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Capillary column gas chromatography–ammonia and deuterated ammonia chemical ionization mass spectrometry of sulfur vesicants

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ABSTRACT

Capillary column gas chromatography–ammonia and deuterated ammonia chemical ionization mass spectrometry was found to be a highly specific technique for the detection and identification of three long-chain sulfur vesicants, 2-chloroethyl (2-chloroethoxy)ethyl sulfide, sesquimustard and bis[(2-chloroethylthio)ethyl]ether. All three vesicants exhibited significant $(M + NX_4)^+$ (where X = H or ^2H) pseudo-molecular ions and structurally significant chemical ionization fragmentation ions during capillary column gas chromatographic–ammonia chemical ionization mass spectrometric analysis. This method was utilized during analysis of contaminated painted panels circulated during the 3rd round robin verification exercise (1991). Chemical ionization data obtained during this exercise complemented the electron impact data obtained for sesquimustard and bis[(2-chloroethylthio)ethyl]ether and the specificity of the technique enabled the confirmation of 2-chloroethyl (2-chloroethoxy)ethyl sulfide, a compound masked by hydrocarbons in the painted panel extracts.

INTRODUCTION

The possible ratification of a United Nations Chemical Weapons Convention has prompted many nations to consider the development of appropriate analytical techniques for chemical warfare agent detection and confirmation. Capillary column gas chromatography (GC) with flame ionization detection (FID) may be used for the routine screening of samples for the presence of mustard and other sulfur vesicants [1,2]. However, it is generally agreed that confirmation of the chemical warfare agents or their degradation products requires identification by mass spectrometry (MS).

Electron impact (EI), the traditional MS method of ionization, has gained wide acceptance for the verification of sulfur vesicants, as the EI mass spectra of numerous chemical warfare agents, their decomposition products and related compounds have been published [3–9]. EI mass spectra generally provide excellent structural information, but the presence of little or no molecular ion information for longer chain sulfur vesicants often hinders the identification of these compounds. Isobutane chemical ionization (CI) MS, a milder ionization technique, has been used to provide molecular ion information for these sulfur vesicants and related compounds [7]. However, isobutane lacks the specificity of ammonia and in hydrocarbon contaminated samples difficulties may occur in the detection of trace levels of sulfur vesicant contamination.

The efficacy of ammonia CI-MS [10] has been demonstrated for the detection of organophosphorus chemical warfare agents, their decomposition products and related impurities [11–15], including those contaminated with high levels of hydrocarbons [16]. Ammonia CI-MS has been used for long chain and cyclic mustard degradation products [8], but has not been previously utilized for long chain sulfur vesicants. The primary objective of this study was the evaluation of capillary column GC–ammonia and deuterated ammonia CI-MS for the detec-

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tion and confirmation of long-chain sulfur vesicants controlled under the proposed United Nations Chemical Weapons Convention. The sulfur vesicants studied exhibited significant $(M + NX_4)^+$ (where X = H or ^2H) pseudo-molecular ions and structurally significant CI fragmentation ions during capillary column GC–ammonia CI-MS analysis. The specificity of this technique was recently demonstrated during the analysis of contaminated painted panels circulated to fourteen United Nations Conference on Disarmament Technical Group national laboratories during the 3rd round robin verification exercise.

EXPERIMENTAL

Standards and sample handling

2-Chloroethyl (2-chloroethoxy)ethyl sulfide, sesquimustard [bis(2-chloroethylthio)ethane] and bis[(2-chloroethylthio)ethyl]ether were provided by the Defence Research Establishment Suffield Organic Chemistry Laboratory. Distilled-in-glass hexane was purchased from BDH (Edmonton, Canada). Anhydrous-grade ammonia (99.99% ; Liquid Carbonic) and deuterated ammonia (99% ; MDS Isotopes) were used during all CI-MS analyses.

Painted metal panels (2 cm × 4 cm with 60 μm paint), provided by Prins Maurits Laboratory TNO (Netherlands) as part of the 3rd round robin verification exercise, were placed in the bottom of a 100-ml glass beaker containing 10 ml of hexane. The panel was extracted by ultrasonic vibration for 5 min and the hexane removed and concentrated by nitrogen blowdown to 1 ml prior to analysis. All sample extracts and standards were stored in 1.8-ml PTFE-lined screw-capped vials at 4°C prior to GC analysis.

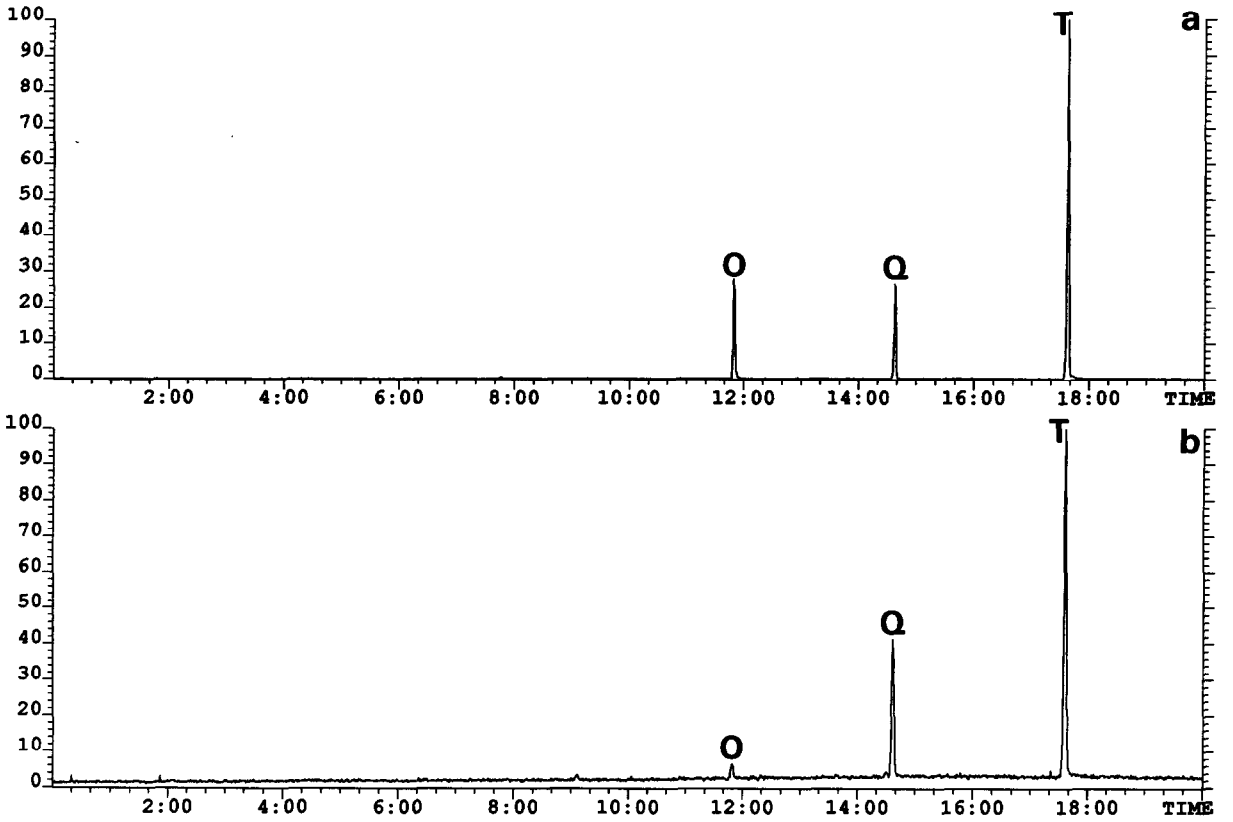

Fig. 1. Capillary column GC–MS (ammonia CI) chromatograms (200 to 300 u) of (a) a standard containing 2-chloroethyl (2-chloroethoxy)ethyl sulfide (O), sesquimustard (Q) and bis[(2-chloroethylthio)ethyl]ether (T) and (b) a hexane extract of round robin painted panel. Time in min; *y*-axis: relative intensity in %.

Instrumental

Capillary column GC–MS analyses were performed with an Autospec-Q hybrid tandem mass spectrometer (VG Analytical, Wythenshawe, UK) interfaced to a Hewlett-Packard 5890 gas chromatograph under the following chromatographic conditions. All injections were on-column [1] at 40°C onto a 15 m × 0.32 mm ID J&W DB-1701 (0.25 μm) capillary column with a 40°C (2 min) → 10°C/min → 280°C (5 min) temperature program. EI-MS operating conditions were as follows: accelerating voltage, 8 kV; emission, 0.2 mA; electron energy, 70 eV; source temperature, 200°C and source pressure, $2 \cdot 10^{-6}$ Torr. CI-MS operating conditions were as follows: accelerating voltage, 8 kV; emission, 0.3 mA; electron energy, 50 eV; source temperature, 120°C and source pressure (near source), $8 \cdot 10^{-5}$ Torr. The ratio of NH_4^+: $NH_3^{+\cdot}$ was approximately 15:1 in the VG Autopsec EI/CI source. Full scanning EI and CI data were collected over the 400 to 40 u mass range at 0.5 s/decade.

RESULTS AND DISCUSSION

Fig. 1 illustrates capillary GC–ammonia CI-MS chromatograms for a standard containing three long chain sulfur vesicants, 2-chloroethyl (2-chloroethoxy)ethyl sulfide, sesquimustard and bis[(2-chloroethylthio)ethyl]ether and the hexane extract of a round robin painted panel contaminated with an envelope of hydrocarbons and the same sulfur vesicants. The envelope of hydrocarbons in the hexane extract of the painted panels did not hinder the EI-MS detection and confirmation of sesquimustard and bis[(2-chloroethylthio)ethyl]ether (Fig. 2).

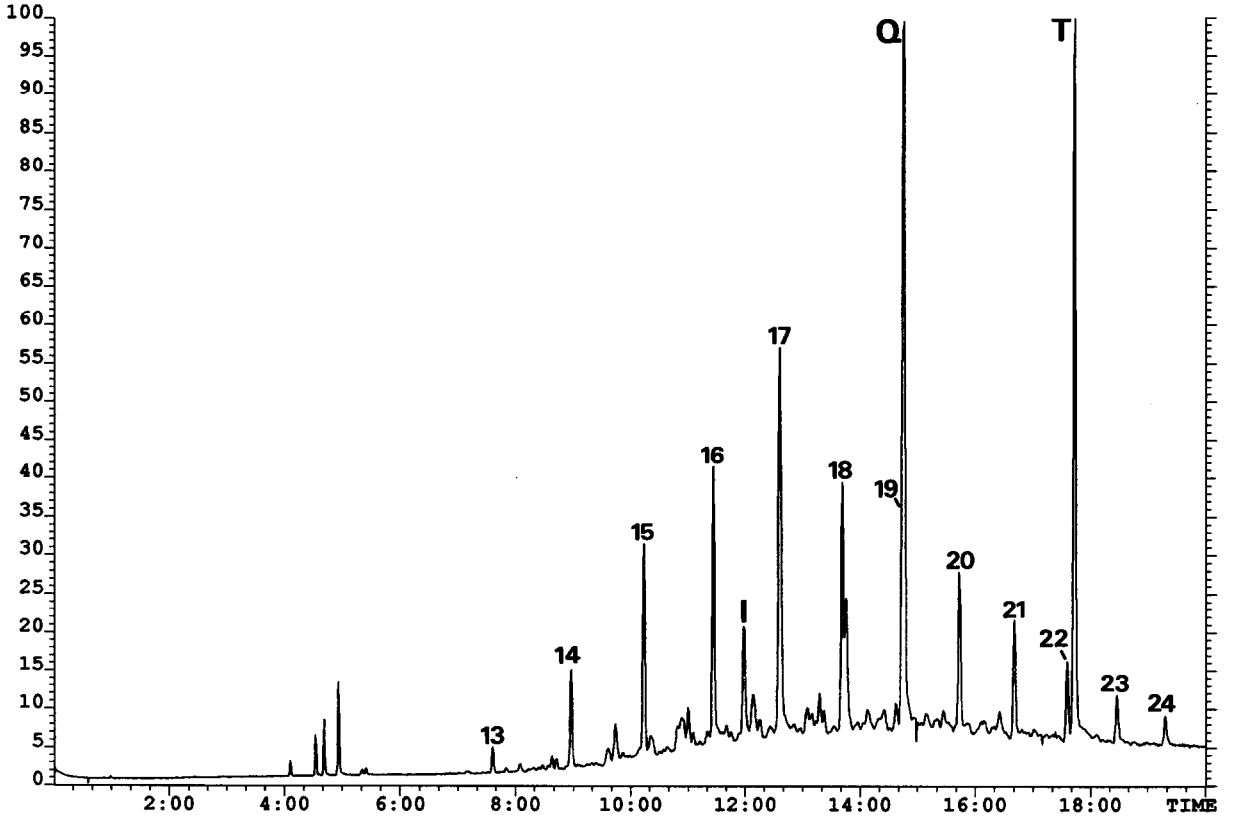

Fig. 2. Capillary column GC–MS (EI) chromatogram (40 to 400 u) of a hexane extract of round robin painted panel containing 2-chloroethyl (2-chloroethoxy)ethyl sulfide [masked by interference (I)], sesquimustard (Q) and bis[(2-chloroethylthio)ethyl]ether (T). The numbered components indicate the carbon number of *n*-alkanes. Scales as in Fig. 1.

However, the presence of co-eluting hydrocarbon(s) hindered the identification of 2-chloroethyl (2-chloroethoxy)ethyl sulfide, present at 4 ng level in the extract chromatogram (Fig. 1b). EI-MS identification was tentative at best. However under ammonia CI-MS the co-eluting hydrocarbon(s) were not ionized and this compound was detected and confirmed along with the other two higher-level sulfur vesicants in the painted panel extract. A full scanning ammonia CI-MS detection limit of about 1 ng was estimated based on the detection of 2-chloroethyl (2-chloroethoxy)ethyl sulfide.

The ammonia CI mass spectra of the compounds found in the painted panel hexane extract (Fig. 3) were characterized by the presence of intense $(M + NH_4)^+$ pseudo-molecular ions and ammonia CI fragmentation ions due to $(M + H)^+$, $(M + NH_4 - 34)^+$, $(M + NH_4 - NH_4Cl)^+$, $[C_2H_4SC_2H_4Cl]^+$ and $(M + NH_4 - C_2H_4S - 34)^+$. Most of the ions, listed in Table I were readily interpreted with the exception of those involving loss of 34. It was apparent from the isotopic abundance data that the loss involved chlorine, but there was uncertainty as to the source of the additional hydrogen. Deuterated ammonia CI-MS was performed on the standards in an attempt to ascertain whether the ammonia CI gas was involved in the gain of hydrogen by these ions. Fig. 4 illustrates the deuterated ammonia CI mass spectra for 2-chloroethyl (2-chloroethoxy)ethyl sulfide, sesquimustard and bis-[(2-chloroethylthio)ethyl]ether. Gains in mass (5 u) by the deuterated ammonia CI fragmentation ions confirmed that the ions in question were due to $(M + NX_4 - Cl + X)^+$ and $(M + NX_4 - Cl - C_2H_4S + X)^+$ (where X = H or ^2H). The other deuterated ammonia CI ions correlated well with

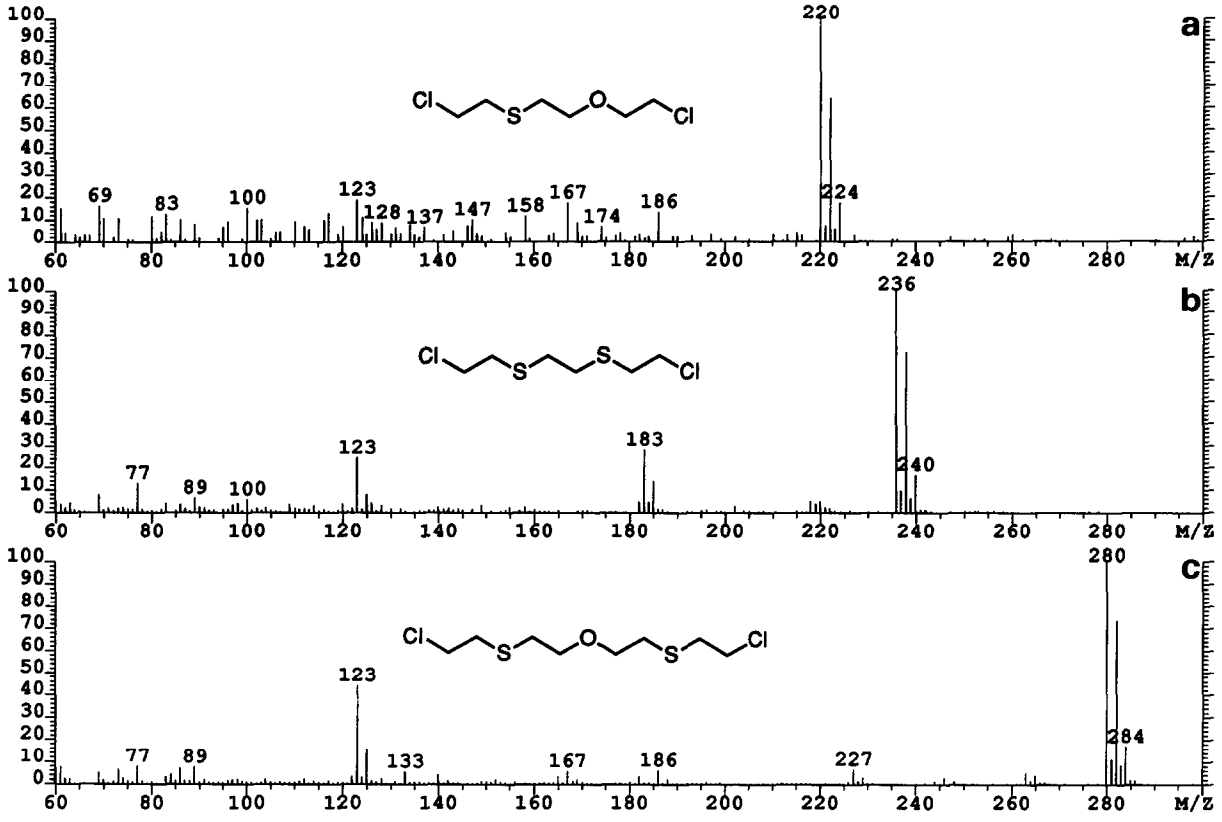

Fig. 3. Ammonia chemical ionization mass spectra of (a) 4 ng of 2-chloroethyl (2-chloroethoxy)ethyl sulfide, (b) 35 ng of sesquimustard and (c) 50 ng of bis[(2-chloroethylthio)ethyl]ether found in the hexane extract of the round robin painted panel (refer to Fig. 1b). *y*-axis: relative intensity in %.

TABLE I

NX_3 (X = H OR ^2H) CHEMICAL IONIZATION MASS SPECTROMETRIC DATA FOR 2-CHLOROETHYL (2-CHLOROETHOXY)ETHYL SULFIDE (O), SESQUIMUSTARD (Q) AND BIS[(2-CHLOROETHYLTHIO)ETHYL]ETHER (T)

Ion structure	*m/z* (% Relative intensity)					
	X = H			X = ^2H		
	O	Q	T	O	Q	T
$(M + NX_4)^+$	220 (100)	236 (100)	280 (100)	224 (100)	240 (100)	284 (100)
$(M + X)^+$	203 (1.4)	219 (3.5)	263 (4.8)	204 (1.6)	220 (5.8)	264 (3.9)
$(M + NX_4 - Cl + X)^+$	186 (6.4)	202 (3.0)	246 (3.0)	191 (3.1)	207 (2.2)	251 (2.1)
$(M + NX_4 - NX_4Cl)^+$	167 (17)	183 (28)	227 (6.1)	167 (11)	183 (13)	227 (5.3)
$(M + NX_4 - Cl - C_2H_4S + X)^+$	–	–	186 (4.0)	–	–	191 (4.5)
$[C_2H_4SC_2H_4Cl]^+$	123 (16)	123 (35)	123 (40)	123 (20)	123 (27)	123 (30)

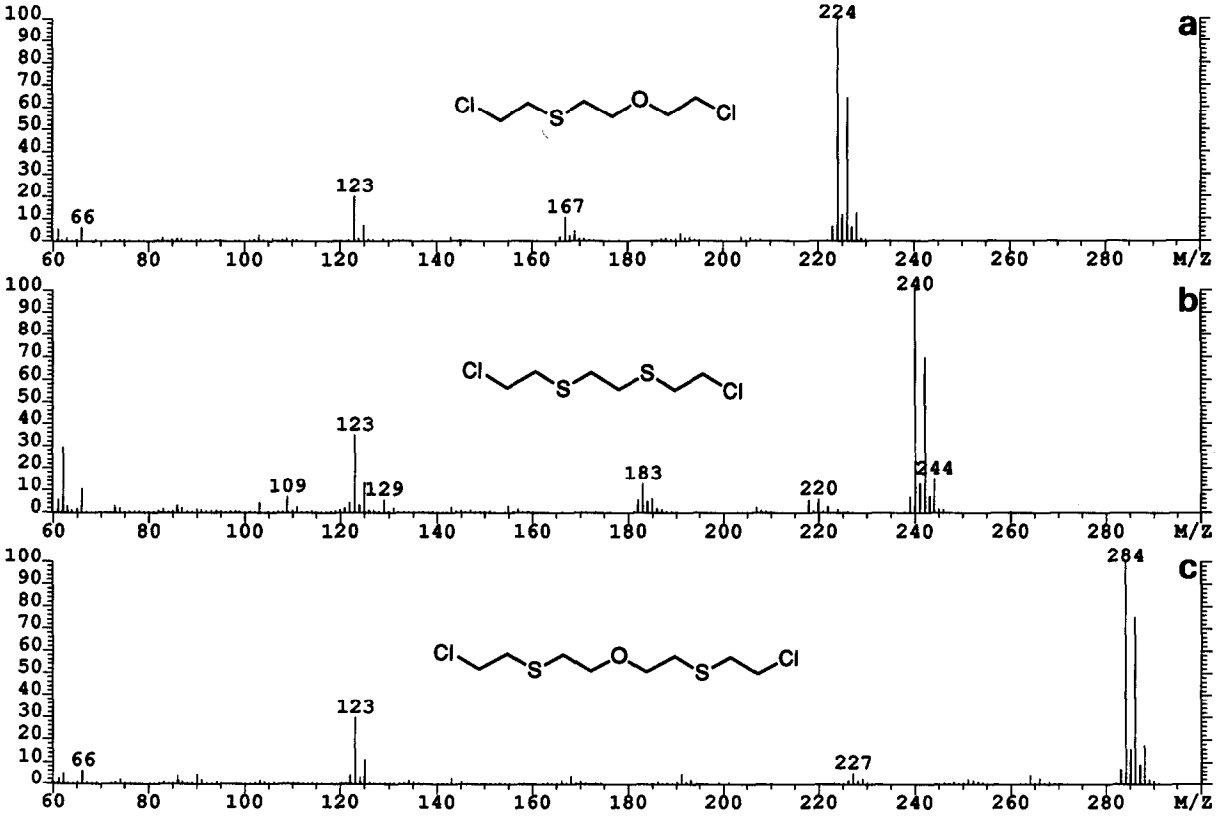

Fig. 4. Deuterated ammonia chemical ionization mass spectra of (a) 2-chloroethyl (2-chloroethoxy)ethyl sulfide, (b) sesquimustard and (c) bis[(2-chloroethylthio)ethyl]ether. *y*-axis: relative intensity in %.

the ammonia CI data and Table I compares the deuterated ammonia and ammonia CI ions observed under similar source conditions.

CONCLUSIONS

Capillary column GC–ammonia and deuterated ammonia CI-MS was found to be a highly specific technique for the detection and identification of three long-chain sulfur vesicants, 2-chloroethyl (2-chloroethoxy)ethyl sulfide, sesquimustard and bis-[(2-chloroethylthio)ethyl]ether. All three vesicants exhibited significant $(M + NX_4)^+$ (where X = H or ^2H) pseudo-molecular ions and structurally significant CI fragmentation ions during capillary column GC–ammonia CI-MS analysis. Deuterated ammonia CI data were acquired for all three compounds to confirm the identity of two unusual CI fragmentation ions.

This new approach to vesicant analysis was demonstrated during analysis of contaminated painted panels circulated during the 3rd round robin verification exercise (1991). CI data obtained during this exercise complemented the EI data obtained for sesquimustard and bis[(2-chloroethylthio)ethyl]ether and the specificity of the technique enabled the confirmation of 2-chloroethyl (2-chloroethoxy) ethyl sulfide, a compound masked by the presence of hydrocarbons during EI-MS analysis of the painted panel extracts. The CI data provided are sufficient for the detection and confirmation of three long-chain sulfur vesicants controlled under the proposed United Nations Chemical Weapons Convention and application of this highly specific technique appears to be likely during future analyses.

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