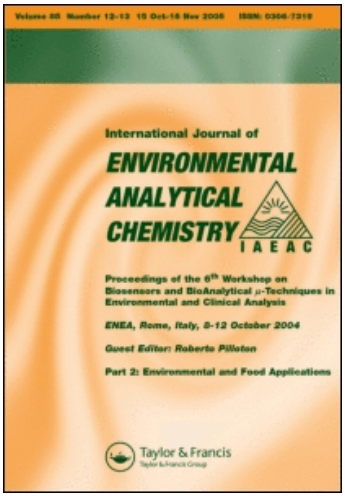
This article was downloaded by:
On: *18 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



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

Isolation, Concentration and Subsequent Analysis by Capillary Gas Chromatography of Trace Amounts of Organophosphorus Compounds from Aqueous Samples

A. Verweij[a]; M. A. Van liempt-Van Houten[a]; H. L. Boter[a]
[a] Prins Maurits Laboratory TNO, AA Rijswijk, The Netherlands

To cite this Article Verweij, A. , Houten, M. A. Van liempt-Van and Boter, H. L.(1985) 'Isolation, Concentration and Subsequent Analysis by Capillary Gas Chromatography of Trace Amounts of Organophosphorus Compounds from Aqueous Samples', International Journal of Environmental Analytical Chemistry, 21: 1, 63 — 77
To link to this Article: DOI: 10.1080/03067318508078371
URL: http://dx.doi.org/10.1080/03067318508078371

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Intern. J. Environ. Anal. Chem., 1985, Vol. 21, pp. 63–77
0306-7319/85/2102-0063 $18.50/0
© 1985 Gordon and Breach, Science Publishers, Inc. and OPA Ltd.
Printed in Great Britain

Downloaded At: 20:17 18 January 2011

Isolation, Concentration and Subsequent Analysis by Capillary Gas Chromatography of Trace Amounts of Organophosphorus Compounds from Aqueous Samples†

A. VERWEIJ, M. A. VAN LIEMPT-VAN HOUTEN and H. L. BOTER

Prins Maurits Laboratory TNO, Lange Kleiweg 137, P.O. Box 45, 2280 AA Rijswijk The Netherlands

(*Received January 14, 1985*)

Trace amounts (ppb or less) of phosphorus containing compounds present in aqueous samples are adsorbed on XAD-4 and subsequently eluted by means of ethyl acetate. The solvent and the eluted compounds are evaporated and swept over a Tenax-GC tube. This gas stripping method traps the phosphorus containing compounds together with only a small amount of the solvent whereas the water entrapped in the XAD step is removed simultaneously. The compounds are desorbed from the Tenax-GC tube and injected into the gas chromatograph using the combination of thermal desorption, cold trapping and flash heating. The subsequent analysis is carried out on a capillary column and the compounds are detected by means of a flame photometric detector. The various steps of the analytical procedure are discussed, including the recoveries of the different compounds studied and some instrumental aspects.

KEY WORDS: Organophosphorus compounds, aqueous samples, gas chromatography, flame photometric detector.

---

†Presented at the 14th Annual Symposium on the Analytical Chemistry of Pollutants, Barcelona, November 21–23, 1984.

INTRODUCTION

A procedure to determine PCH_3-containing compounds in surface water was published in 1980[1] as a method to verify a possible production of chemical warfare agents. This procedure comprises hydrolysis, derivatization with diazomethane and subsequent gas chromatographic analysis. The method lacks specificity in that intact PCH_3-containing chemical warfare agents or their decomposition products are all transformed into the same compound: dimethyl methylphosphonate.

The aim of this investigation was to develop a verification procedure for the detection of intact chemical warfare agents of the organophosphorus type in surface waters. Because of their similarity in properties a number of insecticides and polymer additives would also be included. Generally speaking the concentration of these compounds in surface water, if at all present, will be very small because the majority of the compounds are unstable in water with the exception of the additives (e.g. trialkyl phosphates). Moreover, a production plant will try to keep its waste water effluent as clean as possible for environmental and security reasons. As a consequence it seemed wise to aim at a procedure which could be used at a ppb concentration level, being comparable with the detection limit of the above-mentioned PCH_3-procedure. For practical reasons the sampling had to be relatively simple, fast and suitable for limited, small amounts of aqueous samples to be taken in the field. During the transport of the samplers to the laboratory and awaiting the analysis the isolated compounds should be preserved in their original undecomposed form.

Besides, the procedure had to be applied in pharmacokinetic studies as a sensitive detection of chemical warfare agents such as soman in biological samples like blood or urine.

Trace amounts of organic compounds can be isolated from water using adsorption tubes packed with a porous polymer as the adsorbent. The compounds are eluted from the adsorbent in several ml of solvent.

Subsequently μl aliquots of the eluate may be analysed by gas chromatography, which means a 1000-fold loss in sensitivity. A far more sensitive determination is achieved if the total amount of adsorbed compounds is thermally desorbed from the adsorbent and subsequently analysed on-line by gas chromatography.

Downloaded At: 20:17 18 January 2011

Experiments were carried out to determine the recoveries of the compounds from water by investigating the influence of such parameters as desorption temperature and amount of water left in the adsorbent. Amongst the problems met were irreproducible and low recoveries, residual water that interfered with the thermodesorption analysis by freezing the cold trap, and a simultaneous decomposition of thermally unstable and hydrolytic sensitive organic compounds like soman. To perform a more systematic investigation the different steps of the complete procedure were studied separately. This paper describes the different optimization experiments as well as some results obtained with the complete procedure.

EXPERIMENTAL PART

Chemicals

Compounds investigated: Table I shows the compounds investigated together with some relevant physical properties.

The aim of the study was to develop a procedure for the isolation and detection of a variety of phosphorous containing chemical warfare agents possibly present in surface waters. Therefore, preliminary experiments were carried out using compounds with a wide range of solubility and volatility (Table I: compounds 1–7) so as to investigate the yield of adsorption by the adsorbent XAD-4 and the desorption by means of extraction.

Because of the additional need for a sensitive procedure to detect chemical warfare agents in body fluids in pharmacokinetic studies the majority of the experiments to investigate the different steps of the procedure were carried out with soman and a number of related agents, phosphates and phosphonate esters (Table I: compounds 8–18). Because of their hydrolytic and thermal instability the methylphosphonofluoridates (Table I: compounds 8–11) are critical test compounds.

To prepare the spiked aqueous samples it proved to be essential to start with a stock solution (μg/ml level) in alcohol. On addition of the neat compounds to water they strongly adhered to the glass wall of the sample container. All aqueous samples were prepared by the addition of the alcoholic stock solution to water in a minimum ratio of 1:100. Nevertheless, in the case of nonane the severe loss due to

Downloaded At: 20:17 18 January 2011

Downloaded At: 20:17 18 January 2011

TABLE I
Physical properties of compounds used in this investigation

No.	Compound	Boiling point (K)	Solubility in water (g/100 ml)	(K)
1	methyl isobutyl ketone	391	1.5	(293)
2	toluene	384	0.047	(283)
3	nonane	424	i	
4	o-dichlorobenzene	453	0.0145	(298)
5	malathion	429–430 (0.7 mm)	1.45	(293)
6	parathion	430–435 (0.6 mm)	0.24	(293)
7	diazinon	356–357 (0.002 mm)	0.40	(293)
8	soman—pinacolyl methylphosphonofluoridate	258 (15 mm)	2.1	(298)
9	sarin—isopropyl methylphosphonofluoridate	330 (15 mm)	∞	
10	DFP—diisopropyl phosphorofluoridate	346 (16 mm)	1.5	(293)
11	tabun—ethyl N,N-dimethylphosphoramidocyanidate	381 (12 mm)	10	(298)
12	ethyl pinacolyl methylphosphonate (EPM)	333–334 (0.5 mm)	s	
13	n-propyl pinacolyl methylphosphonate (PPM)	341–343 (0.4 mm)	s	
14	dipinacolyl methylphosphonate (DPM)	343 (0.5 mm)	s	
15	trimethyl phosphate (TMP)	470	s	
16	triethyl phosphate (TEP)	489	s	
17	tri-n-propyl phosphate (TPP)	525	s	
18	tri-n-butyl phosphate (TBP)	562	s	

s = slightly soluble but sufficient for the concentration range applied
i = insoluble
∞ = infinite

The data of compounds 1–4 and 15–18 have been derived from Ref. 2, those of compounds 5–7 from Ref. 3 and those of compounds 8–11 from Ref. 4.

the glass wall adsorption remained; the use of an emulsifier did not give any improvement.

Adsorbents: To concentrate organic compounds from water Amberlite XAD-4 (a divinylbenzene-styrene polymer) was chosen, because it has a great adsorption capacity and a low affinity for water in comparison with other types of XAD-polymers as can be seen from Table II. Moreover, a polymer resin like XAD may be expected to be a safe medium for organophosphorus compounds.[5]

The XAD-4 was purified by successive soxhlet extraction with methanol, acetonitrile and ether according to Ref. 8 and stored under methanol.

For thermal desorption experiments in the complete procedure Tenax-GC was used. Tenax-GC packed in the concentrating trap was purified by heating for 8 hrs at 543 K while a small stream of helium flows through the tube.

Downloaded At: 20:17 18 January 2011

TABLE II
Properties of some XAD-polymers

Amberlite type	Surface area (m^2/g) (Ref. 6)	Water uptake (g/g of dry polymer) (Ref. 7)
XAD-1	100	0.061
XAD-2	330	0.072
XAD-4	750	0.055
XAD-7	450	2.29

Equipment

Adsorption tube: The adsorption tube is made from Pyrex glass 15 cm × 2.5 mm i.d. packed with 50 mg of dry XAD-4 material. Small plugs of quartz-wool were inserted on either end of the adsorption column to hold the resin in place.

Before adsorption of the aqueous sample the resin bed was percolated with a small amount of water to remove air bubbles by moving the water up and down the tube using a rubber bulb. When the tube was packed from a resin slurry in methanol followed by an

elution with water too many air bubbles remained in the adsorption column giving rise to an irregular and slow passage of the aqueous samples. Sample volumes of 100–500 ml were forced under pressure through the column with a flow of about 1 ml/min. In case of a 10–20 ml sample a gravity flow of about 0.3 ml/min was obtained. In Ref. 9 the authors retained organic impurities from water efficiently on similar columns using a flow of 4–5 ml/min.

Concentrating trap: After extracting the compounds from the adsorption tube, the total amount of extract (0.5 ml) is concentrated on an adsorbent (XAD-4 or Tenax-GC) in a concentrating trap using a method which is comparable with the procedure used in Refs. 10–11.

The dimensions of the concentrating trap are the same as those of the adsorption tube except that the length of the loosely packed quartz-wool plug on top of the adsorbent is enlarged to about 6 cm. While taking care not to wet the resin the extract is deposited in portions onto the large quartz-wool plug. While the solvent is evaporated in a nitrogen flow (30 ml/min purified by a charcoal filter) through the tube, the organic compounds and a small amount of the solvent are retained on the adsorbent in the concentrating trap. Next, an additional amount of solvent is removed by maintaining the nitrogen flow for 15 minutes.

Gas chromatographic apparatus: A Perkin Elmer Sigma 3b was used equipped with a Flame Photometric Detector (FPD) and a Flame Ionization Detector (FID) and two injection systems:

1) Standard injection port, with splitter (ratio 1:20) only in combination with capillary columns,
2) Thermal desorption-Cold trap-Flash heating-Injector (TCFI).

A wide bore SE-30 column was used to analyse samples containing the organic compounds 1–7 (Table I), a Carbowax-20 M capillary column was applied in case of the recovery experiments for the complete procedure with compounds 8–18 (Table I).

Thermal desorption-cold trap-flash heating-injector unit: To inject the samples from the concentrating trap as a small vapour plug onto the chromatographic column, a thermal desorption-cold trap-flash heating-injector (TCFI)-unit (Figure 1) was used.

Downloaded At: 20:17 18 January 2011

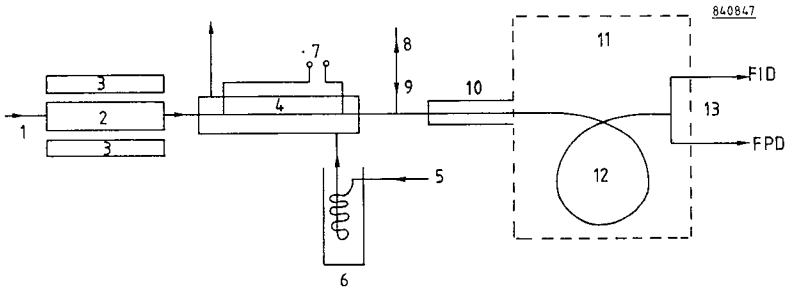


FIGURE 1 Thermal desorption-cold trap-flash heating-injector unit.

1. carrier gas (helium)
2. concentrating trap
3. desorption oven
4. cold trap
5. cooling gas (helium)
6. Dewar with liquid N_2
7. flash heating
8. vent
9. bypass
10. GC-injector
11. GC-oven
12. GC-column
13. detectors

Downloaded At: 20:17 18 January 2011

The concentrating trap (2) is placed in the desorption oven (3). Subsequently the compounds are thermally desorbed and simultaneously transferred with the carrier gas (1) (30 ml/min) to the cold trap (4) while the vent (8) between cold trap and GC-column (12) is open. The cold trap, cooled by a flow of helium (5) passing a Dewar (6) filled with liquid nitrogen, is assembled from a fused silica tube (i.d. 0.3 mm) tightly enclosed in a metal tube being the resistance wire for the flash heating unit (7).

After the vent is closed and a small bypass of helium (9) for the GC-column is restored, the cold trap is flash heated in 10 seconds to 523 K. The trapped compounds are vaporized and swept by the carrier gas onto the GC-column giving an optimum injection. It is very important to avoid cold spots at the couplings being in that case condensation sites. In our apparatus we used heating tapes.

OPERATION OF THE DIFFERENT PARTS OF THE PROCEDURE

Adsorption on XAD-4 and desorption by means of extraction

To investigate the adsorption and desorption capability of 50 mg of

XAD-4 for mg amounts of compounds 1–4 (Table I) the following procedure was used:

The adsorption tube was pre-washed with 5 ml of distilled water taking care to prevent the resin-bed from dryness. A quantity of 50 μl of an ethanolic solution containing 0.5 μg of the organic compounds 1–4 was introduced onto the top of the resin column. After 10 minutes the tube was washed with 10 ml of distilled water. The main part of the interstitial water was subsequently removed by pressing air through the tube until the appearance of water droplets on the outlet ceased. The adsorbed compounds were desorbed by extracting the tube twice with 500 μl of ethanol.

The model compounds were recovered for 85–95% which quantity was present almost exclusively in the first 500 μl of the ethanol extract. Thus it may be expected that 500 μl of ethanol will be sufficient to desorb compounds 1–4 and comparable lipophilic substances after adsorption on the XAD-4 when sampling water spiked with these compounds. Further it seems allowable to use an additional amount of water after desorption to remove adhered impurities (e.g. salts) probably present when analysing surface waters.

Next, adsorption-desorption experiments were carried out with 100 ml of aqueous samples containing 1 μg of compounds 1–4. For the desorption 500 μl of ethanol was used. The results are presented in Table III.

As can be seen, about 2/3 of the amounts added could be recovered but the results varied considerably. Especially, in case of

TABLE III
Recoveries of adsorption-desorption experiments with compounds 1–7

Compound	Recovery (%)
1. methyl isobutyl ketone	73 ± 9
2. toluene	57 ± 10
3. nonane	—
4. o-dichlorobenzene	58 ± 7
5. diazinon	75 ± 15
6. malathion	97 ± 18
7. parathion	72 ± 20

(— = too unreliable to be calculated)

Downloaded At: 20:17 18 January 2011

nonane the losses are probably due to an adsorption onto the glass wall of the sample container. Further, it was found that air bubbles frequently remaining in the resin-bed influenced the recovery to a great extent, probably due to an irregular flow through the column. When the aqueous sample doped with the compounds 1–4 was prepared by homogenizing it with a Teflon-coated magnetic stirring bar, low recoveries were found, possibly due to an adsorption of the organic compounds onto the Teflon material.

An aqueous sample spiked with the insecticides was made by diluting the stock solution in ethanol with water to a final concentration of 10 μg/100 ml. The adsorbed compounds were desorbed with 500 μl of ethanol. Table III shows the recovery results for the three organophosphorus insecticides.

Aqueous samples spiked with soman were prepared by adding 20 μl of a stock solution in isopropanol containing 1 μg of soman to 20 ml of sodium formate/formic acid buffer (0.025 Molar, pH 5.4). In the pH range 4–6 the hydrolysis rate is minimal ($t_{\frac{1}{2}} = 381$ h at pH 4.5–5).

After sampling and removing the main part of the interstitial water the adsorption tube was purged with a flow of nitrogen (30 ml/min) until the resin was visibly dry. However, residual amounts of water on the XAD-4 will be extracted as well with ethanol and as found in some preliminary experiments soman was partly decomposed when analysing the extract by gas chromatography, probably accelerated by the high temperature in the injection port. As a consequence it was preferred to use ethyl acetate as the extractant. In this way the adsorption/desorption recovery of soman was found to be 86%.

Afterwards on performing the experiments with the complete procedure it proved that the bulk of water remaining in the adsorption tube after the passage of the aqueous sample was efficiently removed by centrifugation[12] during 5 min until the resin was visibly dry.

Transfer onto the concentrating trap

To investigate whether a mixture of soman and a number of related compounds (compound 8–11, Table I) were retained quantitatively on XAD-4 in the concentrating trap, several experiments were

Downloaded At: 20:17 18 January 2011

carried out with 0.5 ml of ethyl acetate solutions containing the four model compounds at a μg/ml concentration level.

After the removal of residual amounts of solvent the efficiency of the retainment was determined by extracting the concentrating trap with 500 μl of ethyl acetate and analysing the extract by gas chromatography.

The results presented in Table IV indicate that the concentrating trap retains quantitatively μg amounts of soman and comparable compounds from 0.5 ml of ethyl acetate solutions.

TABLE IV

Retainment of μg amounts in the concentrating trap from 0.5 ml ethyl acetate solutions

Compound	Recovery (%)
8. pinacolyl methylphosphonofluoridate (soman)	91 ± 7
12. ethyl pinacolyl methylphosphonate	89 ± 2
13. n-propyl pinacolyl methylphosphonate	93 ± 7
14. dipinacolyl methylphosphonate	94 ± 1

Downloaded At: 20:17 18 January 2011

Thermal desorption

To investigate the thermal desorption, the performance of three different temperature programmes (Table V) in the desorption oven were compared. The recoveries of compounds 8, 12, 13 and 14 (Table I) on desorption from XAD-4 were determined.

After the application of the compounds on the concentrating trap (XAD-4) the tube was placed in the desorption oven. Then compounds were thermally desorbed from the XAD-4 which was purged with a helium flow (30 ml/min). To determine the amount of desorbed material the compounds were collected on a second XAD-4 tube placed in series and situated outside the desorption oven.

From an occasionally used third adsorption tube which was connected to the second tube only blank values for all test compounds were obtained.

The residual amounts on the concentrating trap as well as the transferred amount isolated on the second tube were determined by extraction and gas chromatographic analysis.

Downloaded At: 20:17 18 January 2011

TABLE V
Recoveries of the thermal desorption from XAD-4

Programming rate (K/min)[c]	7		14		28	
Compound	Desorbed[a]	Residue[b]	Desorbed	Residue	Desorbed	Residue
8. pinacolyl methylphosphonofluoridate (soman)	70	0	53	0	56	0
12. ethyl pinacolyl methylphosphonate	90	0	79	0–20	47	0–30
13. n-propyl pinacolyl methylphosphonate	88	0	53	0–60	27	32
14. dipinacolyl methylphosphonate	50	0–30	0	80	0	63

[a]found on second adsorption tube (%)
[b]left on desorbed concentration trap (%)
[c]initial temperature = ambient
final temperature = 503 K

On application of the three temperature programmes the amounts of compounds 12–14 recovered from the second adsorption tube decreased using increasing heating rates which is probably due to a low volatility in combination with a short heating period. Using 7 K/min the recovery of compounds 12 and 13 from the second adsorption tube was at least 85%. In this case, only compound 14 desorbed incompletely, leaving a residue on the concentrating trap. By using shorter heating periods the desorption efficiencies of compounds 12–14 decreased considerably.

From Table V it can be seen that about 60% of soman can be thermally desorbed from the XAD-4 concentrating trap but the remaining part (40%) is lost, probably due to its instability.

From an energy point of view a slow heating programme will be comparable with a fast programme if the final temperature is prolonged for some minutes.

Consequently, for practical and instrumental reasons the following temperature programme for the desorption oven was selected to be applied in the total procedure:

initial temperature: ambient
heating rate : 28 K/min
final temperature : 503 K hold→5.5 min

Tenax-GC was preferred to XAD-4 in the concentration trap as it can withstand higher temperatures (~370 K). For high-boiling compounds the relatively low maximum allowable temperature of XAD-4 (270 K) may give rise to incomplete recovery (Table V, e.g. dipinacolyl methylphosphonate) because of slow desorption. Moreover, Tenax-GC has a much lower surface area than XAD-4, 18.6 m^2/g[13] against 750 m^2/g respectively. So, especially in case of heat sensitive compounds the desorption from Tenax-GC may proceed more efficiently in comparison to that from XAD-4.

COMPLETE PROCEDURE

The complete procedure as given in Figure 2 is composed from the separate steps which were investigated and accordingly optimized as outlined in the preceding paragraphs.

The performance of the procedure was checked by determination

Downloaded At: 20:17 18 January 2011

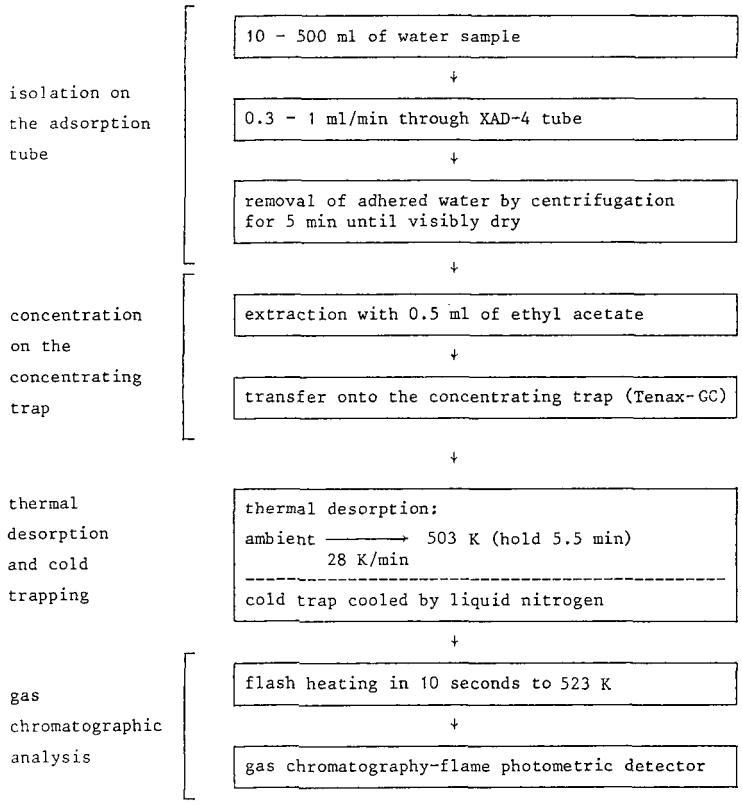


FIGURE 2 Scheme of the total procedure composed of isolation, concentration and gas chromatographic analysis.

of the recoveries of the test compounds (Table I; compounds 8–15) analyzing 10 ml samples of distilled water spiked at a concentration of 0.5 ng/ml. The resulting chromatographic peaks were compared in a quantitative way with those obtained from separate experiments in which the compounds were deposited directly onto the Tenax-GC in the concentrating trap. As can be seen from Table VI the different compounds can be isolated almost quantitatively from water at a 0.5 ppb concentration level. The low recovery of TMP (trimethyl

Downloaded At: 20:17 18 January 2011

TABLE VI
Recoveries obtained for a mixture of 11 model compounds from spiked water sampled (10 ml) at a concentration level of 0.5 ppb using the complete procedure

Compound[a]	Recovery (%)
8. soman	68
9. sarin	54
10. DFP	96
11. tabun	59
12. (EPM)	97
13. (PPM)	91
14. (DPM)[b]	~80
15. (TMP)	40
16. (TEP)	87
17. (TPP)[a]	~80
18. (TBP)	83

[a]For explanation see Table I.
[b]Compounds 14 and 17 give rise to partly merged peaks in the chromatogram; therefore only approximate values can be given.

Downloaded At: 20:17 18 January 2011

phosphate) is probably due to its relatively high solubility in water. The results were checked by direct injection of the same compounds onto the gas chromatographic column. In this way a chromatogram was obtained which was similar to those obtained from the water samples on application of the complete procedure.

CONCLUSIONS

The procedure presented in this paper permits the detection of ppb (or less) amounts of phosphorus containing compounds in 10 ml of water. Additional experiments currently being carried out aim to verify the applicability of the procedure to other aqueous samples (e.g. surface water, blood and urine) so as to examine the influence of the sample matrix.

References

1. A. Verweij, C. E. A. M. Degenhardt and H. L. Boter, *Chemosphere* **3,** 115 (1979).
2. CRC Handbook of Chemistry and Physics.
3. H. Adolphi, Insektizide 1975, BASF Landw. Versuchsstation Limburgerhof.
4. S. Franke, Lehrbuch der Militärchemie. Band 1 Deutscher Militärverlag, Berlin, 1967.
5. K. Berkane, G. E. Caissie and V. N. Mallet, *J. of Chromatog.* **139,** 386 (1979).
6. R. Kunin, *Pure Appl. Chem.* **46,** 205 (1976).
7. D. J. Pietrzyk and C. Chu, *Analytical Chemistry* **49,** 757 (1977).
8. G. A. Junk, J. J. Richard, M.D. Grieser, D. Witiak, J. U. Witiak, M. D. Arguello, R. Vick, H. J. Svec, J. S. Fritz and G. V. Calder, *J. of Chromatog.* **99,** 745 (1974).
9. J. P. Ryan and J. S. Fritz, *J. of Chromatographic Sc.* **16,** 488 (1978).
10. W. K. Fowler, J. E. Smith and H. C. Miller, *Analytica Chimica Acta* **124,** 225 (1981).
11. P. Kirchmer and M. Oehne, *J. High Res. Chrom. and Chrom. Comm.* **7,** 306 (1984).
12. J. F. Pankow and L. M. Isabelle, *J. of Chromatog.* **237,** 25 (1982).
13. K. Sakodynskii, L. Panina and N. Klinskaya, *Chromatographia* **7,** 339 (1974).

Downloaded At: 20:17 18 January 2011