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Mass Spectrometry Technology at the Jet Propulsion Laboratory (JPL)

by
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INTRODUCTION

The purpose of this presentation is to inform the members of the NASA Human Productivity Working Group about recent developments in the field of mass spectrometery taking place at the Caltech Jet Propulsion Laboratory. The pertinent research and development is aimed at producing an ultra-high sensitivity mass spectrograph for both spaceflight and terrestrial applications. The unique aspect of the JPL developed technology is an integrating focal plane ion detector that obviates the need for spectral scanning since all ions over a wide mass range are monitored simultaneously. The ion detector utilizes electro-optical technology and is therefore referred to as an Electro-Optical Ion Detector (EOID). A technical description of the JPL MS/EOID, some of the current applications, and its potential benefits for internal contamination analysis are discussed below.

MS/EOID TECHNOLOGY

Figure 1 illustrates the comparison between a scanning mass spectrometer and a non-scanning mass spectrograph. Simply put, the spectrometer can monitor only one ion species at a time while the spectrograph monitors simultaneously all ion species illuminating the focal plane. For high sensitivity, the spectrometer utilizes an electron multiplier for an ion detector which can achieve the ability to detect single ions passing through the image slit. Classically, the mass spectrograph has used a photoplate to simultaneously monitor all the ion species along the focal plane but required approximately 10,000 ions to generate a detectable image in the photographic emulsion. The duty cycle (i.e., the fraction of time spent measuring individual

ion currents during a spectral scan period) of a scanning mass spectrometer can be as low as 0.01% per mass peak over a mass range of 20:1. The mass spectrograph has a 100% duty cycle. Hence several orders of magnitude increase in spectral sensitivity can be achieved with a spectrograph fitted with an ion detector capable of detecting single ions. The EOID achieves this requirement.

Figure 2 illustrates the EOID concept. Ions exiting the magnetic field of a mass spectrograph impinge on a two dimensionsal microchannel electron multiplier array (MCA). For each ion entering a microchannel 10^4 electrons exit the channel and are accelerated to the phosphored surface of a fiber optic vacuum window. Approximately 100 photons are generated for each impinging electron giving an overall ion-to-photon gain of 10^6. The photons are guided fiber optically to a self-scanned linear photodiode array (PDA) where signals are integrated, coverted back to electrons and sent to a computer. Figure 3 is a photograph of "ion" images appearing on the exit face of the fiber optic window arising from a sample of perfluoro-iso-octane (MW = 438 amu).

Figure 4 is a schematic representation of the MS/EOID hardware implementation. The focal plane is 12.7 cm long and is viewed by five 1024 element PDAs interdigitated fiber-optically for mechanical reasons. Hence the MS/EOID has 5120 individual detector elements (photodiodes) continuously observing the mass spectral signal. Each photodiode is inactive for only 8.3 μs while it is being readout to the computer. Spectral integration time can be varied from several tens of milliseconds to tens of seconds. Figure 5 is a summary of the existing "miniaturized" MS/EOID specifications and Figure 6 is a photograph of the instrument.

APPLICATIONS

Inherent in the MS/EOID concept is the potential for both high sensitivity as well as rapid transient response. Different applications may stress one over the other and in some cases both are required. In general, however, the preservation of complete spectral information while detecting ion currents with single ion sensitivity has opened up some interesting fields of research.

An application stressing sensitivity is that of amino acid analysis from protein molecules sequenced by the Edman degradation chemical process. Determination of the protein structure is accomplished by successively clipping amino acids, one by one off the protein molecule in the sequenator, and analyzing each sample for the prominent amino acid in that residue. Liquid chromotography coupled with UV detection is typically used. This is both time consuming and not very sensitive (30 minutes for an LC run and ~1 ng detectability). An automated MS/EOID is currently under development at JPL that has an analysis time of one minute and a detectability approaching 1 pg. Figure 7 is a block diagram of the system and Figures 8 and 9 are representative data. Efficient sample acquisition and transport together with sample contamination are areas of concern being presently worked.

An MS/EOID instrument system is currently under development that requires both fast transient response and and high sensitivity. This system will be utilized for the real-time analysis of ambient aerosols and biological particles in air. This system concept is shown schematically in Figure 10. Ambient aerosol particles are extracted from the air and formed into a beam by a differentially pumped capillary/skimmer system. As the particles strike a hot rhenium filament, they are volatilized and the plume of vapor is subsequently ionized by an electron beam. The burst of ions thus genrated (in a time span of ~100-200 μs) is accelerated into the mass analyzer, separated according to mass, and integrated by the EOID. Complete mass spectra from each volatilized/ionized particle can be read out at intervals as

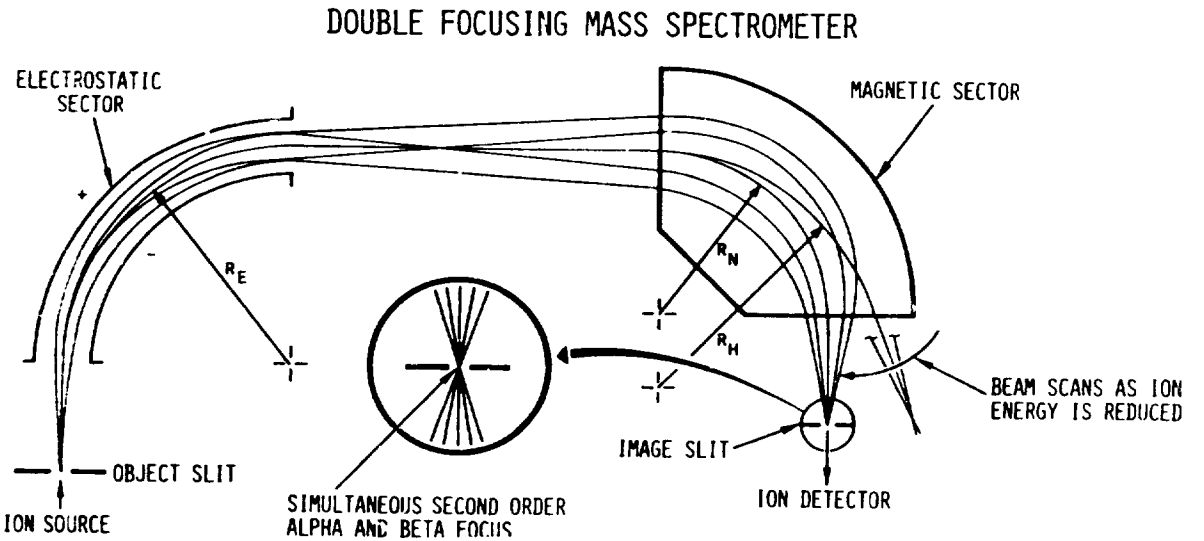
closely spaced as 40 ms. Figures 11 and 12 are data gathered from 1.7 μm diameter potassium biphthalate particles and three different bacterial particles without the benefit of MS/EOID. In these cases approximately 1000 particles per peak were required to generate the statistics necessary to quantitate the ion intensity measurements using a quadrupole mass filter in the manual scan mode. The MS/EOID for the particle analysis research is currently being assembled and will be operational by early spring. A laser ionization method is also under development and will be studied in detail after the MS/EOID is interfaced to the particle beam inlet system.

APPLICATION TO SPACE STATION INTERNAL CONTAMINATION

It is the author's opinion that the potential role MS/EOID could play in the area of internal contamination would be as a quantitiative analysis tool for the elucidation of atmospheric contaminants aboard Space Station. With the hundreds of contaminants found over the years in spacecraft environments, it would appear that combined gas chromotography-mass spectrometery offers the best chance for accurately assessing potentially hazardous conditions in the environment.

The existing MS/EOID at JPL covers a much broader mass range than is required (a maximum mass limit of 300 amu should be adequate). A small MS/EOID at the University of Minnesota (built for upper atmosphere ballon borne measurements) is too small with a maximum mass limit of 50 amu. Preliminary calculations show that if one limits the focal plane length to 6.4 cm a medium size MS/EOID could be constructed covering a mass range from 15 amu to 300 amu while taking advantage of the latest state-of-the-art high resolution microchannel electron multiplier array and photodiode array devices available on the market.

The rational for using an MS/EOID over a more conventional mass spectrometer is speed of response coupled with high sensitivity. Were a micro GC column (silicon wafer type) developed that could effect the required separation of contaminant species then the MS/EOID would likely be the only mass spectrometer that could measure the spectra of the very narrow (fractional second) peaks eluting from the GC. Because of its small size, the silicon wafer GC also utilizes very small sample aliquots thus requiring a high sensitivity detector for the quantitiatve measurement of trace species.



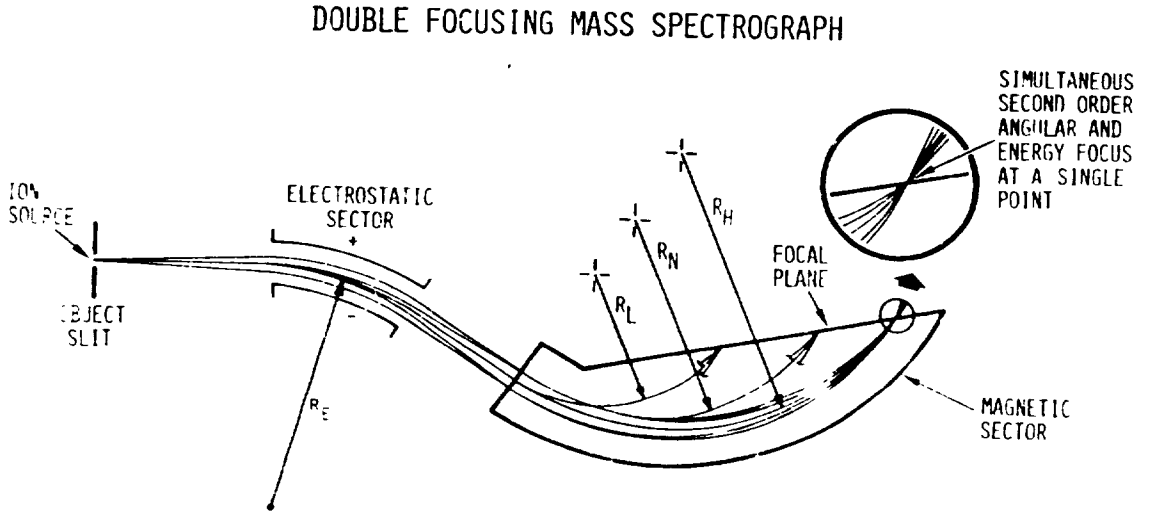


Figure 1 - Comparison of Spectrometer and Spectrograph Geometries

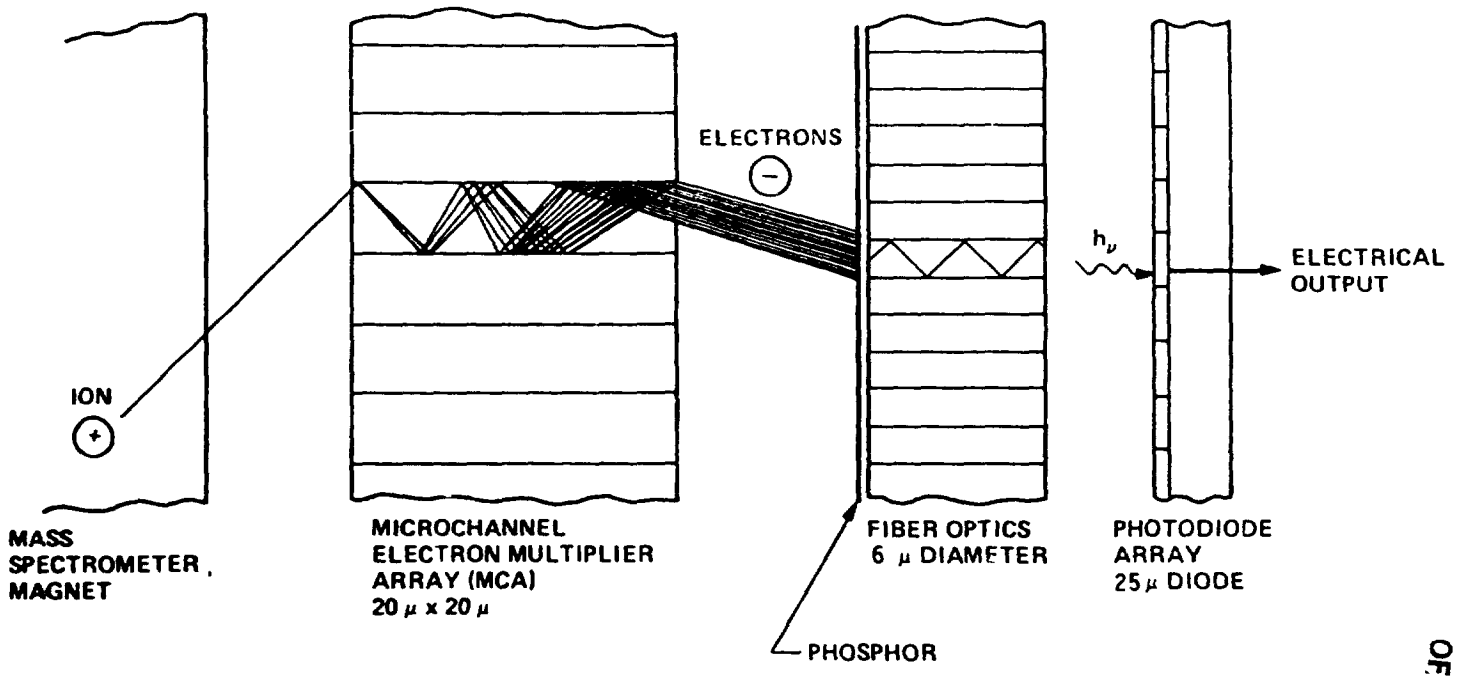


Figure 2 - Electro-Optical Ion Detector Schematic

Figure 3 Ion Images from MS/FOIL

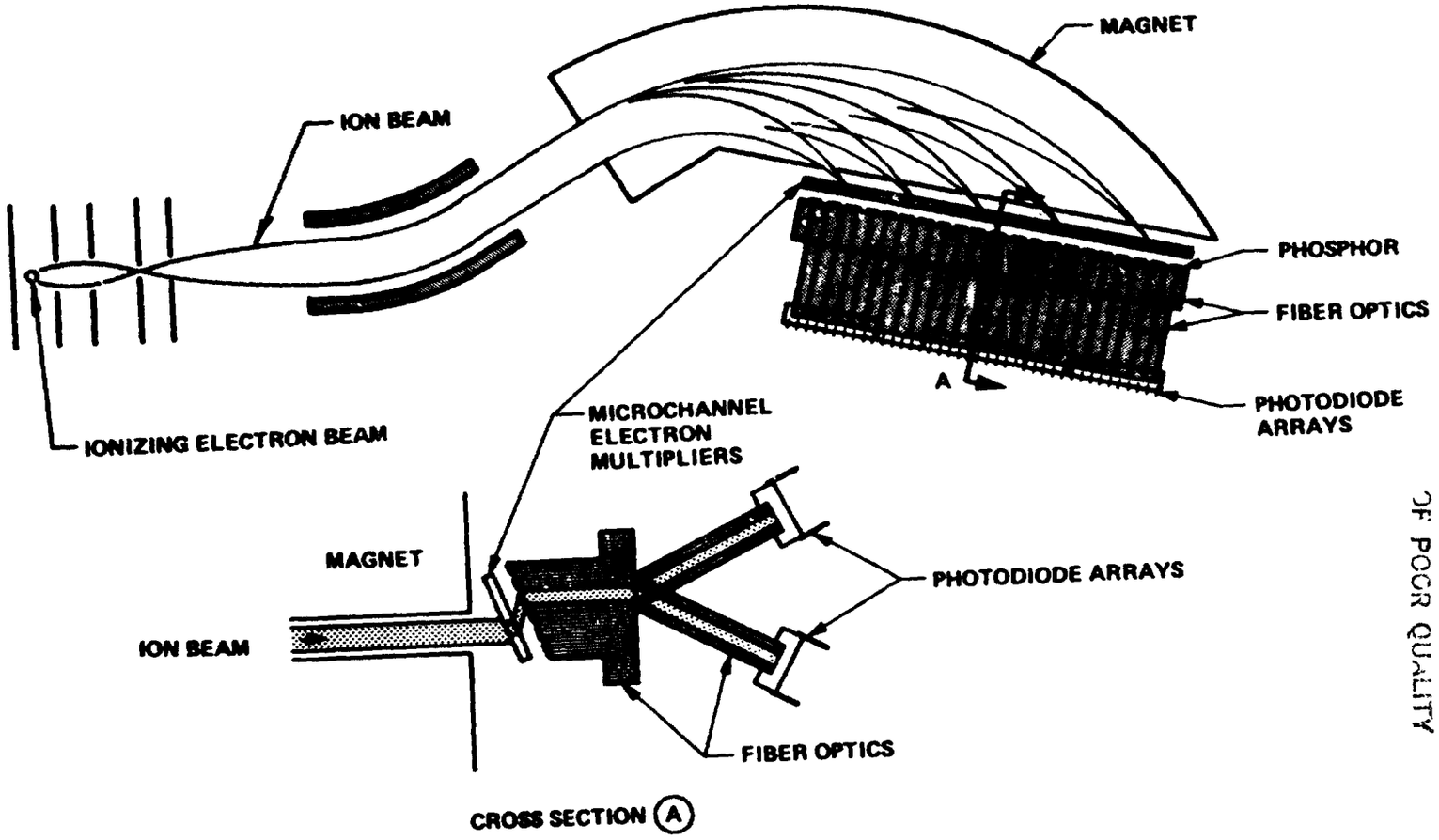


Figure 4 MS/EOID IMPLEMENTATION SCHEMATIC

MS/EOID PERFORMANCE

• MASS RANGE	25 - 500 AMU
• MASS RESOLUTION	$(M/\Delta M)_{10\%} = 515$
• DYNAMIC RANGE	1.5×10^4
• SPECTRAL READOUT TIME	40 MILLISECONDS
• DETECTABILITY (WITH 100:1 SPECTRAL DYNAMIC RANGE)	$\sim 1 \times 10^{-15}$ GRAM*

*APPROXIMATELY EQUIVALENT TO 0.1 μM DIAMETER PARTICLE OF UNIT DENSITY

Figure 5

DOUBLE FOCUSING FOCAL PLANE MASS SPECTROGRAPH WITH AN ELECTRO-OPTICAL ION DETECTOR

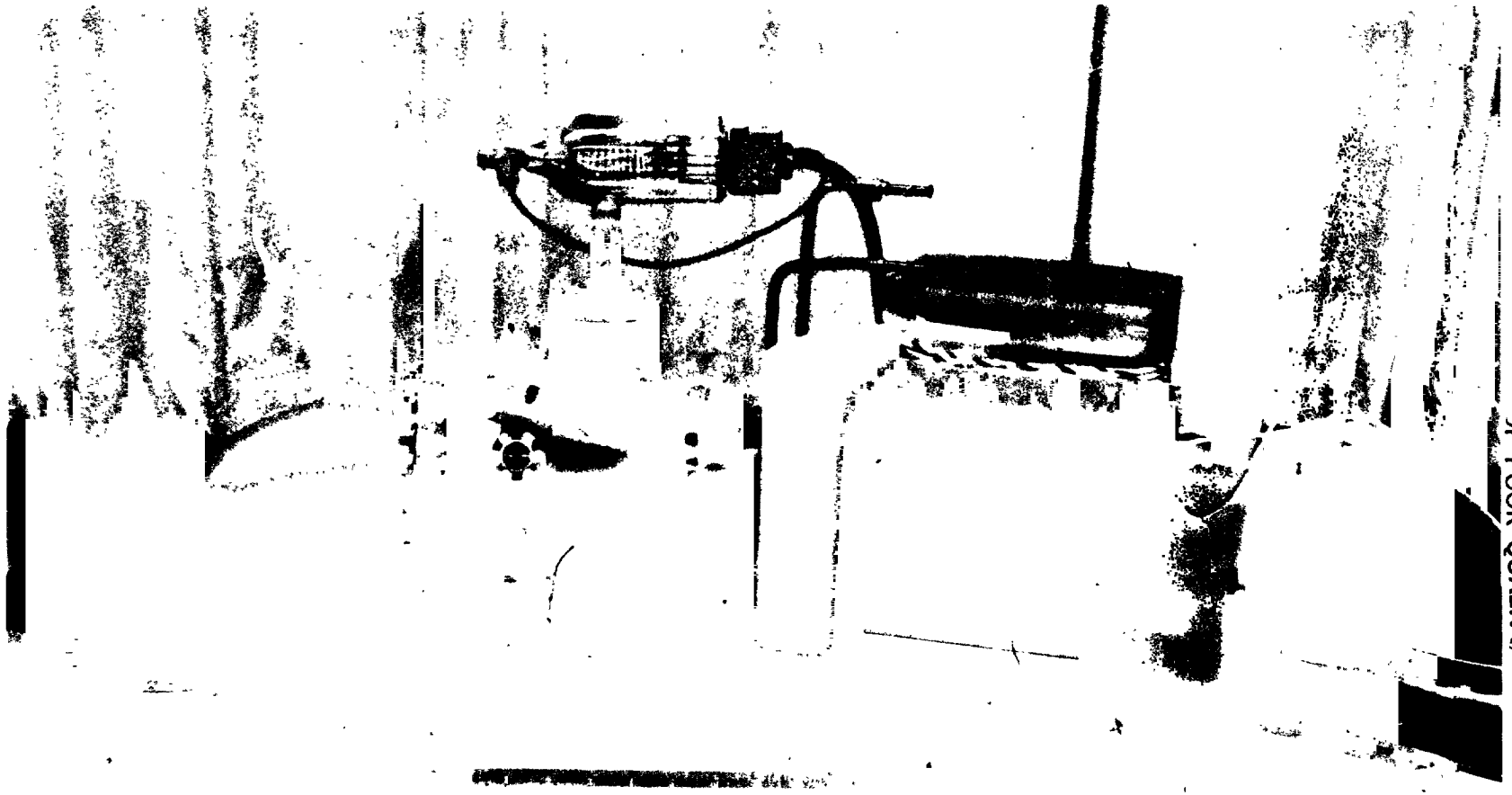


Figure 6

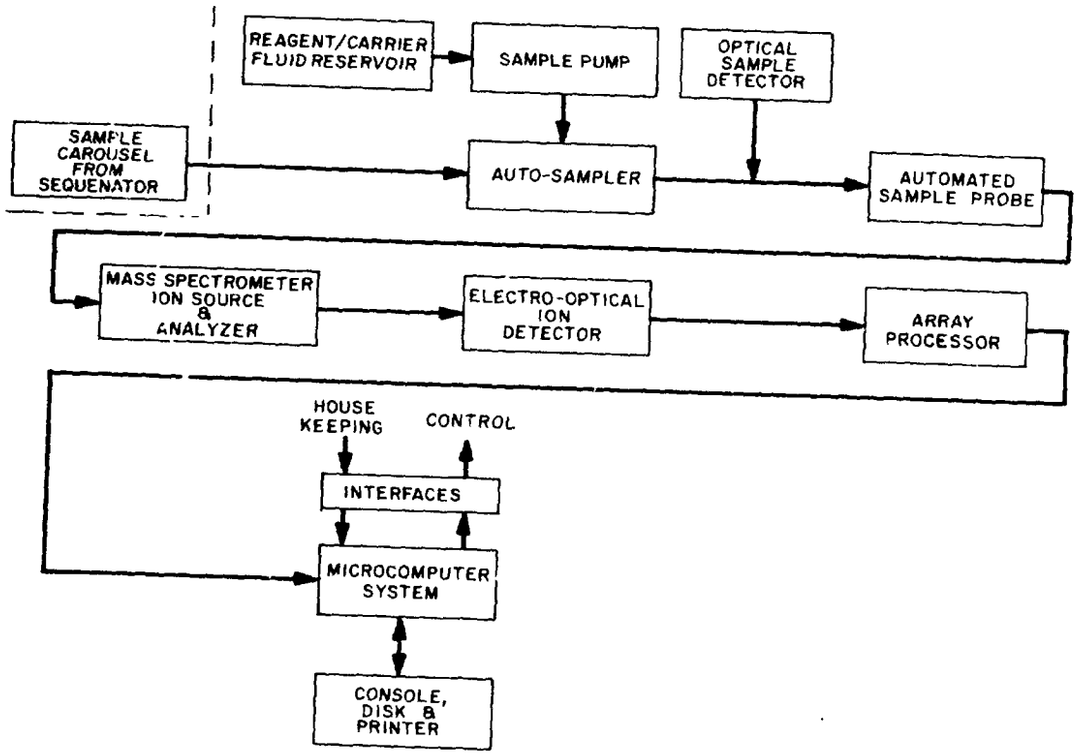
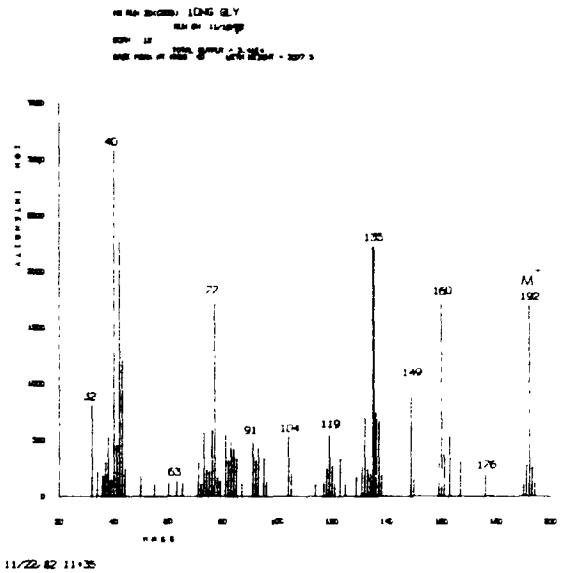
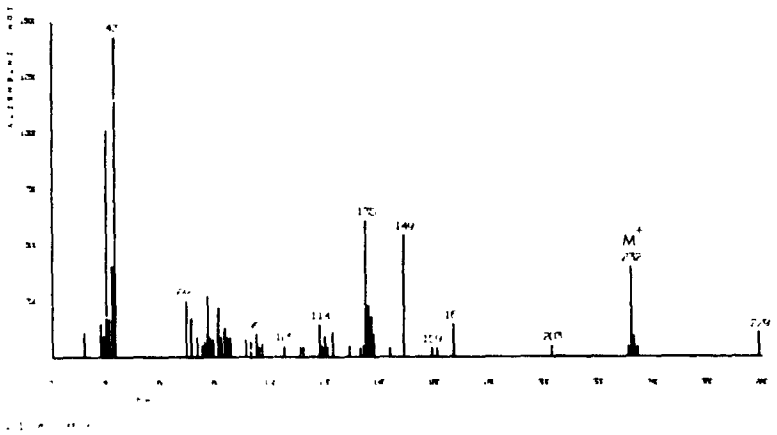


Figure 7: Mass Spectrograph System for Amino Acid Analysis



(a)



(b)

Figure 8 Representative Line Spectra;
(a) Glycine-PTH, (b) Proline-PTH,
(c) Leucine-PTH

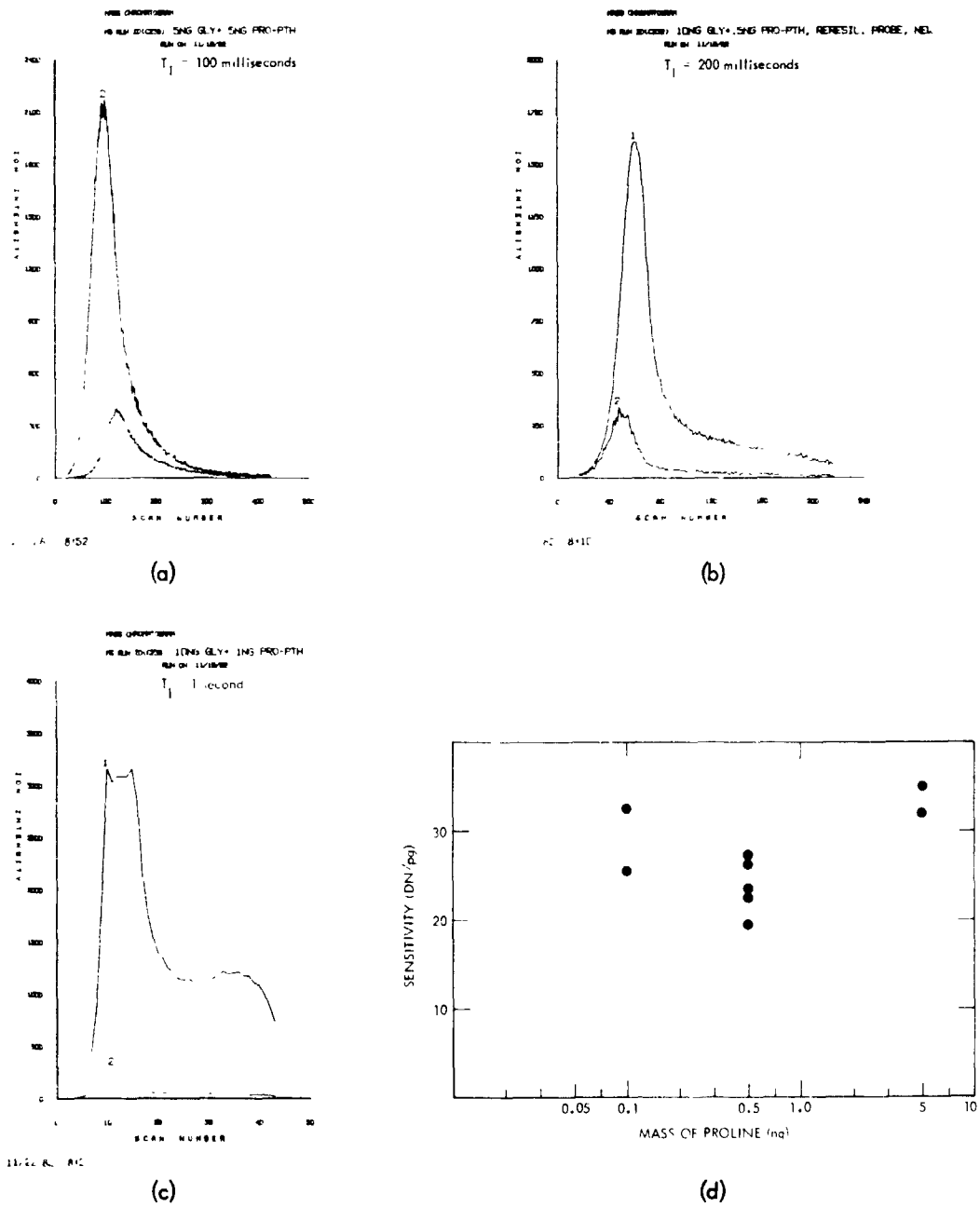


Figure 9 Glycine/Proline-PTH Elution Characteristics and Sensitivity
Curve #1: m/e = 192, Curve #2: m/e = 232,
T_I = Spectral Integration Time

PAMS WITH ELECTRO-OPTICAL ION DETECTION

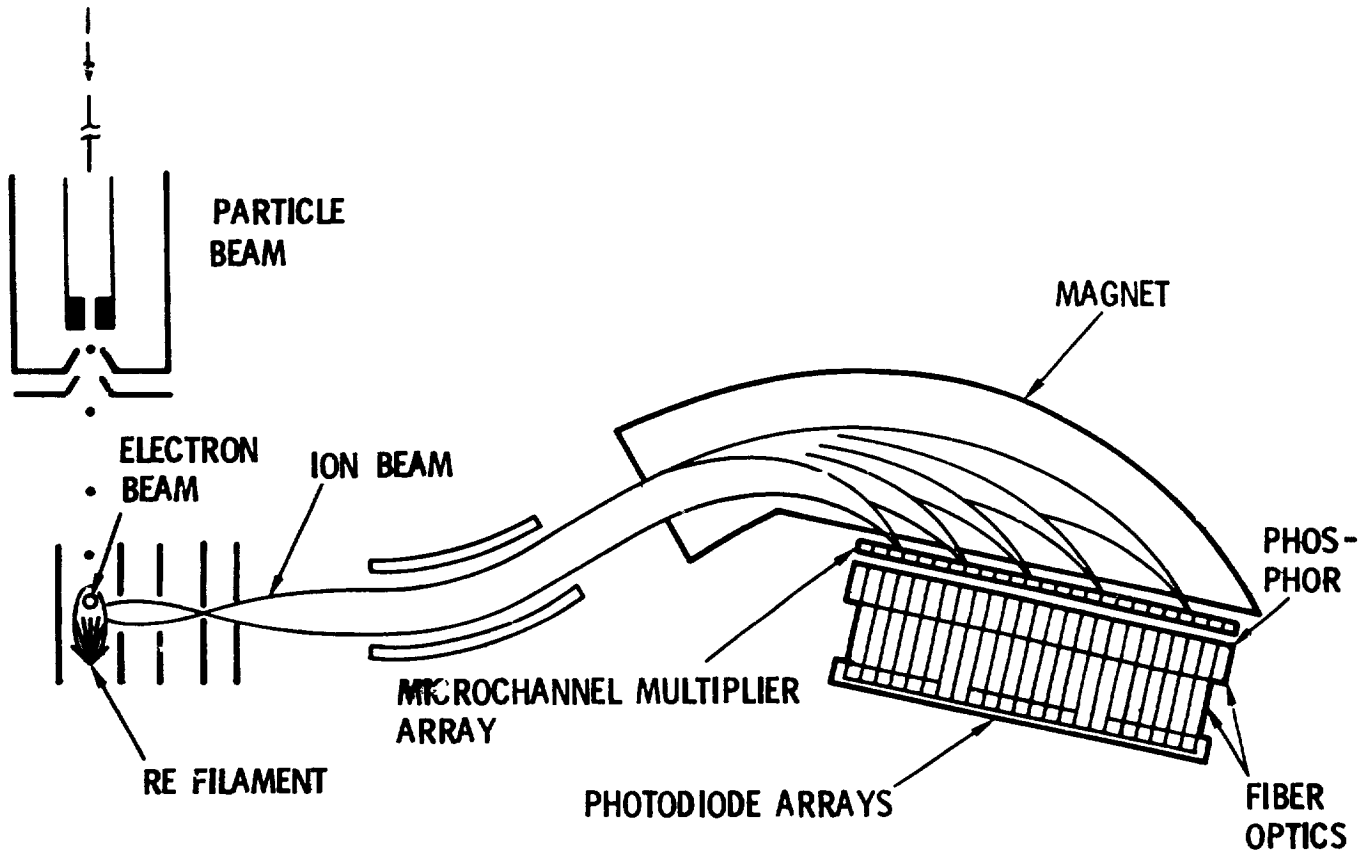


Figure 10

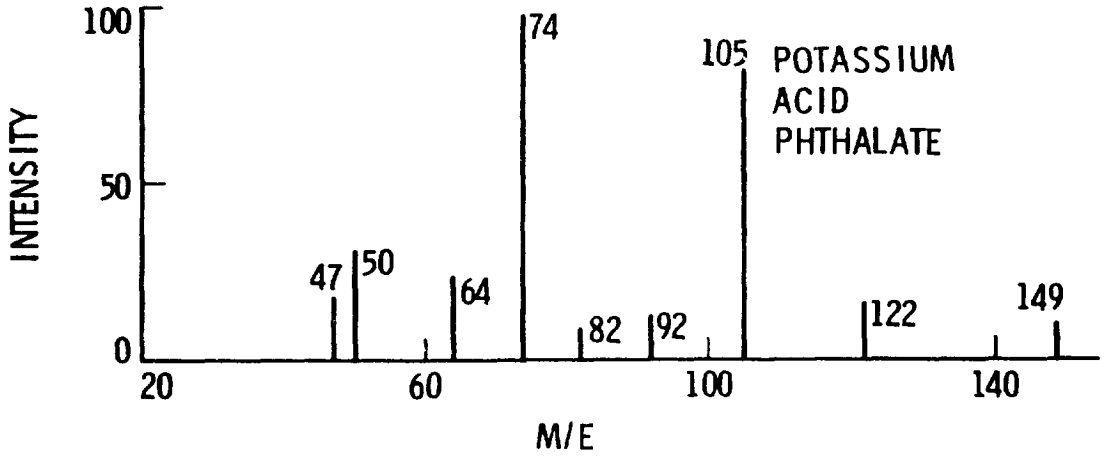


Figure 11a Mass spectrum obtained from potassium biphthalate particles of 1.7 μm diameter.

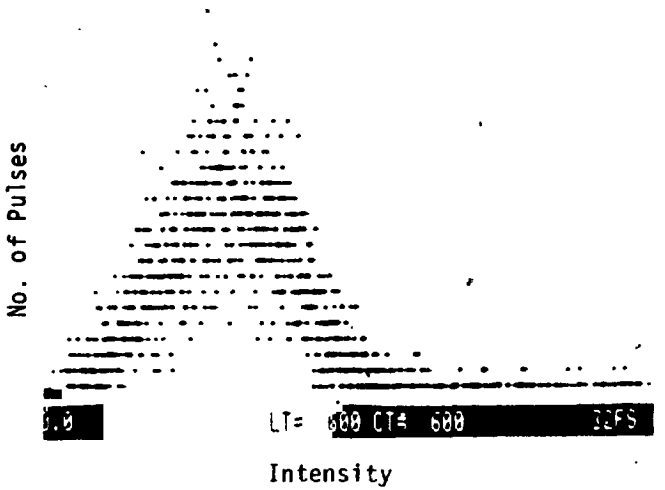


Figure 11b Pulse height Distribution of ion pulses at 50 amu resulting from 1.7 μm diameter KBP particles.

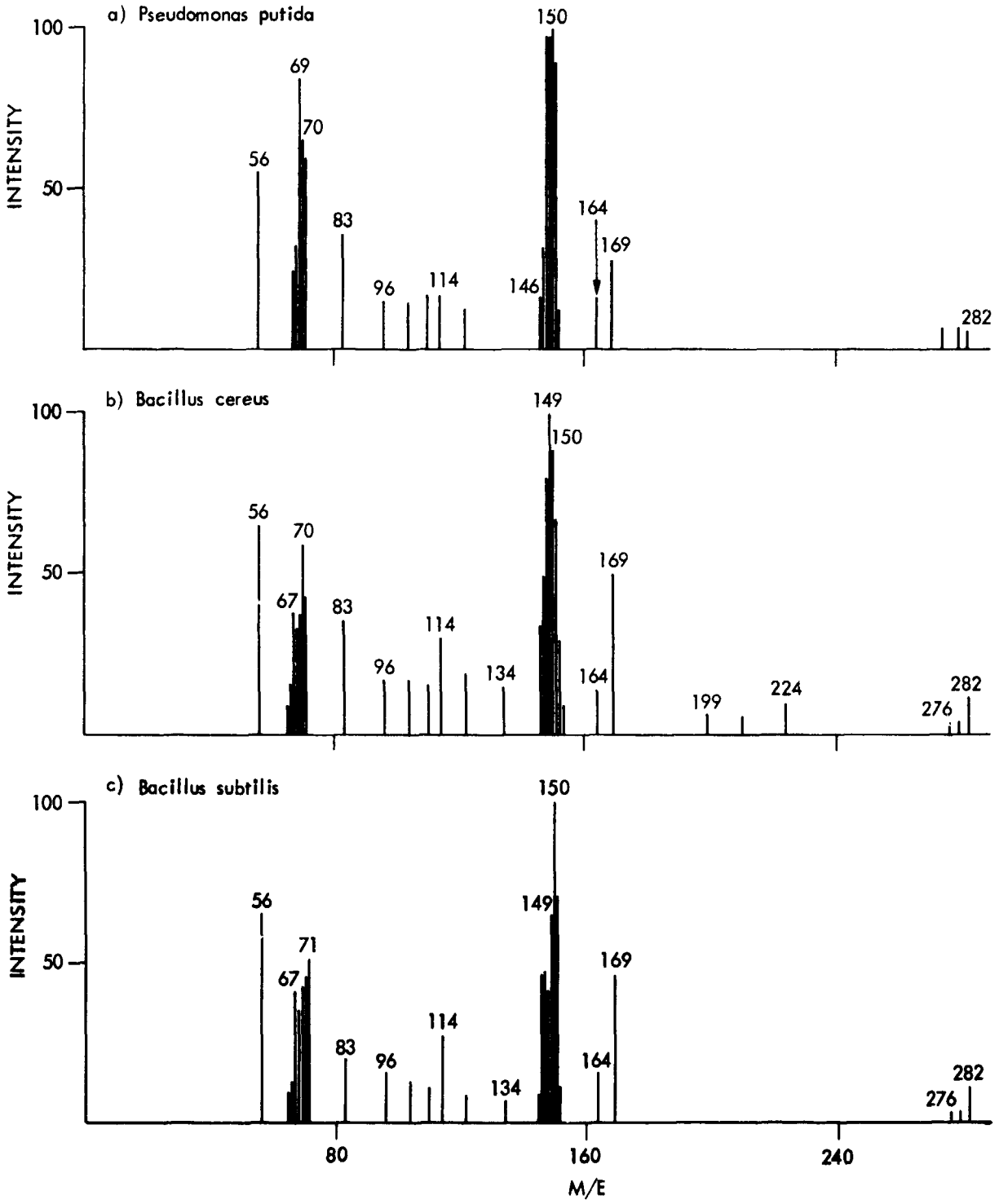


Figure 12 MASS SPECTRA FROM BACTERIAL PARTICLES