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Rugged Miniaturized Mass Sensors for Use in Plutonium Conversion Processes

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A HIGHER EDUCATION CONSORTIUM

A Report on

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Abstract

Ionization is produced either through Plasma Desorption, in the case of a solid, using fission fragments from a Cf-252 source; or in the case of a gas, via an electron avalanche from the impact on a microsphere detector of α particles from a radioactive source.

The gaseous compound analysis yielded multiple peaks on parent ion and

molecular fragments. In the solid compound analysis, the results indicated that solid-state mass spectrometry will provide important information about the degradation of materials by measured changes in molecular weight.

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1. INTRODUCTION

This report covers the first year efforts of an anticipated three-year project devoted to the development of mass analyzers suitable for process and field applications. The aim is to achieve the following instrument specifications: mass range of 1-500 amu, subpicogram sensitivity, mass resolution of ~100; rugged, compact and portable (to fit in an attaché case). The concept is based on a miniaturized time-of-flight, ToF, mass spectrometer. The instrument has two

innovative means of ionization, one for gaseous compounds, the other for solids. Ionization is produced either through Plasma Desorption, in the case of a solid, using fission fragments from a Cf-252 source; or in the case of a gas, via an electron avalanche from the impact on a microsphere detector of α particles from a radioactive source. The performance of initial prototypes with the two ionization modes is described in the following sections.



2. INSTRUMENTATION

A general outline of the instrument is presented in Figure 1. The instrument, which is about 25 cm long and 5 cm in diameter, operates under vacuum ($\sim 5 \times 10^{-6}$ torr). vacuum chamber as small as 1L can house the instrument. The chamber with pumps and measurement electronics can readily fit into an attaché case. In the present prototype configuration, the instrument uses high voltage (3-5 kV) power supplies (TC 952A Oxford) to bias the detectors and to accelerate the ions, a turbo pump (TPU-062 Balzers) to maintain the operating pressure of the system. The electronics units include an amplifier (op amp CLC 414 National Semiconductor), a constant fraction discriminator (TC 454 Oxford) and a time-to-digital converter (Schmidt Instruments). Data processing, display, and archiving are handled by a 386 PC, which, in a portable configuration, could be a laptop PC.

As already noted, the instrument can be configured for the analysis of gases or solids. In the first case, an electron avalanche (EA) is produced from the impact of an α particle on a microsphere or a microchannel plate assembly. The EA (electrons of ~ 70 eV) produces ions from a gaseous sample by the electron impact, EI, process. The α particles are generated by a radioactive source (Th-230 or Am-241) of $\sim 0.1 \mu\text{Ci}$. This mode of gas ionization, described in U.S. Patent 5,659,170 produces ion pulses with ~ 10 ns time resolution. For the analysis of solids, including particulate matter, we use Plasma Desorption, PD, as a means of ionization. In

PD, elemental and molecular species are volatilized/ionized from a solid surface by the impact of a heavy high-energy ion, typically a fission fragment from a Cf-252 source. The latter decays in part via spontaneous fission and thus provides a naturally pulsed means of ionization. A small Cf-252 source (10-50 μCi) is adequate for plasma desorption time-of-flight mass spectrometry, PD-ToF-MS. This technique is well-described in the literature. Our PD instrument operates at $\sim 5 \times 10^{-6}$ torr and is one of only a very few miniaturized versions.

Regardless of the type of sample, i.e., mode of ionization, the pulse of ions generated by an electron avalanche or the impact of a fission fragment are accelerated to 5 kV, and then drift in a fieldfree region before hitting a microchannel or microsphere assembly which serves as a stop detector. Ion flight times are measured by obtaining a start signal when the ionization pulse (EA or fission fragment) hits the sample. It may be recalled that flight times are proportional to the square root of the ion mass. The analog pulses from the start and stop detectors are converted into logic pulses using constant fraction discriminators and are then fed into a time-to-digital converter for a flight time measurement, which is recorded in a PC. The procedure described here amounts to pulse counting and assumes for quantitative measurements that ion multiplicity, i.e., occurrence of multiple isobaric ions, in any given ion pulse is negligible.

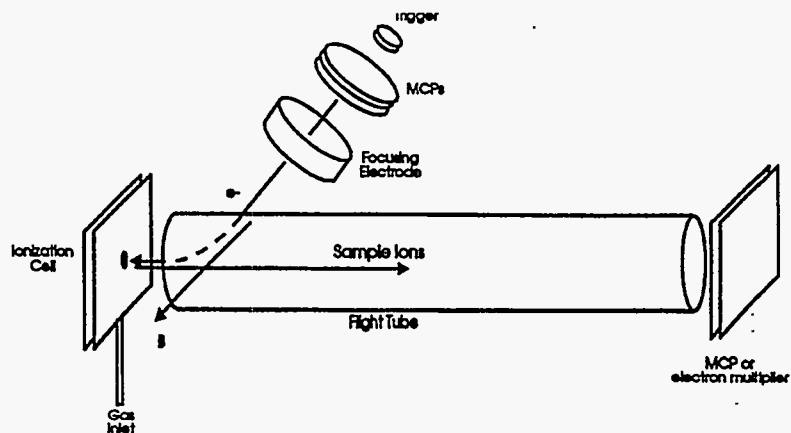


Figure 1: The ToF mass analyzer is shown in the configuration for analyzing gaseous samples using an electron avalanche generated by a microchannel/microsphere assembly itself triggered by an α particle from a Th-230 or Am-241 source. In the Plasma Desorption configuration, the α source, microchannel assembly and focusing electrode are removed. A Cf-252 source is placed close to and in line-of-sight to a solid sample which is positioned at the site shown here for the ionization container.

3. ANALYSIS OF GASEOUS COMPOUNDS

An example of a gaseous sample (octane thiol) analyzed with the EA mode is shown in Figure 2. The analysis, carried out in 5 minutes, yielded multiple peaks (parent ion and molecular fragments). Such fingerprints are indispensable for the accurate identification of significant volatile organics (octane thiol is a synthetic precursor to a chemical warfare agent). The octane thiol spectrum was obtained by simply leaking trace vapors into the mass spectrometer. The addition of an ionization chamber confined the sample in a small volume at increased pressure and resulted in a ten-fold increase in detection sensitivity as demonstrated in Figure 3. Performance characteristics for the gaseous mass analyzer at the completion of the first project year are as follows. A detection limit of 20 ppm was achieved for octane in an air-octane mixture at 1.5×10^{-6} torr in a measurement time of 50 seconds.

The challenge for the second project year will be to optimize ionization conditions to enhance weak parent peaks for heightened accuracy in compound identification and improved detection sensitivity. Further improvements are feasible by increasing the magnitude of the electron avalanche and by switching from electron impact to chemical ionization, CI. The literature suggests that many organic can be efficiently ionized under CI conditions thus further enhancing prospects for detection at ultra-low concentrations. The success of this approach will depend on choosing a CI reagent, which will transfer a proton with little exothermicity to induce fragmentation. Estimates for the proton affinity of volatile organics can be determined by quantum chemistry techniques. Professor G. I. Gellene at Texas Tech University will perform these calculations as part of our second year effort.

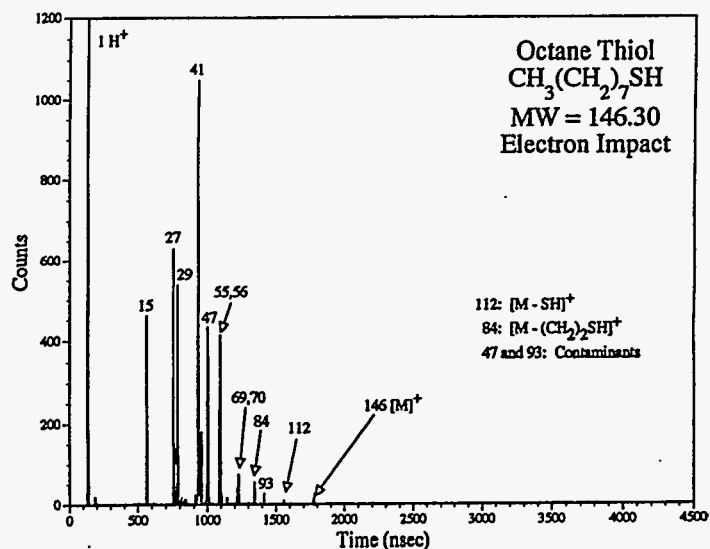


Figure 2: Time-of-Flight Spectrum of Octane Thiol.
Analysis time: 5 min. (Flight Times are Proportional to the Square Root of the Ion Mass)

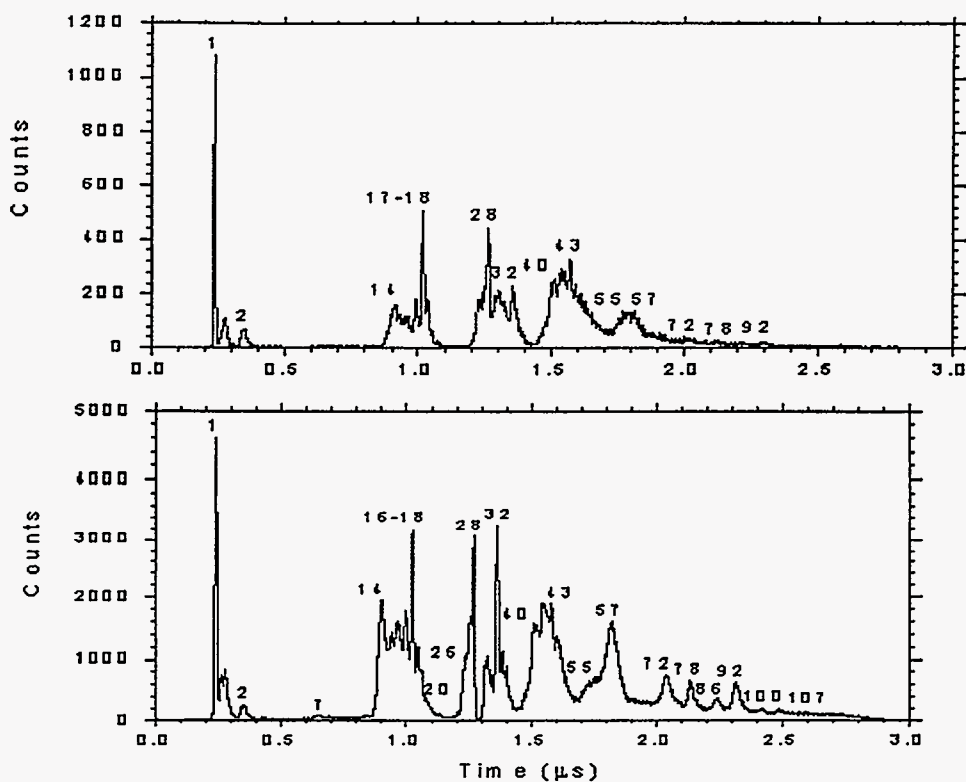


Figure 3: (a) Octane in air (~ 20 ppm octane) at 1×10^{-6} torr. Spectrum taken without ionization chamber. Acquisition time: 60 sec. (b) Octane in air (~ 20 ppm octane) at 1.5×10^{-6} torr. Spectrum taken with ionization chamber. Note peaks from octane at $m/z = 72, 78, 92$. Acquisition time: 50 sec.

4. ANALYSIS OF SOLIDS

We have demonstrated that a miniaturized Plasma Desorption Mass Spectrometer (PDMS) can provide comprehensive mass spectra from solid samples. Further, when PDMS is combined with a coincidence counting method developed in our laboratory, we can determine not only the surface composition but also the microhomogeneity of mixtures. An important problem where these capabilities should be most useful is the characterization of decomposition products in complex high explosive mixtures. Our effort on weapons related organic materials is carried out in association with Drs. Woodyard and Burgess (WTAMU), Rainwater (TTU) and Lightfoot (Pantex). Materials examined

to date include Irganox 1010 (antioxidant), Estane 5301 (polymer) and TATB (high explosive). To our knowledge, the mass spectra for Irganox 1010 and TATB (Figures 4 and 5) are the first such measurements obtained directly from these solids without sample dissolution or derivatization. The results indicate that our solid-state mass spectrometry will provide important information about the degradation of these materials via measured changes in molecular weight. For instance, the oxidation of Irganox by a reaction with free radical species can be monitored by a reduction in molecular weight by 1 amu, corresponding to the conversion of a hindered phenol to quinone type structure.

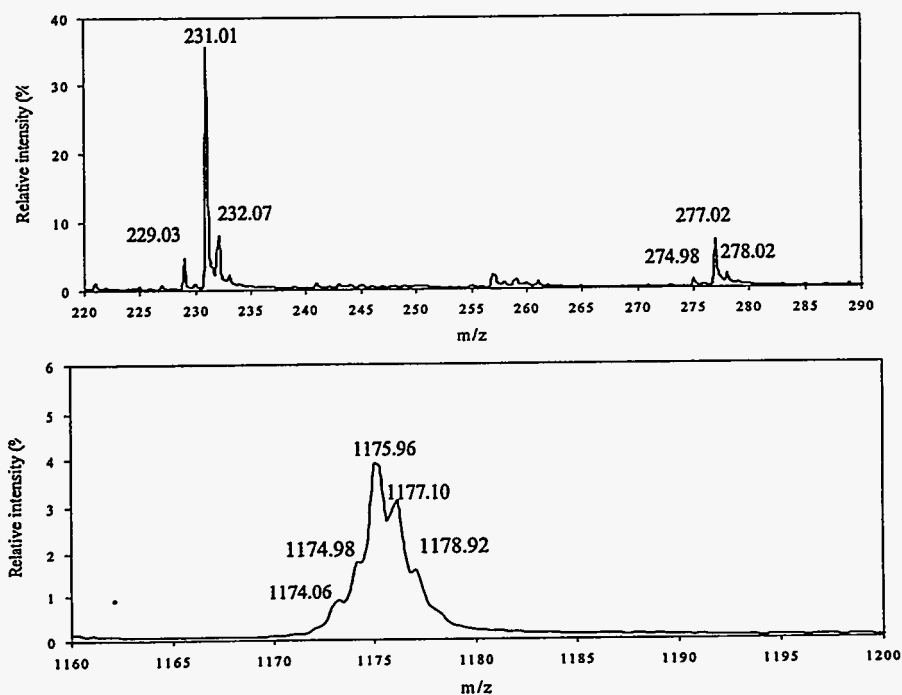


Figure 4: Irganox 1010 (antioxidant): (a) Negative Mass Spectrum from Plasma Desorption; (b) Analytically Significant Detail of Mass Spectrum at Molecular Ion Peak, Nominal Molecular Mass of Intact Molecule is 1176 amu.

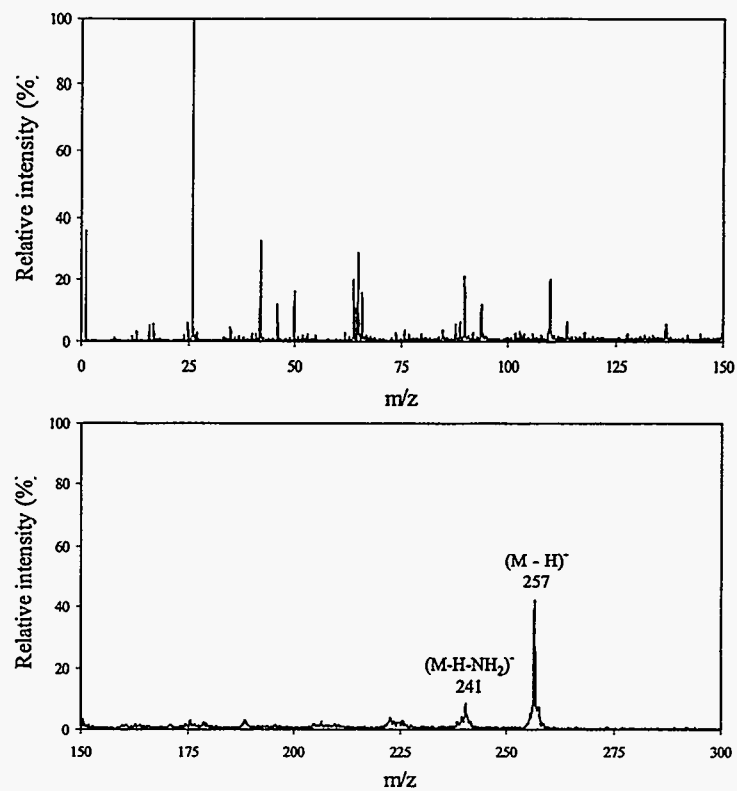


Figure 5: Triamino-trinitrobenzene: (a) Negative Mass Spectrum; (b) Analytically Significant Part of Mass Spectrum at the Deprotonated Molecular Ion, $M - H$.

REFERENCES

There were no references cited for this report.