Y/DZ-2162

Y-12

**OAK RIDGE
Y-12
PLANT**

**Solid Phase Microextraction and Miniature
Time-of-Flight Mass Spectrometer**

John. M. Hiller

Chemistry & Chemical Engineering Department
Development Division

Issue Date: January 25, 1999

MANAGED BY
LOCKHEED MARTIN ENERGY SYSTEMS
FOR THE UNITED STATES
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Prepared by the
Oak Ridge Y-12 Plant
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Solid Phase Microextraction and Miniature Time-of-Flight Mass Spectrometer

A miniature mass spectrometer, based on the time-of-flight principle, has been developed for the detection of chemical warfare agent precursor molecules. The instrument, with minor modifications, could fulfill many of the needs for sensing organic molecules in various Defense Programs, including Enhanced Surveillance. The basic footprint of the instrument is about that of a lunch box. The instrument has a mass range to about 300, has parts-per-trillion detection limits, and can return spectra in less than a second. The instrument can also detect permanent gases and is especially sensitive to hydrogen. In volume, the device could be manufactured for under $5000.

The military and intelligence communities have recognized that existing methods of detecting poisonous gases are not satisfactory; the methods are too slow, are too cumbersome, generate a high level of false alarms, and require the dedicated attention of a skilled operator. A small, rugged, and easy to operate instrument was required. Against these general guidelines, a miniature mass spectrometer was designed and built at the Department of Energy's Y-12 Plant[1].

The prototype instrument, being inherently simple and low-cost, could see additional uses including: sampling and analysis of hazardous atmospheres by first-response personnel (such as firemen), monitoring suspected drug and chemical warfare agent manufacturing sites, CW attack/all clear signal systems, and explosives detection.

The complete paper has details on the instrument including hardware, software, representative spectra, and the results of simulations using ion-optics modeling software. The paper also contains an outline of plans to upgrade the instrument to accommodate a miniature gas chromatograph.

Technology

The detection of gases by mass spectrometry dates to the early 1900's—hence, a well established technology. Of the various forms of MS, perhaps the simplest, most reliable, and most sensitive is based on the time-of-flight (TOF) principle. In TOF, gaseous molecules are ionized, the ions accelerate down a flight tube, and strike a detector. The length of time it takes an ion to reach the detector is a measure of its mass. The number of ions that reach the detector is a measure of the gas's concentration. The pattern of masses and their respective abundances is characteristic of the chemical being sensed.

The design of the TOFMS has always been governed by three considerations: (1) the ions must not bump into gases or other ions on the way to the detector, (2) the "flight" start time of the ions must be about the same, and (3) the electronics has to be fast enough to record the small differences in transit times of the individual ions. In a conventional TOFMS, the physics and technology dictate an instrument about six-feet long, a heavy-duty vacuum system, and a rack of electronic equipment—certainly outside the description of a portable, low-cost device. The electronics for recording of ion flight times was the "weak link" in building a small TOFMS instrument.

Fortunately, electronics has dramatically improved, making the miniaturization of the TOFMS possible. In the conventional instrument, the electronics is only able to provide a time resolution

[1] Managed by Lockheed Martin Energy Systems, Inc. for the U. S. Department Of Energy under contract DE-AC05-84OR21400.

of about 1 μs. The Y-12 instrument has a time resolution of under 1 ns—a thousand-fold improvement.   The ns-time resolution directly maps into the ion-optics design (Figure 1) to create an instrument a few centimeters long.

The shorter instrument allows total system miniaturization by reducing the demands of the vacuum system necessary for operation. The shorter path reduces the opportunity for ions to collide with gases (Condition 1, the "mean free path" constraint) which directly allows operation at a higher pressure. The shorter path reduces the volume of the vacuum system which reduces the needed volumetric pumping capacity. Collectively, the demands of the vacuum system have been reduced from the 100 pounds of vacuum pump and associated "plumbing" in the conventional system to about one pound in the Y-12 instrument.

The final design consideration is the need to start the ions toward the detector at about the same time. In a conventional instrument, this is done by creating ions with a hot filament and pushing the ions into an electrostatic region by applying a brief high-voltage pulse to a "repeller" electrode. Creating extremely short high voltage pulses is traditionally accomplished with a battery of large electronics modules; the pulses generated are typically in the tens of ns long. The Y-12 instrument uses a recently patented method based on electron multipliers. The weight savings in this feature is about 25 pounds; and, the pulses are less than 1 ns long.

Apparatus

<u>Sample introduction</u>. Samples are introduced to the vacuum system of the MS through a leak valve and through a stainless steel capillary tube that opens into the ionization region. Most of the history of the instrument has been obtained with materials that are gases at room temperature. We have introduced "liquids" by venting the head space over the liquids into the vacuum chamber.

Because the basic platform of the instrument is quite flexible, it should be possible to place a solid-phase microextraction fiber near the sample introduction inlet. The fiber could be heated to rapidly desorb the molecules into the ionization region of the MS. This would tend to further improve sensitivity and minimize the introduction of unwanted atmospheric gases. Also, this would enable analyses for less volatile compounds (the mass range of the TOFMS can easily be adjusted to accommodate higher molecular weights).

<u>Ionization source</u>. The ionization source consists of a small ^{241}Am alpha particle source juxtaposed to a pair of electron multiplier plates. The alpha particles strike the front surface of the electron multiplier pair creating an avalanche of electrons out of the back surface. Each alpha particle could create about 10^8 electrons, depending on the applied bias voltage. The emitted electrons are directed through the sample gas creating (1) ions and (2) the start signals for the time-of-flight measurement. The alpha source is nominally about 1 μCi. For reference, an alpha particle source was selected because of the high detection efficiency on the microchannel plate as well as the limited range of alpha particles (an alpha particle can not pass through the walls of the mass spectrometer). The alpha particle source is less radioactive than the ionization element in a home smoke detector.

<u>Acceleration and drift regions</u>. From the ionization region, positive ions are attracted to a negatively charged grid, through a region of increasingly negative voltage, through a flight tube at the same voltage as the last acceleration plate, and eventually strike a detector. The detector, operated in ion counting mode, creates the stop signal for the TOF measurement. The stop detector is made with electron multiplier plates.

Supporting electronics. The TOF measurement is now performed using a commercially available time-to-digital converter manufactured by Ionwerks of Houston, Texas. We will replace the Ionwerks device with a single-board TDC based on a field-programmable gate array.

Status

The Y-12 instrument is now a functioning prototype device (Figure 2). The device has demonstrated parts-per-trillion detection limits for a number of chemical warfare agent precursors as well as routine laboratory chemicals. Interest in the device has been expressed by the government and private sectors.

Near-term Plans

Simulations of the ion optics are being performed to improve the ion collection efficiency of the instrument. Likewise, the electronics are being redesigned to accommodate a much faster data acquisition rate. Both of these activities are prerequisites for interfacing the existing prototype instrument to a portable gas chromatograph.

Contact Information

John Hiller, Lockheed Martin Energy Systems, Inc., Post Office Box 2009, Building 9202, Mail Stop 8094, Oak Ridge, Tennessee, 37831-8094. Voice at 423-574-0287, e-mail at hillerjm@ornl.gov.

Figure 1. Ion-optics model of the Y-12 time-of-flight mass spectrometer. This model was created by the software package Simion, Version 6.0, developed at the Idaho National Engineering Laboratory.

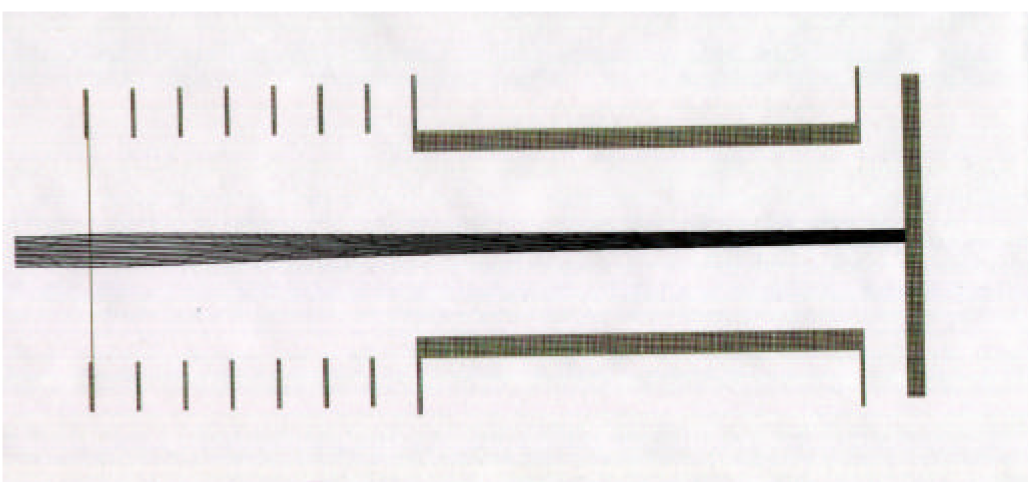
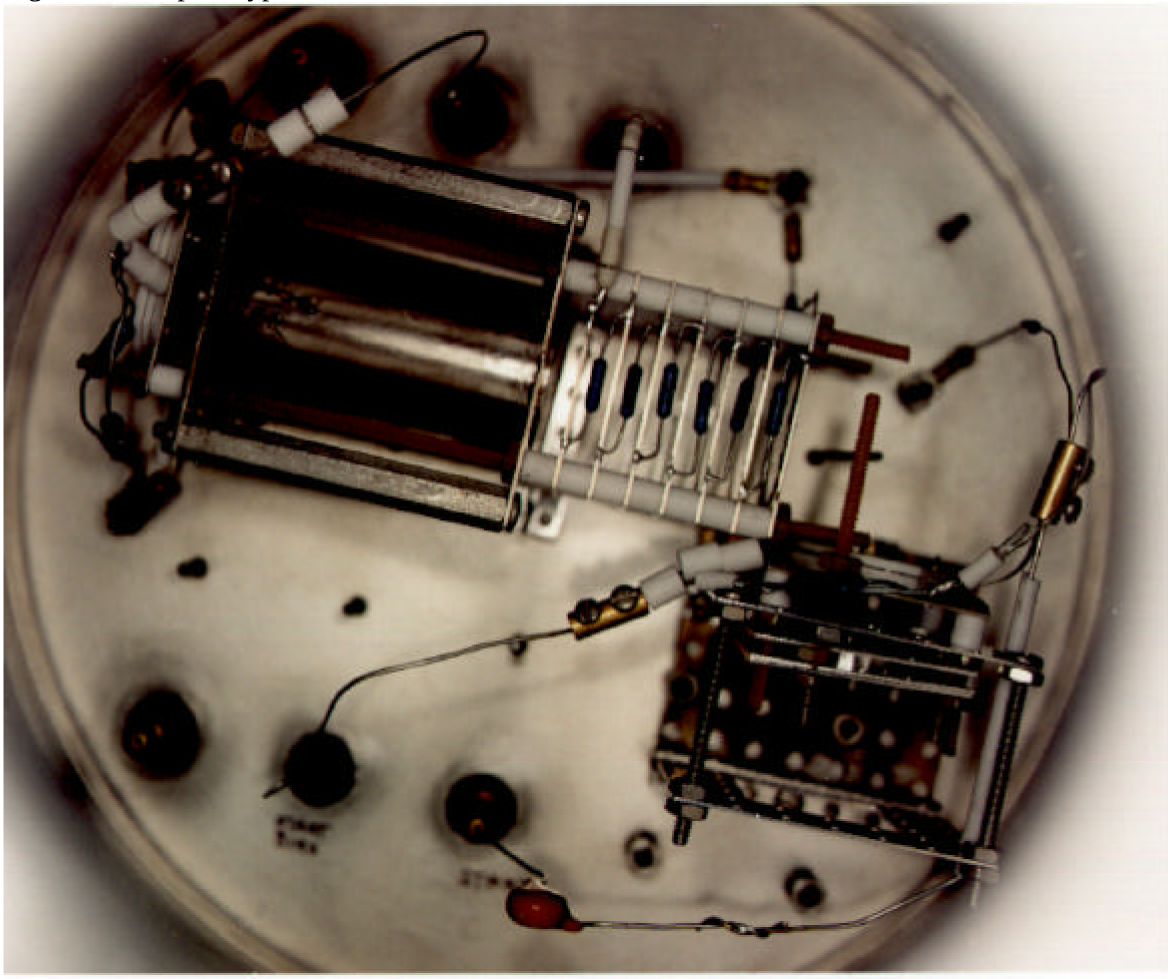


Figure 2. The prototype instrument.



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John Hiller
Lockheed Martin Energy Systems, Inc.
Y-12 Plant
January 25, 1999

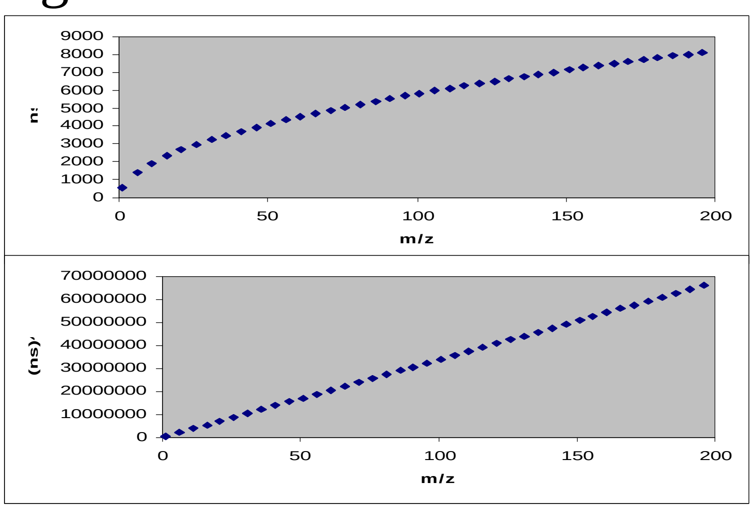
Objectives Over Time

- Initially: demonstrate feasibility of a miniature TOF-MS
- Then: small device for detection of chemical; instrument to be mounted on drone aircraft
- Next: disposable instrument for highly toxic materials; absolute confidence of no cross-contamination
- Now: miniature low-end GC/MS, principally for first-responders

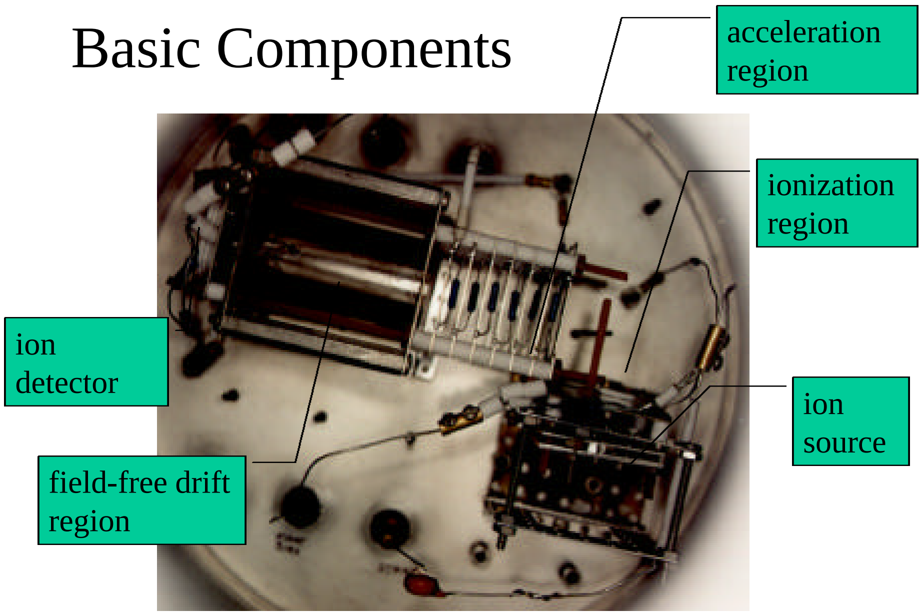
Time-of-flight

- Basic principle
- Benefit relative to scanning instrument
  - Collects all masses simultaneously
    - no need for selected ion monitoring to increase sensitivity
  - Electronics simpler
    - no need to vary potentials
  - Mechanical aspects simpler
    - no precision machining or alignment

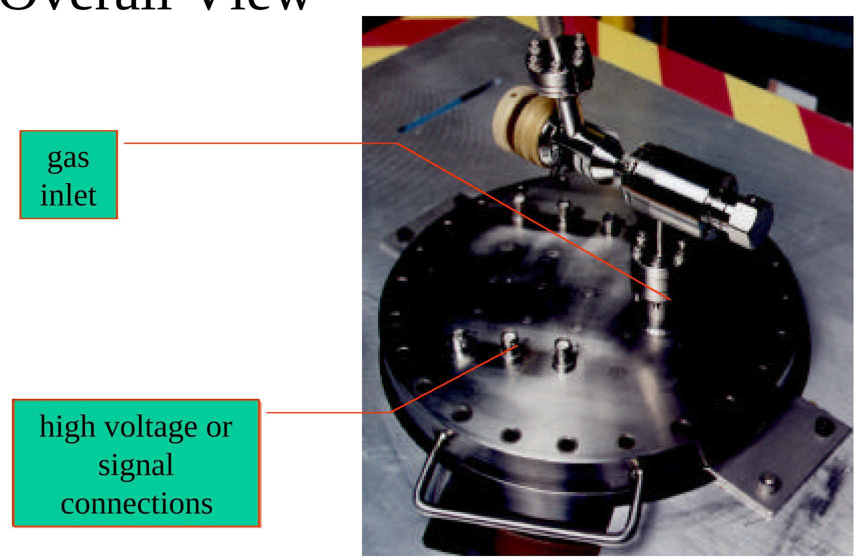
Flight Time



Basic Components

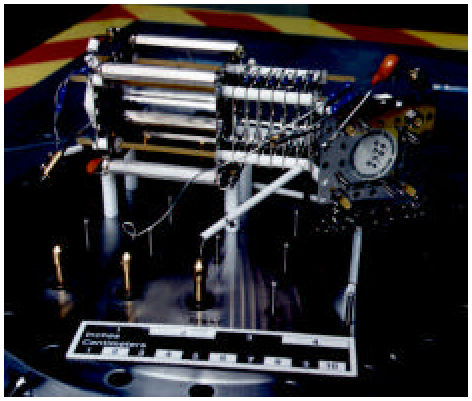


Overall View



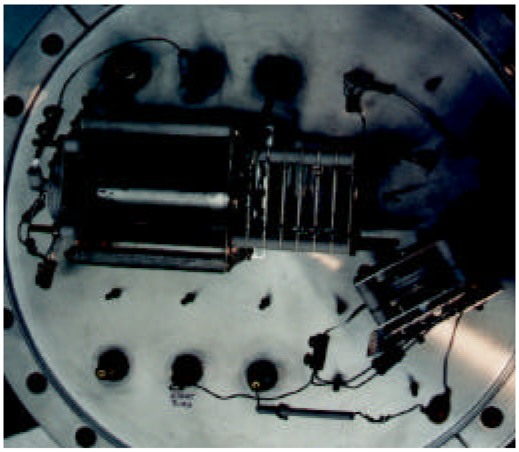
Ion Source

- Unique, based on electron multiplier
- ^{241}Am alpha source
- Microchannel plates arranged as “chevrons”



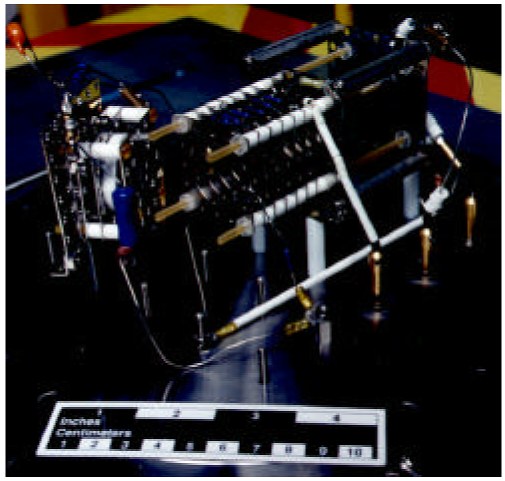
Ion Source Operation

- Benefits
  - Extremely short (sub-ns) pulses)
  - Low input power
  - High gain (10^8)



Ionization Region

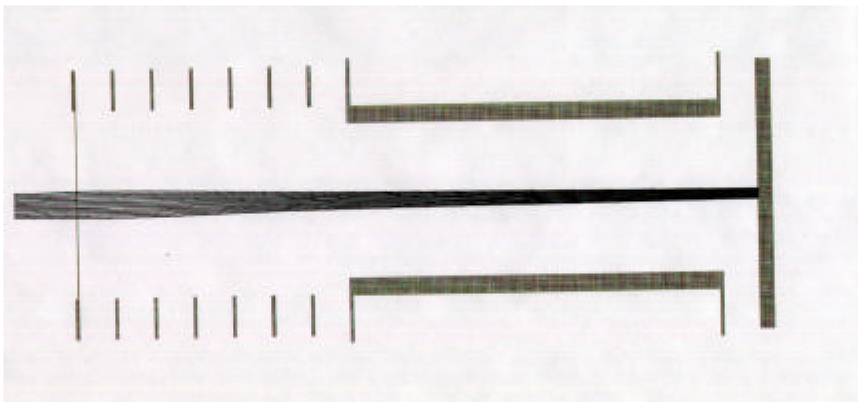
- Now using ion source at an obtuse angle from the balance of the instrument
- Expect to use linear arrangement to increase collection efficiency and improve resolution



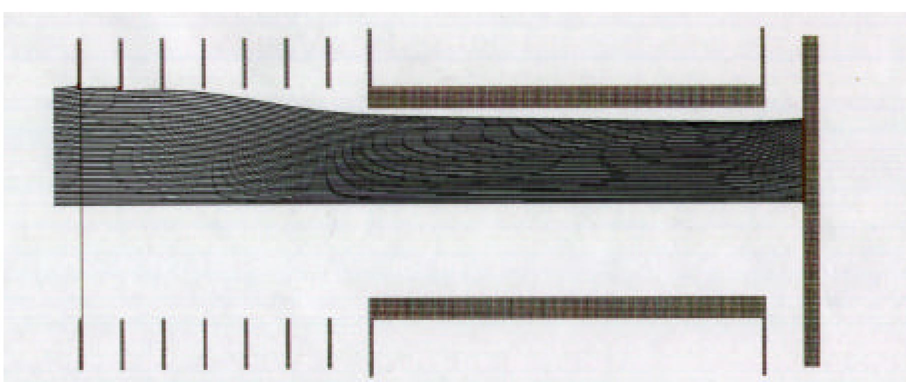
Acceleration Region

- Now using linear array
- Plan on using a non-linear array
- Data to support plan

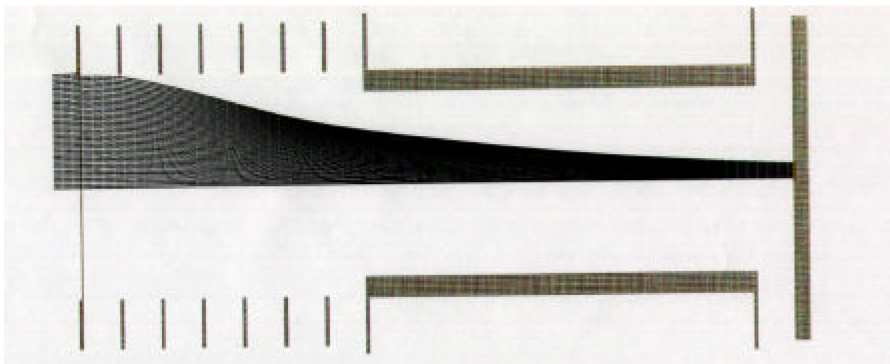
Simion Simulation



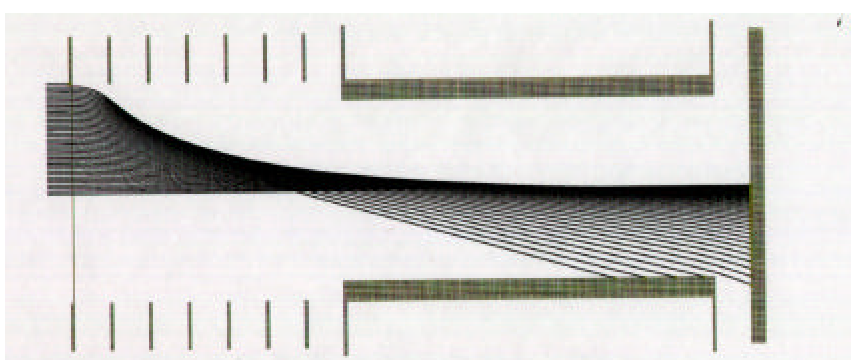
Grid Voltage: -110 VDC



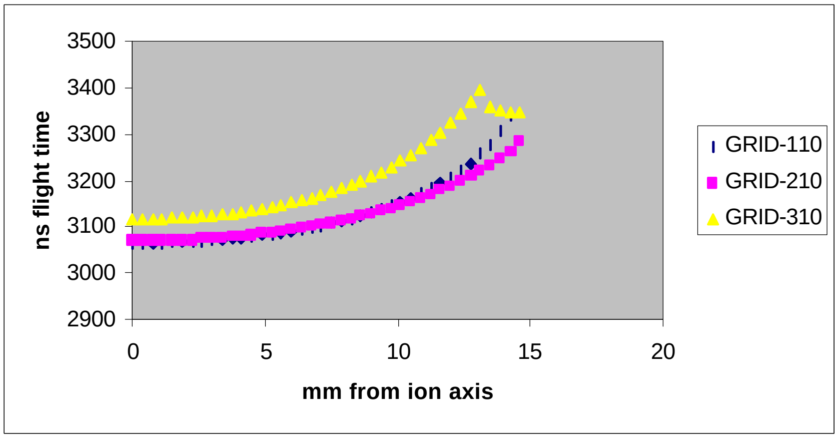
Grid Voltage: -210 VDC



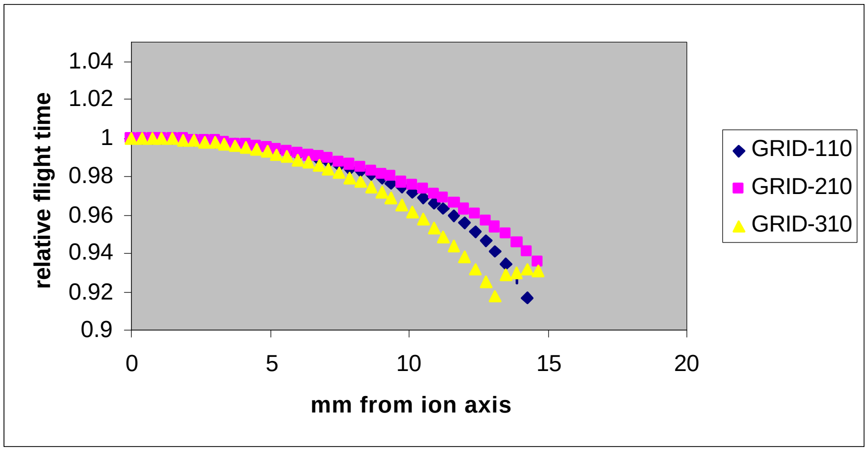
Grid Voltage: -310 VDC



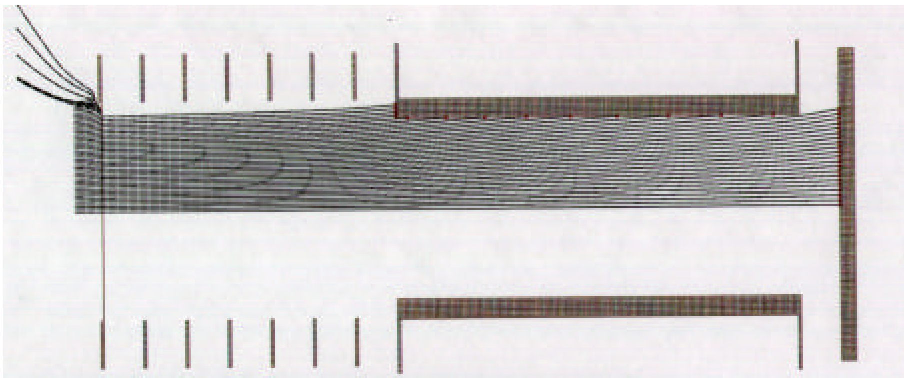
Grid Voltages



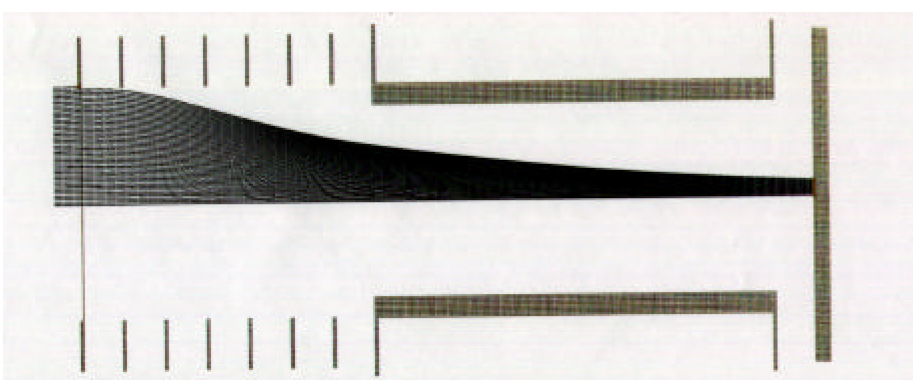
Grid Voltages



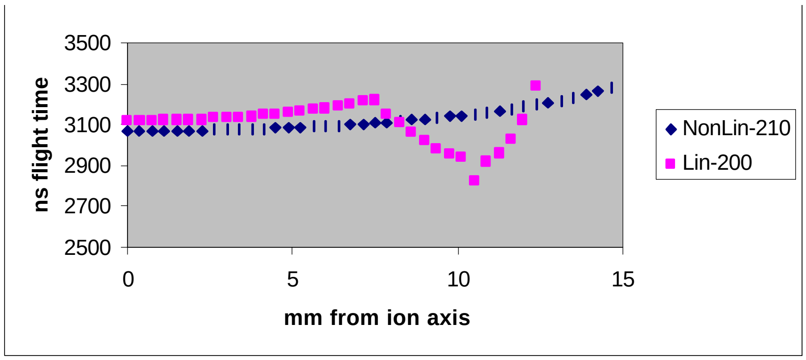
Linear/Nonlinear



Linear/Nonlinear

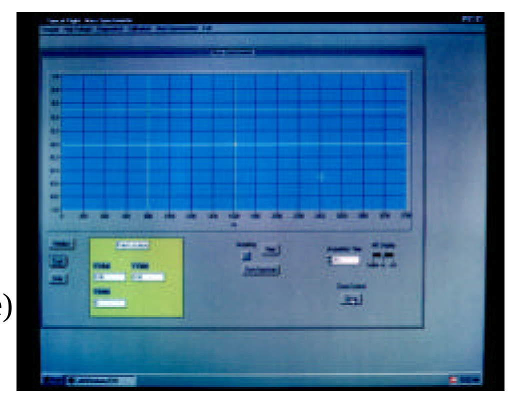


Linear/Nonlinear

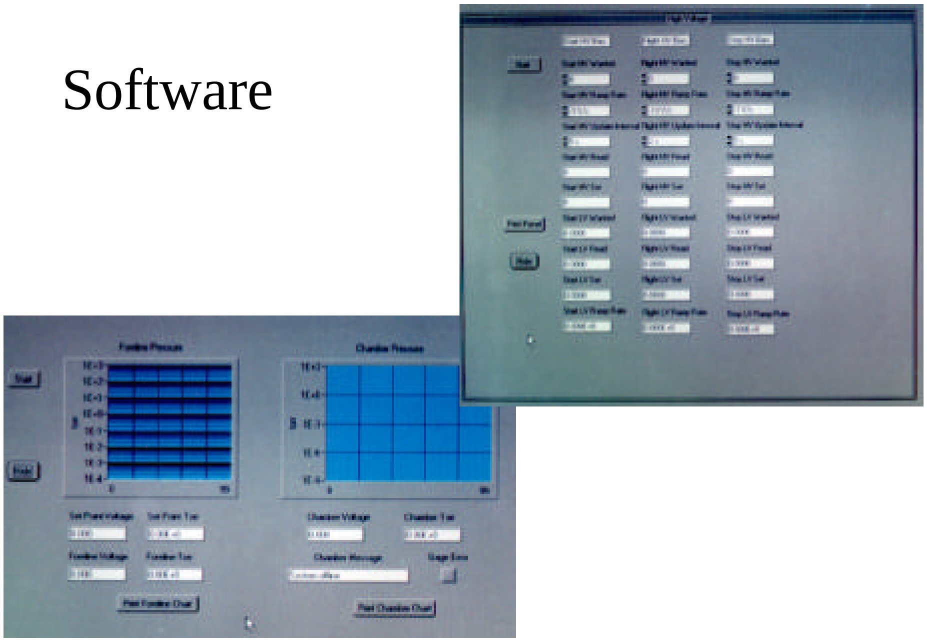


Software

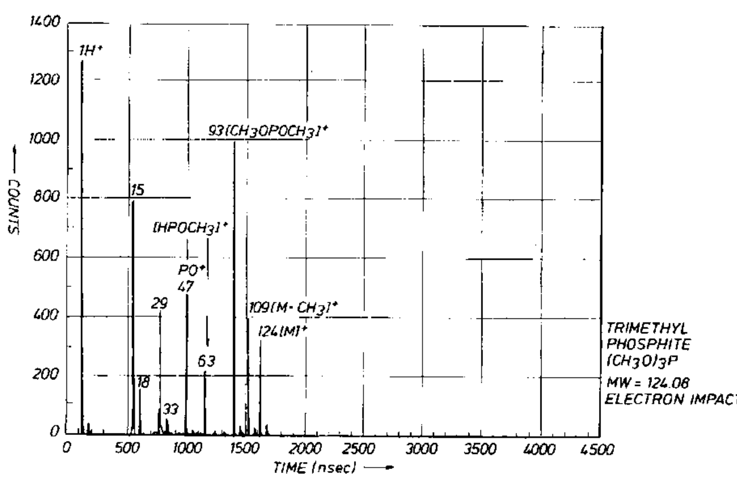
- Primarily internal code using National Instruments product LabWindows/CVI
- Custom driver for Ionwerks time-to-digital converter
- Custom driver for (future) FPGA



Software

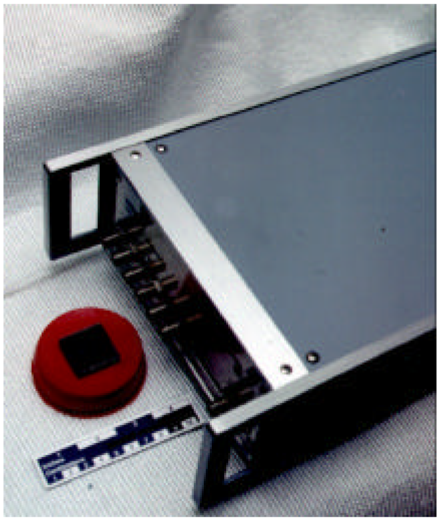


Phosphite



Future Work

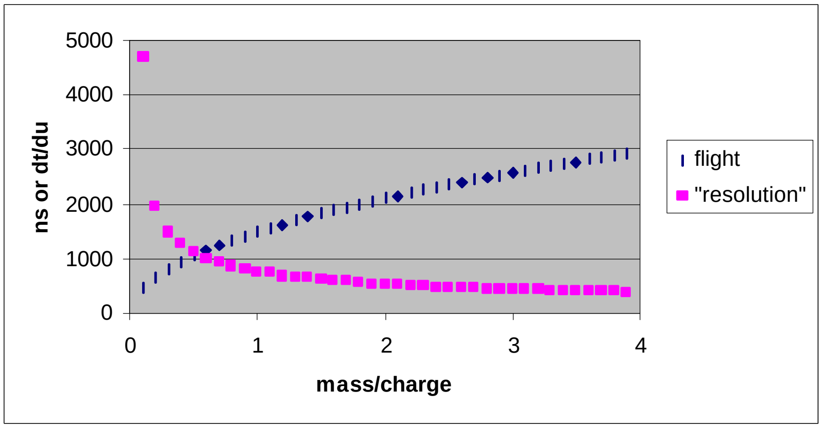
- Miniaturize electronics
  - Expect to replace half-rack electronics module with FPGA (field-programmable gate array)
  - $100 versus $12,000 (after non-recurring engineering costs)
  - 100 g versus 5kg
  - battery versus line voltage



Future Work (continued)

- Improve ion optics for collection efficiency
- Interface instrument to a capillary (miniature) gas chromatograph
- Test compounds, as specified by sponsor

Potential Work--Hydrogen



Questions

Distribution:

V. M. Baylor
J. M. Hiller
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