Issues Related to Gas Chromatography-Mass Spectrometry Analysis in the Field for O-Ethyl S-2-Diisopropylaminoethyl Methylphosphonothiolate (VX) and VX Degradation Products

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Objectives

Discuss Three Approaches used for Detection and Identification of VX-Related Compounds in the Field by GC-MS

(1) 70 eV EI, Transmission Quadrupole Analysis

(2) 70 eV EI/Self-Cl, Cylindrical Ion Trap Analysis

(3) Combination of 70 eV EI, Transmission Quadrupole Analysis and use of GC Retention Index values

Briefly discuss the use of field-portable GC-MS in solving exposure assessment problems
Types of Real-Time Exposure Assessment Tools

Level 1
- Small Colorimetric Single-use Detectors

Level 2
- Handheld Quantitative Detectors

Level 3
- Man-portable (Derived from Level 4)

Level 4
- Transportable

Increasing cost, expertise, complexity
VX-Related Mass Spectra
GC-MS, 70 eV EI, Quadrupole Mass Filter

A

B

Ion Current Intensity

<table>
<thead>
<tr>
<th>Mass</th>
<th>Intensity</th>
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<tbody>
<tr>
<td>114</td>
<td></td>
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<tr>
<td>127</td>
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<tr>
<td>167</td>
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<td>252</td>
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Ion Current Intensity

<table>
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<tr>
<th>Mass</th>
<th>Intensity</th>
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<tbody>
<tr>
<td>72</td>
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<td>103</td>
<td></td>
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<tr>
<td>203</td>
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USMC Mobile Laboratory

LTM GC, 70 °C/min Ramp Rate
<table>
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<tr>
<th>Quadropole Mass Filter Instruments</th>
<th>Ion Trap Instruments</th>
</tr>
</thead>
</table>

**Field-Portable GC-MS**

- **Transportable**
- **Person-portable**
VX-Related Mass Spectrum

NH₃ Cl, Quadrupole Mass Filter

Ion Current Intensity

m/z

50 100 150 200 250 300 350

102 114 128 204
VX Mass Spectrum
Self-CI with CIT Analysis Producing \([M+H]^+\)

25 ng VX Injected

![VX Mass Spectrum Image]
VX Mass Spectrum
Self-Cl with CIT Analysis Producing [M+H]^+ but Space Charge Effects Also

100 ng VX Injected

Ion Current Intensity

m/z

*85
*115
*129
268
Space Charge Issues

Diagram:

A: Scan 213
- M/z 87*
- M/z 102
- M/z 103

B: Scan 214
- M/z 86
- M/z 100
- M/z 102
- M/z 103

Annotations:
- 100: "N"
Space Charge Issues
Toroidal Ion Trap Shows Consistent Mass Resolution Across Entire GC Peak
With no Mass Axis Shifts, Same SPME Sample Conditions as in Previous Slide
10 ng sarin produces relatively tame mass spectrum in CIT; @ 50 ng dimerization dominates:
Use of GC Data to Supplement GC-MS

GC Column and Heating Development

James and Martin, 1951
1st Practiced GC; packed column

Golay, 1957
Open Tubular GC; metal columns at first

Early 1960s
Glass Capillaries Used for OTGC

Early 1980s
Fused Silica Used for OTGC; inert and strong

2009
Oven convection heating still dominant, even though the FSOTGC column has very low thermal mass
Recent Developments in Low Thermal Mass GC Provide for High-Performance GC-MS...
Agilent GC: 900 W

LTM GC: 200 W
Rapid Combined Sampling/Analysis

5 min SPME sample from contaminated water

- GA 162 AMU
- GD 182 AMU
- GB 140 AMU
- HD 158 AMU
- VX 267 AMU
- T2 Toxin 466 AMU

LTM resistively heated column in place of air bath GC oven

Use of GC Data to Supplement GC-MS

Conclusions

(1) 70 eV El, Transmission quadrupole GC-MS analysis without considering RI data does not work well for analysis of VX and VX degradation products.

(2) 70 eV El, Transmission quadrupole GC-MS analysis benefits from use of RI data for analysis of VX and VX degradation products.

(3) 70 eV El/Self-Cl with CIT GC-MS analysis provides “Cl” data for VX and many VX degradation products, space charge effects also possible.

Both (2) and (3) bring additional variables for young, relatively inexperienced military GC-MS users.
What are we Currently Missing in Exposure Assessments?

p-dichlorobenzene
What are we Currently Missing in Exposure Assessments?

Field identification was required at the point of contaminant generation to answer fundamental exposure assessment questions; numerous volatile, irritating chemicals were shown to be produced by the irradiation process.
Initial GC-MS Instrumentation Used

Typical GC air bath oven
Initial screening samples showed a rich mix of volatile organic compounds; poor GC resolution meant that a different column was needed...
GC/MS Analyses for Irradiated Mail Project Moved into Laboratory...