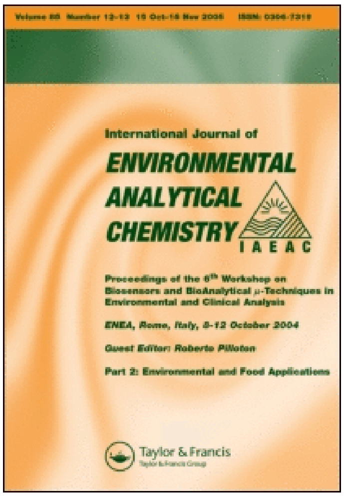

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John Aasulf Tørnes[a]; Aase Mari Opstad[a]; Bjørn Arne Johnsen[a]
[a] Division for Environmental Toxicology, Norwegian Defence Research Establishment, Kjeller, Norway

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USE OF SOLID-PHASE EXTRACTION IN DETERMINATION OF CHEMICAL WARFARE AGENTS

Part II Determination of Chemical Warfare Agents in Samples from a Battlefield Environment

JOHN AASULF TØRNES, AASE MARI OPSTAD and
BJØRN ARNE JOHNSEN

Norwegian Defence Research Establishment,
Division for Environmental Toxicology,
P.O. Box 25, N-2007 Kjeller, Norway.

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The chemical warfare agents Tabun, Sarin, Soman, VX and mustard gas and the Sarin impurity diispropyl methylphosphonate have been isolated from different samples from a battlefield environment. 50 ml of water, 2 g of grass, soil, sand, paper, neoprene or butyl rubber or 1 g of silicone, a polyurethane foam with activated charcoal or a polyester/cotton fabric were spiked with either 1 mg and 1 μg of the various compounds. The samples were extracted with water, and the aqueous solution passed through cartridges filled with C_{18} sorbent. The compounds were then eluted with chloroform and quantitatively analyzed by gas chromatography with a flame ionization detector. The highest yields of the investigated compounds were obtained from water, sand and paper and the lowest from grass, butyl rubber and polyurethane foam with activated charcoal.

KEY WORDS: Chemical warfare agents, determination, environmental samples, polymeric materials, solid-phase extraction, gas chromatography.

1 INTRODUCTION

As the negotiations in Geneva on a Chemical Weapons Convention seem to go to completion, the need for analytical procedures for verification of the convention becomes important. To control alleged violation of the convention, methods are needed for verification of use, destruction and non-production of chemical warfare agents.

When the convention enters into force, it is suggested that a technical secretariat should be put together in order to verify alleged violation of the convention[1]. For such a secretariat to draw correct conclusions from the results of different samples provided by different laboratories, it is important that all parts of the sampling and sample preparation procedures are carried out properly. Several different sampling and sample preparation procedures have been proposed. The most commonly described procedure has been the collection of soil or sand samples which are cooled and transported in air-tight containers to a laboratory where the samples preparation and analysis will take place[2–8]. Sampling of high or low volume air samples on different filters has also been prepared[2,9–12].

In order to reduce the sample amounts which have to be transported to the laboratory, the preparation of the samples should preferably be carried out close to where they are collected. Possible degradation of the chemical warfare agents during transport is thereby also diminished. The use of solid-phase extraction in preparation of samples containing chemical warfare agents was described in Part I of this study[13]. This technique allows a wide range of chemical warfare agents to be isolated from aqueous solutions. Solid-phase extraction is based on trapping the chemical compounds from a sample solution on a sorbent material packed in a small cartridge and subsequent elution with an organic solvent. The cartridges used to retain the compounds by this technique have the advantage of being small, easy to handle, rapid in use and inexpensive.

This paper describes the isolation of the chemical warfare agents ethyl *N*, *N*-dimethylphosphoramidocyanidate (Tabun, GA), isopropyl methylphosphonofluoridate (Sarin, GB), 1,2,2-trimethylpropyl methylphosphonofluoridate (Soman, GD), O-ethyl S-2-diisopropylaminoethyl methylphosphonothiolate (VX) and bis(2-chloroethyl)sulphide (mustard gas, H) and the Sarin production impurity diisopropyl methylphosphonate (DIPMP) from different sample materials. The materials used were water, grass, soil, sand, paper, silicone, butyl rubber, neoprene, a polyurethane foam with activated charcoal and a polyester/cotton fabric. Of these ten materials, the latter five are derived from protective clothing.

2 EXPERIMENTAL

2.1 Sorbent and chemicals

The cartridges filled with octadecylsilane (C_{18}) sorbent used in the experiments were obtained from Analytichem International, and a Vac-Elut rack from the same company was used for simultaneous preparation of up to 10 samples. Methanol and chloroform used were Uvasol grade from Merck. The chemical warfare agents, GA, GB, GD and H and the phosphonate ester DIPMP were sythesized and purified ($>95\%$) in our laboratory. Stock solutions of 1 mg/ml of the model compounds were prepared in chloroform every day and used for spiking the samples with the lowest concentrations. Hexadecane from Koch-Light Laboratories was used as internal standard in the gas chromatographic analyses.

The frit filters used to filter the aqueous samples had pore sizes of 70 μm and were obtained from Analytichem International. They had a form that fitted into the reservoirs used for addition of the samples to the sorbent.

2.2 *Chromatographic equipment and conditions*

The quantitative determinations of the model compounds were performed on a Carlo Erba model 5160 gas chromatograph equipped with a flame ionization detector and a 30 m × 0.242 mm I.D. capillary column with 0·25 μm DB-WAX liquid phase. The injection was splitless with 40 sec splitless time. A multistep temperature programme from 60°C to 250°C was used for the column [60°C (2 min) – 30°C/min – 90°C (3 min) – 16°C/min – 250°C (3 min)], and the injector and detector temperatures were maintained at 270°C.

2.3 *Sample preparation*

Samples of about 50 ml of water, 2 g of soil, sand, grass, paper, neoprene or butyl rubber, or about 1 g of silicone, a polyester foam with activated charcoal or a polyester/cotton fabric were spiked with 1 mg or 1 μg of the chemical warfare agents GA, GB, GD and H and the phosphonate ester DIPMP. For VX only 1 mg was used.

After adding the model compounds, the samples were placed in closed vials for 30 min and then extracted by shaking with 50 ml distilled water for 1 min. The extracts from the grass, sand and soil samples were first filtered through frit filters with 70 μm pore sizes to remove particulate matter. All aqueous solutions were then immediately passed through cartridges filled with 200 mg C_{18} sorbent which had previously been wetted with 1 ml methanol and 4 ml water. Finally, the compounds were eluted from the cartridges with 600 μl chloroform, an internal standard was added and the sample was analyzed by gas chromatography. Five replicate experiments were conducted for each combination of model compound, concentration and sample material.

3 RESULTS AND DISCUSSION

The yields (means ± standard deviations) of the various experiments are shown in Tables 1 and 2 for samples containing 1 mg and 1 μg respectively of the chemical warfare agents and related compound. The data show that the majority of yields are somewhat lower for samples containing 1 μg than 1 mg of the model compounds. In addition, the differences between the sample materials seem to be larger for the 1 μg samples.

For GA at the highest spiking level, 60 to 90% could be recovered from all sample materials except polyurethane. For samples containing 1 μg GA, the yields showed large variations, from 80% with paper and 78% with soil to 8% with grass and 4% with polyurethane as sample materials. For GB at the highest spiking level, 30–35% was recovered from all materials except polyurethane. Water, soil and paper showed the highest yields at the lowest spiking level, with values of 64–75%, while butyl rubber, grass and silicone gave lower values. For GD at the highest spiking level, the yields were about 50% for all sample materials except grass and polyurethane. For samples containing 1 μg GD, the yields varied from 86% with paper to 8% with

Table 1 Amounts recovered (%) from different sample materials contaminated with 1 mg of the model compounds.

Sample material	*Percentage yields of*					
	GA	*GB*	*GD*	*VX*	*H*	*DIPMP*
Water	86 ± 11	54 ± 3	98 ± 3	36 ± 12	12 ± 1	87 ± 10
Grass	72 ± 22	29 ± 10	27 ± 19	32 ± 21	38 ± 4	86 ± 19
Soil	62 ± 11	36 ± 11	84 ± 6	8 ± 6	29 ± 9	66 ± 7
Sand	77 ± 7	36 ± 6	73 ± 24	36 ± 6	34 ± 3	87 ± 9
Paper	82 ± 17	37 ± 5	53 ± 5	18 ± 2	11 ± 1	71 ± 10
Silicone	88 ± 13	35 ± 3	47 ± 18	28 ± 8	48 ± 13	67 ± 5
Butyl	79 ± 12	48 ± 9	79 ± 19	17 ± 8	46 ± 2	67 ± 4
Neoprene	83 ± 12	32 ± 4	62 ± 4	13 ± 2	24 ± 9	53 ± 27
Polyurethane	48 ± 14	15 ± 2	23 ± 11	19 ± 8	5 ± 1	45 ± 8
Polyester/ cotton	81 ± 9	55 ± 7	83 ± 18	38 ± 5	32 ± 3	61 ± 26

butyl rubber and 3% with polyurethane as sample materials. The yields were only established for samples containing 1 mg VX due to poor chromatography at the low spiking level. At the highest level, 8–38% was recovered, with water, sand and polyester/cotton fabric being the most suited and soil the least suited sample material(s). For samples containing 1 mg H, the yields varied from 48% with silicone and 46% with butyl-rubber to 5% with polyurethane as sample material. At the lower spiking level, the yields were below 21% from all sample materials, except paper (57%). The amount of H recovered from neoprene and polyurethane at this level was below the detection limit of the chromatographic method used. More than 45% was recovered from all sample materials containing 1 mg DIPMP, with water, grass and sand as the most suitable sample materials. At the lower spiking level, the

Table 2 Amounts recovered (%) from different sample materials contaminated with 1 μg of the model compounds.

Sample material	*Percentage yields of*				
	GA	*GB*	*GD*	*H*	*DIPMP*
Water	56 ± 8	64 ± 5	68 ± 8	11 ± 2	46 ± 4
Grass	8 ± 6	18 ± 17	10 ± 7	9 ± 10	40 ± 16
Soil	78 ± 19	65 ± 13	77 ± 18	21 ± 4	90 ± 15
Sand	33 ± 12	40 ± 11	63 ± 17	17 ± 8	86 ± 15
Paper	80 ± 12	75 ± 9	86 ± 3	57 ± 6	91 ± 8
Silicone	15 ± 4	19 ± 3	11 ± 4	1 ± 3	19 ± 3
Butyl	10 ± 1	11 ± 3	8 ± 2	1 ± 2	12 ± 3
Neoprene	13 ± 4	27 ± 22	12 ± 3	—	20 ± 5
Polyurethane	4 ± 1	24 ± 22	3 ± 1	—	11 ± 1
Polyester/ cotton	33 ± 7	45 ± 24	58 ± 13	14 ± 4	47 ± 8

–, Amount below detection limit.

yields varied form 91% with paper and 86% with sand to 12% with butyl rubber and 11% with polyurethane.

The rather low yields for some of the compounds (e.g. H and VX) could obviously have been improved if the solid-phase extraction technique had been optimized for one agent at a time. The present procedure has, however, been developed as a general screening procedure for samples suspected to be contaminated by chemical warfare agents.

The low yield for H is probably also the result of its low solubility in water.

4 CONCLUSIONS

Some conclusions can be drawn with respect to the type of samples to be preferred for screening purposes to determine chemical warfare agents. The yields were highest with water, sand and paper and lowest with grass, butyl rubber and polyurethane foam with activated charcoal. The yields for soil were high for all compounds except VX and H. These results should, however, be related to earlier experiments[14], where samples were exposed to prevailing weather conditions for up to four weeks before analysis. The latter experiments showed that polymer materials like silicone, neoprene and polyurethane foam with activated charcoal preserved the chemical agents to such an extent that small amounts still remained after four weeks of exposure under summer conditions. Thus, although the yields of chemical warfare agents are low for such polymer materials when using the present sample preparation procedure, they can become important sample types when analysis after long-term exposure is desired. In principle, therefore, all the materials tested in this paper can be used for the verification of alleged violation of a chemical weapons convention.

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