fig. 1), the elution strength of methanol and acetone is comparable, whereas chloroform exhibits an elution strength too low to be applicable to the elution of these pesticides. Since the eluates had to be treated for HPLC analysis with UV detection, acetone (b.p. 56 °C) was given preference over methanol (b.p. 65 °C). Chloroform, on the other hand, was found suitable for the elution of the triazine herbicides (Fig. 2). Figures 1 and 2 can serve to assess not only the minimum solvent volumes required for a quantitative elution but also the average recoveries.

The pesticides studied are medium polar substances, and so the process of their sorption was expected to be affected by the pH of the water sample. This assumption was correct, as Figs 3 and 4 demonstrate. The range of pH 2.5 – 7.5 was examined. The limits of this range were determined by two factors, by the stability and usability of the sorbent¹⁹ and by the stability of the pesticides^{20–22}. Figures 3 and 4 show that pH 5.5 – 6.5 is suitable for the preconcentration of the carbamate and phenylurea pesticides. The lower recoveries in the strongly acid and neutral regions can be due to a partial degradation of the pesticides and also to the nature of their molecules and the related chromatographic behaviour during the preconcentration. It would be difficult to specify exactly the interactions involved, and this was beyond the scope of this work. For the

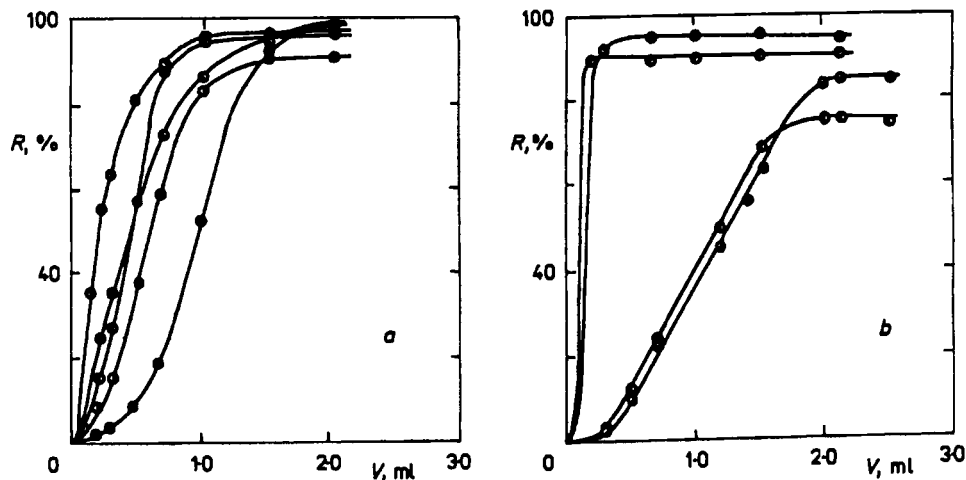


FIG. 2
Elution curves for ● hexazinone, ● simazine, ● terbutryn, ● terbutylazine, ● metoprotryn, ● prometryn, ● atrazine. Eluting solvent: *a* chloroform, *b* acetone

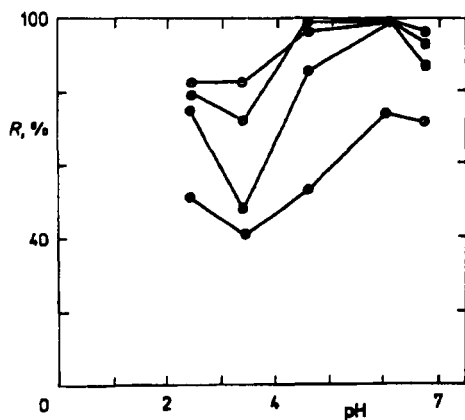


FIG. 3
Dependence of recovery on water sample pH for \ominus carbaryl, \bullet linuron, \ominus phenmedipham, \oplus propham. Eluting solvent: acetone

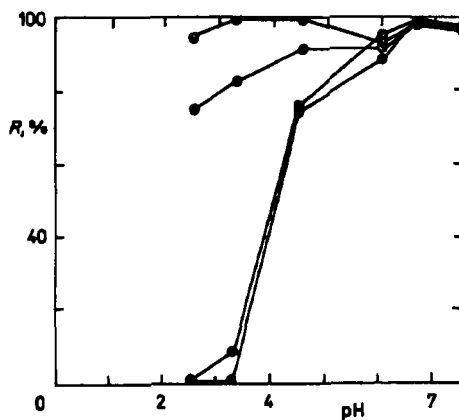


FIG. 4
Dependence of recovery on water sample pH for \bullet terbutryn, \ominus prometryn, \bullet terbuthylazine, \bullet atrazine. Eluting solvent: chloroform

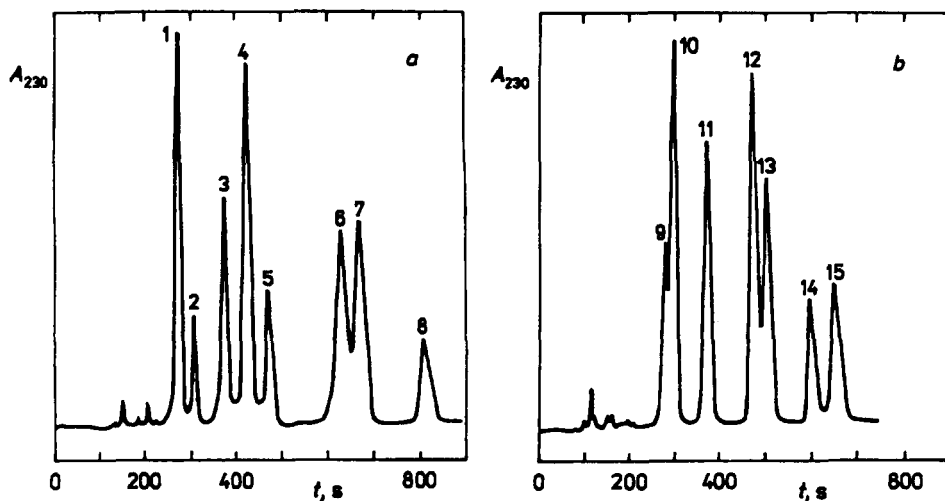


FIG. 5
Chromatogram of the extract of a drinking water sample (100 ml) contaminated with carbamate and phenylurea pesticides (a) and with triazine herbicides (b). Peaks: 1 metoxuron, 2 bendiocarb, 3 carbaryl, 4 propham, 5 propoxur, 6 desmedipham, 7 phenmedipham, 8 linurol, 9 hexazinone, 10 simazine, 11 terbutryn, 12 prometryn, 13 terbuthylazine, 14 atrazine, 15 metoprotryn

triazine herbicides, the acidity of the water sample had to be adjusted to pH 6.5 – 7.5 to achieve the highest recovery (Fig. 4). The pH adjustment is of particular importance for metoprotryn, prometryn and atrazin. At pH \approx 3 the recovery is so low that the analysis is precluded.

The consumption of the eluting solvents increases with increasing weight of the sorbent. Elution from 1 000 mg of the C18 sorbent requires a minimum of 1.8 ml of acetone for the carbamate and phenylurea pesticides, and 2.5 ml of chloroform for the triazine pesticides. The amount of 1 000 mg of sorbent is necessary for the preconcentration from water sample volumes larger than 500 ml.

The results were evaluated and employed to develop the optimized procedures as given in Experimental. The recoveries obtained in the sample treatment by the optimized procedures are given in Table I along with the limits of determination, calculated as $L_D = 10 s_b$, where s_b is the standard deviation of a sample of uncontaminated drinking water.

Chromatograms of extracts of 100 ml of drinking water contaminated with the pesticides under study (Table I) are shown in Fig. 5. Interfering background is minimal, and

TABLE I
Recovery (R) and limit of determination (L_D) of carbamate, phenylurea and triazine pesticides in waters

Pesticide	c , $\mu\text{g} / 100 \text{ ml}$	R , %	L_D , $\mu\text{g} / \text{l}$
Metoxuron	4.58	98.1	0.10
Bendiocarb	1.98	97.9	0.40
Carbaryl	4.52	98.7	0.15
Propham	2.34	74.0	0.09
Propoxur	3.08	85.7	0.30
Desmedipham	1.64	98.4	0.09
Phenmedipham	2.26	98.3	0.09
Linuron	2.50	98.5	0.15
Hexazinone	2.18	94.5	0.90
Simazine	2.02	89.1	0.50
Terbutryn	2.30	98.9	0.05
Prometryn	1.80	98.2	0.05
Terbutylazine	1.50	96.2	0.05
Atrazine	1.78	99.8	0.05
Metoprotryn	3.90	98.2	0.04

the chromatogram of the blank exhibits no peak whose retention time coincides with that of any of the pesticides.

The authors wish to thank J. T. Baker manufacturers for Bakerbond spe C18 sorption cartridges.

REFERENCES

1. Agostino A., Caselli M., Provenzano M.: *Water, Air, Soil Pollut.* 19, 309 (1983).
2. Levesque D., Mallet V.: *Int. J. Environ. Anal. Chem.* 16, 139 (1983).
3. Popl M., Tatar V., Vozňáková Z.: *Fresenius Z. Anal. Chem.* 313, 137 (1982).
4. Bruner F., Crescentini G., Mangani F., Petty R.: *Anal. Chem.* 55, 793 (1983).
5. Tatar V., Popl M.: *Fresenius Z. Anal. Chem.* 322, 419 (1985).
6. Oehmichen U., Kerrenbrock F., Haberer K.: *Fresenius Z. Anal. Chem.* 327, 715 (1987).
7. Johnson W. E., Fendinger N. J., Plimmer J. R.: *Anal. Chem.* 63, 1510 (1991).
8. Richard J. J., Junk G. A.: *Mikrochim. Acta* 1986, 385.
9. Weber W. H.: *4th Symposium on Handling of Environmental and Biological Samples in Chromatography, Basel 1988.*
10. Junk G. A., Richard J. J.: *Anal. Chem.* 60, 451 (1988).
11. Nash R. G.: *J. Assoc. Off. Anal. Chem.* 73, 438 (1990).
12. Marvin Ch. H., Brindle I. D., Hall C. D., Chiba M.: *Anal. Chem.* 62, 1492 (1990).
13. Tatkovičová V.: *Collect. Czech. Chem. Commun.* 55, 2146 (1990).
14. Stahl M., Luhrmann M., Kicinski H. G., Kettrup A.: *Z. Wasser Abwasser Forsch.* 22, 124 (1989).
15. Scherma J.: *J. Liq. Chromatogr.* 9, 3433 (1986).
16. Tatkovičová V.: *Innovation Proposal No. 15/90.* Palacký University, Olomouc 1990.
17. Tatkovičová V.: *Thesis.* Palacký University, Olomouc 1990.
18. Tatkovičová V., Stránský Z.: *Proceedings of the Seminary on Separation Methods, Prague 1991*, p. 63. PDS, Prague 1991.
19. Zief M., Kiser R.: *Solid Phase Extraction for Sample Preparation*, manual. J. T. Baker, Phillipsburg 1988.
20. Röder C. H., Jenny N. A., Otnad M. in: *Analytical Methods for Pesticides, Plant Growth Regulators and Food Additives* (G. Zweig, Ed.), Vol. X, p. 293. Academic Press, New York 1978.
21. Kossman K., Jenny N. A. in: *Analytical Methods for Pesticides, Plant Growth Regulators and Food Additives* (G. Zweig, Ed.), Vol. VII, p. 611. Academic Press, New York 1974.
22. Bergson M., Hamida N. B., Calmon J.-P.: *J. Agric. Food Chem.* 33, 577 (1985).

Translated by P. Adámek.