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Field-portable gas chromatography with transmission quadrupole and cylindrical ion trap mass spectrometric detection: Chromatographic retention index data and ion/molecule interactions for chemical warfare agent identification

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ABSTRACT

Field-portable gas chromatography–mass spectrometry (GC–MS) is well-suited for the reliable identification of dangerous chemicals. The chemical warfare agent (CWA) *O*-ethyl-*S*-2-diisopropylaminoethyl methylphosphonothiolate (VX) and many VX degradation products are challenging GC–MS analytes for a transmission quadrupole detector, as resulting 70 eV electron ionization mass spectra contain little high mass information. Approaches were explored to detect these analytes using two field-portable GC–MS systems having either a transmission quadrupole or a cylindrical ion trap (CIT) detector. Spectral matching alone for the transmission instrument did not unambiguously identify VX and several related analytes, while use of mass spectra and retention index information resulted in accurate identification. Ion/neutral interactions in the CIT produced pseudomolecular ions ($[M+H]^+$) for VX-related compounds and also for other CWA nerve agent compounds. In addition to $[M+H]^+$, protonated dimers ($[2M+H]^+$) were produced in the CIT for phosphonofluoridate compounds such as sarin. The CIT ion/molecule reactions were concentration-dependent, and mass assignment shifts were not unusual with increasing analyte concentrations. For these reasons the CIT detector is potentially problematic for reliable chemical identification by technician-level users under non-laboratory conditions.

1. Introduction

Accurate detection and identification of dangerous chemicals, including chemical warfare agent (CWA) analytes is important to protect military forces and for public safety, and gas chromatography–mass spectrometry (GC–MS) has been used in this role. Following September 11, 2001 expanded market demand for small, rapid GC–MS systems have continued to drive development of innovative GC column heating technologies, and several research and commercial groups have also worked to develop small mass spectrometric detectors [1,2]. Resistive heating of a low thermal mass (LTM) GC column assembly described by Sloan et al. [3] has been the basis for several commercially available GC–MS systems designed for field use [2,4]. This LTM GC assembly is compact, consumes relatively little power, and is capable of high chromatographic performance.

Transmission quadrupole mass spectrometers are commonly used for fieldable GC–MS systems, and are known to provide consistent 70 eV electron ionization (EI) mass spectra for CWA analytes. However the neurotoxic CWA *O*-ethyl-*S*-2-diisopropylaminoethyl methylphosphonothiolate (VX) and a number of VX degradation products yield similar EI fragmentation patterns with this type of detector, with little or no diagnostic high mass information [5–7]. One GC–MS approach that can compensate for this involves the use of GC retention data combined with mass spectral information. The methods of Van den Dool and Kratz [8] allow comparison of linear temperature program GC retention information using a series of reference standards (commonly *n*-alkanes) analyzed with a chosen stationary phase material. The retention characteristics for unknown chemicals analyzed with the same conditions and stationary phase are then related to those of the reference compounds.

Another approach to clearly identify VX and VX-related analytes would be through the use of GC–MS analyses with chemical ionization (CI). As typically carried out, CI is not well-suited for

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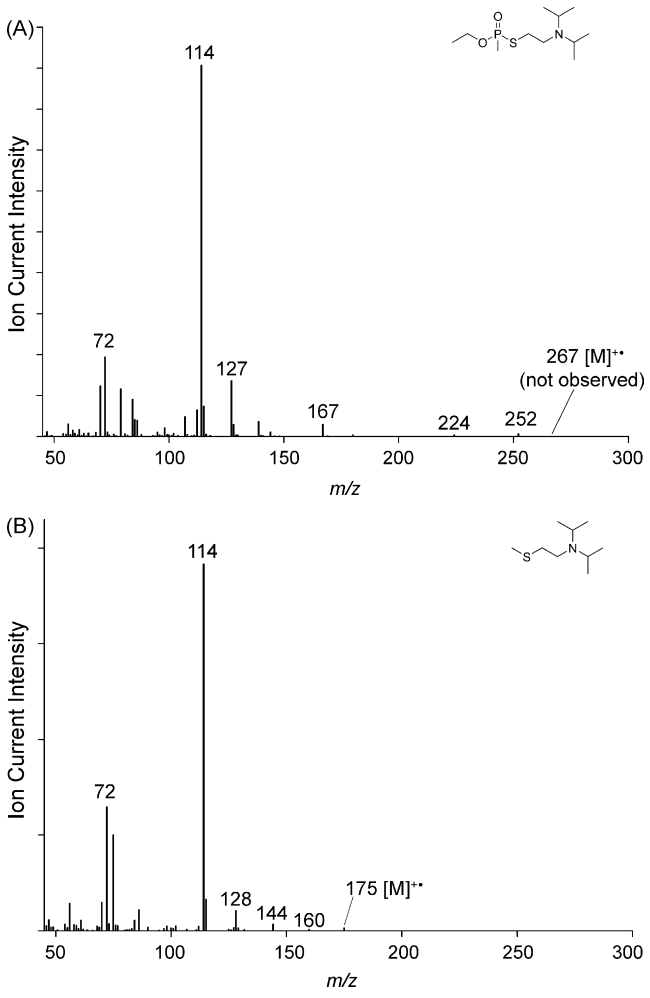

Fig. 1. Transmission quadrupole mass spectra for (A) VX, and for (B) the VX degradation product 2-(diisopropylaminoethyl)methyl sulfide.

a field-portable instrument that must be used to identify a wide range of unknown analytes, as the specific reagent used will limit the applicability of the method. Also, for many unknown analytes CI mass spectra are often not amenable to interpretation by technician-level analysts.

One benefit of using a mass spectrometric detector that relies upon ion storage is that ion/molecule interactions resulting in self-chemical ionization (self-CI) are possible [9–11]. Given time to interact, molecules within an ion trap that escape the EI process uncharged may react with trapped ionic species to create pseudomolecular ions. A pure CI reagent gas is not needed, but the resulting pseudomolecular ions are dependent on the specific chemistry between an analyte and the trapped ions derived from it, and their relative concentrations. Also, space charge effects become a factor in an ion storage mass spectrometer if ion density is not adequately controlled, potentially impacting mass resolution and mass assignment [10].

In this work, three possible strategies were explored for the detection of VX-related analytes and other CWA nerve agent compounds in the field during defensive military training exercises using two types of GC–MS systems with either a transmission quadrupole or a cylindrical ion trap (CIT) [1] detector. Spectral matching alone, and spectral matching in combination with retention index information were used with the transmission quadrupole, while the third approach used the CIT to produce pseudomolecular ions through self-CI to attempt nerve agent identification.

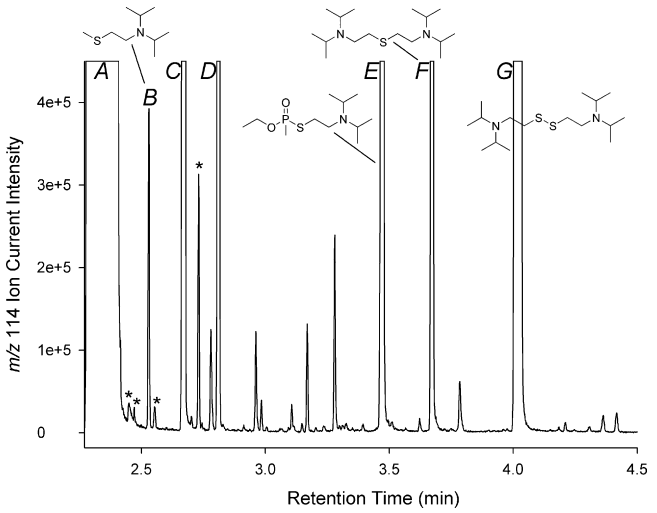

Fig. 2. Extracted ion chromatogram for *m*/*z* 114, degraded VX sampled by SPME and analyzed using van-mounted GC–MS system with transmission quadrupole mass spectrometric detection. A base peak of *m*/*z* 114 was observed in mass spectra of all GC peaks in this chromatogram, except for the four marked with a single asterisk. Around 20 analytes with *m*/*z* 114 as the most intense mass spectral peak are represented in the chromatogram, and for each of these the relative ion current intensity for mass spectral peaks greater than *m*/*z* 127 was <10%. Identities of labeled peaks: (A) 2-diisopropylaminoethanethiol; (B) 2-(diisopropylaminoethyl)methyl sulfide; (C) 2-(diisopropylaminoethyl)ethyl sulfide; (D) 2-(diisopropylaminoethyl)isopropyl sulfide; (E) VX; ***F***, bis(diisopropylaminoethyl)sulfide; (G) bis(diisopropylaminoethyl)disulfide.

2. Experimental

A field-portable GC–MS system with a miniature CIT mass spectrometric detector (model 450, ICX-Griffin, West Lafayette, IN) was used with ultra high purity He carrier gas to obtain mass spectra from liquid injections with varied concentrations of CWA analytes dissolved in solvent. Retention index comparisons to identify VX and VX-related degradation products were obtained from a van-mounted Agilent Technologies (Wilmington, DE) 5975 transmission quadrupole mass spectrometer combined with a 6890 GC system using high purity H_2 carrier gas generated electrolytically on-site.

Both GC–MS systems used LTM GC column heating for fast analysis, with identically manufactured open tubular columns (Agilent Technologies) having DB-5 stationary phase with 25 μm film thickness, 30 m length, and 0.25 mm I.D. For both instruments the initial column temperature was held at 40 °C for 0.5 min. Following the initial temperature hold time the built-in LTM GC system of the Griffin instrument raised the column temperature 40 °C min^{-1} to 300 °C, with no hold time at the terminal temperature. The retrofit LTM GC module of the Agilent instrument heated at 75 °C min^{-1} to 300 °C, with 2 min terminal temperature hold time. The injector temperature was 250 °C for each instrument and both were operated in splitless injection mode, with 22.5% split flow applied to the Griffin instrument at 0.5 min, and 50 ml min^{-1} purge flow at 0.75 min for the Agilent instrument. The GC transfer lines for the Griffin system were maintained at 200 °C while the corresponding temperature was 250 °C for the Agilent system.

The ion source and quadrupole assembly of the Agilent system were maintained at 230 and 150 °C respectively, and this instrument relied on standard 70 eV electron ionization (EI). The temperature of the CIT was held at 150 °C during analyses, and the voltage bias between the EI filament and the trap entrance was 13.8 eV. In this instrument the RF trapping field imparts additional energy to the electrons produced at the filament, providing ionization with molecular energy deposition similar to