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**THE NETHERLANDS****WORKING PAPER CONCERNING THE VERIFICATION OF THE PRESENCE OF NERVE AGENTS,  
THEIR DECOMPOSITION PRODUCTS OR STARTING MATERIALS DOWNSTREAM OF CHEMICAL  
PRODUCTION PLANTS****INTRODUCTION**

In 1977 the Netherlands tabled a document (CCD/533 dated 22 April 1977, now reissued as document CD/306) describing a relatively non-intrusive method to determine the presence of nerve agents, their decomposition products or starting materials downstream of chemical production plants. The rationale behind this method is that most of the super-toxic nerve agents contain a phosphorusmethyl (P-Me) bond which is very stable towards chemical reactions and can be used as a kind of "fingerprint".

In the last paragraph of the aforementioned document two subjects for further studies were announced, viz. an investigation into the applicability of the method with regard to precursors for binary nerve agents and a study into the background of P-Me compounds present in several types of water. This document addresses both problems.

A part of this work has been reported in references 1-4.

**THE METHOD**

Since the appearance of CCD/533 the verification procedure has been slightly modified. Details of this modification are given in Annex I.

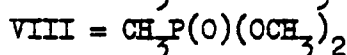
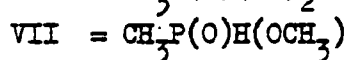
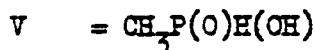
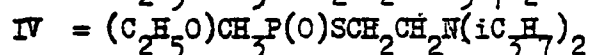
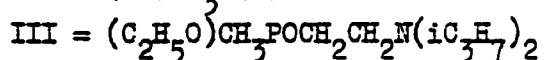
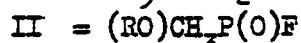
**BINARY NERVE AGENTS**

As has been mentioned above, the P-Me bond occurring in the most toxic nerve agents is chemically very stable. It is also relatively difficult to produce. Thus it is highly improbable that this chemical bond is formed during the short period in which the chemical precursors are in contact with each other in a binary (a multicomponent for that matter) weapon. So one has to assume that one of the precursors does already contain the P-Me bond and as a consequence will be liable to the fingerprinting method. Two types of P-Me precursors can be distinguished. The first type is represented by methylphosphonic difluoride (I) which has been

mentioned as a precursor for the production of the so-called G-agents (II). This compound is very reactive and hydrolyses in water very rapidly while forming methylphosphonic acid. Consequently the verification procedure can be applied without any change.

In case of the so-called V-agents, methylphosphonites may be used as precursors. A representative of these compounds is ethyl diisopropylaminoethyl methylphosphonite, better known by its code name QL (III), which is a precursor of the nerve agent VX (IV) (5). In water QL decomposes completely and very rapidly into methylphosphinic acid (V). By using the verification procedure only a small amount of methylphosphonic acid (VI) is formed. On methylation with diazomethane the aforementioned compounds are converted into methyl hydrogen methylphosphinate (VII) and dimethyl methylphosphonate (VIII) respectively. Application of the clean-up procedure - a necessity for the proper analysis of the phosphonate - was not very satisfactory as the phosphinate eluted only partially. However, by means of gas chromatographic analysis carried out before the clean-up procedure the phosphinate was identified on basis of its retention index.

In conclusion it may be stated that binary precursors like QL are detected by means of the verification procedure and moreover may be distinguished from other compounds originating from nerve agents and starting materials.



#### ENVIRONMENTAL BACKGROUND LEVELS OF COMPOUNDS CONTAINING THE P-ME BOND

A search was carried out to get acquainted with the occurrence of P-Me containing compounds in water from natural or industrial origin as these will also give rise to dimethyl methylphosphonate on application of the verification procedure. The concentration of P-Me containing compounds was determined in several surface waters sampled in a number of countries in Europe and North-America (2,3). According to the grades of pollution as indicated by the sampling authorities the water samples were divided into four distinct groups. The results are summarized in Table 1. The mean values of the dimethyl methylphosphonate concentration of the different groups increase in accordance with their grade of pollution. This suggests that the background of P-Me containing compounds is due to industrial sources.

Table I: The concentration of P-Me containing compounds (determined as dimethyl methylphosphonate) of the surface water samples arranged in accordance with the different pollution grades

Classification	dimethyl methylphosphonate conc. ( $\mu\text{g}/\text{l}$ )*
very clean	-
clean	0.2
industrially polluted	0.5
waste water	13

\* = mean value

- = nothing or below detection limit of  $0.14 \mu\text{g}/\text{l}$

The commercially available P-Me containing flame retardants (3) or the corresponding starting materials and decomposition products will give rise to dimethyl methylphosphonate on application of the verification procedure. Another source for the background may be methylphospholane dichloride ( $\text{CH}_3\text{PCl}_2$ ) which is commercially available and is a starting material for many other products (3). Many of these products will be hydrolysed to methylphosphinic acid [ $\text{CH}_3\text{P}(\text{O})(\text{OH})$ ] which is susceptible to oxidation and will be detected as dimethyl methylphosphonate by means of the verification method. These commercially available, industrially produced P-Me containing compounds may be sources of the background as mentioned in Table I.

What are the consequences of these background values of P-Me containing compounds for the applicability of verification method?

For economic, environmental and security reasons it is reasonable to expect that the amount of nerve agents or their decomposition products in the discharge will not exceed 0.01 per mil of the agents produced (4). This means that a nerve agent production facility designed to produce 12 tons per day, as mentioned in a publication of the United States Arms Control and Disarmament Agency (6), may carry off 120 g of a nerve agent (or more probably an equivalent amount of its decomposition products) per day into a waste stream with a flow rate of  $7 \text{ litre sec}^{-1}$  (4); this results in a concentration of about  $200 \mu\text{g litre}^{-1}$ , which far exceeds the detection limit of the verification procedure ( $0.14 \mu\text{g litre}^{-1}$ ). Ultimately, the waste stream may flow into a river. In the case of a river flow below  $2000 \text{ m}^3 \text{ sec}^{-1}$  the concentration of the nerve agent (or the P-Me containing decomposition compounds) originating from the waste stream will be above the detection limit within a few hundred meters downstream of the waste outlet (4). To establish if a certain plant carries off compounds

containing the P-Me linkage and to correct for a background of these compounds it is necessary to compare a downstream sample with an upstream sample. The size of both samples must be such that a specified difference in terms of standard deviation will be found statistically significant according to the t-test with a chosen level of significance in a specified percentage of cases. With a level of significance of 0.05, a difference of two standard deviations will be found with a probability of 0.95 if both sample sizes are chosen to be seven or more (4). In our measurements we found that the standard deviation was about 12 per cent of the determined value. Consequently with a background of  $0.5 \mu\text{g litre}^{-1}$  (the mean value of industrially polluted surface waters; see Table I) a downstream concentration originating from the waste stream of  $0.12 \mu\text{g litre}^{-1}$  would be detected. As this concentration is comparable with the detection limit of  $0.14 \mu\text{g}$  it may be concluded that the above-mentioned background does not affect the maximum distance of a few hundred meters downstream where samples could be taken.

#### FUTURE WORK

The P-Me verification procedure is sensitive even in heavily polluted water. It gives a simple yes or no answer to the question of whether compounds related to chemical warfare nerve gases containing the P-Me linkage are present or not. Nevertheless the method lacks specificity. The intact P-Me containing chemical warfare agents or their decomposition products are all transformed into the same compound: dimethyl methylphosphonate. Experiments are now started to concentrate trace amounts of chemical warfare agents from water using adsorption tubes packed with the porous polymers XAD or TENAX as adsorbent. After a thorough removal of the water adhered onto the adsorption material the isolated chemical warfare agent will be desorbed thermally from the tubes and analysed on-line in a qualitative and quantitative way by capillary gas chromatography combined with a phosphorus-specific detector or a mass spectrometer. It may be expected that relatively high volumes of water samples can be handled, thus ensuring high sensitivity. This will be necessary because generally, after a natural or manual-induced decomposition or after adsorption processes only trace amounts of the original, intact chemical warfare agents will be present in the water samples.

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4. A. Verweij, H.L. Boter and C.E.A.M. Degenhardt, Science 204(1979)616
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#### ANNEX

In this annex a summary of the verification procedure is given including the modification.

The water samples are hydrolysed at pH 3 during 24 hours. The resulting acids are concentrated on an ion-exchanger and after elution converted into methyl esters by means of diazomethane. Methyl hydrogen methylphosphinate [ $\text{CH}_3\text{P}(\text{O})\text{H}(\text{OCH}_3)$ ] and dimethyl methylphosphonate [ $\text{CH}_3\text{P}(\text{O})(\text{OCH}_3)_2$ ] are analysed by gas chromatography on a wide-bore capillary column coated with Carbowax 20 M. The analysis of these compounds is performed respectively before and after the application of the silica gel clean-up column. The Kovats retention indices are 1645 and 1659 respectively at  $110^\circ\text{C}$ . The detection was carried out by a thermionic, phosphorus-specific detector. Further details are given in ref. 1-4.

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1. CCD/533, 22 April 1977, The Netherlands
2. A. Verweij, H.L. Boter and C.E.A.M. Degenhardt, Science 204(1979)616
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