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Working paper concerning the verification of the presence of nerve agents, their decomposition products or starting materials downstream of chemical production plants

1.1. A NON-INTRUSIVE METHOD TO VERIFY A BAN ON THE PRODUCTION OF NERVE AGENTS

One of the functions of an effective verification system with respect to a ban on the development, production and stockpiling of chemical weapons is to deter the production of chemical weapons, in particular the very dangerous nerve agents. To achieve adequate deterrence, procedures are necessary to ensure that a sufficient chance exists that clandestine production of nerve agents will be detected. On the other hand, one always strives for verification methods which are as non-intrusive as possible.

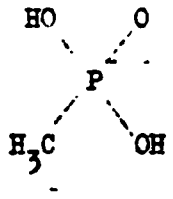
As a contribution to solve part of the problems involved, a highly sensitive method will be described to analyse waste water downstream of chemical production plants and to compare this with an upstream sample with the purpose of detecting the presence therein of nerve agents, their decomposition products or starting materials. The analytical procedure may be carried out in every laboratory equipped with a gas chromotograph and the method is sufficiently sensitive to give a positive indication even after extensive water purification.

From the results it may be concluded that the reported procedure gives a practically unambiguous and simple yes or no answer to the question whether nerve agents, their decomposition products or starting materials are present or not. After a positive detection -- which would only make the plant suspected -- a visit to the plant could be made to reveal the identity of the product manufactured.

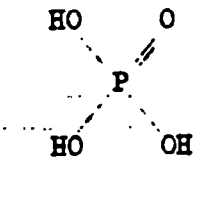
1.2. BASIS OF THE METHOD

The nerve agents are organophosphorus compounds and structurally related to pesticides. Generally both types of compounds may be prepared in similar production plants. However, an important structural difference between both types of compounds exists. The majority of the nerve agents is related to methylphosphonic acid (I),

whereas most of the commercially available organophosphorus pesticides have phosphoric acid (II) as their basic structure apart from a few pesticides based on I which generally have an experimental status[3-5].



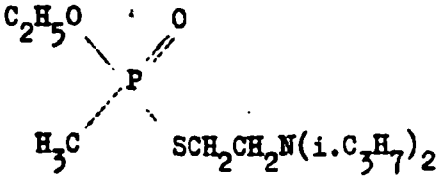
I



II

The Japanese delegation to the Conference of the Committee on Disarmament drew attention to the fact that the phosphurus-carbon bond is not cleaved under mild decomposing conditions. Besides gas chromatography in combination with a specific detection was mentioned as a suitable method to detect organophosphorus compounds at very low concentrations.[6]

A verification procedure, based on the above-mentioned considerations, is presented in this report. Samples from the Rhine and Meuse, both considered as heavily polluted rivers, were used as models for substantially diluted waste water downstream of chemical production plants. As such the procedure provides a rather non-intrusive inspection method. Ethyl S-2-di-isopropylaminoethyl methylphosphonotioate (VX).



was used as a representative of the nerve agents.

After a discussion of the investigations concerning the different aspects of the procedure in part 2 the ultimate procedure is described in part 3. Part 4 comprises some results obtained on application of the ultimate verification procedure on Rhine and Meuse river water samples. Some directions for future work conclude the report as part 5.

2. EVALUATION OF THE VERIFICATION PROCEDURE

2.1. Materials

Rhine river water samples were collected from the Lek at Bergambacht and analysed by the Dune Water Works of the Hague. The Meuse river was sampled at Keizerzveer and analysed by the Drinking Water Works of Rotterdam. The samples were stored in a refrigerating room. The chemical analyses of the water samples are listed in Table 1.

Table 1
Chemical analyses of Rhine and Meuse river samples

component		Rhine						Meuse
		12-12-'73	12-8-'74	20-11-'74	8-1-'75	25-8-'75	3-3-'76	23-2-'76
chloride	(mg/l)	230	175	168	83	140	196	37
sulphate	"	89	86	85	59	70	94	54
bicarbonate	"	140	146	156	146	149	193	134
nitrate	"	11.5	10.8	12.2	14.0	12.7	17.6	17.0
Kjeldahl nitrogen	"	4.4	1.7	2.2	1.5	1.0	2.6	1.9
orthophosphate		0.62	0.55	0.75	0.41	0.98	0.97	0.73
unfiltered	"	1.95	1.27	1.70	1.10	1.61	1.92	1.4
total organic carbon	"	6.2	7.8	5.9	8.0	5.5	8.2	6.9
silt	"	64	10	19	46	33	23	26
cholinesterase inhibition in parathion eq.	(µg/l)	0.17	0.25	0.24	0.04	0.08	0.13	-
pH		7.55	7.60	7.50	7.65	7.70	7.50	7.6
flow	(m^3/sec)	2572*	1648*	2870*	3497*	1964*	1329*	350**

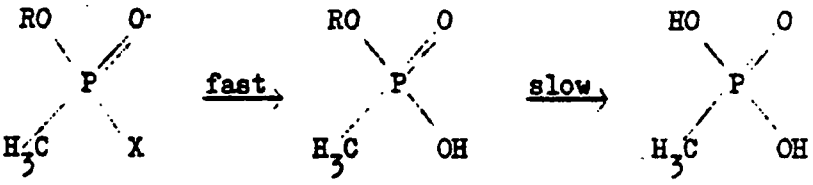
* Lobith.
** Lith.

For each experiment new glassware was used to preclude cross-contamination. ^{32}P-labelled methylphosphonic acid (specific activity 1 mCi/g) and ^{32}P-labelled VX (specific activity 20 mCi/g) as well as the corresponding unlabelled compounds were synthesized in this laboratory. Diazomethane was prepared and used in diethyl ether solution[7].

2.2. Hydrolysis

As stated in Chapter 1 gas chromatography in combination with a specific phosphorus detection is a suitable technique for the tracing of nerve agents in water at very low concentrations. To make the gas chromatographic picture as simple as possible (section 2.6) a complete hydrolysis should be carried out after which most

phosphorus-containing nerve agents will present themselves as methylphosphonic acid (equation 1), whereas organophosphorus pesticides will give rise to phosphoric acid (equation 2).

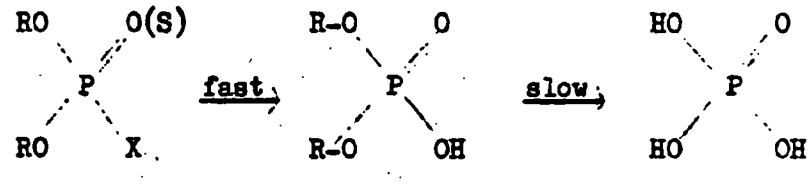


(1)

III IV I

Example of III: VX, in which R = C_2H_5 and X = $SCH_2CH_2N(i.C_3H_7)_2$

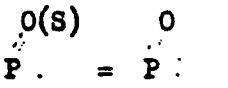
Sarin, in which R = $i.C_3H_7$ and X = F.



(2)

V VI II

Example of V: Parathion, in which R = C_2H_5, and X = $OC_6H_4NO_2$-p and

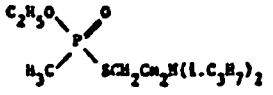
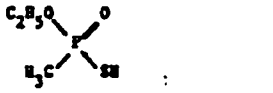
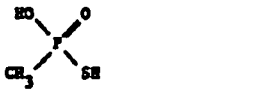
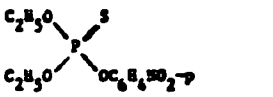
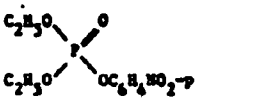
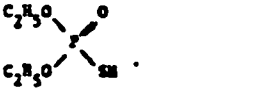
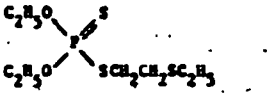
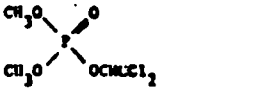
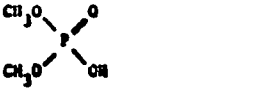
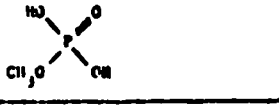


A strong acidic medium is a prerequisite to ensure a complete hydrolysis of both chemical warfare agents and pesticides with chemical formulae represented in equations 1 and 2 respectively. Moreover the process of hydrolysis should take place in a reasonable period of time. In order to establish optimum conditions, hydrolytic data of a number of organophosphorus compounds were collected.

In addition to some hydrolytic half-life values derived from literature a number of model compounds has been selected to determine their rates of hydrolysis. Experiments were carried out in 1 ml sealed glass ampoules containing 0.5 ml of 0.05 M sodium citrate/citric acid buffer at pH 3. The concentration of the different model compounds was 0.02 M. The ampoules were heated in an oil-bath at 130°C. From the quantitative analysis of the reaction mixture using high-voltage paper electrophoresis, paper chromatography, gas chromatography and ultraviolet spectroscopy the respective hydrolytic half-life values were determined[8], Table 2 comprises hydrolytic data of a representative of the nerve agents (VX), of some pesticides (Parathion, Disyston and DDVP) and of intermediates that might appear during hydrolysis. To motivate the presence of some of these intermediates it is to be remarked that in the acid hydrolysis of nerve agents (equation 1) and pesticides (equation 2) to I and II respectively, the

Table 2

Hydrolytic half-life values of some compounds related to phosphorus-containing nerve agents and pesticides at pH 3

	compound	systematic or trivial name	hydrolysis temp. (°C)	$t_{\frac{1}{2}}$ (h)	ref.
1		VX	130	0.24	-
2		ethyl hydrogen methylphosphonate	130	10	-
3		ethyl hydrogen methylthiophosphonate	130	9.8	-
4		methylphosphonothioic acid	130	0.36	-
5		Parathion	70	21	13
6		Paraoxon	70	23[a]	13
7		diethyl hydrogen phosphate	130	82	-
8		ethyl dihydrogen phosphate	130	1.42	-
9		diethyl hydrogen phosphorothioate	130	61	-
10		Disyston	70	62[a]	13
11		diethyl S-hydrogen phosphorodithioate	130	0.97	-
12		monothiophosphoric acid	92.8	1.2	14
13		DDVP	70	3.4[a]	13
14		dimethyl hydrogen phosphate	100	110	15
15		methyl dihydrogen phosphate	100	0.25	9

hydrolysis of the intermediately formed alkyl hydrogen methylphosphonate (IV) and dialkyl hydrogen phosphate (VI) is the rate determining step. Therefore hydrolytic data on these compounds are included.

The rates of hydrolysis of phosphates and phosphonates are known to be pH-dependent. The hydrolysis of alkyl dihydrogen phosphates[9] generally shows a maximum rate at pH 4; the hydrolysis rates of dialkyl hydrogen phosphates[10] and phosphonates[11] rise progressively when lowering the pH-value. Thiophosphates[12] show a maximum rate at pH 3. As a compromise and for practical reasons a pH 3 was selected for all hydrolysis experiments: acidic solutions below pH 3 may affect the performances (e.g. the capacity) of the anion-exchange column in the second step of the procedure (section 2.3).

A temperature of 130°C was selected to obtain measurable rates of hydrolysis in a four-days period.

From Table 2 it may be concluded that nerve agents, pesticides and their decomposition products hydrolyse to I and II respectively in a reasonable period of time at pH 3 and 130°C. In the ultimate procedure the temperature was increased to 160°C to obtain a complete hydrolysis of organophosphorus esters in 24 hours.

2.3. Isolation and concentration

After the hydrolysis the water samples of the Rhine and the Meuse river are passed through glass-fibre papers to remove solid particles (silt) preceding the use of the anion-exchange column. In this way the resin could be reused by means of a regeneration process*/ and a possible disturbance of the sample flow through the column was excluded. The adsorption of I onto the solid particles in the river samples is negligible as was determined by means of ^{32}P-labelled I. After filtration through the filter paper ng quantities of I were recovered quantitatively in the eluate.

A strong anion-exchange resin [type ϕ-$N(CH_3)_3^{(+)}$] is used to adsorb the methylphosphonate anion from the hydrolysed water samples. A simultaneous adsorption of other anions occurs e.g. chloride, sulphate and phosphate, which are generally present in excess when compared with the amount of compound I. The bicarbonate ion and other anions or weak acids are not adsorbed. A 2-3 fold excess in adsorption capacity of the anion-exchange column is used which is based on the average amount (3.5 meq.) of anions present in 0.5 litre of Rhine water in addition to the methylphosphonate ion and the added amount (about 3 meq.) of hydrochloric acid used to adjust the pH to 3. The first experiments were carried out with the commercially available anion-exchange resin

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*/ According to BIO-RAD: (step 1) resin-$Cl^{(-)}$ + NaOH → resin-$OH^{(-)}$; (step 2) resin-$OH^{(-)}$ + formic acid → resin-$formate^{(-)}$.

Amberlite IRA-400 in the chloride (Cl^-) form. On a column packed with this resin a quantity of 0.1 meq. of the methylphosphonate anion proved to be adsorbed incompletely from one litre of the water sample. 50-60 per cent of the added amount of I was not retained on the column. A quantitative adsorption of I was obtained when the resin was converted into the formate ($HCOO^-$) form. Afterwards a commercially available resin, type BIO-RAD AG 1-X8 ($HCOO^-$) was used. By means of a breakthrough chromatogram using a 0.5 litre sample containing 815 mg of chloride or 1200 mg of sulphate and 225 µg of ^{32}P-labelled I it was found that during the isolation I moved as a narrow band on the column in front of the chloride and the sulphate ions. Compound I eluted from the column only when the anion-content in the water sample surpassed the anion-exchange capacity of the column.

After the passage of the water sample the resin is washed with methanol to remove the interstitial water together with some neutral and basic compounds present in the original water sample. It is important that the hydrochloric acid-methanol solution, which is then used to elute the methylphosphonate anion, is dry because the subsequent evaporation of this solution in the presence of water gives rise to considerable losses of compound I.

A recovery of compound I amounting to 75-100 per cent was found after evaporation as was checked by experiments with ^{32}P-labelled I.

2.4. Derivatization

Compound I itself cannot be gas chromatographed but has to be converted into a volatile derivative to achieve a sensitive gas chromatographic detection and separation. The compound was transformed into dimethyl methylphosphonate using diazomethane in diethyl ether solution[7]. The yield of the esterification was nearly quantitative (95 per cent) as determined by gas chromatography (Chapter 3). Other acids such as phosphoric acid and sulphuric acid are methylated simultaneously. These acids may be present in the ion-exchange column eluate coming from the original water sample and trapped on the resin together with compound I.

2.5. Clean-up

This part of the complete verification procedure was introduced to obtain a proper gas chromatographic analysis of dimethyl methylphosphonate as outlined in section 2.6.

Ether as well as methanol are removed from the esterified sample (section 2.4) by means of boiling under reflux in a Vigreux column until a residual volume of 3-4 ml persists. This concentration step was checked by means of a number of experiments with mixtures containing 10 ml of benzene, 10 ml of ether, 1 ml of methanol and 3 µg of dimethyl methylphosphonate. A recovery of 90-100 per cent of the phosphonate was found as determined by gas chromatographic analysis.

The procedure according to reference 16 using a small silica gel column removes the majority of trimethyl phosphate and dimethyl sulphate from the methylated sample solution. Details of the gas chromatographic interferences of dimethyl sulphate are given in section 4. The silica gel column is successively eluted with benzene, ethyl acetate, and methanol. It was found that the benzene fraction contains mainly dimethyl sulphate, the ethyl acetate fraction trimethyl phosphate and the first ml of the methanol fraction about 80 per cent of the added amount of dimethyl methylphosphonate.

2.6. Gas chromatographic analysis

For the separation of dimethyl methylphosphonate and trimethyl phosphate the performances (e.g. resolution and peak symmetry) of a number of different stationary phases such as SE-30, QF-1, FFAP, OV-225, DEGS and Triton X-305 were evaluated. Triton X-305 turned out to be the best.

The optimum column temperature was found to be 140-150°C. Due to an increased column bleeding at higher temperatures the column-life decreased considerably whereas an increase in detector noise and detector contamination occurred.

Besides the use of diazomethane for the esterification of methylphosphonic acid and phosphoric acid it is possible to use other diazoalkanes. The resolution of the resulting trialkyl phosphates and dialkyl methylphosphonates may be expressed by:

$$R_s = 2\,\frac{t_r(\text{trialkyl phosphate}) - t_r(\text{dialkyl methylphosphonate})}{y\,(\text{trialkyl phosphate}) + y(\text{dialkyl methylphosphonate})} \qquad (3)$$

where R_s stands for the resolution, t_r for the retention time and y for the peak width at the base. The results together with the retention time relative to dimethyl methylphosphonate are given in Table 3.

Table 3
Resolution and retention times relative to dimethyl methylphosphonate*/ of a number of methylphosphonates and phosphates

$(RO)_2P(O)CH_3$ R =	relative retention	$(RO)_3P(O)$ R =	relative retention	resolution
CH_3	1.00	CH_3	1.33	2.1
C_2H_5	1.29	C_2H_5	2.07	4.0
$n.C_3H_7$	2.57	$n.C_3H_7$	5.53	4.1
$i.C_3H_7$	1.09**/	$i.C_3H_7$	1.58	2.8

*/ Retention time is 200 sec, column temperature 140°C, for further gas chromatographic conditions see Chapter 3.

**/ Tailing peak.

From the results given in Table 3 it might be concluded that it is advisable to prepare either the ethyl or the n.propyl esters instead of the methyl esters. Nevertheless the use of the methyl esters is to be preferred for the following reasons:

(a) Dimethyl methylphosphonate is detected at least two times more sensitive than diethyl methylphosphonate and dipropyl methylphosphonate.

(b) When using the ethyl esters or n. propyl esters the analysis time will be increased two or four times respectively in comparison with that needed for the methyl esters.

(c) Methanol is used as a main component of the eluent system to desorb methylphosphonic acid from the anion-exchange column. In that case the use of diazomethane[17] is recommended.

Owing to its specificity for organophosphorus compounds the thermionic detector was the detector of choice. The mean lowest detectable amount of dimethyl methylphosphonate proved to be 0.23 ng (range 0.15-0.30 ng). The maximum injection volume was found to be 5 µl. More solvent volume caused an extinction of the detector flame.

Dimethyl methylphosphonate can be identified by means of its retention index according to Kovàts[18]. The index amounts to 1427 when determined at 170°C on Triton X-305 as a stationary phase. Under these conditions trimethyl phosphate, which will be detected as well, has a retention index of 1483.

To prove unambiguously that the peak ascribed to dimethyl methylphocphonate is not due to the presence of a non-phosphorus compound in relatively high concentration, the thermionic detector was used in combination with a flame ionization detector. In case o. a non-phosphorus compound the last mentioned detector will give a relatively high pressu-

3. DESCRIPTION OF THE VERIFICATION PROCEDURE

From the results outlined in the preceding Chapter the following method was selected to verify the presence of nerve agents or their decomposition products in waste water.

Hydrolysis: The hydrolysis is carried out in sealed 750 ml Carius tubes containing 500 ml water samples adjusted to pH 3 using 0.5 N hydrochloric acid. The tubes are heated in an oil-bath at 160°C during 24 hours.

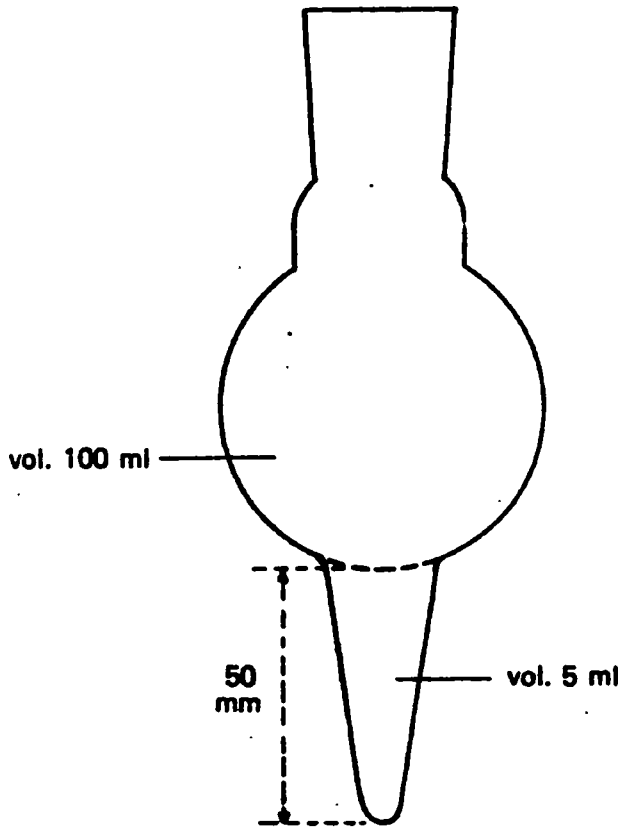

Figure 1. Pear-shaped flask to concentrate the column eluate.

Isolation and concentration: After filtration through glass-fibre paper (Whatman, GF/A) the hydrolyzed sample is passed through an anion-exchange column (length 20 cm, i.d. 11 mm) packed with AG 1-X8 (formate form, BIO-RAD) at a flow rate of 1-2 ml/min. After the passage of the sample the exchange column is washed with 30 ml of methanol. Methylphosphonic acid and other acids adsorbed on the resin are eluted at a flow rate of 0.5-1 ml/min with 20 ml of acidified (with gaseous hydrochloric acid up to 3N) methanol. The eluate, collected in a pear-shaped flask (Fig. 1), is concentrated to a volume of less than 1 ml by evaporation in a water-bath maintained at 50°C, using a gentle stream of air.

Derivation: A solution of diazomethane, generated from N-methyl-N-nitroso-p-toluenesulphonamide and potassium hydroxide[7], in ether is added to the residue of the eluate until a yellow colour persists. The mixture is allowed to stand for 15-20 minutes. The excess of diazomethane is removed by means of a few droplets of acetic acid.

Clean-up procedure: After the addition of 10 ml of benzene the methylated solution is concentrated by boiling under reflux using a Vigreux column (length 19 cm, i.d. 11 mm) until a residual volume of 3-4 ml. To prevent bumping of the boiling liquid use is made of a device consisting of a glass bar bent in a U-form[7]. During boiling the pear-shaped part of the reaction flask (Fig. 1) is immersed in an oil-bath, which is gently heated from room temperature up to 160°C in the course of 45 minutes.

Silica gel, after pretreatment by heating for 48 hours at 135°C, is partially deactivated by shaking with 3 per cent (w/w) distilled water. After four hours the gel is ready for use. To a column (length 19 cm, i.d. 8 mm) plugged with glass wool 1 g of the silica gel is added, followed by 2 g of anhydrous sodium sulphate[16]. The column is prewashed with 10 ml of hexane. The sample solution is transferred to the silica gel column which is successively rinsed with 16 ml of benzene, 24 ml of ethyl acetate and 8 ml of methanol at a flow rate of 0.2-0.4 ml/min. The eluates of benzene, ethyl acetate and the initial 1 ml of methanol are collected separately. The methanol fraction is set aside for further use.

Gas chromatography: The gas chromatographic analyses are carried out on a Becker gas chromatograph, type 409, equipped with a thermionic detector (TID), type 712. The coiled glass column (length 2 m, i.d. 1.5 mm) is packed with Chromosorb W-AW/DMCS 80-100 mesh coated with Triton X-305 (25 per cent w/w) after sieving in the particle range from 149-177 µm. The column, injector and detector are maintained at 150, 200 and 200°C respectively. Gas flow rates are 40 ml/min for nitrogen, 65 ml/min for hydrogen and 250 ml/min for air. Because of the use of a splitter at the end of the column [ratio (3:1)] only 20 ml of nitrogen pro minute reached the TID detector. The remaining part is led to a flame ionization detector. Maximum sample volumes of 5 µl can be injected. Reference samples of comparable concentration are used for quantitative measurements.

4. APPLICATION AND DISCUSSION

Once developed the complete verification procedure was checked by adding varying quantities (0.1 µg - 1 mg) of VX to 1 litre of demineralized water and Rhine river water.

Based on dimethyl methylphosphonate a mean recovery of 73 ± 11 per cent was obtained in demineralized water. The clean-up part of the procedure was omitted in this case. Considerable concentrations of phosphoric acid (approximately 0.2 mg/litre) were found which were detected as trimethyl phosphate by gas chromatography. Phosphoric acid is probably released from the wall of the glassware during hydrolysis.

Samples obtained after the addition of a relatively high quantity (1 mg) of VX to 1 litre of Rhine river water were analysed similarly. A clean-up of the sample before the gas chromatographic analysis proved to be unnecessary because no interfering substances were present at that concentration level and the comparable amounts of dimethyl methylphosphonate and trimethyl phosphate could be sufficiently separated by gas chromatography. Based on dimethyl methylphosphonate a recovery of 78 ± 10% (n=6) was obtained.

In the analytical procedure carried out with small quantities of VX (0.1-1 µg) added to 1 litre of Rhine river water the clean-up method had to be introduced because of interferences in the gas chromatographic analysis. First of all separation of small amounts of dimethyl methylphosphonate from a 1000 fold excess of trimethyl phosphate proved to be insufficient because of overlapping of the peaks. Moreover dimethyl sulphate interfered seriously in the detection of dimethyl methylphosphonate. Depending on the hydrogen flow the thermionic detector gave negative or positive peaks for dimethyl sulphate which influenced the response of dimethyl methylphosphonate, because of peak overlap. Dimethyl sulphate was identified by the combination of gas chromatography and mass spectrometry (type JEOL JMS-01-SG). It is most probably formed by methylation of sulphuric acid present in the Rhine river samples (concentration level of sulphate ≈ 80 mg/litre). The interferences of excess trimethyl phosphate and dimethyl sulphate could be overcome when using a clean-up of the methylated sample before the gas chromatographic analysis. In this way it proved to be possible to analyse concentrations of VX added to Rhine river water samples down to 250 ng/litre. Based on dimethyl methylphosphonate a recovery of 80-90 per cent was found in Rhine river samples taken 25 August 1975.

These recoveries were corrected for an amount of dimethyl methylphosphonate (0.7-0.8 µg/litre) detected in the same Rhine river samples to which no VX was added. The identity of this compound was approved by mass fragmentography on a Finnigan quadrupole gas chromatograph-mass spectrometer, type 3100-003D. The peak was scanned at three characteristic m/e values: 79, 94 and 109 which correspond with $(CH_3O)P(O)H^{(+)}$, $(CH_3O)P(O)H(CH_3)^{(+)}$ and $(CH_3)_2P(O)^{(+)}$. The peak intensity ratio was 6:4.4:1 which

equals the result obtained with a reference sample of dimethyl methylphosphonate. Owing to the small amount the intensity of the molecular ion was too small for scanning.

Later on the same compound was detected in the Rhine river samples of 3 March 1976 (conc. 760 ng/litre) and in the Meuse river sample of 23 F bruary 1976 (180 ng/litre). Obviously one or more emission sources in or at both rivers give rise to the presence of a compound containing a PCH_3 group in the molecule. Literature gives no indication that such compounds occur in nature. It is known that a number of insecticides containing a P-C bond are commercially available e.g. Dyfonate (ethyl S-phenyl ethylphosphonodithioate). As a result of the described analytical procedure dimethyl ethylphosphonate will result. According to its retention index (1468) this compound will not interfere in the gas chromatographic analysis of dimethyl methylphosphonate (retention index 1427, see section 2.6). However, Mecarphon[5] to our knowledge the only commercially available pesticide containing a PCH_3 group will give rise to dimethyl methylphosphonate on application of the analytical procedure and will thus interfere in the verification process.

As stated in section 2.6 the mean lowest amount of dimethyl methylphosphonate detectable by gas chromatography (section 2.6) is 0.23 ng of dimethyl methylphosphonate or 250 ng of VX per litre of water, being corrected for a mean recovery of 80 per cent and an original water sample volume of 0.5 litre, which was concentrated to a volume of 1 ml. This means that if a plant carries off at least 5 kg of VX or an equivalent quantity of its decomposition products or starting materials in 24 hours into a river with a flow of 250 m^3/sec it will be detected A survey of advanced waste treatment technology has revealed that carbon adsorption processes would be capable of reducing a concentration of 1 mg/litre of phosphorus containing insecticides in a waste stream to less than 1 µg/litre[4]. This concentration lies well above the detection limit of the procedure described.

As to the possible presence of PCH_3-containing compounds may also be due to a natural or industrial background a reference sample upstream of the chemical production plant has to be analysed in addition to a downstream sample.

5. FUTURE WORK

Further research is needed to get acquainted with the natural or industrial occurrence of compounds which will deliver dimethyl methylphosphonate after application of the described procedure.

Experiments will be carried out to investigate the applicability of the procedure in case of binary nerve agent systems in which the nerve agent is formed by mixing two compounds during the delivery of the projectile to its target.

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