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Multiple-technique analytical characterization of a mixture containing chemical-weapons simulant from a munition

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Abstract

An amber yellow organic liquid was found in a munition shell at Dugway Proving Grounds, UT, USA, that was likely used as a simulant of chemical weapons. The primary analytical techniques to characterize the mixture were gas chromatography–infrared detection–mass spectral detection (GC–IR–MS); liquid chromatography–mass spectrometry (LC–MS); nuclear magnetic resonance (NMR) using the nuclei ^{1}H, ^{13}C and ^{31}P; and gas chromatography–atomic emission detection (GC–AED). Six major phosphorus-containing components were identified and confirmed by at least three techniques, and several additional phosphorus-containing components of lower concentration have been identified by GC–IR–MS and LC–MS. Five major non-phosphorus components, including ethyl acetate, diethyl sulfide and dibutylamine, have been identified by multiple techniques. The major phosphorus compound (23.9±0.4 wt.%) was *O*,*O*,*O*-triethyl phosphorothioate (I) and the second most abundant (14.4±0.2 wt.%) was *O*,*O*,*S*-triethyl phosphorothioate (III). No VX, G-agent, or pesticide was observed in the sample, although III may be a cholinesterase inhibitor which produces delayed toxic response. III also produces a false hit for the pesticide cyanthoate when analyzed by GC–MS-EI. The mixture appears to have been formulated as a chemical warfare agent simulant, most likely as a challenge of agent detection techniques.

Keywords: Warfare agents; VX; Organophosphorus compounds

1. Introduction

Environmental remediation of US Army bases, for example Dugway Proving Ground (DPG), UT, USA, can uncover munitions with unknown contents. These munitions may contain undetonated explosives, chemical weapons, or they may be 'dummy' rounds with relatively benign fills that were used for targeting or range-finding. The wide range of munitions that have been tested at these bases includes chemical weapons simulants. After firing, the munitions may have been buried in the desert for potentially decades of time, the exterior may be corroded to obscure any markings, and no documentation may exist to describe the contents. As a result, chemical analysis is needed to determine the proper method for disposal of the contents of some of the munitions.

Typically, it is possible to distinguish explosive from nonexplosive munitions by using non-invasive

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methods, including X-ray, acoustic and neutron activation methods [1]. X-ray analysis can show the configuration of the contents. Acoustic analysis indicates the phase of matter of the contents. Neutron activation analysis can provide a chemical elemental analysis. For example, a high nitrogen signal is typical of explosives, while phosphorus, sulfur, or arsenic are characteristic of chemical weapons [1].

A small minority of these munitions are deceptive. If the munition contains compounds that were chosen to simulate chemical weapons, they can give positive signals for phosphorus, sulfur, or arsenic. However, when sampled and analyzed, the results may not correspond to any of the usual chemical warfare (CW) agents, so these results are difficult to interpret with routine analyses or with portable, field instruments. It is also possible that a high concentration of a simulant can interfere with the identification of a trace level of a hazardous compound. In the case of munitions which are even suspected to contain chemical weapons, detailed determination of the identity of the compounds down to trace levels is required for proper safety precautions and disposal.

One such suspect sample was received from DPG during June, 1997, by the Edgewood Chemical and Biological Center (formerly Edgewood Research, Development, and Engineering Center), Aberdeen Proving Ground, MD. The sample of amber yellow organic liquid had been extracted from an obsolete munitions round, and preliminary GC–MS analysis at DPG had indicated the possible presence of trace levels of VX and a commercial pesticide cyanthoate {commercial name Tartan™, manufactured by Montedison; chemical name *S*-[2-[(1-cyano-1-methylethyl)amino]-2-oxoethyl]-*O*,*O*-diethyl phosphorothioate, CAS RN 3734-95-0}. This pesticide is considered obsolete [2]. A characterization of the sample was requested to determine the bulk composition of the sample, in addition to a trace analysis to determine whether the sample contained VX or other chemical weapons agent.

It was very unlikely that the munition contained a biological weapons agent or a biological toxin. Biological weapons are banned by the 1972 Biological Weapons Convention, and World War II vintage biological weapons were destroyed in 1945 [3]. For research purposes, biological weapons have been typically stored in dry powdered form, and munitions are not the preferred method for dispersing the powder [4]. As a result, it is improbable that a munition would be uncovered in the US that contained any biological weapons agent. A munition with liquid contents with a high concentration of phosphorus is indicative of a chemical weapons agent. Analysis of the sample for neat agents that have been weaponized was done at DPG, and the sample was definitely not a neat agent.

2. Experimental methodology

Because gas chromatography–mass spectrometry (GC–MS) was already done on the sample, other analytical methods were used in addition to provide more information. The primary analytical techniques to characterize the mixture were gas chromatography–infrared detection–mass spectral detection (GC–IR–MS), liquid chromatography–mass spectrometry (LC–MS), gas chromatography–atomic emission detection (GC–AED), and nuclear magnetic resonance (NMR) using the nuclei ^{1}H, ^{13}C and ^{31}P. GC–IR–MS and GC–AED provide additional information on the chemical composition of the compounds in the sample. LC–MS and NMR have the advantage of analyzing liquid-phase samples, so they provide information on compounds that may not be detectable by GC analysis. In total, they provide methods that should be able to identify all the possible components of the sample. In addition, quantitative analysis of the sample was done to insure that all major components by weight were accounted for.

GC–IR–MS analysis of the samples was performed on a Hewlett-Packard (Little Falls, DE) 5890 GC with a BioRad (Cambridge, MA) 5965B Fourier Transform Infrared Detector coupled in series with a HP 5971 Mass Spectral Detector operating in electron impact ionization mode (EI). This configuration allows separation and near-simultaneous collection of mass spectra and vapor-phase infrared spectra of the individual components of a liquid injection. The gas chromatograph was equipped with a HP-5 column which was 25 m×0.32 mm I.D. with a phase thickness of 0.17 μm. Injection volumes of 2 μl were made with the GC operating in splitless mode. Samples were prepared by (1) dilution of at least

1:100 in dichloromethane and (2) by mixing with Sylon BFT (Supelco, Bellefonte, PA) to form a trimethylsilyl derivative. GC oven programming started with a 1-min hold at 35°C for dichloromethane and 60°C for trimethylsilylated samples, ramped at 10°C/min to 200°C, then at 20°C/min to 280°C. Infrared spectra were collected in a range from 550 to 4000 cm^{-1} at an optical resolution of 8 cm^{-1}. Mass spectra were acquired at a range of m/z 40–400. In addition to the GC–IR–MS, a separate GC–MS was also used, which gave better sensitivity to the low concentration peaks.

LC–MS analysis was performed using a HP 1090M High Performance Liquid Chromatograph with a UV–Vis diode array detector and a HP 5989A 'MS Engine' Mass Spectrometer with an Analytica of Branford (Branford, CT) Atmospheric Pressure Chemical Ionization (APCI) interface. An ODS Hypersil LC column (HP Part No. 79916OD-552), 100×2.1 mm with a particle size of 5 μm was used. The flow-rate was 0.25 ml/min, and the injection volume was 25 μl. The gradient was 100% 0.05 *M* aqueous ammonium acetate (held for 5 min) to 95% acetonitrile at 40 min. The MS was operated in positive ion scan mode over a mass range of 20–400 Da. The UV–Vis detector was a diode array detector operating between 190 and 450 nm. Samples were prepared by 1:100 dilution of the liquid phase in methanol or acetonitrile. In order to positively correlate the compounds that were observed by LC and GC analysis, fractions were collected from the LC flow and analyzed by GC. For fraction collection, a Jones Chromatography Genesis C_{18} LC column was used with dimensions of 150×4.6 mm and total flow 1.0 ml/min, with the flow to the MS split by 1:4. Since LC analysis diluted the sample, it was necessary to extract the low-concentration analytes from the LC mobile phase to reconcentrate for GC analysis.

Quantitative NMR analysis was performed according to a validated analytical method used for CW agents [5]. All NMR experiments were performed on a Varian Unity Widebore 300-MHz NMR with a 5-mm broadband probe. General 1-D acquisition parameters are provided in Table 1. Samples of the supernatant liquid were prepared by filtration of the sample with a 0.45-μm PVDF cartridge filter. For quantitative ^{31}P NMR analysis, a known weight of hexamethylphosporamide (HMPA, 99+%, Aldrich, Milwaukee, WI, CAS RN 680-31-9) was added as an internal standard. Based on the measured T_1 values, a recycle delay of 20 s was used. Characterization of the grayish solids was achieved by gravity filtration of the sample. The solids dissolved in deuterated trifluoroacetic acid.

Table 1
Varian unity NMR acquisition parameters

Parameter	Nucleus: ^{1}H	Nucleus: ^{13}C	Nucleus: ^{31}P
Tip angle	5–45°	90°	90°
90° pulse	21.5 μs	14.0 μs	15.0 μs
Sweep width	4000 Hz	20 000 Hz	17 000 Hz
File size	16k	40k	68k
FID resolution	0.25 Hz	0.5 Hz	0.25 Hz
Transients	≥32	≥20 000	≥300
Line broadening	0.02 Hz	1.0 Hz	1.0 Hz

An HP 5890/5921A GC–AED was used to identify heteroatoms in the compounds. The atomic emission detector uses a Beenaker-style microwave cavity to produce a helium plasma. As compounds elute from the GC column into the plasma, they are atomized and emit light characteristic of the elements making up the analyte. Because compounds are atomized, the response for a particular element is independent of the chemical compound from which it originated. Compounds that contained multiple heteroatoms could be identified from the GC trace for confirmation of the GC–MS and LC–MS identifications.

Note: even though there was no evidence that the sample was toxic, it did potentially contain or may have been exposed to chemical weapons agents. Thus, the sample was handled as a potentially toxic material in accordance with the operating procedures for chemical weapons agents.

3. Results

The sample was an amber yellow organic liquid with a grayish solid which settled out with time. The liquid portion was analyzed by GC–AED, GC–IR–MS ($MeCl_2$ extract and TMS-derivatized sample), LC–MS and NMR. The solid was characterized after dissolution by NMR.

Fourteen components were identified in the sample, and their structures are shown in Table 2. Each component was confirmed by as many independent methods as possible, and the results for all methods were combined to insure that all the high concentration compounds were identified and quantified.

Six high-concentration phosphorus-containing components were identified and confirmed by GC–IR–MS, LC–MS, GC–AED, and NMR. Several phosphorus-containing components of lower concentration have been identified by GC–MS and LC–MS.

3.1. LC–MS and GC–MS analysis

With LC–MS using APCI ionization, chemical identification is done from the LC retention time, which can be compared to a known standard compound, and the mass spectrum. The mass spectra typically give molecular $[M+H^+]$ ions with small amounts of fragmentation. LC–MS molecular weight and fragmentation data were used to determine the structure of the major components and several minor compounds.

LC–MS analysis showed that two of the compounds, I and III, are isomers with molecular weights of 198 Da, giving $[M+H]^+$ ions at m/z 199. The same was observed in the GC–MS results. II has a molecular weight of 184 Da. VI, molecular weight 182 Da, coelutes with II on the LC under these conditions. In the mass spectrum of I, the fragment peaks at m/z 171, 143, and 115 indicate sequential losses of three ethylene groups, which is consistent with the symmetric *O*,*O*,*O*-triethyl structure. A fraction of this compound was collected, and the EI mass spectrum from analysis of the fraction showed that this peak is consistent with the assignment of the isomers from the GC and IR data. However, the LC–MS spectrum is considerably simpler and easier to interpret than the EI mass spectrum, although the EI spectrum is in the NIST mass spectral database.

LC–MS spectrum for III shows fragment ions from loss of only two ethylene groups, indicating that the *S*-ethyl group is less subject to fragmentation than the two *O*-ethyl groups. The mass spectrum for II also shows only two fragment ions from loss of the ethyl groups.

Fig. 1 shows the liquid chromatographic peaks for most of the identified compounds. IV and V are acidic and elute early in the run, and they have little retention on the C_{18} column. These compounds give $[M+H]^+$ peaks at m/z 157 and 171. They both have fragments from a single loss of ethylene from the *O*-ethyl group. They have poor peak shapes, possibly because they are partially ion paired with the amines that are present in the sample, or because of solvent effects and poor retention. Greater dilution of the sample improves the peak shape, but at the expense of sensitivity to the lower concentration compounds. X and XI are consistent with the peaks at $[M+H]^+$ of m/z 130 and 158.

Fig. 2 illustrates the advantage of using multiple LC detection methods, since different methods have dramatically different sensitivities for different compounds. The MS and UV data for a section of a chromatogram are shown. The conditions for this run were different from that in Fig. 1, using DI water without buffer to improve the UV signal and using the larger column that was used for fraction collection. The chromatograms are shifted slightly in time relative to each other, with the UV peaks about 0.3 min earlier than the MS peaks. The m/z 185 and 199 peaks from compounds II and III have very strong signals in the mass spectral trace but correspond to relatively weak peaks in the UV trace. The largest UV peaks are assigned to compounds VIII and IX, which are sulfur compounds with relatively strong absorption and high concentrations. (Because of the strong signal, the UV peaks are saturated, and the peaks appear to be split from noise spikes or bubbles in the detector.) However, compounds VIII and IX have low proton affinities, so they do not produce strong MS peaks. Small $[M+H]^+$ peaks at m/z 77 and 91 are observed, which confirm the assignments. In addition, a standard of IX (ethyl sulfide, 98%, Aldrich, CAS RN 352-93-2) was analyzed, and it gave a retention time match. These compounds were not identified by GC analysis, since they are volatile and eluted close to the solvent peak. They were confirmed by ^{1}H NMR.

Four lower concentration compounds were also identified both by LC–MS and GC–MS. A section of the LC–MS extracted ion chromatogram is shown in Fig. 3. Three of these compounds, with $[M+H]^+$ of m/z 266, 268 and 282, contain phosphorus and

Table 2
List of major identified compounds

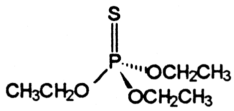
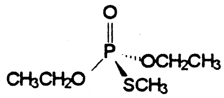
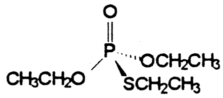
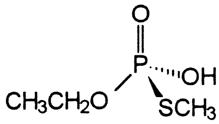
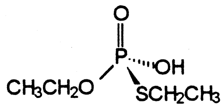
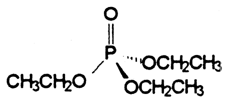
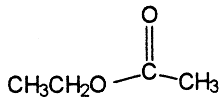
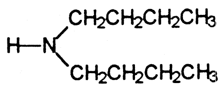
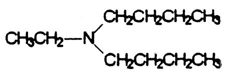
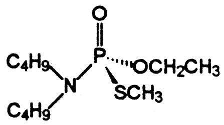
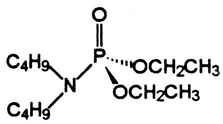
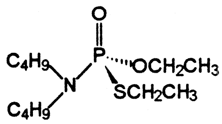
Compound name	Structure	Mol. wt.	CAS RN
I. *O*,*O*,*O*-Triethyl phosphorothionate		198	126-68-1
II. *O*,*O*-Diethyl-*S*-methyl phosphorothioate		184	2404-05-9
III. *O*,*O*,*S*-Triethyl phosphorothioate		198	1186-09-0
IV. *O*-Ethyl-*S*-methyl phosphorothioic acid		228	
V. *O*,*S*-Diethyl phosphorothioic acid		242	
VI. Triethyl phosphate		182	78-40-0
VII. Ethyl acetate		88	141-78-6
VIII. Ethylmethylsulfide	$CH_3CH_2SCH_3$	76	624-89-5
IX. Ethylsulfide	$CH_3CH_2SCH_2CH_3$	90	352-93-2
X. Dibutylamine		129	111-92-2

Table 2. Continued

Compound name	Structure	Mol. wt.	CAS RN
XI. Dibutylethylamine		157	
XII. *O*-Ethyl-*S*-methyl *N*,*N*-dibutylphosphoramidothioate		267	
XIII. *O*,*O*-Diethyl *N*,*N*-dibutylphosphoramidate		265	67828-17-5
XIV. *O*,*S*-Diethyl *N*,*N*-dibutylphosphoramidothioate		281	

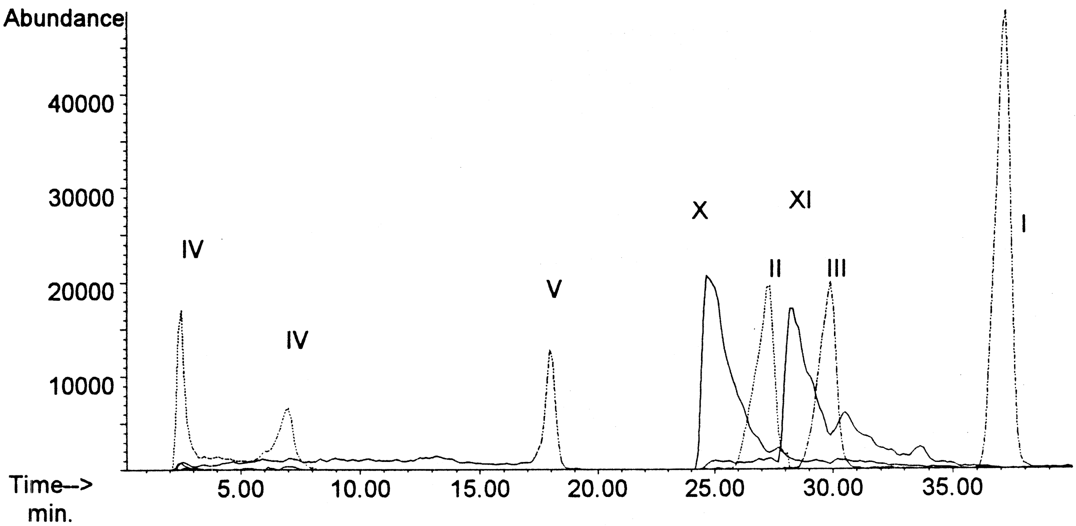


Fig. 1. LC–MS extracted ion chromatogram showing most of the major components of the DPG simulant sample. Roman numerals designate compound numbers in Table 2. Peak heights do not represent relative signals, since in some cases the most abundant ions are not shown. The peaks for compounds I, II, and III are fragment ions at m/z 171 and/or 157, not the more intense m/z 185 and 199 peaks that are the major ions for these compounds. Peak IV is split, and peak V tails strongly due to solvent effects on the chromatography or ion pairing with the amines.

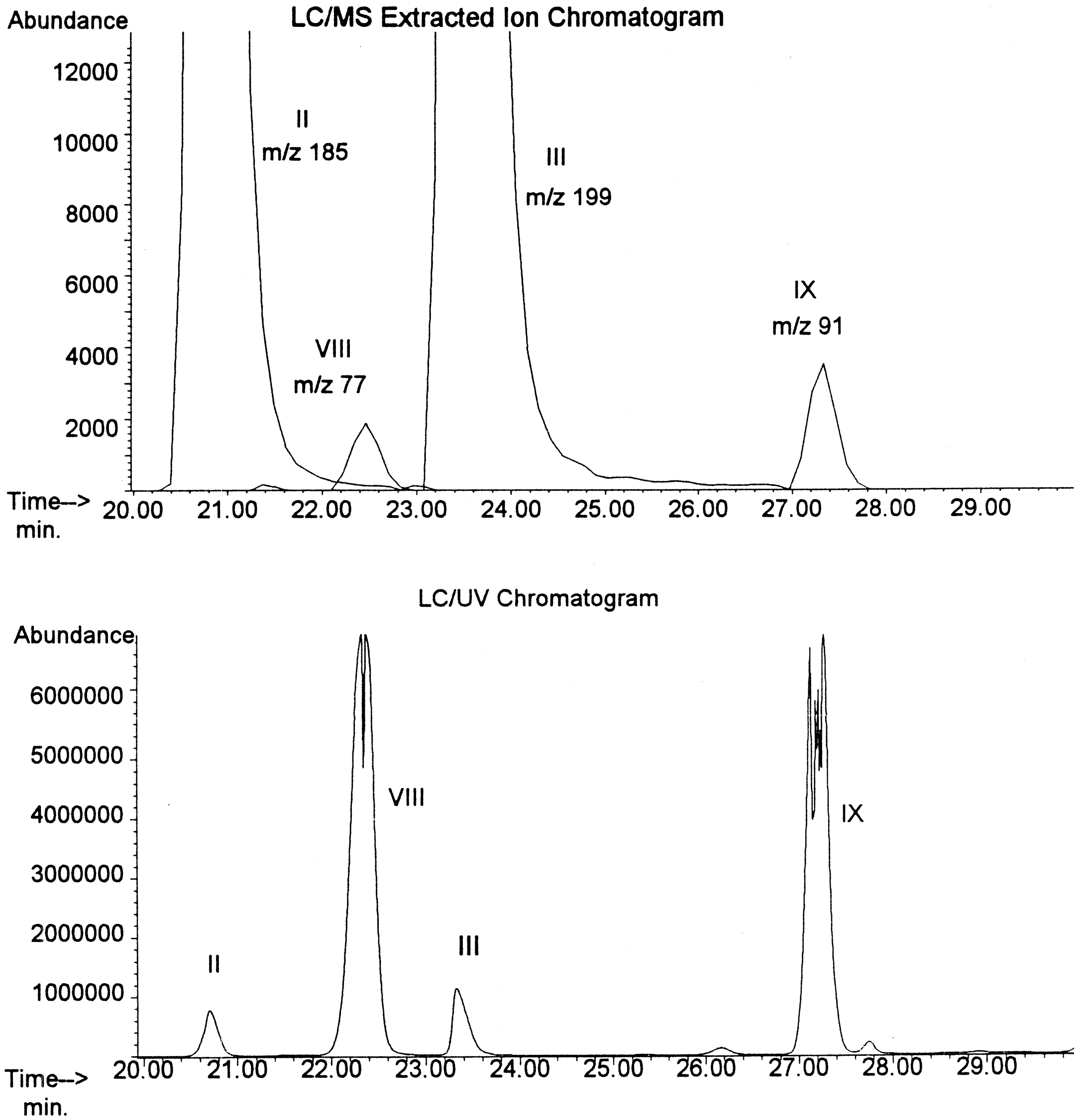


Fig. 2. Partial LC–MS extracted ion chromatogram (top panel) and UV absorption spectrum at 210 nm (bottom panel) showing compounds II, III, VIII, and IX. The strong UV peaks are split due to saturation of the signal, and noise or bubbles in the detector.

nitrogen, as determined by GC–AED. The m/z 268 and 282 compounds also contain sulfur. This implies that the m/z 268 compound (XII) is an isomer of VX, although the EI MS and IR spectra show that it is definitely not VX. The EI mass spectrum is shown in Fig. 4. In comparison, the EI spectrum of VX has predominant m/z 114 and 127 peaks [6]. Fractions of these three compounds were collected and analyzed by GC–MS to confirm the LC identifications. They were all synthesized (F. Berg, unpublished results) as a confirmation of the structures as three esters of *N*,*N*-dibutylphosphoramidate: *O*,*O*-diethyl (XII), *O*-ethyl-*S*-methyl (XII), and *O*,*S*-diethyl (XIV). Another peak at $[M+H]^+$ of m/z 234 was assigned

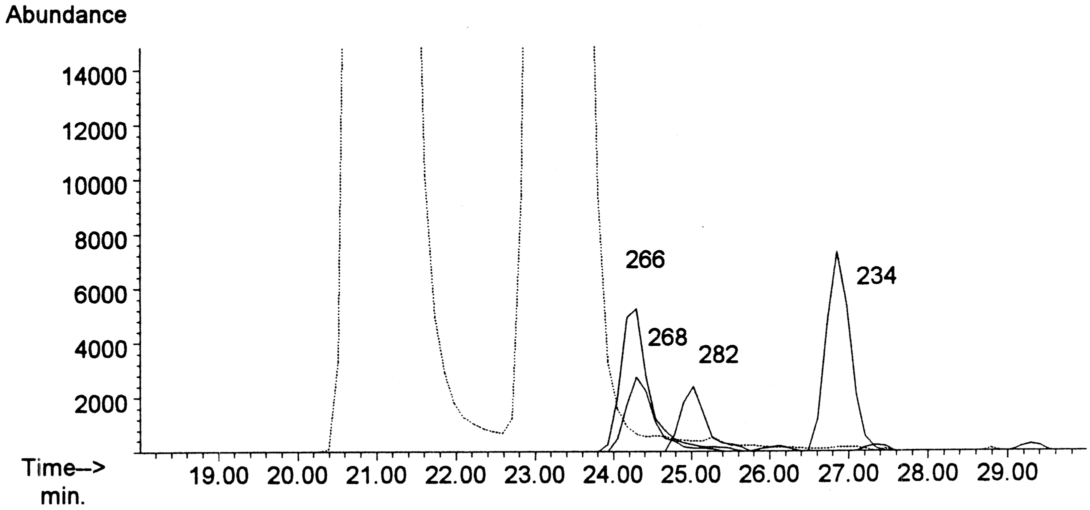


Fig. 3. Partial LC–MS extracted ion chromatogram showing four low-concentration peaks with $[M+H]^+$ ions at m/z 266, 268, 282, and 234. The peaks at m/z 266 and 268 coelute in this chromatogram, but they can be resolved using a longer run time.

as *N*,*N*-dibutylethylcarbamodithioate, which may be a reaction product of a stabilizer. Other low concentration peaks were not assigned.

3.2. GC–IR–MS analysis

The availability of two spectral techniques in a single run is extremely valuable in the identification of unknown materials. With the relative lack of phosphorothioate compounds in the available commercial mass spectral libraries, the additional information provided by the infrared detector provided critical information distinguishing isomeric forms of compounds. However, infrared libraries are also

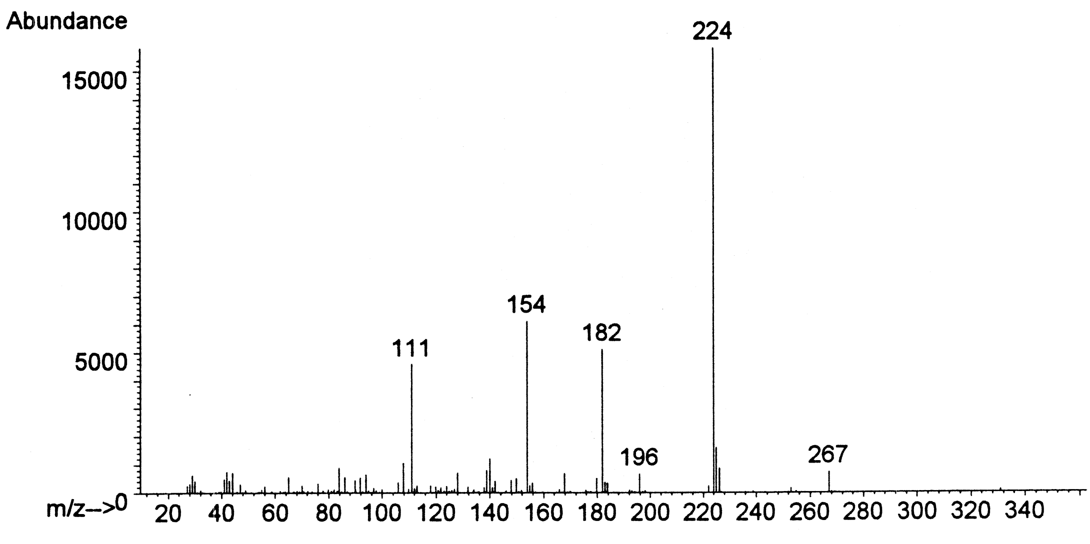


Fig. 4. Electron impact-ionization mass spectrum of compound XII, an isomer of VX.

limited, so a considerable amount of spectral interpretation was required to identify the relevant vibrational bands.

In the case of III, the IR data conclusively showed that the analyte was not the pesticide cyanthoate, although this assignment was not unreasonable on the basis of the mass spectral data alone. During analysis at APG, the search algorithm assigned the unknown spectrum to the pesticide with a match factor of 95%, as shown in Fig. 5. The match is excellent, and the spectrum is complex and has many peaks. The infrared spectrum, shown in Fig. 6, however, was clearly not from cyanthoate. In particular, the absence of bands from carbonyl, cyano, or secondary amino functionalities exclude that assignment.

The compounds identified by GC–IR–MS analysis in the dichloromethane extract are I, II, III, VI, X, XI, and XII. The compounds IV and V were identified as trimethylsilyl derivatives. Identities of I, II, III, XII, XIII, and XIV were confirmed by micro-scale synthesis of the compounds and analysis by GC–IR–MS. This technique had been previously used to synthesize compounds related to chemical warfare agents and was extended to the phosphorothioates and phosphoramidothioates [7]. A more detailed description of the synthesis and analysis of compounds II and XII has been presented [8].

3.3. NMR analysis

Determination of the structure of the major phosphorus and non-phosphorus compounds was accomplished by spectral interpretation of ^{1}H, ^{13}C, ^{31}P, DEPT-135, ^{1}H–^{1}H COSY, ^{13}C–^{1}H HETCOR and ^{31}P–^{1}H HETCOR spectra of the supernatant liquid in $CDCl_3$.

The combination of ^{31}P–^{1}H HETCOR and ^{1}H–^{1}H COSY was sufficient to determine the complete structure of II and III. Fig. 7 shows the ^{31}P–^{1}H HETCOR two-dimensional NMR determination used to identify compounds II and III. The vertical axis is a section of the ^{31}P scale from 21 to 31 ppm, which was expanded to show the detail of the separation of the compounds. Two-dimensional NMR, when used on a mixture, can act as a 'separation' technique to distinguish between different components of the mixture. It is also useful for distinguishing the isomers, since the ethyl groups bonded to S are clearly separated from the ethyl ether groups. The

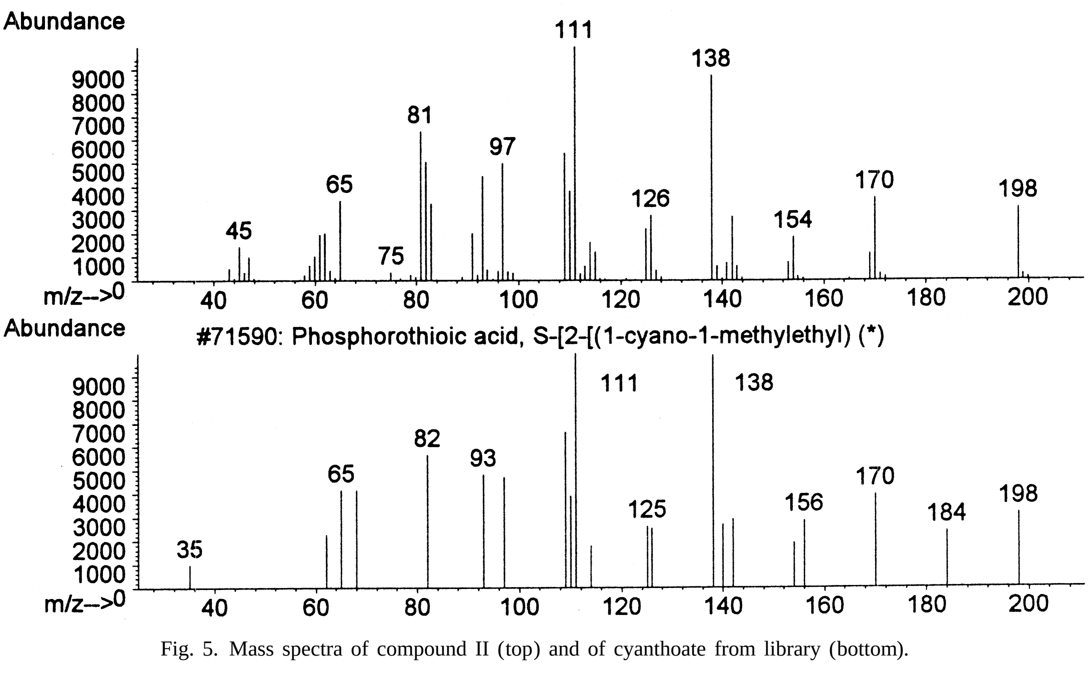


Fig. 5. Mass spectra of compound II (top) and of cyanthoate from library (bottom).

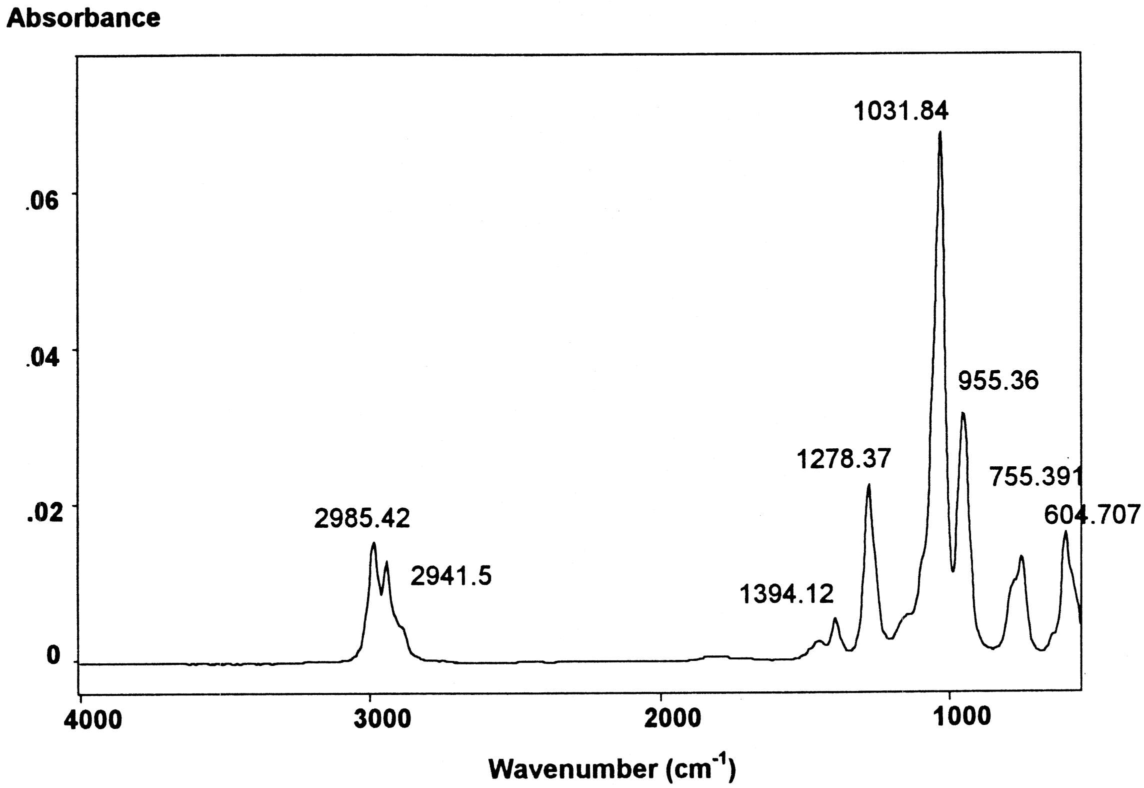


Fig. 6. Infrared spectrum of compound II.

horizontal axis is the ^{1}H axis from 1.1 to 5.0 ppm, which shows all the protons for these compounds. The other P compounds are not present in this section. Compound I has a much different ^{31}P chemical shift at 76 ppm due to the P=S bond, and it was observed in the entire spectrum. The entire structure of I required the molecular weight data from GC–MS and LC–MS, since the identity of the S atom bonded to the P could not be determined unequivocally from just the NMR spectrum of the unknown.

DEPT-135 and ^{13}C–^{1}H HETCOR indicated the structures for IV, V, and VI, but confirmation by GC–IR–MS and LC–MS was crucial. ^{1}H–^{1}H COSY and ^{13}C–^{1}H HETCOR NMR analyses were critical for the identifications of VII, VIII, and IX; ethyl acetate (VII) was not observed by either of the other techniques and the sulfides (VIII and IX) were not observed by GC–MS–IR because of their relatively high volatility.

Quantitation was relatively simple to do by NMR, once the compounds were identified, since the major components had high concentrations. Quantitation could have been done by GC–AED, but the sample would have had to be diluted, and some major components were not detectable by GC, whereas NMR could account for essentially all of the sample. Quantitative NMR analysis showed that the major phosphorus components (I–VI) account for 58% of the total weight of the liquid portion of the sample. Seven replicate quantitative ^{31}P NMR analyses were performed on a sample with a known weight of HMPA internal standard. The mean of the seven replicate analyses is reported in Table 3 with an error range of ± 2 SD for a 95% confidence interval.

Quantitation of the major non-phosphorus components by ^{1}H NMR shows that ethyl acetate (VII) accounts for 15.5%, ethylmethyl sulfide (VIII) for 4.7%, and ethyl sulfide (IX) for 11.2% of the sample. The bulk of the remaining 10.6% of the

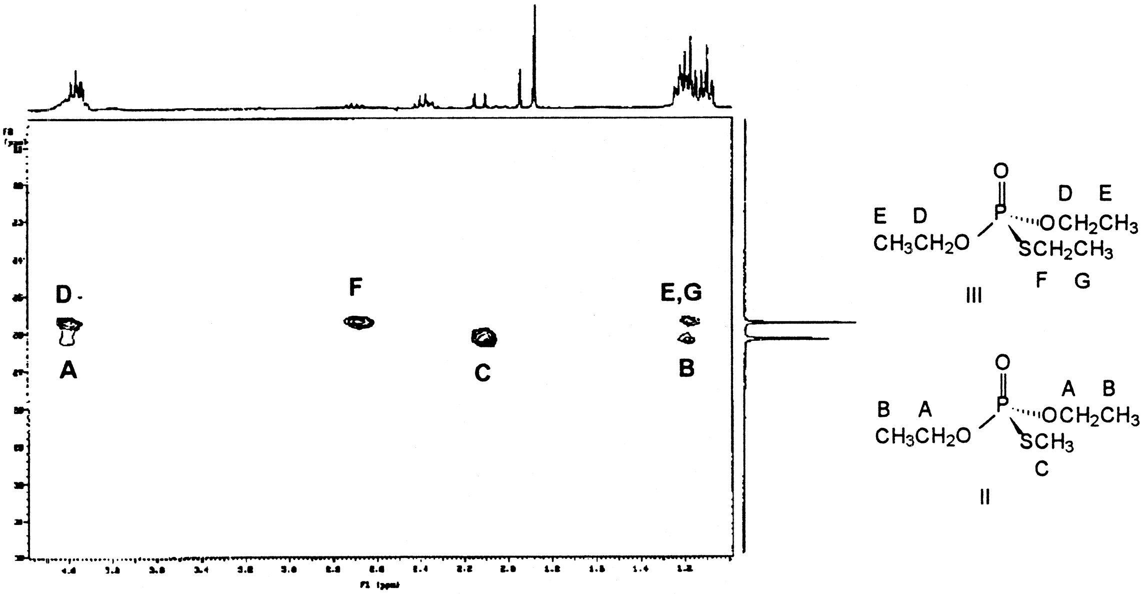


Fig. 7. $^{31}P-^{1}H$ HETCOR two-dimensional NMR determination used to identify compounds II and III. The vertical axis is a section of the ^{31}P scale from 21 to 31 ppm, and the horizontal axis is the ^{1}H axis from 1.1 to 5.0 ppm. The other P compounds are not present in this section, since they have much different ^{13}P chemical shifts.

sample appears to be comprised of the amines, X and XI, which produce broad lines in the NMR spectra. Characterization of the whitish solid, which could only be dissolved in trifluoroacetic acid, indicates that it is also composed primarily of a salt of dibutylamine.

4. Discussion

There were several major conclusions:

(1) Fourteen components were identified in the sample, shown in Table 2.

(2) Six high-concentration phosphorus-containing components were identified and confirmed by GC–IR–MS, LC–MS and NMR.

(3) Several phosphorus-containing components of lower concentration have been identified by GC–IR–MS and LC–MS.

(4) One of these trace compounds was a VX isomer (XII), but VX was not found in the sample.

(5) One of the bulk components, *O,O,S*-triethyl phosphorothioate (III), spuriously tests as the pesticide cyanthoate by GC–MS-EI library matching.

(6) LC–MS and NMR were able to identify the most volatile components (VII, VIII and IX).

(7) Quantitative NMR was able to account for the bulk of the sample composition. Quantitative NMR analysis shows that the major phosphorus components account for 58% of the total weight of the liquid portion of the sample. Quantitation of the major non-phosphorus components shows that they account for most of the remaining 42% of the sample.

(8) Characterization of the whitish solid from the

Table 3
Absolute weight percentages of the major phosphorus compound (±2 SD) in the Dugway Simulant Round as determined by quantitative ^{31}P NMR analysis

I	II	III	IV	V	VI
23.9±0.4%	10.6±0.5%	14.4±0.2%	3.7±0.4%	4.0±0.3%	1.4±0.1%

sample indicates that it is composed primarily of the salt of dibutylamine.

No VX, G-agent or pesticide has been observed as a major component in the sample by any of the methods. The isomer of VX was a low abundance phosphorus compound, but it is not likely to be confused for VX by GC–MS-EI analysis, as its fragmentation pattern is considerably different from that of VX.

The detection limits for particular agents were not determined by spike and recovery experiments in the diluted sample, but they are estimated in the low μg/ml concentration in the original sample. Because the sample is a neat organic liquid, techniques such as solvent extraction or solid-phase extraction are of limited use, without extensive method development. In fact, since the sample was diluted by 1:100 for GC analysis, detection of agents by GC was not necessarily more sensitive than by NMR. NMR detection limits in the neat sample are approximately 20 μg/ml. Related problems have been observed in other studies [9].

The sample was clearly not predominantly composed of agent, but it is not possible to rule out trace (<μg/ml) concentrations, so it should be handled with appropriate precautions. Preliminary review of the toxicology literature shows *O,O,S*-triethylphosphorothioate (III) is a cholinesterase inhibitor which produces delayed toxic response [10]. For this reason alone, the sample should be handled with great care.

The reason for this particular formulation of CW agent simulant is not known. Clearly, the phosphorus compounds are related to the G and V nerve agents. Most CW agent monitors operate by an element-

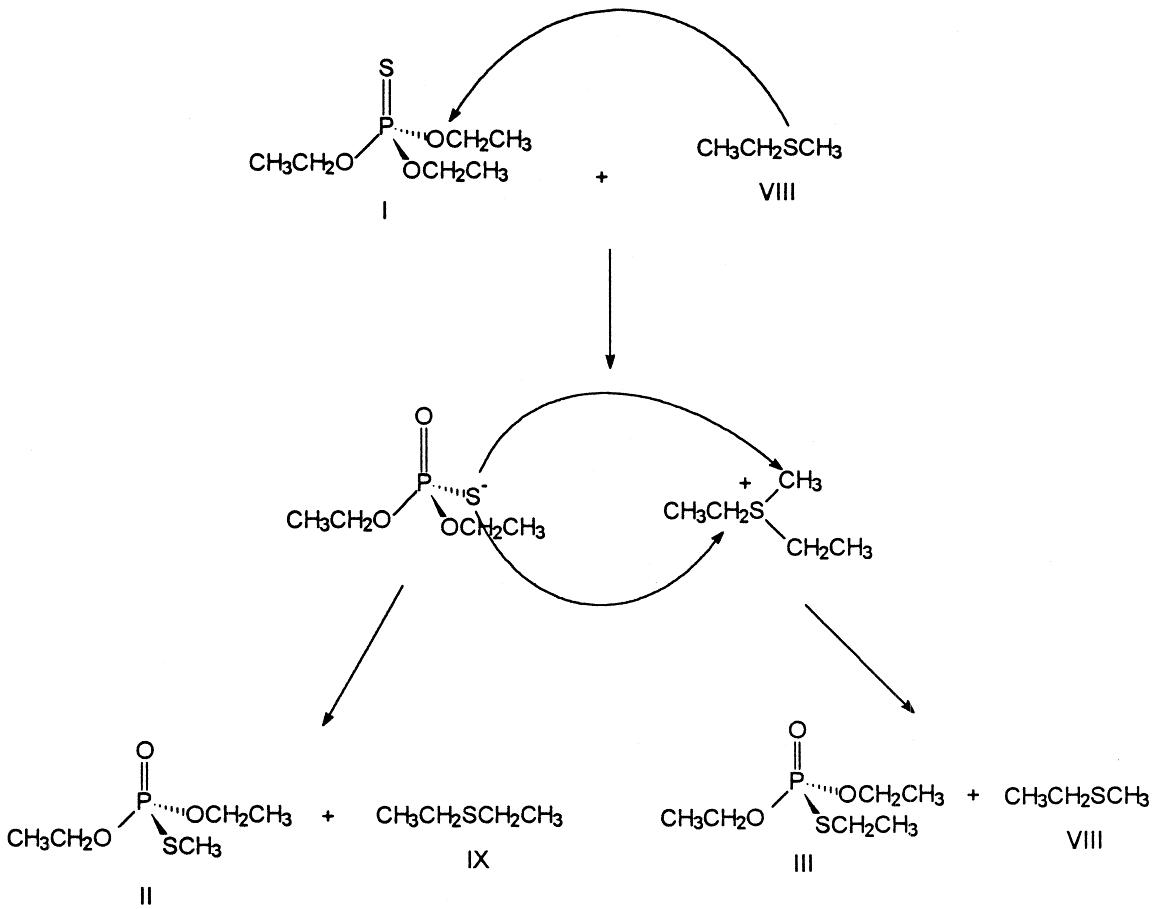


Fig. 8. Possible reaction scheme producing some of the components from compounds I and VII.

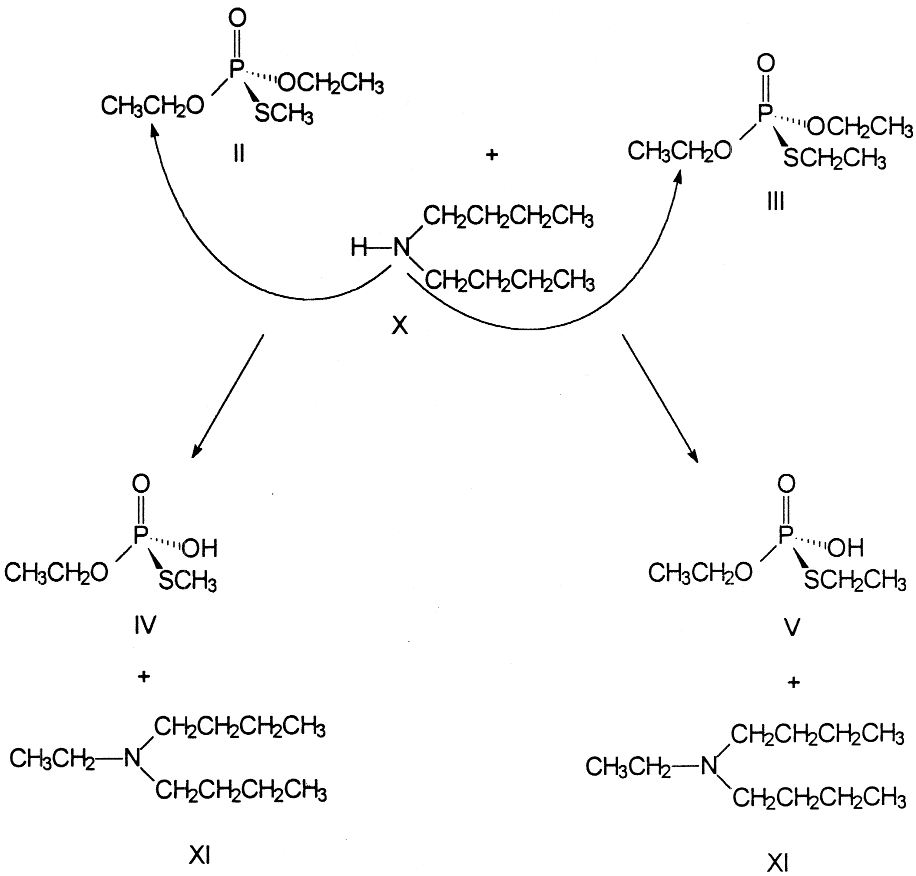


Fig. 9. Possible reaction scheme producing some components from compounds II or III and X.

specific detector such as a flame photometric detector, so these compounds may have been selected to register on this type of detector. However, the sulfur compounds (VIII and IX) are considerably more volatile than sulfur mustard, to the degree that they might not elute in the same GC retention time window. Therefore, their value as simulants is unknown. The amine compounds could be simulants for the amine group of VX or for nitrogen mustard compounds.

It is possible that the original formulation of the mixture was considerably simpler, and many of the components formed by slow reactions. Fig. 8 shows a possible reaction scheme that could form several components from I and VIII. The lower concentration phosphorus compounds are likely to be reaction products between the major compounds. The phosphoramidates are probably reaction products of I or II with the amine X. A possible reaction scheme is shown in Fig. 9. These reaction products, which may have formed during the long storage time, further complicate the mixture and make trace screening for CW agents more difficult.

This study illustrates the necessity for thorough analytical determination of unknown CW-related materials as an assessment of the hazard and the appropriate disposal method. Since the mixture was a complete unknown, the use of several complementary analytical methods was essential. Any one technique gave reasonably good identifications of some of the components, but each technique also missed major components of the mixture. Identification and quantitation of the mixture required cooperative use of all the analytical data.

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