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# A combined microprobe and high-resolution mass spectrometer for materials aging studies

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## Introduction

We are developing a new instrument for studying aging effects in materials, especially those that contain interfaces with organic compounds. The intent is to combine the high spatial resolution provided by focused beam probes with the high mass resolution inherent in ion cyclotron resonance (ICR) mass spectrometry. This will make it possible to closely examine interfacial zones in complex materials for signs of aging and to unambiguously identify any degradation products as well as the location where they are formed. The instrument consists of a sample analysis chamber coupled to an ICR mass spectrometer (MS) and is depicted in Fig. 1. The analysis chamber contains focused laser and ion beam probes, a high precision sample manipulator, a time-of-flight ion detector, and transfer optics to the MS. The ICR–MS is a commercial unit that can be also be used independently for analysis of bulk solids, liquids, and solutions. This paper will give an overview of the instrument, describing it design, capabilities, and current status.

## Sample analysis chamber

The core of the system is the sample analysis chamber, which is a turbo-pumped UHV chamber. Samples, which can be up to 2.5 cm in diameter and 0.5 cm in thickness, are introduced via a vacuum load lock and transfer system. They are inserted onto a manipulator, which is driven by piezo-motors that allow the sample surface to be positioned anywhere within a 2x2x2 cm volume to within 1 μm. There is a provision for an onboard sample heater and thermocouple for sample heating and temperature control up to 1000 °C. In addition, a thermal contact to a liquid nitrogen reservoir permits sample cooling to below –100 °C.

Laser and ion focused beam probes enter the chamber to interrogate the sample. Two types of laser probes are available: infrared (IR) and ultraviolet (UV). For IR, transversely excited atmospheric-pressure (TEA) and continuous wave (CW) carbon dioxide ($CO_2$) lasers are used. The TEA $CO_2$ laser is used for laser ablation and direct ionization of sample material while the lower-power CW $CO_2$ laser is used for transient sample heating. For UV, nitrogen ($N_2$) and neodymium:yttrium-aluminium-garnet (Nd:YAG) lasers are used. The pulsed $N_2$ laser is used for surface desorption and ionization (e.g., matrix-assisted laser desorption ionization, MALDI) while the Nd:YAG laser is used to photoionize desorbed neutral species. The ion beam probe is a liquid gallium ion ($Ga^+$) source attached to an ion optics column for focusing, pulse formation, and rastering. The $Ga^+$ beam can be operated in either a continuous or pulsed mode and is used to sputter material from the surface of the sample. The beam can be focused to less than 100 nm diameter, which enables analysis of selected points on the sample to be conducted or high-resolution secondary electron or secondary ion images of the sample to be generated.

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probe provides information about the surface and near-surface regions. Spatially resolved information is obtained by using the manipulator to move the sample across the path of a stationary laser or by electronically rastering the ion beam over a stationary sample. The variety of probes available facilitates the use of numerous analytical procedures for materials examination, such as line scans across the interface of a sectioned sample, depth profiles of a selected region on the sample, and two-dimensional analytical images.

Secondary ions and post-ionized neutrals desorbed or sputtered from the sample can be mass analyzed in two ways. First, if the beam probe is operated in a pulsed mode, time-of-flight (ToF) analysis of the sample material is accomplished with a simple linear ToF tube and a microchannel plate-type ion detector. This form of mass analysis is rapid, but has relatively low resolution ($M/\Delta M<10^3$) and mass range ($<10^3$ daltons). It is used primarily in conjunction with beam or sample rastering to obtain an elemental image of the sample surface in order to identify regions of interest. Second, for high-resolution mass analysis a selected point on the sample is irradiated by a beam probe and ejected ions are transferred to the ICR-MS. The ICR-MS is capable of much higher mass resolution and range than the ToF analyzer, but the detection process is relatively slow. Consequently, this form of analysis is used to obtain detailed chemical information about one or a few selected points on the sample surface.

## ICR-MS

The ion cyclotron resonance mass spectrometer is a Bruker Daltonics APEX II system, equipped with a 7 Tesla magnet, a cylindrical ICR cell, ion transfer optics, and several types of ion sources. It can be operated independently with an electron or chemical ionization source to provide analysis of gas phase species, with a heated sample probe to analyze volatile solids, and with an electrospray ionization source to analyze compounds in solution. This last type of ion source is often used for the analysis of polymers and biomolecules. Ions are detected in a homogeneous magnetic field following resonant RF excitation, which can be tailored to excite ions having a particular mass or set of masses. Only a small number of ions ($<10^3$) are needed for analysis, so this mass-measuring technique is both precise and sensitive. Because ion-atom collisions scatter ions out of their cyclotron orbits, it is necessary to conduct the analysis under UHV conditions. Like the sample analysis chamber, vacuum (<50 nPa) is maintained by several turbo pumps.

## Capabilities of the instrument

The focused beam microprobes provide a means to examine small areas on a sample. This makes it possible to study compositional variations at interfaces and throughout the bulk of the sample. Interfaces of special interest are found at metal/polymer boundaries, which are prevalent in many weapons components. Aging effects at metal/polymer interfaces can be promoted by segregation of bulk impurities in the metal to the interface and by accumulation of degradation products of the polymer at the interface. These effects may alter the mechanical, electrical, and/or chemical properties of the material. Combining microprobes with an ICR-MS allows such interfaces to be studied in detail.

The ICR-MS has a resolution ($M/\Delta M$) that can exceed $10^6$. This enables unambiguous identification of molecular fragments containing hundreds of atoms, owing to the characteristic mass defect for each stable isotope. For heavier ions, it is possible to first isolate a selected ion mass (by exciting all ions of other masses and clearing them from the cell), break the ion into smaller fragments through either collisions with an injected inert gas or infrared multiphoton dissociation, and then analyze the fragments. This capability allows the molecular structure of

complex compounds to be determined and makes it feasible to identify polymeric compounds and search for their decomposition products.

Some of the materials aging issues that will be addressed with the instrument are (1) study of conductive epoxy/metal interface reliability, (2) evaluation of energetic material stabilizers, (3) degradation of binder/propellant mixtures, and (4) material changes in adhesive/binder layers. Other reactive processes, such as polymer oxidation, decomposition, or cross-linking, and how they affect the integrity of metal/polymer and other interfaces in complex materials will be investigated as the need arises. The instrument is expected to be flexible enough to identify and help understand a wide range of aging processes in materials.

## Current Status

The ICR-MS instrument was installed in early 2000 and became operational in March. It has been used as a stand-alone system to examine various organic compounds, polymeric solutions, energetic materials, and protein digests. The sample analysis chamber has been assembled and evacuated. The sample manipulator stage, transfer system, ion gun, and ToF detector are all operational. The laser probes are being tested. At present, the ICR-MS and sample analysis chamber are being aligned, so that ions generated by the microprobes can be efficiently transmitted to the ICR cell for analysis. We expect the combined instrument to begin operation in early 2001.


## Acknowledgment

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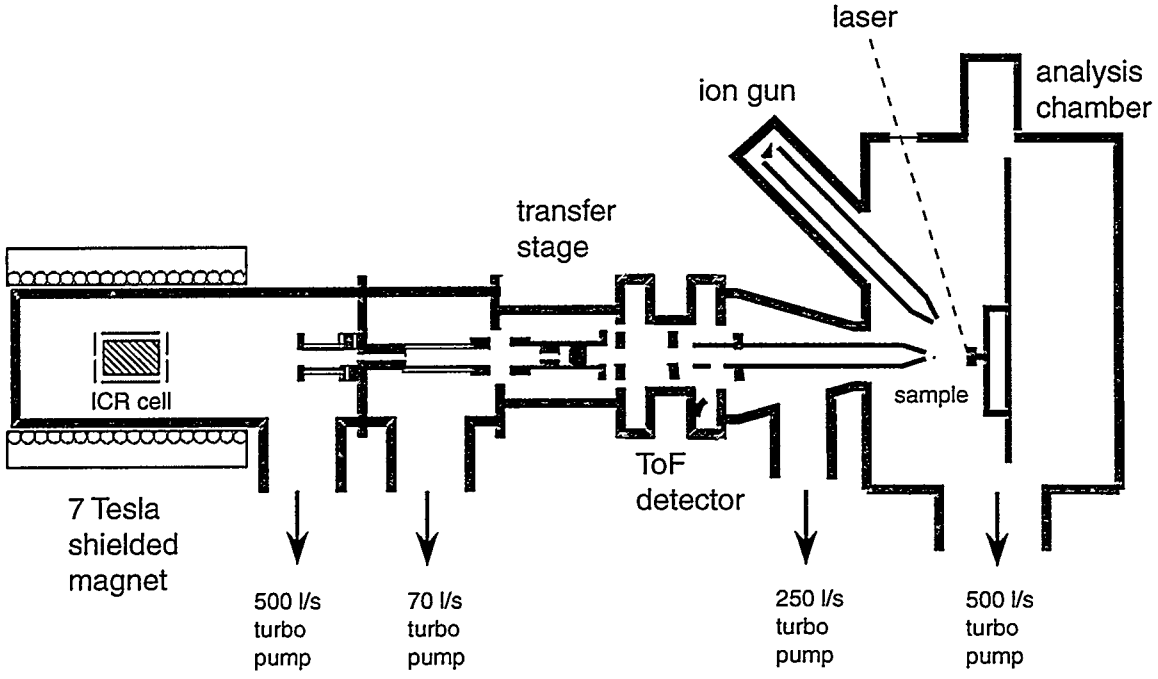


Figure 1. General layout of the combined microprobe and ICR-MS instrument.

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