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Note

An improved gas–liquid chromatographic method for the analysis of bis(2-chloroethyl)sulfide collected from air by solvent entrapment*

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In the gas chromatographic (GC) method reported previously[1] for the entrapment and analysis of low concentrations of mustard gas from air, the use of an electron capture detector (ECD) tended to limit the collection solvent to saturated hydrocarbons and also exhibited the short linear range expected for this detector. Decalin had the best chromatographic properties of the hydrocarbons examined, but solvent and mustard losses were unacceptably high during 24-h collection periods at room temperature. These deficiencies were partially overcome by cooling the traps to −17°, which however introduced an additional complication in the amount of equipment required. In addition, ice sometimes formed in the traps during collections in hot humid weather and occasionally led to blockage of the air flow. Accordingly, we sought a means to eliminate these experimental complications and developed the GC method described herein.

EXPERIMENTAL

Gas chromatography

A Tracor MT 160 DIN Scientific Research Chromatograph equipped with a flame photometric detector (FPD) and a 394-nm filter specific for sulphur was used for all the GC studies. A stainless-steel column, 6 ft. × 1/8 in. O.D., packed with 4% FFAP on Chromosorb W AW-DMCS, 60–80 mesh, was employed. Optimum gas flow-rates and instrumental parameters were determined using a standard solution of mustard in diethyl succinate (10 μg/ml) and were as follows unless otherwise specified (see Table I). Flow-rates: hydrogen, 170 ml/min; oxygen, 20 ml/min; nitrogen, 55 ml/min; air, 40 ml/min; temperatures: injection port, 275°, column, 155°; detector, 160°. These conditions were employed to examine the GC properties of numerous high-boiling solvents which were considered as possible candidates as collection media for mustard, including chlorinated hydrocarbons, succinates, malonates, benzoates, glycerol esters, long-chain aliphatic hydrocarbons, alcohols and diols. The five compounds listed in Table I were judged superior on the basis of their clean and rapid separation from mustard.

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Mustard retention and collection experiments at room temperature using diethyl succinate

The ability of the solvents to retain mustard during 24-h aspiration with dry air at a rate of 100 ml/min at room temperature was examined by using two traps in series, each containing 5 ml of diethyl succinate. Known amounts of mustard were added to the lead traps from standard solutions containing 20, 100, and 200 μg/ml in diethyl succinate. The traps were weighed before and after aspiration to determine the solvent loss during aspiration. The solutions remaining in both traps were analyzed by GC to determine the slippage into the second trap. The peak-height-ratio method of quantitation was used and the peak height varied as the square of the concentration[2], as anticipated for this detector. Standard solutions of mustard in diethyl succinate with concentrations close to those being measured were used for calculation. Results are given in Table I for diethyl succinate and four other solvents which were substituted for it in preliminary studies. Additional studies using diethyl succinate after it had been chosen as the most suitable solvent are summarized in Table II. Dilute solutions of mustard in diethyl succinate were stable for several weeks at room temperature.

For the collection experiments, the procedure was identical with that given for the mustard retention experiments, except that five times 1-μl drops of mustard transferred to small tared watchglasses by means of a microlitre syringe (range 584–684 μg) and weighed on the microbalance were used as sources of mustard vapour. The watchglasses were placed inside stainless-steel cells (sealed with butyl rubber gaskets). Dry air was drawn through these cells at the rate of 100 ml/min for 24 h and then through the traps connected in series. Results are given in Table III.

RESULTS AND DISCUSSION

The method described previously[1] for the entrapment and analysis of low concentrations of mustard gas from air using decalin as the collection solvent and an ECD, although rapid and accurate, had several disadvantages. Firstly, it was necessary to cool the traps to $-17°$ to retain the mustard and the solvent. This requirement for extensive cooling complicated the experimental set-up and sometimes led to difficulties in warm humid weather because of ice formation in the traps, which blocked the air flow. Secondly, the peak height to concentration ratio employing the ECD was linear only over the range 1–8.5 μg/ml (for 1-μl injections), necessitating multiple dilutions for most of the solutions examined. Consequently, we sought a means to avoid these disadvantages by using an instrument equipped with an FPD specific for sulphur, which would allow more freedom in the selection of a solvent with better mustard retentive capacity at room temperature. Numerous high-boiling compounds such as chlorinated hydrocarbons, succinates, malonates, glycerol esters, benzoates, aliphatic and alicyclic hydrocarbons, alcohols and diols were examined for their GC behaviour, using 4% FFAP on Chromosorb W as the column packing. Selection was made on the basis of sharpness of separation of mustard from the solvent, together with short retention times to facilitate rapid replicate analyses. This procedure restricted the choice to the five candidates shown in Table I. Studies on the loss of solvent and mustard during the aspiration of solu-

tions of mustard in these solvents with dry air as described in Experimental restricted the possibilities to diethyl succinate and tributyrin. Diethyl succinate was finally selected as the more suitable because the loss of mustard and solvent during prolonged collection from air streams tended to compensate for one another, whereas there was no loss of solvent from tributyrin solutions while mustard losses were approximately 4%.

TABLE I

CHROMATOGRAPHIC PROPERTIES, MUSTARD SLIPPAGE AND SOLVENT LOSS FROM CANDIDATE SOLVENTS *

Solvent	*B.p. (°C)*	*Retention time (sec)* **	*Mustard slippage (%)*	*Solvent loss (%)*
2-Methyl-2,4-pentanediol	196	35.4***	19.7	2.2
Diethyl succinate	218	41.4***	2.6	2.8
Ethyl benzoate	213	45.0***	3.5	7.5
Tributyrin	315	58.1§	3.6	0
Triacetin	259	67.5§	5.0	0.4

* 24-h aspiration at 100 ml/min.
** Mustard 60.0 sec in first three solvents, 16.9 sec in tributyrin, 37.5 sec in triacetin.
*** Chromatographic conditions as specified in Experimental.
§ 3 ft. × 1/8 in. O.D. stainless-steel column; packing, 4% FFAP on Chromosorb W AW-DCMS 60–80 mesh; gas flow-rates: hydrogen, 175 ml/min; oxygen, 12 ml/min; nitrogen, 118 ml/min (90 ml/min in the case of triacetin); air, 60 ml/min; temperatures: injector, 280°; column, 200° (163° in the case of triacetin); detector, 150°.

Further studies on the retention of solvent and mustard during the aspiration of solutions containing 20–200 μg of mustard/ml of diethyl succinate indicated that solvent and mustard losess of 2.5% and 3.3%, respectively, could be expected, as shown in Table II.

TABLE II

SOLVENT AND MUSTARD LOSS FROM DILUTE SOLUTIONS OF MUSTARD IN DIETHYL SUCCINATE AT ROOM TEMPERATURE *

No. of samples	*Trap*	*Initial mustard conc. (μg/ml)*	*Solvent loss (%)*		*Mustard retained (%)*		*Mustard accounted for (%)*
			Range	*Average*	*Range*	*Average*	
2	lead	20	2.1–2.6	2.4	95.6–97.8	96.7	100.4
2	back-up	0	0	0	3.4– 3.9	3.7**	
2	lead	100	2.3–3.0	2.7	93.4–95.7	94.6	98.0
2	back-up	0	0	0	2.9– 4.0	3.4**	
2	lead	200	2.2–2.3	2.3	96.4–99.4	97.9	100.8
2	back-up	0	0	0	2.8– 2.9	2.9**	

* 24-h aspiration at 100 ml/min.
** Mustard loss from lead trap.

TABLE III

SOLVENT AND MUSTARD LOSS DURING MUSTARD COLLECTION IN DIETHYL SUCCINATE AT ROOM TEMPERATURE*

No. of samples	*Trap*	*Solvent loss (%)*		*Mustard collected (%)*		*Mustard accounted for (%)*
		Range	*Average*	*Range*	*Average*	
6	lead	2.1–3.0	2.4	95.0–100.6	96.6	99.3
6	back-up	0–0.2	0.1	2.2–3.6	2.7**	

* 24-h aspiration at 100 ml/min.
** Mustard loss from lead trap.

The efficiency of collection of mustard vapour from dry air by diethyl succinate was then examined. The results summarized in Table III indicate average solvent and mustard losses of 2.4% and 2.7%, respectively, for the collection of 584–684 μg of mustard. For routine analysis a single trap is used, both solvent and mustard losses are ignored and mustard analyses approximately 1% low are obtained. This result was considered satisfactory for our purposes and compares very favourably with that obtained using the method described previously[1].

For routine analysis a calibration curve was prepared by plotting the square root of the peak height against the mustard concentration for standard solutions in diethyl succinate. This curve was linear over the range 1–120 μg/ml for 1-μl injections. This is a substantial improvement in linearity over the method described previously[1], making it possible to analyze directly most of the solutions resulting from our experiments. Cross checking standard solutions of mustard in diethyl succinate for the linear range indicated an accuracy of $\pm 3\%$. Sample injections can be made every 2 min and the method is capable of detecting as little as 0.2 ng of mustard in a 1-μl injection.

REFERENCES

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