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-CI, 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



### VX-Related Mass Spectra GC-MS, 70 eV EI, Quadrupole Mass Filter



# **USMC** Mobile Laboratory





LTM GC, 70 °C/min Ramp Rate



### **Field-Portable GC-MS**

Quadropole Mass Filter Instruments



#### Person-portable









## VX-Related Mass Spectrum NH<sub>3</sub> CI, Quadrupole Mass Filter



#### VX Mass Spectrum Self-CI with CIT Analysis Producing [M+H]<sup>+</sup>



# **VX Mass Spectrum**

Self-CI with CIT Analysis Producing [M+H]<sup>+</sup> but Space Charge Effects Also



## **Space Charge Issues**



## **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



## **Ion/Neutral Interactions**



10 ng sarin produces relatively tame mass spectrum in CIT; @ 50 ng dimerization dominates:







Stevens et al (in review), J Chromatogr. A, 2009

GC Column and Heating Development



James and Martin, 1951 1<sup>st</sup> 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...

Shunble.











Smith et al , J Chromatogr. A,1067 (2005) 285-294

#### Use of GC Data to Supplement GC-MS



Stevens et al (in review), J Chromatogr. A, 2009



Reference RI Values (10 °C/min): D'Agostino et al , J Chromatogr., 402 (1987) 221-232



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

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

(3)70 eV EI/Self-CI with CIT GC-MS analysis provides "CI" 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?







# 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

- Irradiated Mail

## **Initial GC-MS Instrumentation Used**



Typical GC air bath oven

# GC/MS with Mobile Laboratory

Initial screening samples showed rich mix of volatile organic compounds; poor GC resolution meant that different column was needed...







GC/MS Analyses for Irradiated Mail Project Moved into Laboratory...





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