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Detection of Chemical Agents, Precursors and By-Products Using Ion Trap Technology

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ABSTRACT

The utility of a new field portable ion trap-based instrument, the Generic Detector, for use in chemical weapons treaty verification is assessed. The ability of the instrument to detect targeted chemical agents, precursors and degradation products is examined. Instrumental characteristics (membrane vacuum interface, ion pump, air buffer gas) which resulted from the reduction in size of the instrument are evaluated as to their impact on the detection limits for these selected compounds. Detection limits in the low nanogram range are obtainable for most of the chemical agents, precursors and by-products using both GC/MS and GC/MS/MS analysis

INTRODUCTION

In response to the pending Chemical Weapons Convention treaty, the Defense Nuclear Agency (DNA) has tasked the US Army Edgewood Research Development and Engineering Center (ERDEC) to develop a small, field portable instrument (the "Generic Detector") that is capable of unambiguous detection of chemical warfare agents and their associated precursors and by-products. These compounds are listed in Schedules 1, 2 and 3 of the "Rolling Text" of the Conference on Disarmament¹. The US Army has had a long standing project with Bruker-Franzen Analytik (Bremen, Germany) to develop a chemical and biological warfare agent detector (the "CBMS"). This instrument is based on an ion trap mass spectrometer and is being developed as a rugged, field transportable mass spectrometer that can detect chemical and biological agents in a battlefield environment at sub-toxic levels. The Generic Detector is an modified version of the CBMS which is being developed specifically for treaty verification activities.

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The role of the GD would be two-fold. It is intended for use on-site as a primary detector for chemical agents and other associated compounds covered under the treaty. In addition, it could also be used as an air quality monitor to ensure that the inspectors are not exposed to dangerous levels of other chemicals during the inspection. Concerns by the chemical industry as to the disclosure of proprietary information requires the development of an instrument that is capable of detecting only the targeted treaty compounds while remaining blind to other compounds present at the site but not covered by the treaty. Ion trap mass spectrometry, with its combination of small size, high sensitivity and high selectivity from MS/MS capabilities is uniquely suited for this role.

BACKGROUND and INSTRUMENTATION

Ion traps use high voltage radio frequencies (rf) to trap ions inside a small, three-dimensional cavity². The trajectories of the ions are then typically stabilized by collisions with a helium background (or buffer) gas. As the amplitude of the rf voltage is increased, ions are sequentially ejected from the device according to their mass-to-charge (m/z) ratio. The fact that all ions that are formed are subsequently detected gives ion traps their high sensitivity. Alternate operational modes exist where ions of a single mass-to-charge can be isolated within the trap. These ions can be subsequently fragmented by causing the ions to collide with a background target gas. The resulting second generation fragment ions can then be mass analyzed as described above. This experiment (MS/MS) greatly enhances the selectivity of the analysis.

The Generic Detector ion trap mass spectrometer³ has been specifically design to be a field portable mass spectrometer. The instrument is still in the development stages and as such has not been completely optimized. It is small (75 x 43 x 35 cm), light (less than 45 kg) and operates less than 500 watts of power. In order to ensure compatibility with all international voltage sources, the instrument operates on 24 V_{DC}. No gas cylinders are needed to operate the instrument because the Generic Detector has a unique electrode geometry that allows the instrument to be operated with air and not helium as the buffer gas and the gas chromatographic carrier gas.⁴ The air buffer gas and sample are admitted to the analyzer through a dimethylsilicone membrane vacuum interface. The vacuum manifold is pumped by an 8 l/s ion pump to pressures of approximately 2×10^{-6} torr. A vacuum isolation valve positioned between the membrane interface and the manifold allows the instrument to be powered off for up to several days without substantial loss of vacuum. The small pumping system precludes the use of the high pressures of reagent gas used in chemical ionization (CI). For this reason, only electron impact ionization (EI) is available. A short (3 meter) chromatographic column is used for temporal sample analysis prior to introduction into the mass spectrometer. Samples can be admitted to the column by either directly injecting into a standard GC injector or desorbed from sampling cartridges in a thermal desorption injector. The GC injector and column can be replaced by a direct sampling capillary ground probe which is comprised of another membrane

interface and a 2 meter capillary. A portable PC computer provides the user interface on this prototype version, however plans exist to utilize PCMCIA technology to reduce the computer to a notebook size. Eventually, the final version will incorporate all computer functions within the mass spectrometer chassis. A summary schematic of these features is shown in Figure 1.

FIGURE 1. Schematic of the Bruker-Franzen Generic Detector

EXPERIMENTAL

Nine samples were selected which are representative of the compounds listed in schedules 2 and 3 of the "Rolling Text". In addition, naphthalene was chosen as a sample which would test the best case sensitivity of the instrument. Solutions of each sample were prepared using either methanol or hexane at concentrations ranging from approximately 200 ng/ul to 200 pg/ul. The sample solutions were then analyzed using either single stage (GC/MS) or multiple stage (GC/MS/MS) mass analysis. EI/MS detection limits were determined for each sample as the amount of sample which generated a signal-to-noise equal to 3 for the integrated mass chromatograms.

RESULTS AND DISCUSSION

The detection limit results obtained for the analysis of the nine precursors/by-products are listed in Table 1. Also included is the detection limit obtained for the analysis of naphthalene.

TABLE I
Generic Detector EI/MS Detection Limits for Selected Chemical Agent
Precursors/By-products and Naphthalene

COMPOUND	EI/MS DETECTION LIMITS (ng)
diisopropylmethylphosphonate (DIMP)	6
dimethylmethylphosphonate (DMMP)	1.5
diethylethylphosphonate (DEEP)	4
diethylmethylphosphonate (DEMP)	4
trimethylphospite	20
triethylphosphite	4
1,4-dithiane	0.8
thiodiethylene glycol	6.5
trichloronitromethane	120
naphthalene	0.005

As can be seen from the table, most of the compounds tested have detection limits in the low nanogram range. This is not reflective of the instrument, however, as the detection limits for naphthalene are nearly three orders of magnitude lower. Most of the chemical agent precursors and by-products are relatively polar compared to naphthalene and illuminate a shortcoming, the source of which is still under investigation.

Diisopropylmethylphosphonate (DIMP) is, in addition to being a Schedule 2 compound, an often used simulant for the G-series chemical weapons. The largest intensity fragment ions in the EI spectrum of DIMP are m/z 79 and 97 respectively. Mass-to-charge 97 was isolated in the ion trap and subsequently fragmented under MS/MS conditions to m/z 79. The MS/MS spectrum and mass chromatograms for m/z 79 and 97 are shown in Figure 2 for a 50 ng injection of DIMP. Note that almost all of the MS/MS product ion signal results from m/z 79⁺.

Figure 2. Mass chromatograms of m/z 79⁺ and 97⁺ and the MS/MS spectrum from the analysis of 50 ng DIMP under MS/MS conditions. The parent ion selected was m/z 97⁺.

Figure 3. Comparison of MS/MS mass chromatograms for A) isolation of m/z 97⁺ and B) the resulting fragmentation to m/z 79⁺

Figure 3-A and 3-B compare the results obtained for the injection of 5 ng of DIMP. The resulting signal obtained when isolating m/z 97⁺ with out subsequent fragmentation is shown in Figure 3-A. When m/z 97⁺ is fragmented (almost entirely to m/z 79⁺), the mass chromatogram for m/z 79⁺ is acquired. A peak area integration routine is not yet implemented on this prototype instrument software, however approximate quantitative comparisons can be made from the vertical intensity scale of both figures. Only 20% of the parent ion signal is recovered in the MS/MS product ion signal. This value is typical for this instrument and reflects the poorer MS/MS efficiency obtained when using air instead of helium as the buffer/target gas. MS/MS efficiencies using helium as the target gas typically approach 100%. This reduced efficiency when combined with 50% isolation efficiencies accounts for MS/MS detection limits that are approximately the same as the MS detection limits for DIMP. There is, however, considerable added selectivity for DIMP under these MS/MS conditions as only ion signals for m/z 79⁺ which originate from m/z 97⁺ are recorded.

CONCLUSION

When designing a truly field-transportable mass spectrometer, trade-offs must be made between size (or weight) and optimum analytical performance. The Generic Detector has achieved full transportability while retaining reasonable performance in the analysis of chemical weapons precursors and by-products. Differences in detection limits for polar versus non-polar compounds and MS/MS efficiencies are issues which are still being addressed. The ability to use mass spectrometry to analyze samples directly in the field will have an impact in fields other than treaty verification.

REFERENCES

1. Ember, Lois R. *Chem. Eng. News*, 7 June 1993, 7-18.
2. March, R.E., Hughes, R.J., Quadrupole Storage Mass Spectrometry, John Wiley and Sons, New York, 1989.
3. Franzen, J., U.K. Patent #GB 2,180,687 A, 10 Sept 1986.
4. Franzen, J., *Int. J. Mass Spectrom. Ion Processes*, 106 (1991) 63-78.

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