

## Thermal desorption–gas chromatography of some organophosphates and S-mustard after trapping on Tenax

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### ABSTRACT

Thermal desorption from Tenax coupled with gas chromatographic analysis was performed with bis(2-chloroethyl) sulphide (s-mustard), O,O-diisopropyl phosphorofluoridate (DFP), O-isopropyl methylphosphonofluoridate (sarin), O-(1,2,2-trimethylpropyl) methylphosphonofluoridate (soman) and O,O-dimethyl methylphosphonate (DMMP). Experiments with humidified test atmospheres (48% relative humidity at 20°C) of S-mustard, DFP and soman revealed that the moisture did not impair the sampling of these compounds on Tenax or their thermal desorption from that sorbent. Tenax tubes loaded with the three agents from humidified atmospheres could be stored for up to 2 months without a decrease in recovery.

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### INTRODUCTION

The objective of this work was to study the applicability of Tenax as the sampling material together with automated thermal desorption–gas chromatography (ATD–GC) in monitoring atmospheres for their content of the toxic compounds bis(2-chloroethyl) sulphide (S-mustard), O,O-diisopropyl phosphorofluoridate (DFP), O-isopropyl methylphosphonofluoridate (sarin), O-(1,2,2-trimethylpropyl) methylphosphonofluoridate (soman) and, as a simulant, O,O-dimethyl methylphosphonate (DMMP). Additionally, with S-mustard, DFP and soman, the influence of atmospheric moisture on sampling, ATD–GC and storage of loaded sorbent tubes was investigated.

### EXPERIMENTAL

#### *Materials and equipment*

The chemicals used, with the purity and supplier in parentheses, were Tenax TA, 20–35 mesh (Alltech), 1,1,2-trichlorotrifluoroethane (TCFE; 99%, Aldrich), DMMP (97%, Aldrich), S-mustard (99.7%, Atlanta), DFP (80%, EGA Chemie), sarin (93.5%, Wehrwissenschaftliche Dienststelle der Bundeswehr) and soman (83%, Wehrwissenschaftliche Dienststelle der Bundeswehr). The percentages given for the last three latter compounds were determined by titration according to ref. 1.

For ATD and GC an ATD 50–GC 8500 system with an LCI 100 integrator from Perkin-Elmer was applied. The ATD sorption tubes, made of stainless-steel (8.9 cm × 0.49 cm I.D.), were filled with 175 mg of Tenax and flushed with nitrogen at 250°C overnight to remove volatile impurities.

The ATD 50 (with a multiple split system) was run with the following operating parameters: helium, 150 kPa; purge, 1.5 ml/min; mode 2; box, 140°C; oven, 250°C; cold trap, –30/300°C; desorb I, 10 min, input split closed, output split 18 ml/min; desorb II, 45 s, input split 12 ml/min, output split closed. With these split settings maximum transfer of sample onto the column was achieved. The cold trap was filled with 15 mg of Tenax. In order to exclude contamination of the cold trap by exudations from the septum of the ATD injector, the septum port was replaced with a stainless-steel screw-cap. With this measure, an appreciable decrease in the noise of blank tube runs and in the detection limits was achieved.

The operating parameters of the GC 8500 were as follows: helium, 150 kPa (4 ml/min at 35°C); column, WCOT (25 m × 0.32 mm I.D.), 1 µm PVMS (Perkin-Elmer); oven, 35°C (4.5 min), increased at 30°C/min to 65°C (2 min) and to 110°C (3 min); flame ionization detector, 250°C, with hydrogen at 85 kPa and air at 155 kPa; flame photometric detector, 300°C, with hydrogen at 135 kPa and air at 145 kPa.

#### *Calibration of the gas chromatograph with flame photometric detection (FPD) and the ATD–GC system with flame ionization detection (FID)*

Stock solutions of the test compounds S-mustard, DFP and soman were made up by weight in isooctane. From these, dilutions containing 0.05–1 µg/ml were prepared, so that with 2-µl injections into the GC (FPD) the relevant concentration range could be covered. The calibration functions were linear in each instance.

Another stock solution, also made up by weight, contained a mixture of all five test compounds in TCFE. From this, six different dilutions were prepared covering the concentration range 10–1000 µg/ml. The sorbent beds of ATD tubes were spiked at the upstream side with 1 µl of the six standard mixtures ( $n = 6$ ). The tubes were then subjected to ATD–GC (FID). By means of second ATD runs, it was ensured that a single thermal desorption step was sufficient to remove the sample completely from the sorbent.

As mentioned above, the ATD injector was switched out of operation, so that GC calibrations via the cold trap and the transfer line were not performed.

#### *Test atmospheres*

Test atmospheres of DFP and soman (as a mixture) and S-mustard were prepared by means of a dynamic diffusive vapour generator as described previously<sup>2</sup>. The generator was run with dry air, applying a flow-rate of 100 ml/min (S.T.P.). Based on the operating parameters, the generator should deliver gas concentrations of 0.23 (S-mustard), 0.2 (DFP) and 0.1 ng/ml (soman). The arrangement allowed the admixture of humidified air [ca. 100% relative humidity (R.H.) at 20°C] behind the exit of the generator with a flow-rate of 100 ml/min (S.T.P.). Hence, in the experiments with humidified air, a total flow-rate of 200 ml/min was applied, containing half the concentrations as above and a final humidity, as measured by means of an appropriate sensor, of 48% R.H. (at 20°C).

With the humidified atmosphere a series of control experiments were performed

to check the retention of water vapour on the Tenax bed: 100 ml/min of this atmosphere were conducted through a Tenax tube and the downstream humidity, as measured by a sensor, reached the upstream value of 48% R.H. within 30 s or less.

#### *Sampling and analysis of vapours*

The technical arrangement and the procedure for sampling the gas mixtures delivered by the vapour generator has been described in detail in a previous paper<sup>2</sup>.

For determining the gas concentration, a portion of 80 ml/min was sucked from the main gas stream through two small bubblers, arranged in series in an ice-bath; they were filled by weight with 3 ml of isooctane (density 0.69 g/cm<sup>3</sup>). After the sampling period, their actual contents in isooctane (plus analyte) were determined by weight, followed by GC (FPD) analysis and the agent concentration was calculated on this basis. Sampling in isooctane was carried out only from dry atmospheres; sampling times of 80–100 min were applied, so that amounts of 1–3 µg of the agents should be trapped.

The sampling on Tenax was done by sucking 50 ml/min from the main stream through two tubes coupled in series. For analysis, the tubes were subjected to ATD-GC (FID). Samples were taken from both dry (50 ml/min) and humidified (100 ml/min) atmospheres, applying sampling times of 20–40 min, so that 100–450 ng of the agents should be trapped. The loaded ATD tubes were divided into two series: series 1 was subsequently subjected to ATD-GC analysis; the tubes of series 2 were closed with the usual aluminium caps (with integral Viton O-ring seals), stored at ambient temperature and pressure in an empty desiccator and analysed after different storage times.

## RESULTS AND DISCUSSION

The ATD-GC (FID) analysis of the spiked Tenax tubes yielded a satisfactory separation of the five components (Fig. 1).

The detection limits were calculated to be three times the respective noise levels of the baseline, which was obtained by ATD-GC (FID) of TCFE-spiked tubes ( $n = 6$ ); there was no noticeable difference between TCFE-spiked and blank tubes. Representative chromatograms are given in Fig. 1. After subtracting the respective noise levels from the individual peak areas, linear calibration functions were obtained in each instance. The respective correlation coefficients resulting from linear regression are given together with the retention times and detection limits in Table I.

The results obtained by sampling the standard atmospheres in isooctane followed by GC analysis, and on Tenax with subsequent ATD-GC, are given in Table II. The contents in the second bubblers were  $\leq 10\%$  of the total; in the "back-up" tubes none of the analytes could be detected.

The agreement of the results from the two methods substantiates the reliability of calibrating with spiked tubes (at least for the three compounds concerned) and sampling these agents on Tenax. The concentration values found with the humidified atmospheres are, as expected, 50% of those obtained from dry air sampling. With regard to DFP and soman, there is a discrepancy between the precalculated and the measured concentrations. The probable reasons for these deviations from the theoretical values have been discussed elsewhere<sup>2</sup>.

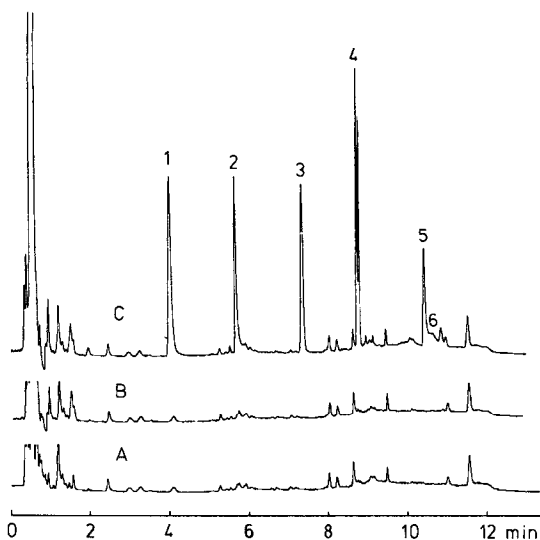


Fig. 1. Chromatograms obtained by ATD-GC with FID (sensitivity, "high"; LCI 100, 10 V, attenuation "2") of Tenax tubes. (A) Blank; (B) spiked with 1  $\mu$ l of TCFE; (C) spiked with (1) 41.0 ng of sarin, (2) 47.9 ng of DMMP, (3) 35.2 ng of DFP, (4) 34.5 ng of soman (doublet on account of stereoisomers) and (5) 53.7 ng of S-mustard in 1  $\mu$ l TCFE; an impurity in the DFP batch appeared at 10.8 min (6).

The influence of storage on the loaded Tenax tubes is illustrated by the data in Table III. For calculating the percentage recoveries, the concentration values in Table I and the individual sampling volumes were used to give the 100% value. The original contents of the tubes were in the range 100–300 ng per agent. Tenax tubes loaded with DFP and soman from a dry atmosphere were not stored. The results show that no obvious decrease in recovery occurred on prolonged storage.

Concerning the influence of moisture on the sampling and analysis procedures, the results indicate that, so far as was measured, the humidity did not impair the sampling efficiency, in the thermal desorption step the water content in the tubes (see

TABLE I

ATD-GC (FID) OF THE TEST COMPOUNDS: CORRELATION COEFFICIENTS OF THE CALIBRATION FUNCTIONS, RETENTION TIMES AND DETECTION LIMITS

<i>Compound</i>	<i>Correlation coefficient (n = 6)</i>	<i>Retention time (min)</i>	<i>Detection limit (ng per tube)</i>
Sarin	0.9997	4.0	10
DMMP	0.995	5.8	10
DFP	0.99990	7.2	5
Soman	0.99990	8.8	5
S-Mustard	0.9998	10.4	20 <sup>a</sup>

<sup>a</sup> 5 ng per tube as a single compound.

TABLE II  
ANALYSIS OF STANDARD ATMOSPHERES

Compound	Precalculated <sup>2</sup> concentration ( $\mu\text{g/l}$ )	Concentration after sampling ( $\mu\text{g/l}$ )					
		In isooctane (GC)			On Tenax (ATD-GC)		
		Concentration	S.D.	n	Concentration	S.D.	n
S-Mustard:							
Dry	230	221	7	6	229	6	12
Humidified	115				117	5	11
DFP:							
Dry	200	150	11	4	166	8	4
Humidified	100				85	7	4
Soman:							
Dry	100	74	8	4	86	7	4
Humidified	50				42	3	4

TABLE III

ATD-GC RECOVERY OF S-MUSTARD (I), DFP (II) AND SOMAN (III) FROM TENAX AFTER TRAPPING FROM DRY AND HUMIDIFIED ATMOSPHERES AND PROLONGED STORAGE

Storage time (h) <sup>a</sup>	Recovery (%) after trapping from			
	Dry atmosphere: <i>I</i> <sup>b</sup>	Humidified atmosphere		
		<i>I</i>	<i>II</i>	<i>III</i>
0.5	94.4	109.7		
	97.4	109.4		
	104.3	94.0		
1.5			75	103
2.3			99	104
23			99	98
26	97.4	99.1		
96	105.6	103.4		
	99.6	99.7		
	95.7	100.9		
221			102	92
308	97.8	103.4		
370		105.1		
			104	98
			97	94
860	106.1	100.0		
1465	80.5	99.1		
Average	97.9	102.1	96	98
S.D.	7.4	4.7	11	5

<sup>a</sup> Excluding analysis time.

<sup>b</sup> With II and III, no samples were stored.

below) did not cause any reduction in the recovery and there was no loss of analyte in the tubes on storage for up to 2 months.

The small influence, if any, of water on the sampling efficiency of Tenax has already been reported by other workers and has been ascribed to the hydrophobic properties of this polymer<sup>3,4</sup>. The lack of effect on the recovery could be due to the purge step in the ATD operation, by which both air and water vapour are removed from the cold tube before the thermal desorption begins.

The stability on storage of samples taken from the humidified atmosphere was unexpected, however. The hydrolytic half-lives of these agents in aqueous solution at 20°C are<sup>5</sup> 16 min (S-mustard), 61 h (DFP) and 23 h (soman). Without any water adsorption taken into account, the tubes still contained in their free volume the atmospheric moisture of 48% R.H.; with a sorbent weight of 175 mg, its specific density of 1.2 g/cm<sup>3</sup> (ref. 6) and geometric data, this free volume is calculated to be 1.53 cm<sup>3</sup>, corresponding to a water content of 12.7 µg per tube, which is, e.g., 40 times more than the content in S-mustard.

Obviously the state of sorption of these compounds prevents the access of (and/or reaction with) water molecules. It seems reasonable to assume that absorption is the reason for this protective effect.

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