

Detection of Chemical/Biological Agents and Simulants using Quadrupole Ion Trap Mass Spectrometry

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A new detector for chemical and biological agents is being developed for the U.S. Army under the Chemical & Biological Mass Spectrometer Block II program. The CBMS Block II is designed to optimize detection of both chemical and biological agents through the use of direct sampling inlets [1], a multi-ported sampling valve and a turbo-based vacuum system to support chemical ionization. Unit mass resolution using air as the buffer gas [2] has been obtained using this design. Software to control the instrument and to analyze the data generated from the instrument has also been newly developed.

Detection of chemical agents can be accomplished using the CBMS Block II design via one of two inlets - a 1/16" stainless steel sample line -Chemical Warfare Air (CW Air) or a ground probe with enclosed capillary currently in use by the US Army - CW Ground. The Block II design is capable of both electron ionization and chemical ionization. Ethanol is being used as the CI reagent based on a study indicating best performance for the Biological Warfare (BW) detection task [3]. Data showing good signal to noise for 500 pg of methyl salicylate injected into the CW Air inlet, 50 ng of dimethylmethylphosphonate exposed to the CW Ground probe and 5 ng of methyl stearate analyzed using the pyrolyzer inlet were presented.

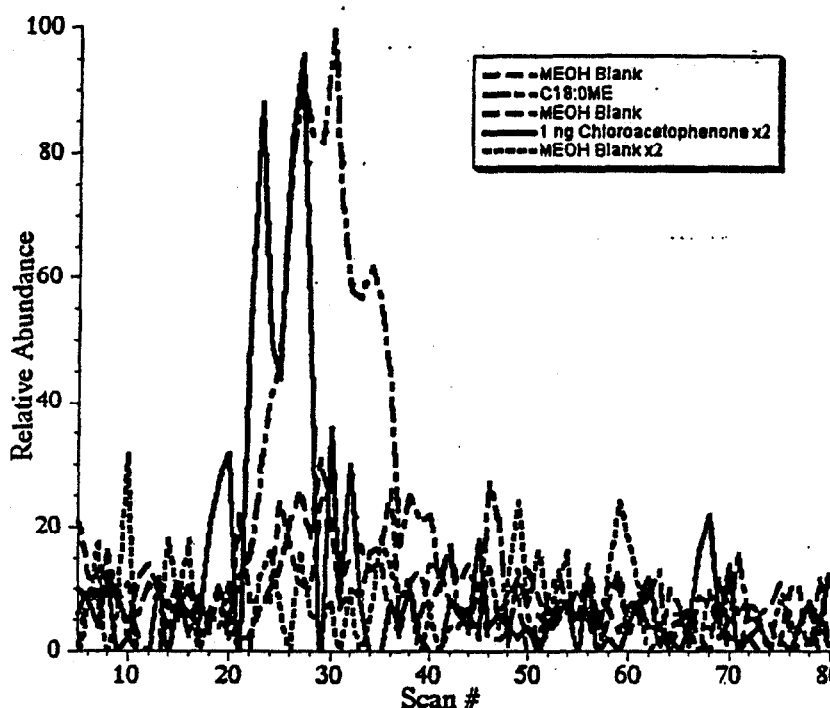
Biological agents are sampled using a "bio-concentrator" unit that is designed to concentrate particles in the low micron range. Particles are collected in the bottom of a quartz pyrolyzer tube. An automated injector is being developed to deliver approximately 2 μ L of a methylating reagent, tetramethylammonium-hydroxide to the collected particles. Pyrolysis occurs by rapid heating to ca. 550°C. Biological agents are then characterized by their fatty acid methyl ester profiles and by other biomarkers.

A library of ETOH-CI/pyrolysis MS data of microorganisms used for a recently published study [3] has been expanded with additional bacteria and fungi. These spectra were acquired on a Finnigan Magnum ion trap using helium buffer gas. A new database of CI spectra of microorganisms is planned using the CBMS Block II instrument and air as the buffer gas. Using the current database, the fatty acid composition of the organisms was compared using the percentage of the ion current attributable to fatty acids. The data presented suggest promising rules for discrimination of these organisms. Strain, growth media and vegetative state do contribute to some of the distributions observed in the data. However, the data distributions observed in the current study only reflect our experience to date and do not fully represent the variability that might be expected in practice.

Acquisition of MS/MS spectra has begun (using He and air buffer gas) of the protonated molecular ion of a variety of fatty acids and for a number of ions nominally assigned as fatty acids from microorganisms. These spectra will be used to help verify fatty acid

assignments and to provide a means to identify fatty acids in the presence of an interferant. For example, similar MS/MS spectra of the m/z 257 ion have been obtained from a C15:0 standard and from *Bacillus anthracis*. MS/MS may also afford additional discrimination among the fatty acid isomers [4]. For example, under the ion trap conditions used on a Varian Saturn 2000, MS/MS spectra of *n*- and iso-C15:0 fatty acid standards displayed a m/z 215 ion while the MS/MS spectrum of the anteiso isomer was lacking this ion.

A helium stream used as a carrier/buffer gas was purged through a vial containing diesel fuel and subsequently through a thermal desorber to illustrate the capability of ETOH-CI/MS/MS to enhance selectivity for agents and simulants in the presence of battlefield contamination. Selected product ion profiles for injections of 1 ng of methyl stearate ($[M+H]^+$, m/z 299) and chloroacetophenone ($[M+H]^+$, m/z 155) dissolved in methanol into the thermal desorber were clearly distinguishable from the profiles obtained for blank methanol injections (shown below).



1 M.B. Wise, C.V. Thompson, R. Merriweather and M.R. Guerin, *Field Anal. Chem. Technol.* **1998**, 1, 251; 2 S.A. Lammert and J.M. Wells, *Rapid Commun. Mass Spectrom.* **1996**, 10, 361; 3 S.A. Barshick, D.A. Wolf and A.A. Vass, *Anal. Chem.* **1999**, 71, 633; 4 F. Basile, K.J. Voorhees and T.L. Hadfield, *Appl. Environ. Microbiol.* **1995**, 61, 1534.

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