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GAS CHROMATOGRAPHIC DIFFERENTIATION AND ESTIMATION OF SOME SULFUR AND NITROGEN MUSTARDS USING A MULTIDETECTOR TECHNIQUE

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SUMMARY

A simultaneous multidetector system for gas chromatography was designed and applied to a series of sulfur and nitrogen mustard compounds. It was found possible to detect and estimate species even when very proximate in retention time. Up to four detectors could be operative at the same time with a single injection of nanograms to micrograms of sample. Parathion was selected as a compound sensitive to all the detectors.

INTRODUCTION

Some sulfur and nitrogen mustards have been found to be relatively persistent and a few have even been considered or even applied as chemotherapeutic agents because of their cytotoxicity. The need existed for a trace analytical system that could be used to identify and estimate these species as residues from a wide variety of media, both physical and biological. Among these compounds were bis(2-chloroethyl)sulfide (H), bis(2-chloroethyl)ethylamine (HN-1), bis(2-chloroethyl)methylamine (HN-2), tris(2-chloroethyl)amine (HN-3), bis(2-chloroethylthio)ethane (Q) and bis(2-chloroethylthioethyl)ether (T). Also of interest in the past were mixtures such as H and Q (HQ) and H and T (HT). At a time when no single method had been available with the capability of differentiating between the mustards at the low milligram to nanogram range, gas chromatography (GC) was shown to be highly effective for this purpose[1]. In this investigative work, beginning circa 1965, the electron-capture detector (ECD) which had become generally available for GC, was evaluated and thence employed in our laboratories for both identification and trace quantitative estimation of these compounds.

Since that time a number of investigators have reported on the application of GC to the analysis of mustard "gas" [bis(2-chloroethyl)sulfide] and related compounds[2–5].

With the advent of the flame photometric detector (FPD) for phosphorus and sulfur[6], plus the Coulson[7,8] and then the Hall[9] nitrogen detector, the concept of GC with multidetector finish became one of potential practical application. For this pur-

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pose, we had originally equipped an F&M Scientific (now Hewlett-Packard) Model 5750 gas chromatograph having a flame ionization detector (FID) and an ECD, with a Microtech photometric head having phosphorus (526-nm) and sulfur (394-nm) filters and an electrometer. This equipment thus gave the capability for determining the mustards with the identical GC column, but sampled separately for different detectors. The added advantage observed by combining selectivity of detection with proximity of retention times brought us to the point of specifying design of equipment that would produce simultaneous recordings or printouts relating the retention time found with the respective detectors and even the relative quantity of compound as represented by integrated peak areas. An obvious additional benefit, especially when the amount of available sample might be limited, is the fact that at least three detector outputs could be obtained with only a single injection of solution or of air sample. The request for bid thus included our specifications to best meet, within the then state of the art, our requirements. We selected parathion of certified purity as the test compound for acceptance of instrument. This report describes our application of the multidetector concept to the determination of trace quantities of some mustards, and parathion as a representative of a phosphorus pesticide.

EXPERIMENTAL

Equipment and materials

The gas chromatograph which most closely approximated our specifications was the Tracor Microtek MT 220 which at that time was the sole licensee for flame photometry, the Coulson nitrogen detector and later the Hall, on a commercial basis. The design of the basic instrument was such that phosphorus and sulfur were detectable simultaneously on a dual head flame photometer[6]. Four ports were available for injection and the instrument was capable of holding four different columns. According to our design, each column could be connected to a separate detector or the output from any single column could be split two or three ways for separate and simultaneous detection such as by ECD (pulsed or d.c. mode), FID and FPD in the combined P and S mode, or a three-way combination that could include the Coulson or Hall nitrogen detector. Four recordings could be obtained simultaneously by means of two dual needle recorders. The peaks could be quantitated by means of ball and disc integrators or measured separately using electronic integrators. Included in the instrumentation capability was a teletypewriter which served for data handling as well as programming. Microweighing was done on a Cahn Electrobalance and injections were performed using Hamilton microliter and gas-tight syringes. The column coatings and supports were obtained from Applied Science Labs., State College, PA, U.S.A. Solvents used were of CP grade except for the nanograde hexane used in determinations that involved the ECD.

Sample standards

The sulfur and nitrogen mustards used as standards were available samples further purified where necessary. This was accomplished by either fractional distillation or preparative GC as for H, Q, and T, and by fractional crystallization as for the nitrogen mustards which were stored as their hydrochlorides. The free bases of nitrogen mustard compounds are very unstable, being susceptible to *in situ* intra-

and intermolecular alkylation. HD (distilled mustard) samples were of purities no lower than 96.5% as determined by freezing point depression, alkylation titration employing thiosulfate[10], thin-layer chromatography[11] and by GC employing thermal conductivity detection (F&M Scientific, Model No. 810). Q (or sesquisulfur mustard) was 98.5% pure as determined by melting point, the alkylation titration, elemental analysis and GC. HN-1, HN-2, and HN-3 as their hydrochloride salts were 95, 97 and 97% pure, respectively, on the basis of elemental analysis, alkylation titration, and by GC after conversion to their free bases, as described later.

HQ was a mixture of H and Q (50:50, w/w). Parathion was of 95%+ purity as obtained from Shell Chemical.

Procedure

Purity determination by GC. The basic instrumentation employed in this investigation included a Tracor Model MT 220 gas chromatograph equipped with a dual head, an FPD (phosphorus and sulfur filters), an FID; the Model M5 Coulson (CCD) and later the Model 700 Hall electrolytic conductivity detector (HCD), both in the nitrogen mode; and the Tracor pulsed-mode and d.c.-mode electron capture (^{63}Ni) modules which could be alternately tied into the system. Each of the detectors were separately equipped with their own dual channel electrometers. Data handling was performed with the Infotronics CRS-208 electronic integrator, and the Hewlett-Packard Model 3380A report integrator, two Westronic M-22 dual-pen recorders of 0–1 mV range and a Teletype 33T2 teletypewriter. Switching for detector selection was accomplished by means of Cat. No. 4011, Carle valves (Carle Inst., Fullerton, CA, U.S.A.).

The arrangement of columns and valves on the modified Tracor MT-220 to allow for multidetection is shown in Fig. 1.

In our configuration with the capability for four columns, the sample could be directed to a single detector or to simultaneous multidetection. The columns could contain the same packings or allow a variety of choice. Fig. 1 illustrates the arrange-

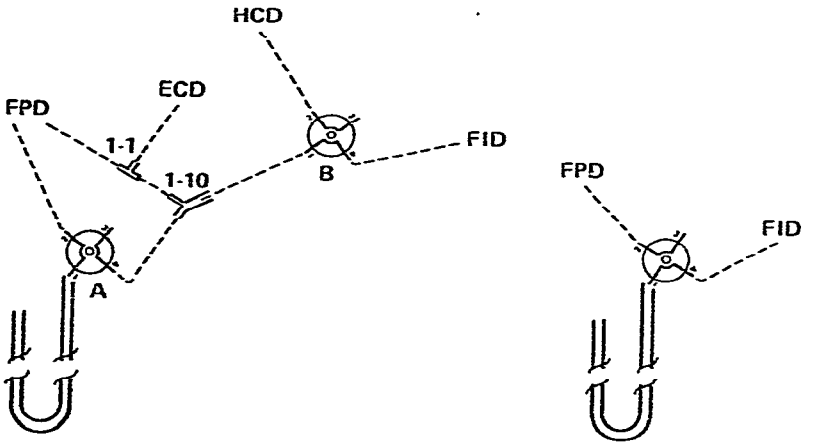


Fig. 1. Examples of column arrangements which allowed up to four simultaneous detector responses. A and B are two way valves; splitters are 1:10 and 1:1 as indicated. (Parathion gave simultaneous response for FPD-S and -P, ECD, and FID or HCD.)

ment whereby the valve off the column (valve A) allows either direct FPD or flow to a two-way splitter. The first two-way splitter directs column effluent as a one (FPD and ECD) to ten [Hall nitrogen (HCD) or FID] feed. The 1:1 splitter feeds an equal amount of effluent to FPD and ECD. Replumbing could allow a split wherein FPD might be eliminated in favor of ECD, FID and HCD or, with the elimination of ECD, to allow inclusion of FPD, FID and HCD. Column 2 of the equipment was dedicated to ECD and columns 3 and 4 were each connected via a valve that gave the capability for separate detectors and the same or different packings.

Purified samples (or samples of known purity, 90% and better) of sulfur mustards were dissolved in hexane or chloroform to obtain a concentration of about 50 mg/ml of solution.

For nitrogen mustards of known purity (90% and better) as the hydrochloride salts, weighed quantities were dissolved in chloroform (also at a concentration of about 50 mg/ml). Sufficient sodium carbonate (roughly equal to the weight of the sample) was added to a vial, followed by an amount of water approximating the quantity of chloroform. After shaking for about 30 sec, all of the nitrogen mustard as the free base was found in the chloroform layer.

Aliquots of the chloroform solutions of the sulfur and nitrogen mustards in the range of 5 μl (0.23 μl, 1.0 mg) were subjected to GC, fitted with the thermal conductivity detector (TCD). A calibration curve of peak area *versus* weight of compound (corrected for known purity) was prepared. This curve was found to be linear over the range of 0.25 to 1.0 mg of mustard.

Samples resubmitted to the determination of purity were weighed and dissolved in chloroform in the range of 50 mg/ml and then treated in the same manner as the known purity compounds used in the calibration. Aliquots (10 μl) of the chloroform were injected and the actual mustard content was extrapolated from the calibration curve. This value divided by the calculated weight of material injected times 100, gave the purity of the material being analyzed.

Using calibration based on known purity mustard, the standard deviation was of the order of 1%.

The conditions used for the purity determination, while employing an F&M Model 810 gas chromatograph, follow: bridge current (TCD): 150 mA; attenuation: × 16; sample size: 10-μl aliquot from 50 mg/ml of solution; carrier gas flow-rate: helium, 90 ml/min; detector temperature: 310°C; injection chamber temperature: 200°C; column: 6 ft., Pyrex glass, 1/4 in. O.D.; column coating: 10% QF-1; column support: Gas-Chrom Q (60–80 mesh).

Procedures for estimation of trace quantities. Conditions were established whereby each trace detector system could be calibrated separately, or together with the other detector(s) being employed. Helium was the carrier gas of choice to fit all of the detectors except the ECD. For electron capture in the conventional pulsed mode, argon–methane was used as the carrier and purge gas. For the d.c. mode, nitrogen served as the carrier and purge gas, with helium used as the carrier gas only when in the multidetector phase.

Chromatography was performed both under temperature-programmed conditions and isothermally. The former was useful for aiding in the identification of the species and for determining the most reasonable isothermal temperatures for analysis of the specific compounds.

Dual flame-ionization detection. The 6 ft., 3% QF-1 GC column employing FID or other detectors was programmed at 8°C/min from 60 to 230°C. For FID, quantities of mustards or parathion were at the concentration level of 100 μg/ml of solvent or greater and 3 μg or more of the compounds were injected for assay or calibration purposes. The elution temperatures found for the various mustards, using the 6 ft. 3% QF-1 column under temperature programming (8°C/min from 60 to 230°C), are listed in Table I.

TABLE I

ELUTION TEMPERATURES AND RETENTION TIMES OF THE MUSTARDS

Programmed at 8°C/min from 60°C. (B) = free base.

Agent	*Peak elution*	
	Temperature (°C)	*Retention time (min)*
HN-1	100	5
H	100	5
HN-2 (B)	110	6.3
HN-3 (B)	120	7.5
Q	165	13.1

Electron-capture detection. When employing the ECD in the pulsed mode (PM-ECD) calibration curves and linearity checks were made by injecting measured volumes of a variety of concentrations, *e.g.*, 1, 10, 25 and 50 ng/μl, of sulfur mustards dissolved in hexane instead of chloroform. Unknown solutions and vapor concentrations of the mustards were estimated based on these calibration curves. Calibrations were performed daily for each agent being analyzed to compensate for any sensitivity changes that might occur in the chromatographic system.

Similar calibration curves were prepared for the nitrogen mustards in hexane after conversion of the salts to the free bases. The concentration of sample subjected to chromatography was similar to that used for the sulfur mustards mentioned above. Salts of the nitrogen mustards, in the proportion of 1 mg/ml of hexane, were treated with approximately 0.05 g of sodium carbonate followed immediately with 10 ml of water and mixing. Aliquots from the hexane layer were used in the preparation of the standard solutions for calibration in the same increments as mentioned previously.

Solutions of mustards of uncertain concentration were analyzed using sample volumes from 0.5 to 30 μl, starting with the lower volume to minimize the possibility of detector overload. Similar precautions were taken with vapor samples, where volumes in a range from 0.5 to 5 ml are recommended.

A listing of the chromatographic conditions common to all of the mustards, and parathion, when using the various detectors, follows: column: 6 ft. × 2 mm I.D. Pyrex glass, packed with 3% QF-1 on 100–120 mesh Gas-Chrom Q; column temperature: programmed at 8°C/min from 60 to 230°C. Isothermal as shown in Table II; inlet temperature: 200°C; transfer temperature at valves: 210°C; detector temperature: FID 250°C, FPD 185°C, HCD solvent transfer, 220°C, furnace 875°C, d.c.-ECD 220°C, PM-ECD 250°C; carrier gas: helium at 40 ml/min for all detectors

TABLE II

RETENTION TIMES FROM DIFFERENT ISOTHERMAL COLUMN TEMPERATURES

a = 4.5 ft. 10% QF-1, b = 6 ft. 3% QF-1.

Agent	*Column temperature (isotherm) (°C)*		*Retention time (peak maximum) (sec)*	
	a	*b*	*a*	*b*
H	110	90	240	140
HN-1	120	90	240	125
HN-2	120	105	180	70
HN-3	140	110	480	330
Q	170	155	390	80
T	200		390	
Parathion	200		390	

except argon–methane at 90 ml/min for PM-ECD, and preferably nitrogen at 30 ml/min for d.c.-ECD only when the latter is not in a multi-detector phase; purge gas: HCD, helium at 40 ml/min and as make-up gas when the solvent was vented before it reached the reaction furnace; d.c.-ECD, nitrogen at 30 ml/min; PM-ECD, argon–methane (90:10) at 10 ml/min; reaction gas: HCD, hydrogen at 50 ml/min; fuel gas: FPD: hydrogen at 120 ml/min, oxygen at 20 ml/min and air at 35 ml/min; FID: hydrogen at 40 ml/min and air at 35 ml/min with helium at 20 ml/min as equilibrator gas.

RESULTS AND DISCUSSION

Tests with a variety of column substrates had indicated that the subject mustard compounds were reasonably elutable when present in microgram or larger amounts. Among the coatings tested were dodecyl phthalate, SE-30, Apiezon N, Versamid 900 and QF-1. Prior experience with relatively reactive compounds such as the mustards described here[1] and the irritant type compounds CA (bromobenzylcyanide), CN (chloroacetophenone) and CS (*o*-chlorobenzylidenemalononitrile)[12], and some pesticides[13] had indicated that the QF-1 coating yielded the sharpest peaks even at the low nanogram level. Gas-Chrom Q was the support material found to give optimum results. To preclude direct reaction with the column, metal-catalyzed decomposition or thermolability, a glass column and the on-column injection technique were utilized.

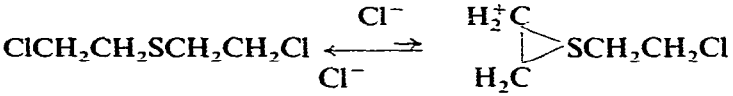
Initial studies made using a sample of unknown purity started with a semi-quantitative GC assessment (thermal conductivity) based on the ratio of agent peak area to total peak area. H, Q, T and parathion were injected as chloroform solutions, and the nitrogen mustards were run as their respective free bases after partitioning into chloroform from aqueous solution, via sodium carbonate treatment.

Experiments similar to those described above, were made employing the dual hydrogen FID but on more dilute solutions (μg to mg/ml). This study aided in the selection of optimum column conditions (temperature and flow-rate).

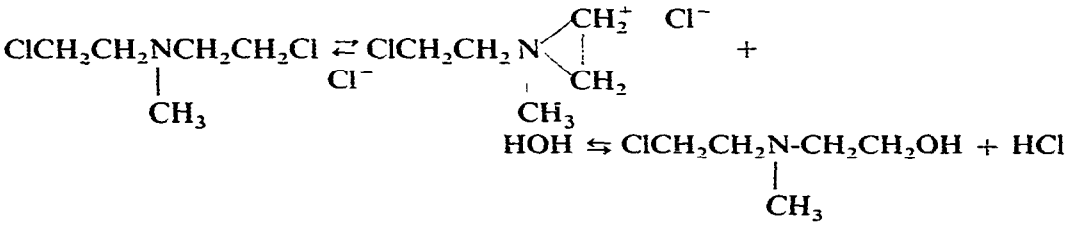
As with all analysis employing the ECD, especially in the case of halo com-

pounds, great care was exercised to keep the amount of each mustard agent chromatographed initially in the low (1 to 10) nanogram range. Once the degree of response was established at this low level, progressively larger samples (10 to 20 ng increments) were injected to establish the linear region of the response curves and to insure against severe detector overload. Hydrogen chloride and methylene chloride can be present as decomposition products of H, Q and T. Dilute solutions of the sulfur mustards and parathion were prepared in spectrophotometrically pure hexane. It was also found possible to determine low concentrations of the salts of the nitrogen mustards by their conversion to the free base with aqueous sodium carbonate and a simultaneous extraction into hexane. Very little loss through hydrolysis of the mustard agent was observed while using this conversion procedure.

Freshly prepared solutions of H (10 to 50 ng/ml) in 1 l of saline–water (1:10) were extracted almost immediately with 100 ml of hexane, in a separatory funnel. Aliquots of the supernatant hexane were subjected to GC, fitted with the ECD. With the original favorable increase in concentration of 10 to 1, due to solvent transfer (1000 ml reduced to 100 ml) plus the sensitivity of the detector to nanogram quantities of mustard, it appeared possible to measure residual H present in aqueous media at the level of ppt (10^{12}). This scheme should also have application to the measurement of unreacted mustards in physiological media. The rate determining step for hydrolysis of sulfur mustards (H, Q and T) is the cyclization to the ethylenesulfonium ion



Chloride ion supresses the sulfonium ion formation thus giving a degree of stability to the mustard dissolved in the water. The rate determining step for hydrolysis of the nitrogen mustards is the hydration of the relatively stable ethyleneimonium complex



Solution concentrations were measured for all the mustard agents and parathion from 1 to 100 ng and up to micrograms (FID) employing each of the appropriate detectors. The responses observed for practical linearity are summarized in Table III.

The characteristics of the separate detectors relating to response sensitivity and thus linearity and reproducibility can vary with the state of the art in instrumentation. The multidetector arrangement that we have established using the modified Tracor MT-220, with its accompanying detectors, could be applied to equipment from other sources. The essential difference might be in the relative sensitivities, and possibly specificity, when compared to later detector systems, *i.e.*, "light pipe" for FPD[14] and

TABLE III

LINEARITY RANGE OF DETECTORS FOR APPROPRIATE COMPOUNDS

Agent	*Linearity range**					
	FPD-S (ng)	*FID (μg)*	*d.c.-ECD (ng)***	*PM-ECD (ng)*	*HCD-N (ng, 30 V)*	*FPD-P (ng)*
H	10–100	0.5–500	5–100	5–200	50–200	–
HN-1	–	0.5–500	5–100	5–100	50–200	–
HN-2	–	0.5–500	5–50	5–50	50–200	–
HN-3	–	0.5–500	5–100	5–100	50–200	–
Q	10–100	0.5–500	5–100	5–70	–	–
Parathion	10–100	0.5–500	10–100	5–100	50–200	5–100

* No attempt was made to test any of the agents for linearity in excess of the cited ranges. Wider ranges of concentrations were analyzed simply by varying the sample size.

** ECD, pulse interval of 50 μsec, d.c.-ECD (30 V).

the alkali thermionic detectors for nitrogen and phosphorus[15,16] along with electronic filter/electrometer improvements for baseline maintenance and signal-to-noise ratio advantages. The detectors available to us were evaluated for each of the mustards and for parathion using attenuation settings that would permit quantitative measurement of column effluent via three way splitting. For simplicity, "equalized" thirds of sample would be supplied to the respective detectors. The goal was to determine the sensitivity thresholds of the detectors for the respective compounds, as well as the concentrations *versus* instrument settings for near equal responses. The

TABLE IV

RESPONSE OF DETECTORS FOR MUSTARDS AND PARATHION

	HN-1	*HN-2*	*HN-3*	*H*	*Q*	*Parathion*
FPD-S						
Attenuation				32 × 10	32 × 10	32 × 10
Minimum detectable limit (ng)				2	2	2
At 10:1 signal-to-noise level (ng)				5	5	7
d.c.-ECD 30 V						
Attenuation	32 × 10	32 × 10	32 × 10	32 × 10	32 × 10	32 × 10
Minimum detectable limit, (ng)	0.2	0.2	0.3	0.3	2	0.3
At 10:1 signal-to-noise level (ng)	2	2	4	3	4	4
FID						
Attenuation	4 × 10	4 × 10	4 × 10	4 × 10	4 × 10	4 × 10
Minimum detectable limit (ng)	60	40	70	60	40	40
At 10:1 signal-to-noise level (μg)	0.5	0.5	0.7	0.5	0.5	0.5
HCD-N						
Attenuation	2 × 10	2 × 10	2 × 10			2 × 10
Minimum detectable limit (ng)	10	5	10			5
At 10:1 signal-to-noise level (ng)	40	20	40			25
FPD-P						
Attenuation						32×10^2
Minimum detectable limit (ng)						0.7
At 10:1 signal-to-noise level (ng)						5

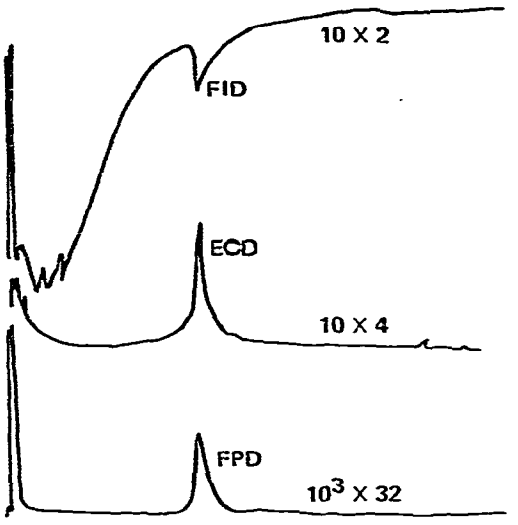


Fig. 2. Simultaneous detector response for purified H using two recorders.

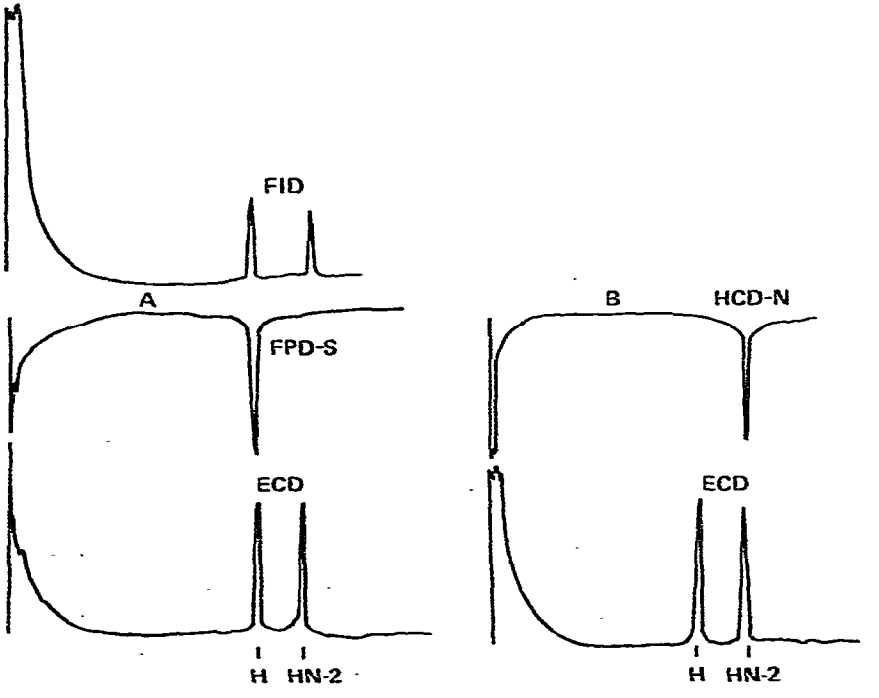


Fig. 3. Simultaneous detector response for a mixture of H and HN-2. Left: ECD, FPD-S and FID; right: ECD and HCD-N.

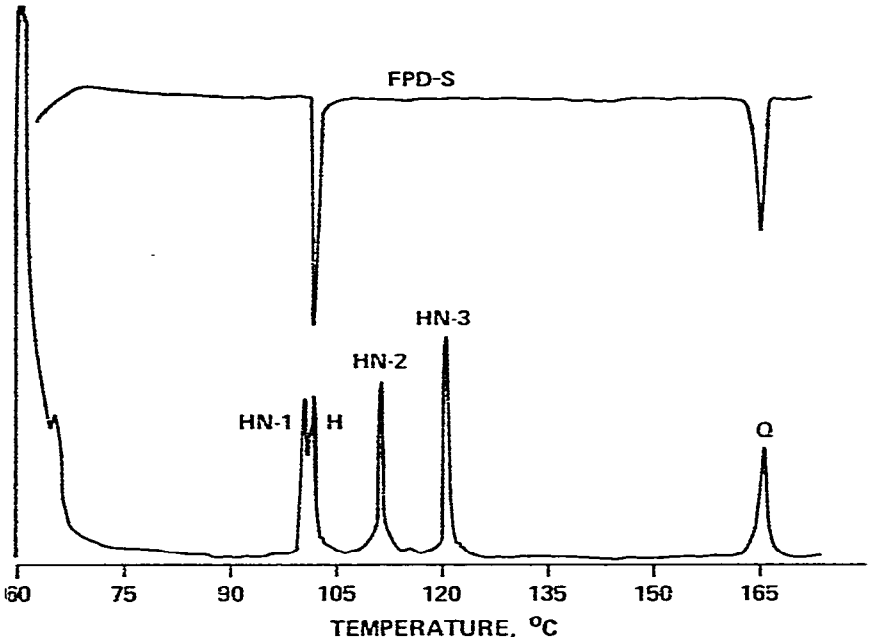


Fig. 4. Composite chromatography of the mustards employing FID and FPD-S, programmed at 8°C/min from 60°C. Similar chromatograms were obtained using other detectors. Parathion gave simultaneous responses for FPD-S and -P, ECD, and FID or HCD; and T was detectable via FPD-S, FID and ECD.

relative sensitivities of the detectors for these compounds in decreasing order are d.c.-ECD > FPD > FID > Hall nitrogen > Coulson nitrogen. Dilutions of the compounds in their respective solvents were injected into the GC column (210°C) under single, dual and multidetector configurations. With the optimum electrometer attenuations set for the respective detectors it was possible to determine the minimum detection limits for the mustards. Also estimated were the analytical limits wherein a 10:1 signal-to-noise level could be obtained. These results are shown in Table IV.

d.c.-ECD was originally selected for the multidetector approach because it could use a carrier gas more common to the other detectors. An ECD capable of operation in the constant mode has since been reported[14] as having a similar advantage. d.c.-ECD is less specific than when in the pulsed mode, and can be advantageous since it is applicable to the detection of a broader number of compounds. It should be pointed out that at least one of our four columns was dedicated to PM-ECD. With the pulsed mode detector the range could be extended by decreasing the pulse interval to 15 μsec or less, if desired. The minimum detectable quantity using an ECD for all the compounds was found to be approximately 4 ng with a signal-to-noise ratio of 10:1; similarly 5 to 7 ng for FPD-P or -S were applicable (Table IV). This would correspond to a solution concentration (assuming 30 μl as the maximum liquid sample volume) of about 160 ng/ml. Similarly, assuming a maximum vapor sample size of 5 ml, vapor concentrations as low as 1 ng/ml, or 1 mg/m^3, could be readily monitored. An average of replicate determinations (peak areas) in the 1 to 100 ng range indicated that the standard deviation for an aliquot containing 50 ng of a

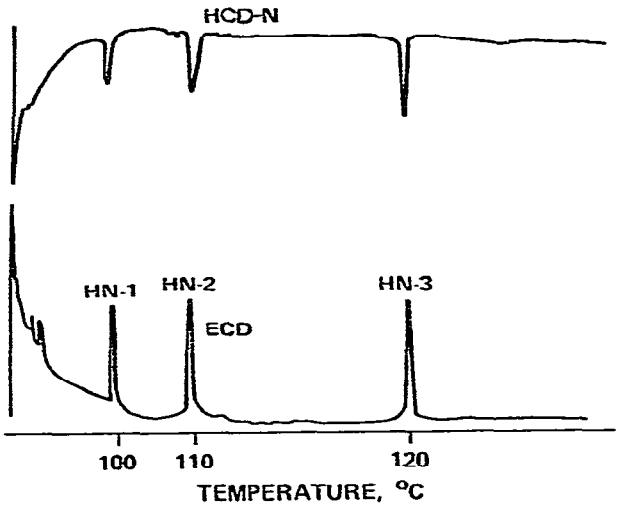


Fig. 5. Chromatogram of nitrogen mustards employing ECD and HCD.

mustard is 2.2% (±1.1 ng). These data were obtained using solutions similar to those prepared for determining linearity.

The design of column and valves included also the requirement for venting sufficient solvent prior to the detector(s) thus allowing a near return to base line for sample analysis. The column assemblies for single, dual and simultaneous multidetection are illustrated in Fig. 1.

Sulfur mustards were injected mostly from solution in hexane but also out of chloroform. Since these compounds contain no nitrogen the valves were configured to give simultaneous readings from ECD, FID and FPD-S. The nitrogen mustards were detected via ECD, FID and HCD. Parathion was detected via ECD, FPD-P and -S, and FID or HCD. The respective combined chromatograms for the mustards are illustrated in Figs. 2–5.

Referring back to Table I it can be seen that under temperature-programmed conditions HN-1 (B) and H show an elution peak and retention time that could be superposable if in the same mixture. When determined via multidetector, HN-1 shows no FPD-S, while H shows no HCD-N. Similarly, although not shown here, a wide variety of potential break-down products or related compounds were found resolvable based on detector specificity. A few of these compounds were described in reported thin-layer chromatography studies[11].

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