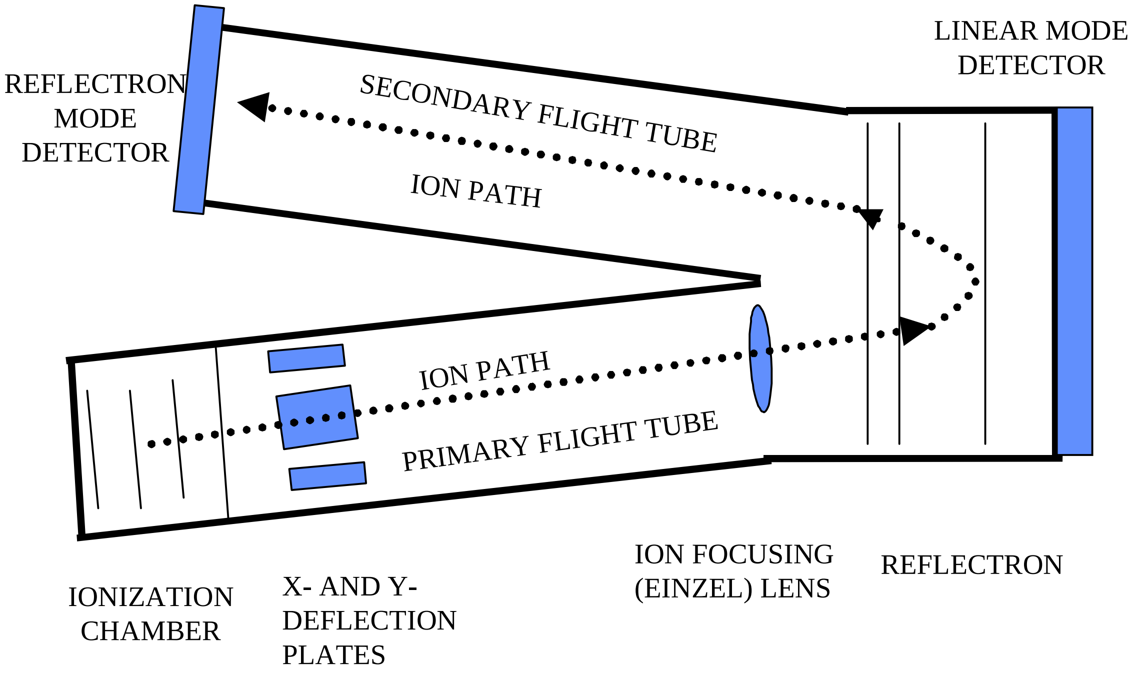
CHAPTER II. EXPERIMENTAL SETUP

II.1-- INSTRUMENTAL DESIGN OVERVIEW

Analyses are performed on a custom Comstock Reflectron Time-of-Flight Mass Spectrometer model LI RTOF/210 designed with a laser ionization source chamber. The TOF-MS is operated in positive-ion detection mode, with polarities chosen accordingly for ion extraction (positive voltage extraction pulse), acceleration (negative voltage), and detection (negative bias). Its design allows for either linear mode or reflectron mode operation, with detection following the first or second flight tubes, respectively. Overall, the instrument can be considered a system of several regions, the ionization chamber, primary flight tube, reflectron, secondary flight tube, and detectors. A schematic is shown in Figure II.1 with the corresponding flight tube, voltage plates, and reflectron distances noted in Tables II.1 and II.2.

II.2-- VACUUM SYSTEM

A vacuum requirement of less than ~10^{-5} torr is achieved by a two-pump system. A Varian turbomolecular pump is used in conjunction with an Alcatel two-stage mechanical forepump. A Bayard-Alpert style nude ionization gauge measures the pressure in the flight tube. For most applications, the flight tube pressure is maintained between 5×10^{-7} and 5×10^{-6} torr, while the forepump pressure remains between 3.5×10^{-3} and 2.0×10^{-3} torr.



Overall TOF-MS schematic

Figure II. 1: Our complete reflectron-design TOF-MS.

Table II. 1: Voltage ranges for components of the TOF-MS.

Lens/Grid/Plate	**Operating potentials**
Extraction (Repeller) plate	0 to ± 450 V
Acceleration grid (V_{TOF})	0 to ± 5000 V
Primary flight tube	0 V
Secondary flight tube	0 V
Reflectron front/entrance lens	0 to ± 2000 V
Reflectron rear/exit lens	0 to ± 2000 V
Ion focusing lens	V_{TOF} +0 to V_{TOF} +500 V
Vertical and Horizontal Deflection plates	V_{TOF} +0 to V_{TOF} ± 500 V
Detector Bias	0 to ± 5000 V

Table II. 2: Distance specifications of the TOF-MS.

TOF-MS REGION	DISTANCE	Refer to Figure #
Extraction/source region (s)	~1.35 cm	II.2
Acceleration region (d)	~1.35 cm	II.2
Primary flight tube	1 m	II.1
Secondary flight tube	0.8 m	II.1

II.3-- IONIZATION CHAMBER

The heart of the ionization chamber consists of the ion extraction (repeller) plate and acceleration grid for a two-stage drawout system (See Figure II.2). Samples are mounted on a rotatable stainless steel sample probe, and the laser beam strikes the sample surface orthogonally (0°) from above. Following ion formation, a positive voltage extraction pulse is applied to the repeller plate. The pulse has a variable delay time (0 to 100 μs), amplitude (0 to +500 V), and width (0 to 10 μs), which are adjusted and optimized for the operation mode and analytical conditions. The positive extraction ("Repeller") pulse propels ions out of the ionization region and transmits them through the ground grid (Ni mesh) into the acceleration region. A constant negative bias (0 to -5 kV, with a safe limit of –3 kV) on the acceleration grid accelerates ions into the field-free primary drift tube (approximately 2 cm in diameter).

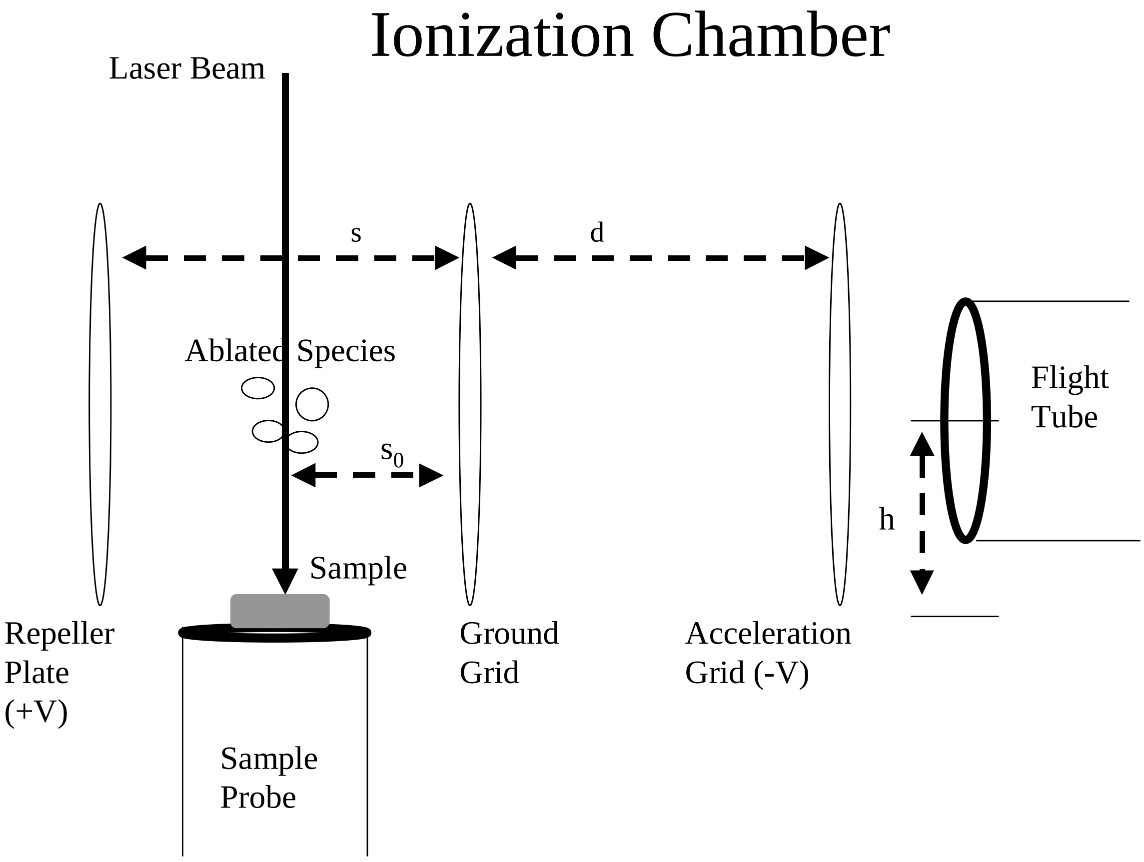


Figure II. 2: Dual-stage ionization chamber of our LI-TOF-MS.

II.4-- FLIGHT TUBES

Following the ionization chamber, ions are focused into the 1-meter long electric-field-free primary flight tube. This field-free region allows ions to drift and separate based on their mass/charge ratios. At the beginning of the first flight tube, horizontal (X) and vertical (Y) deflection plates (0 to ±500 V) may be used to better direct ions into the linear detector. For reflectron operation, these plates help steer the ions from the primary flight tube into the reflection region (offset by 6°) for subsequent reflection into the secondary flight tube. Although optional in linear mode, the deflection plates are mandatory for ion channeling when using the reflectron. Positional ion focusing is further achieved by experimentally optimizing the Einzel ion lens (0 to +500 V) for maximum sensitivity.

After the reflectron, the field-free secondary flight tube (0.8 meters long) further separates ions based on their different mass/charge ratios. In addition, ion packets of same-mass species sharpen after the initial kinetic energy distributions have been compensated by the reflectron. The secondary flight tube terminates at the second detector.

II.5-- REFLECTRON

The energy-focusing reflectron is of dual stage design, with an entrance lens and exit lens (See Figure II.3), which are adjusted to achieve second-order focusing for improved resolution. The entrance lens is at a constant negative bias (0 to –2000 V) to draw ions into the reflection region, while the exit lens is at a constant positive potential (0 to +2000 V) for reflection into the secondary flight tube. The magnitude of each lens is adjusted to optimize resolution, with the entrance lens affecting both the initial ion space focusing and second-order energy correction. The exit voltage governs the depth of penetration into the reflectron to achieve maximum correction of the initial kinetic energy distribution of same-mass ions. The gridless construction of the reflectron maximizes ion transmission from the primary flight tube into the secondary flight tube.

Dual-Stage Reflectron schematic (for positive ion reflection)

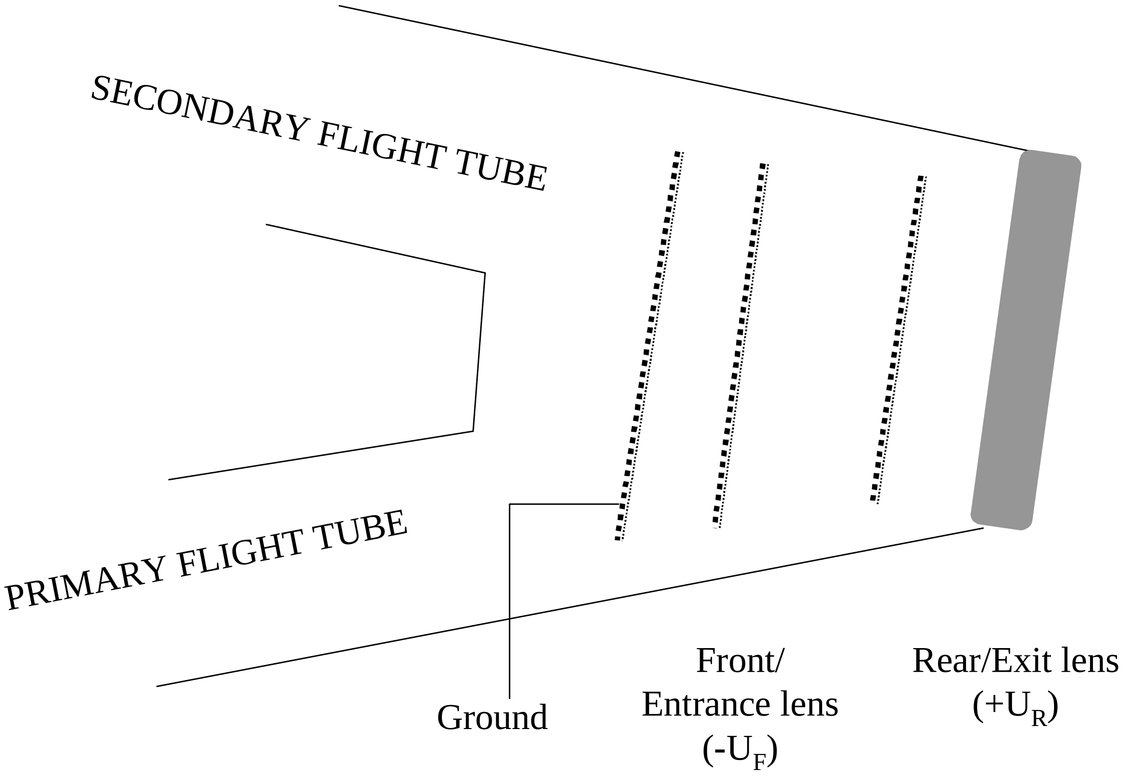


Figure II. 3: Two-stage reflectron design for second-order space focusing in our LI-TOF-MS.

II.6-- LASER IONIZATION

Ions are both ablated and ionized from the sample surface with a frequency-tripled (355-nm) Nd^{3+}:YAG laser (Continuum Surelite II). The laser is pulsed (4-6 ns pulse length) and has a repetition rate of 10 hertz, so it mates well with the TOF-MS to obtain a new spectrum every 100 ms. A xenon flashlamp voltage of 1.60 kV to 1.63 kV is used, and laser energies are controlled through an adjustment of the Q-switch delay time; the longer the delay, the lower the energy output.

As noted above, the laser beam is oriented perpendicularly to the sample surface. The high intensity beam ablates material from the surface and several underlying monolayers to generate the microplasma and ionize the species produced. Because of the polarities chosen on the mass spectrometer, only positive ions are analyzed.

II.6.1-- Optics

The beam from the Nd^{3+}: YAG laser is directed to the sample with three dielectric mirrors of ~99.9% reflectivity (for 355 nm). Following the final mirror is a focusing lens with a focal length of 25 cm, and the beam is then transmitted through a quartz window into the mass spectrometer.

II.6.2-- Laser Energy

Laser energies are chosen based on the ease of ablation for the particular sample, intensity of the observed signal, and degree of fragmentation desired. Care is taken to avoid signal saturation effects and damage to the multichannel plate detectors. To gauge the laser energy, a Digirad radiometer with a pyroelectric detection head optionally intercepts the laser beam after the second mirror. The observed spectral energy at this location is reduced by an approximate factor of 0.92 to account for ~4% losses on each side of the quartz window on the mass spectrometer. For most analyses, the energy range was selected between 1 and 100 μJ.

To determine that the beam is focused on the sample, the lens height is adjusted to maximize the ion yield observed on the oscilloscope. The beam size is viewed on a white card and measured with a Vernier caliper at the 25-cm focal length lens. The measured beam radius depends on the laser energy used, as higher laser energies produce a larger beam radius (~0.35 cm) and lower energies yield a smaller radius (~0.20 cm). For typical analyses with an energy setting of ~20 μJ, the radius is approximately 0.25 to 0.30 cm. The measured radius at the lens can be used to approximate the beam spot size at the focal point according to the Gaussian spot size relation (Equation II.1)[41]

$$2r = \frac{4f\lambda}{\pi d_0}$$

Equation II. 1: Laser spot size on sample surface.

where r represents the beam radius at the focal point of the lens, f represents the focal length of the lens, λ is the wavelength of the laser light, and d_0 is the beam diameter as measured at the lens.

The beam size at the sample surface thus translates to a radius of 9.4 μm to 11 μm, yielding an area of 279 μm^2 to 401 μm^2. Laser energy densities when using 20 μJ are then calculated to between 49.9 and 71.7 mJ/mm^2.

II.7-- DETECTORS

Detection is selected following either the first flight tube while in linear operation mode, or after reflection and the secondary flight tube while in reflectron mode (See Figure II.1). The electronics configuration precludes simultaneous use of both detectors.

Each of the identical detectors, a Galileo multichannel plate detector (MCP), is operated for positive-ion detection. Following impact by the positive ion, the first plate produces an electron output which is subsequently amplified to more electrons to provide a gain on the ion signal. The detector gain is governed by the potential applied to the plates (0 to -5 kV). For detector potentials of -1000 V to -2000 V, the nonlinear gain profile is between 10^4 and 10^5 [42]. Because of considerable signal ringing and poor signal quality, a maximum safe operating voltage on the detector is -2300 V, with most analyses employing potentials between -1600 and -1900 V. The gain selected is determined by the intensity of the ion signal observed on the oscilloscope, and signal saturation is avoided

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[41] J.R. Meyer-Arendt. *Introduction to Classical and Modern OPTICS*. Englewood Cliffs, N.J.: Prentice Hall, 1995.

[42] Microchannel Plate Detector Manual. Comstock, Inc.

by lowering the detector voltage. The detection efficiency of the MCP varies considerably based on the velocity of the impinging ions. For positive ions with acceleration potentials of 1500 to 2500 eV, the efficiency is approximately 20% to 60%[42]. The output of the detector is an electron current that is transmitted through a BNC cable to the oscilloscope and terminated in a 50-ohm resistance.

II.8-- ELECTRONICS AND TRIGGERING

Coordination of the ionization and extraction events is vital for optimum instrument operation and data integrity. As Figure II.4 shows, a photodiode responds to the laser beam pulse to ensure that timing begins on the actual laser output rather than on an internal laser trigger. The photodiode output is transmitted through a BNC cable to a digital pulse generator (Stanford Research Systems) to produce a +5 Volt TTL signal. The TTL signal is transmitted by a BNC cable into the Repeller Power Supply (RPS) and begins the extraction pulse delay time. After the user-determined "repeller" delay, the repelling plate is pulsed with the positive voltage specified for ion extraction. Concurrently, the RPS transmits a +5 Volt signal to the oscilloscope trigger to begin data collection. The time-of-flight is therefore defined as initiating from the true extraction pulse on the repeller plate and is independent of the extraction pulse delay time between the laser firing and the repelling pulse. A timing summary is presented in Figure II.5.

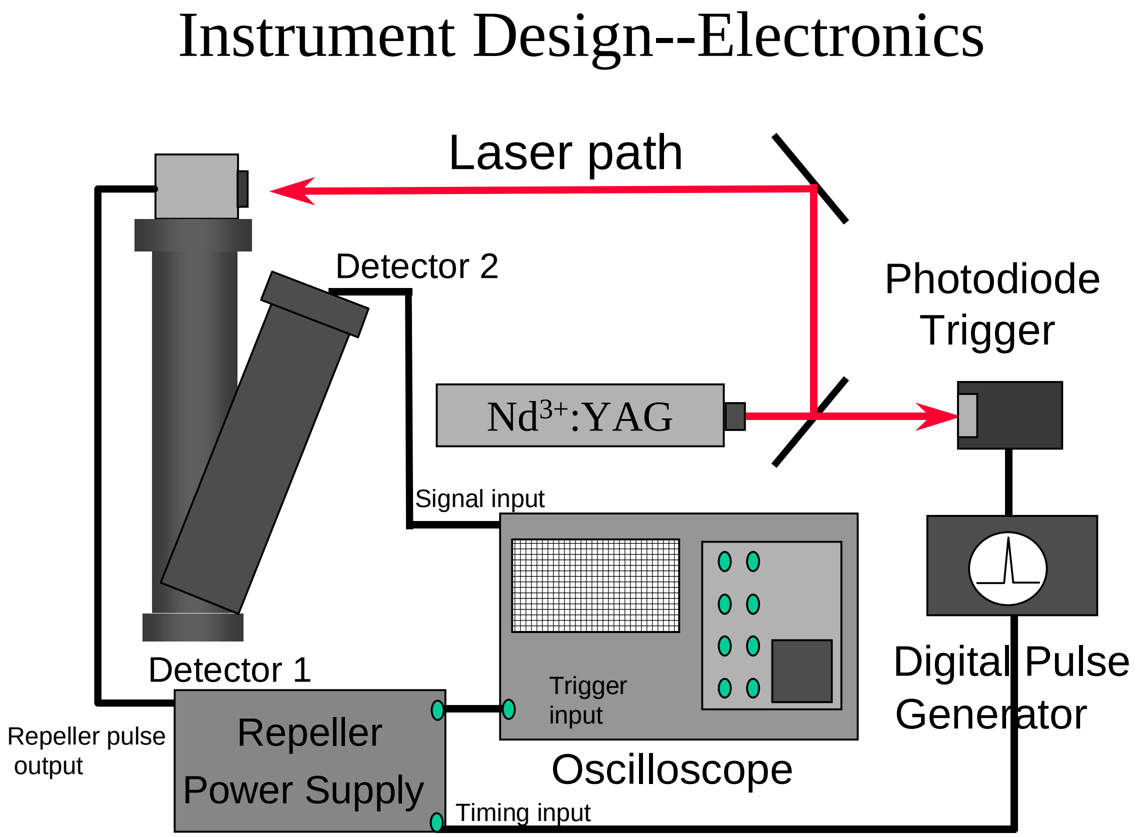

Figure II. 4: Electronics configuration and triggering for the LI-TOF-MS.

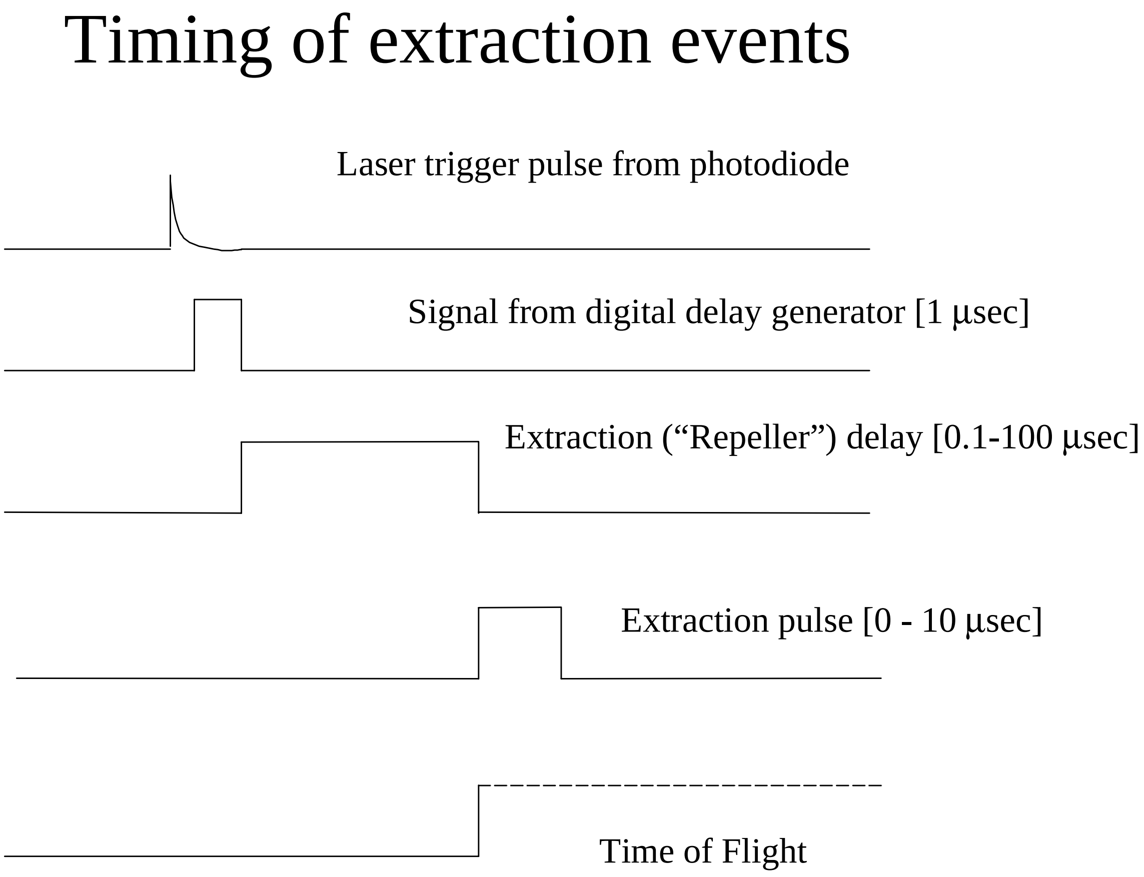

Figure II. 5: Timing of ion generation and extraction events.

II.9-- DATA HANDLING

II.9.1-- Data Recording

Waveforms are recorded and stored on a Tektronix Model 520A digital oscilloscope. After a 50-ohm internal resistor the ion (electron) signal from the MCP (-Voltage) is plotted against the time following the repeller trigger (the time-of-flight in seconds). For small data sets, the oscilloscope is capable of digitizations of up to 500 Megasamples/second and a bandwidth of 500 MHz. For most analyses, the tradeoff is made to widen the range of detected times-of-flight (typically 50 to 500 μs) at the expense of slower data sampling rates (typically 10 to 100 Megasamples/second).

II.9.2-- Data Display

Waveforms from the oscilloscope are stored in an oscilloscope-readable waveform file onto a PC-format floppy disk. The waveform file is transferred to a PC and a "converting waveforms" executable computer program converts the waveform data to ASCII format.

The ASCII data is then imported into the Origin 4.0/4.1 scientific graphing program. A user-created spreadsheet template inverts the -Voltage ion signal to produce an intensity versus time-of-flight spectral display, with horizontal baseline and ion peaks rising vertically. Following mass calibration the time-of-flight (x-axis) can be converted to a mass-to-charge (M/Z) scale if desired.