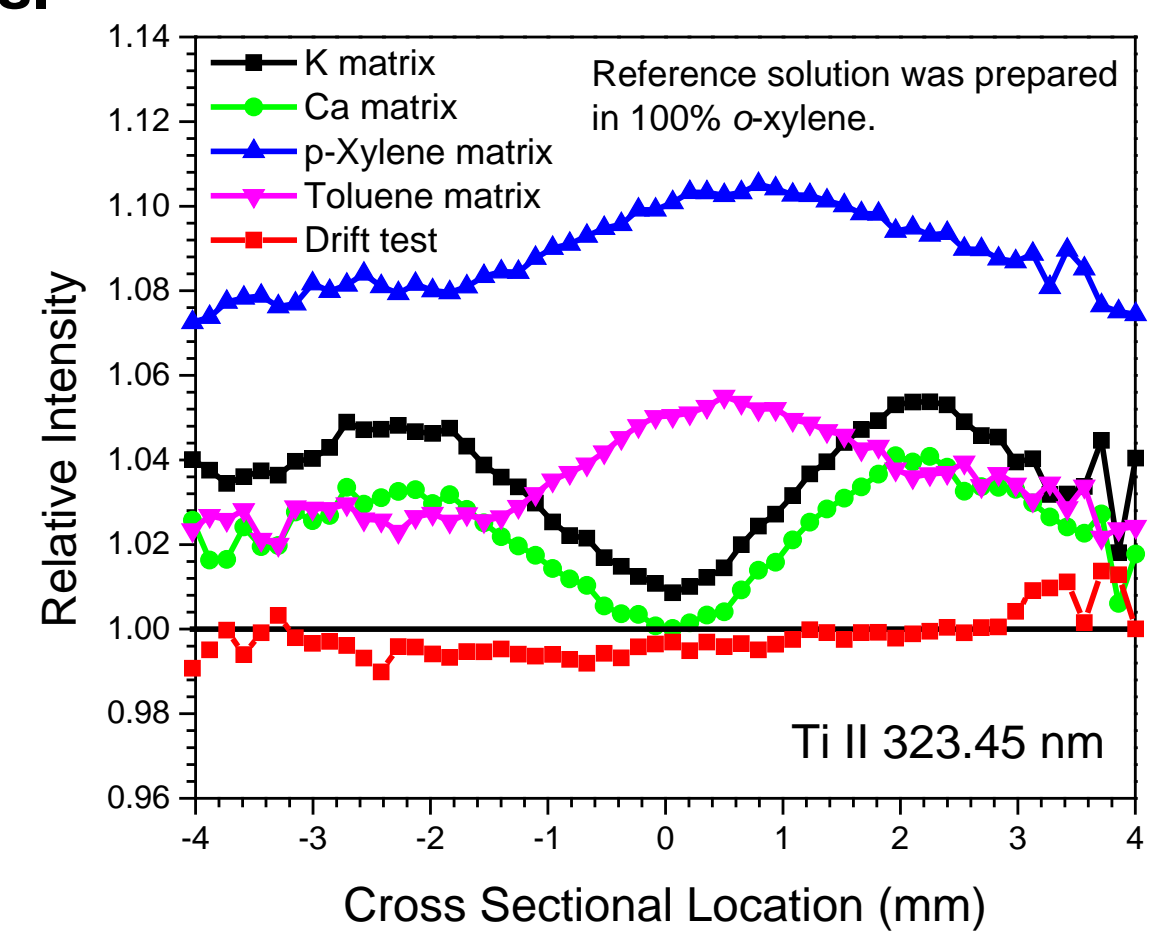


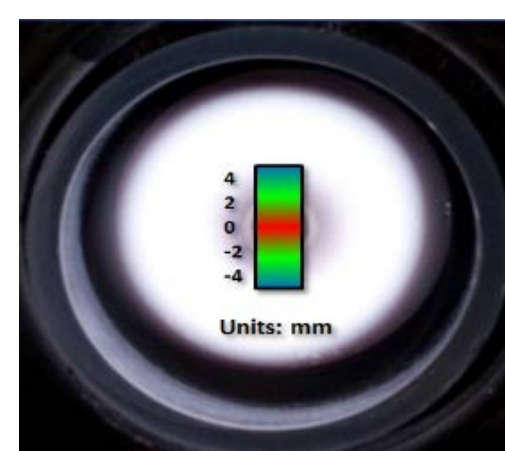
# Inductively Coupled Plasma: Techniques for Overcoming Matrix Effects

## Plasma Spatial Emission Profiles

The signal response of atomic emission lines in the ICP under the influence of different categories of interferences were examined. For each type of interference tested a spatial variation in the signal response was found along the plasma axis (either radial or axial axis). This spatial dependence translates into different determined concentrations (relative intensity) of the analyte species at various locations in the plasma, and thus allows the matrix interference to be flagged. In order to use spatially dependent signal responses to flag matrix interferences, a calibration is performed, using prepared standards, at each spatial location. The unknown sample is then analyzed at each location using the corresponding calibration curve. If the sample exhibits no matrix interference it will exhibit the same behavior as the standards, so all determined concentrations will be the same. In contrast, if an interference exists, the determined concentrations will not be the same but will be spatially dependent. This method was successfully used as matrix-effect indicator in both radial- and axial-viewing ICP for aqueous- and organic-solvents. The figure on the left below shows results for axial-viewing ICP in organic-solvent based analysis.

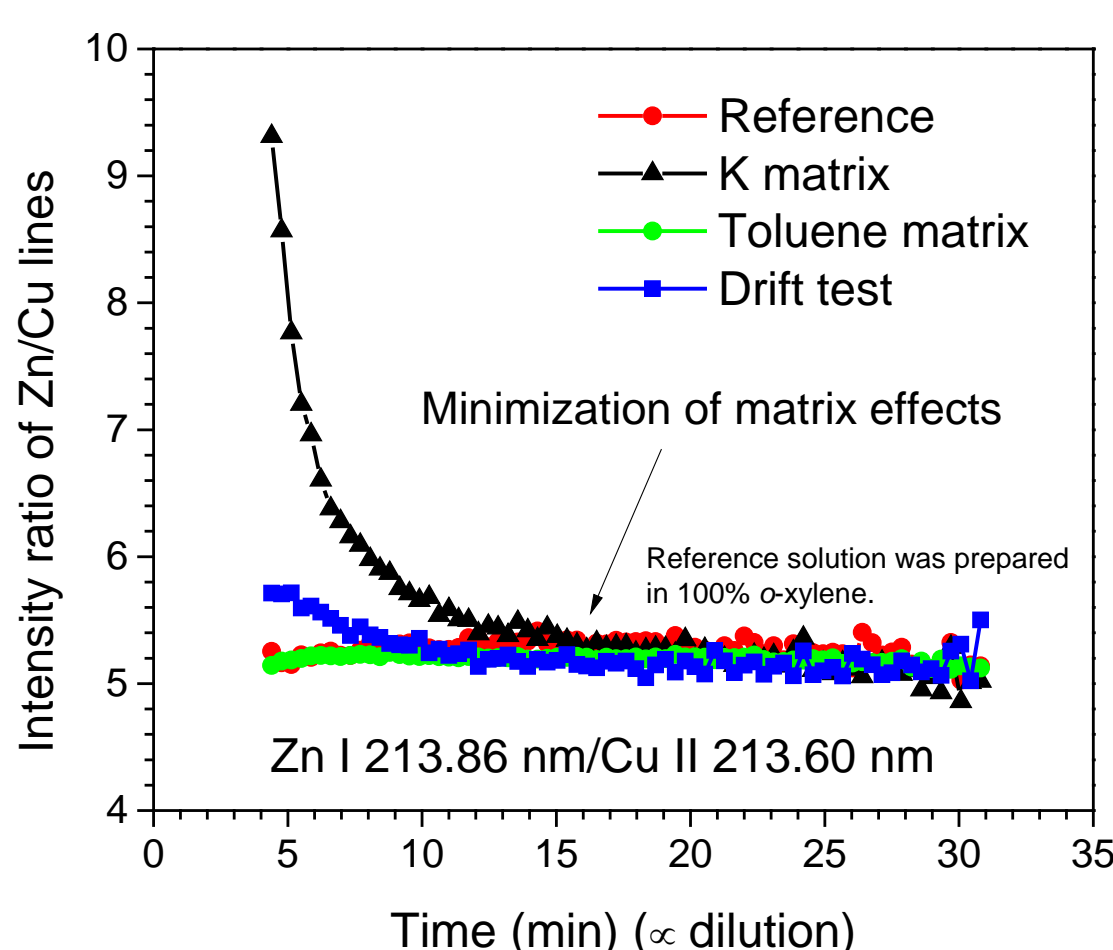


(Left) Spatial profiles of Ti II 323.45 nm emission line in four different matrices. Curved profiles were observed, flagging the presence of non-spectral interference. All sample solutions were prepared in *o*-xylene. (Below) White light image of plasma cross sectional locations.



## Intensity Ratio of Two Emission Lines From Gradient Dilutions

A gradient pump designed for delivering the mobile phase in liquid chromatography was coupled with ICP-AES in order to flag matrix interferences. The pump was used prior to the nebulizer to introduce sample solvent in a gradual and controlled way. The intensity ratio of two emission lines is monitored as the dilution of the sample solution increases. A flat profile of this ratio can be observed for sample without matrix interferences present. However, for a sample with an interference present the ratio will have a curved profile, owing to difference in lines energies between two emission lines. A suitable dilution factor can be determined when the ratio profile becomes flat (calculated from Equation 1). Unlike the traditional dilution methods, with this method analytical results free from interference can be obtained in a timely and online fashion.

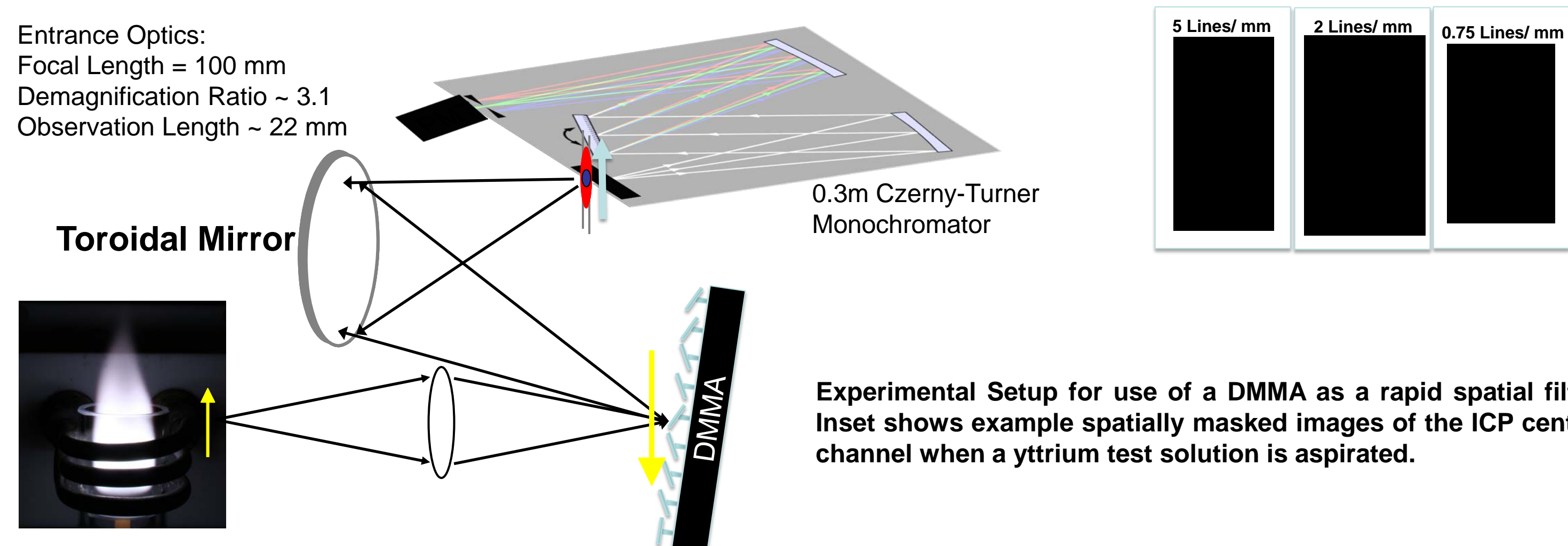


$$\text{Dilution Factor (DF)} = \frac{\text{Total analysis time (T)}}{\text{Total analysis time (T)} - \text{Time of data collection (t)}}$$

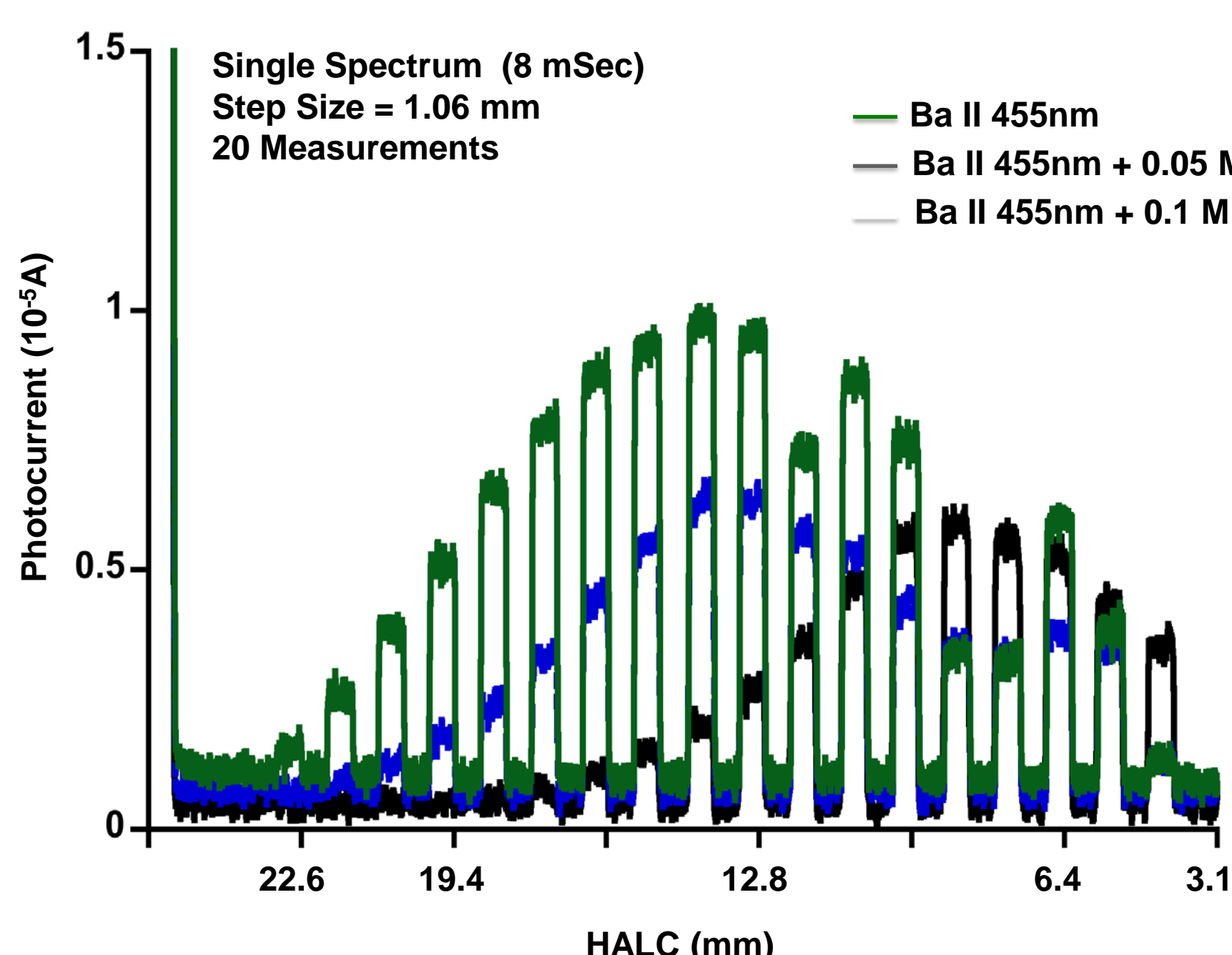
Temporal intensity-ratio profiles of Zn/Cu in the absence of a matrix (red trace), and presence of 400 ppm K (black trace) and 10% v/v toluene matrices (green trace). Drift test (blue trace) indicates there was no instrumentation drift during this analysis.

## Rapid Spatial Profiling with a Digital Micro-Mirror Array (DMMA)

The DMMA is a microelectromechanical system (MEMS) component often employed in consumer electronics (e.g. projectors). DMMA's are composed of a large number (500k-9M) of individually-addressable mirror elements, each of which can be toggled between an 'ON' and 'OFF' state under computer control and at a very rapid rate (>10kHz). Here, an inexpensive DMMA was used as an adaptable, spatially selective image filter to obtain the spatial emission profile of a plasma utilizing only a single-element detection system. As shown below in the experimental diagram, the plasma (ICP) was imaged onto the surface of a 604 x 680 pixel DMMA (Texas Instruments 0.3WVGA). When a pixel element was held in the ON state, that portion of the ICP image was reflected onwards to be reflected by a toroidal mirror onto the entrance slit of a monochromator. When a pixel was held in the 'OFF' state, that portion of the image was reflected out of the light path and lost. By this method, any portion of the plasma image could be selected for spectroscopic analysis in a rapid fashion (>4kHz). The inset to the right of the experimental diagram shows the ICP imaged through spatial masks with different line segments vertical dimension. Of course, the masks can be programmed to interrogate any arbitrary subset of pixels.



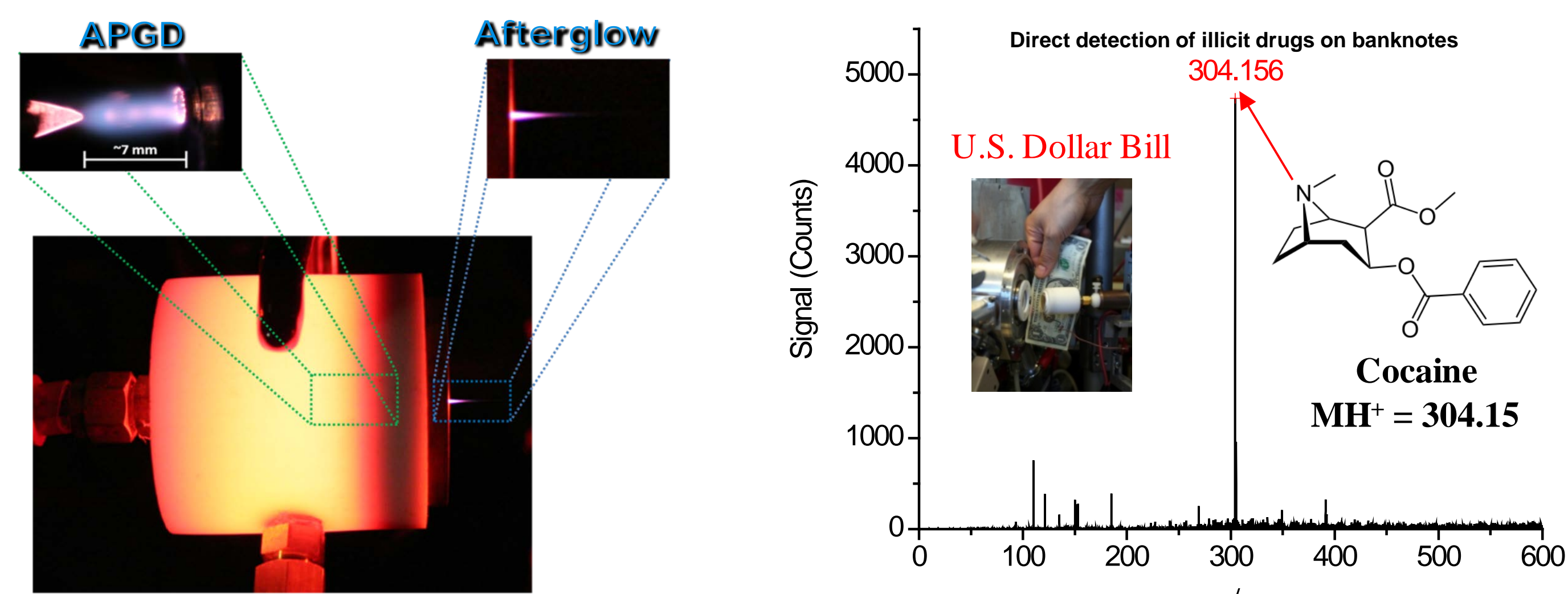
The vertical emission profile of atomic emission of a standard solution was compared with solutions containing a high concentration of concomitant matrix species sufficient to cause a matrix effect. As shown in Figure X, the vertical profile of emission of Ca(I) is markedly changed with the addition of the matrix interference species, showing enhancement low in the ICP and suppression at greater HALC values. This strategy is currently being adapted for use with a polychromator. By replacing the single channel monochromator with a simultaneous readout system, all wavelengths of interest will be monitored simultaneously and with spatial resolution.



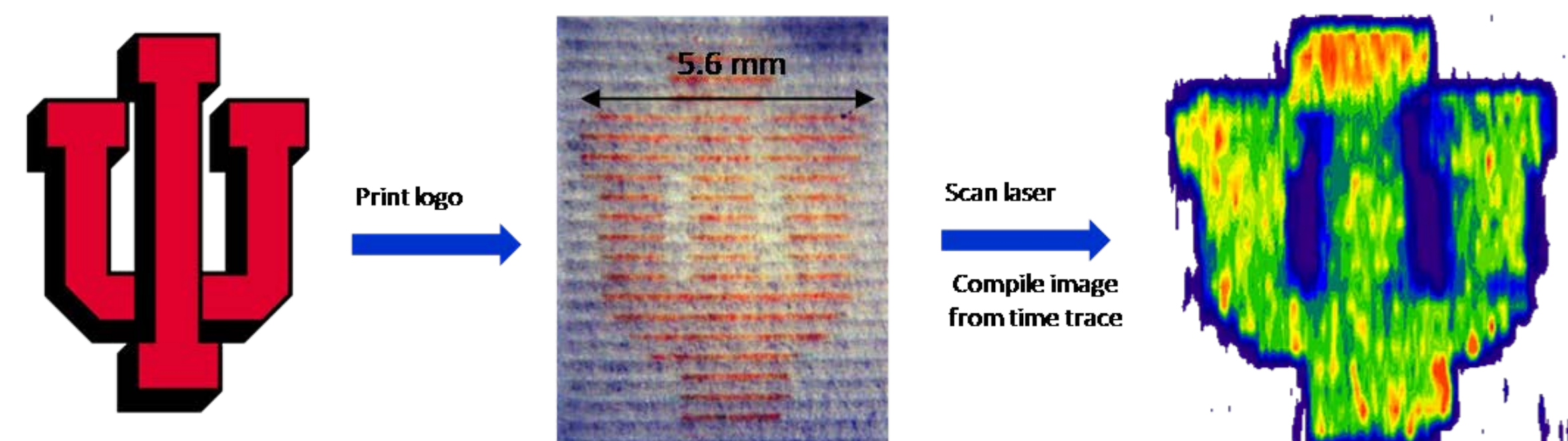
Vertical emission pattern of barium ion atomic emission in absence (green) and presence of increasing concentrations of matrix (sodium). Relative enhancement of signal at low HALC and depression of signal at higher HALC is indicative of a matrix effect.

# New Sources for Spectrochemical Analysis

## Flowing Atmospheric-Pressure Afterglow for Ambient Mass Spectrometry

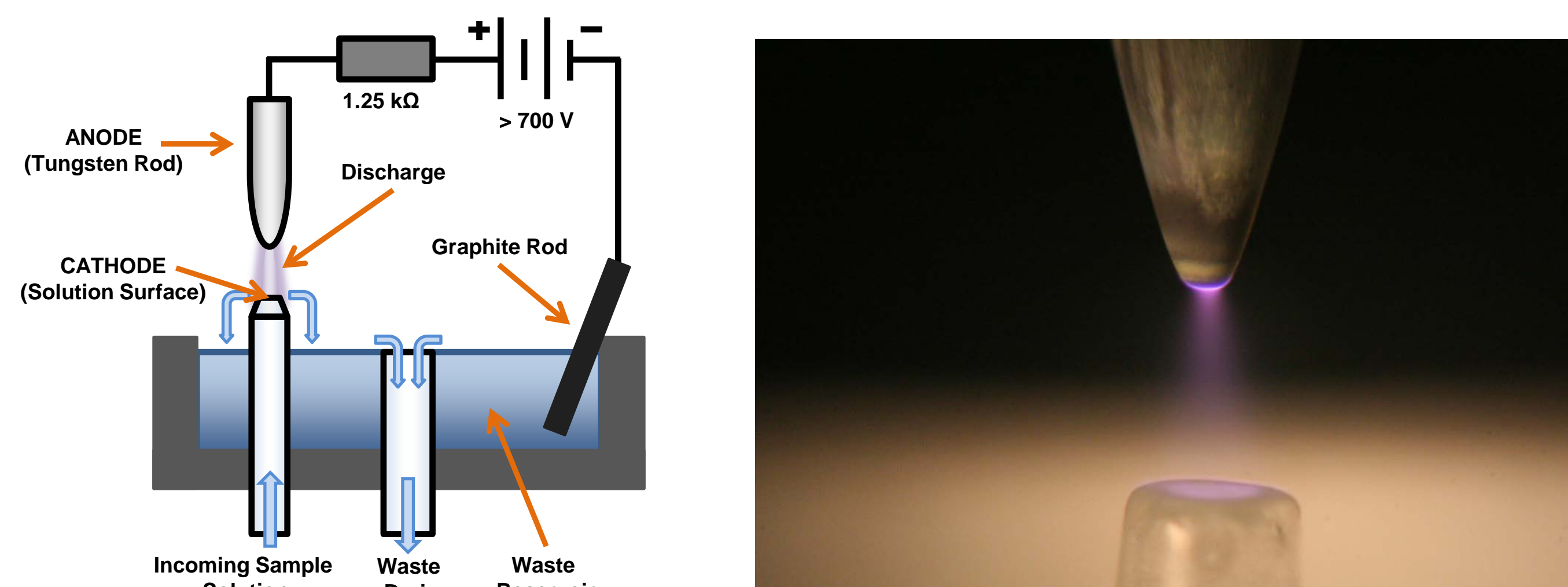


In the Hieftje lab, we are developing a novel ionization source for mass spectrometry that desorbs and ionizes analytes directly from their native substrate without the need for sample pre-treatment. The Flowing Atmospheric-Pressure Afterglow (FAPA) source is a helium atmospheric-pressure glow discharge sustained between a pin cathode and a plate anode. Ions and excited species generated by the discharge flow into the atmosphere, through a hole in the plate, yielding atmospheric reagent ions used for the chemical ionization of organic compounds. When solids or liquids are exposed to the afterglow, the signal for the molecular ions can be easily detected.

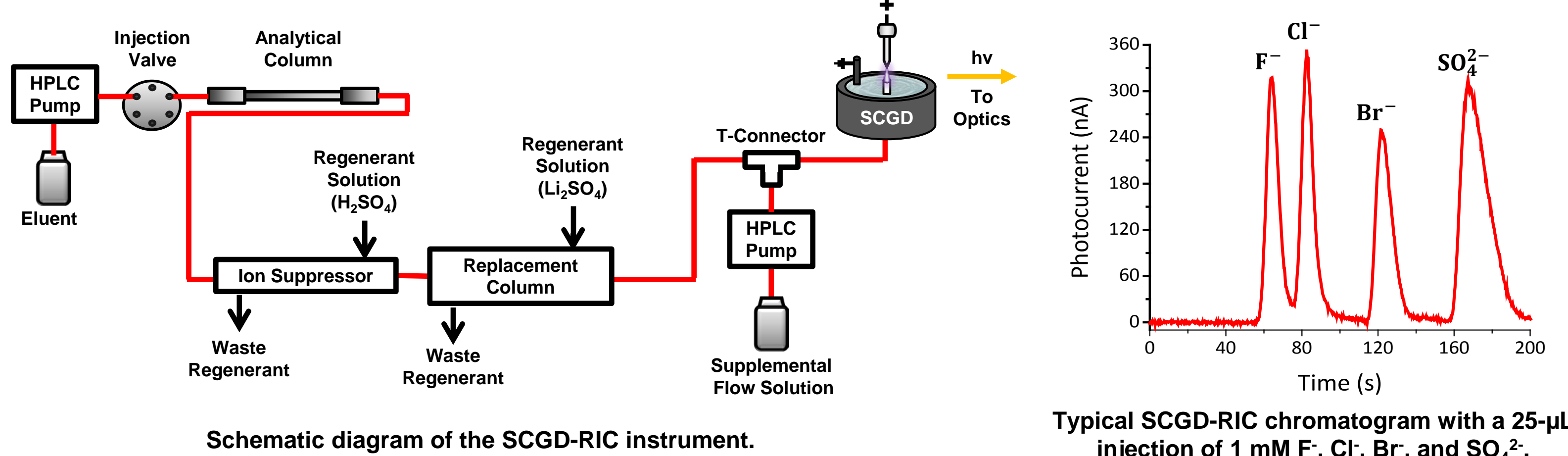


Detection limits on the order of 1 to 100 fmol and sensitivities greater than 10 counts/fmol have been achieved for a wide variety of compounds. In addition, the FAPA source has been found to be useful in chemical imaging by either raster scanning the sample under the source or by coupling with laser ablation (LA). Spatial resolutions of <20 μm have been achieved with the LA-FAPA combination.

## Solution-Cathode Glow Discharge



We are currently developing an atmospheric-pressure glow discharge sustained directly on a liquid surface for use in atomic emission spectroscopy. This unique glow discharge structure permits the plasma to eject species from the liquid directly and desolvate, atomize, and excite the elements in a single location. Elemental analysis can then be conducted by collecting atomic emission directly from the plasma-liquid interface. The solution-cathode glow discharge (SCGD) is of simple construction, consisting of a glow discharge sustained between a flowing liquid cathode (the sample solution) and a metal anode. It has shown detection capabilities on-par with much more expensive and elaborate instruments (i.e. ICP-AES). Further, the SCGD operates in the open atmosphere, uses no compressed gases, and requires very little power (e.g. 65 W).



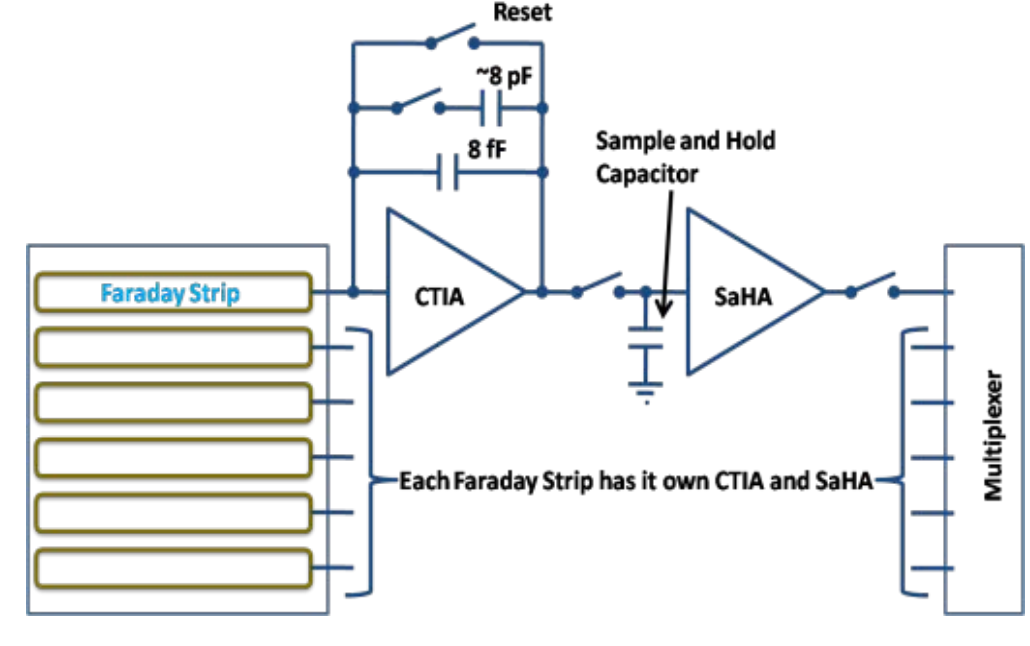
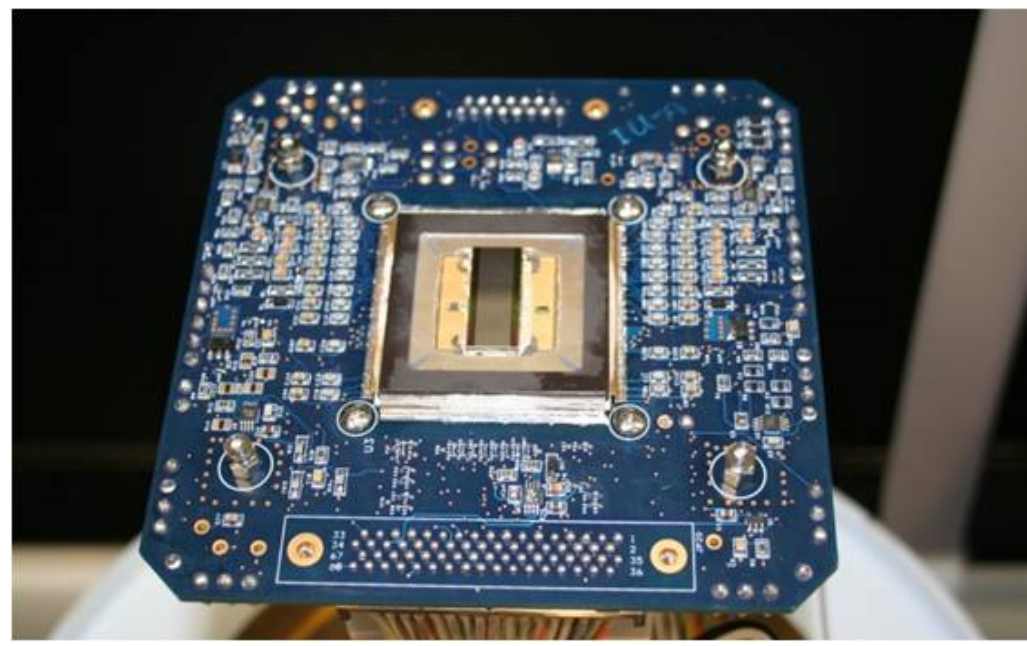
Replacement-ion chromatography (RIC) is an alternative scheme for universal ion chromatography (IC) detection in which a third ion-exchange device, referred to as the replacement column, is positioned downstream from the analytical column and ion suppressor of a traditional suppressed-IC system. The replacement column is functionalized with a desired "replacement ion," so separated analyte ions (or their counter-ions) that enter the replacement column are stoichiometrically exchanged for the replacement ions, which are then monitored downstream with a suitable detector.

The analyte replacement aspect of RIC offers a number of inherent advantages. First, since all sample ions are stoichiometrically replaced by a common replacement ion, each is detected with the same sensitivity and dynamic range, independent of its original chemical form. As a consequence, each eluted species can be quantified from a single calibration curve. Apart from benefits to calibration, detectors employed in RIC need to be optimized for only the replacement ion, so selective IC detectors can be used as universal detectors if an appropriate replacement ion is selected. In addition, the combination of detector and replacement ion can be chosen to provide exceptional sensitivity.

Recent work has focused on use of the SCGD as a detector for RIC. The SCGD is an attractive detector for RIC for many reasons. First, because the SCGD samples directly from a flowing stream of sample solution, the detector response is very rapid, promoting chromatographic resolution. Further, since the surface of the flowing solution is continually replenished, the detector system experiences no memory effects or lingering contamination from the analysis of highly concentrated samples. Most importantly, the SCGD has demonstrated exceptional sensitivity for alkali metal species. Thus, when an alkali metal is selected as the replacement species in an SCGD-RIC setup, the system has the potential to be highly sensitive for RIC detection.

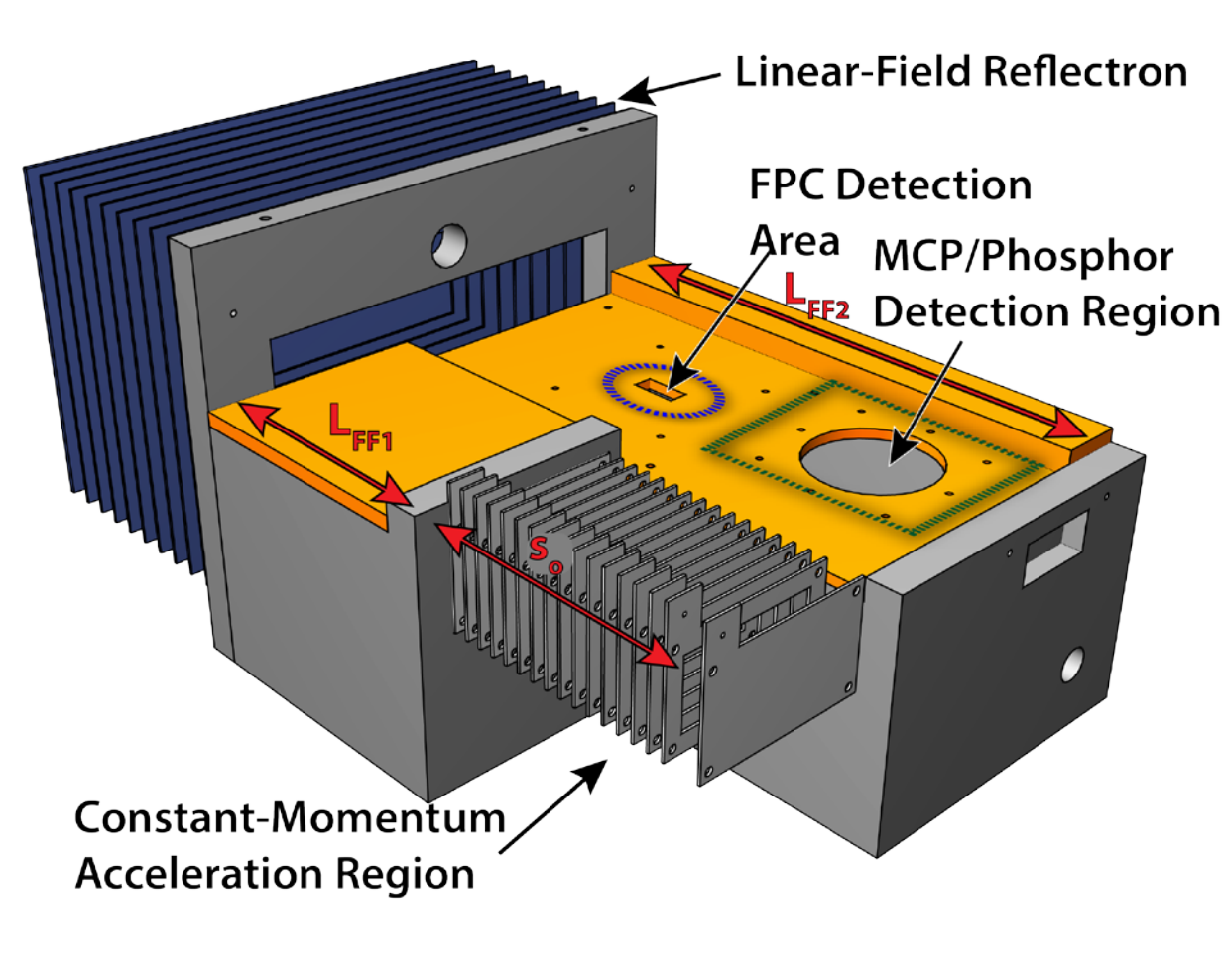
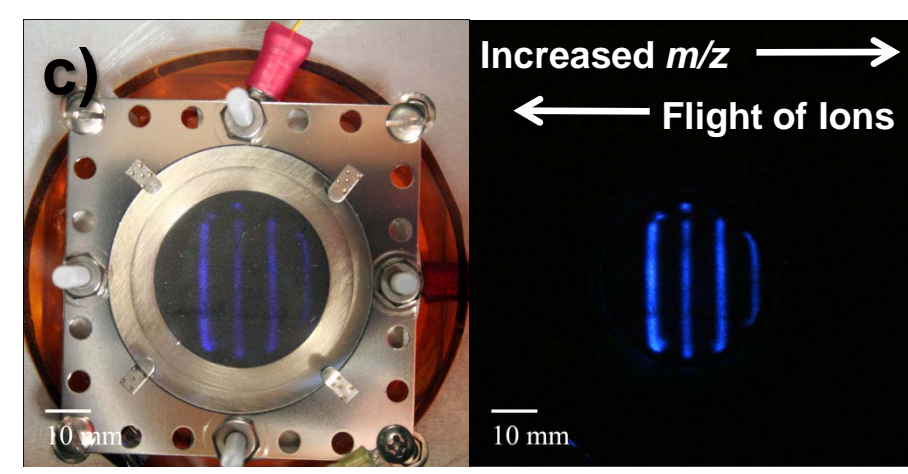
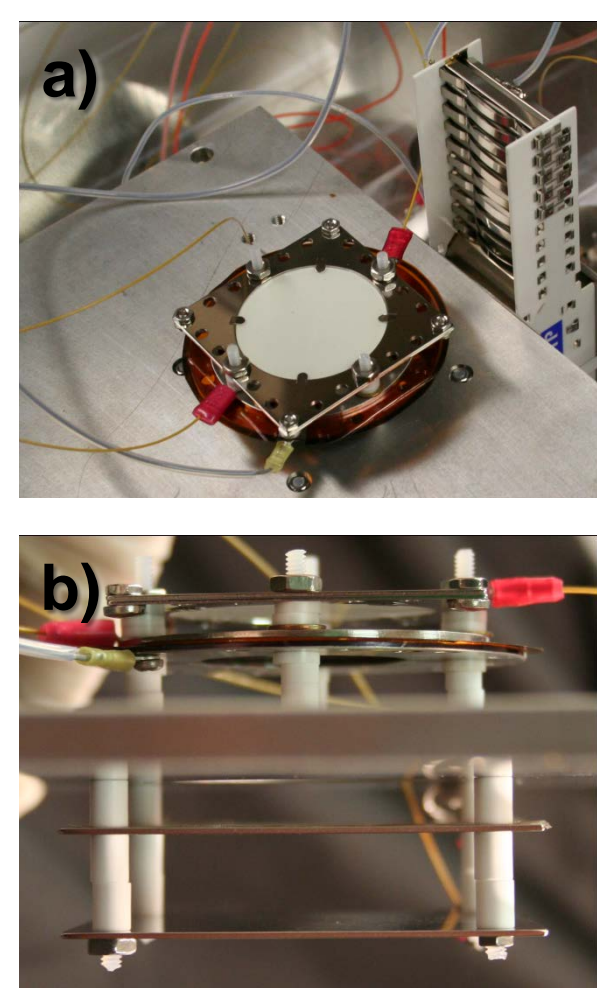
# Novel Mass Spectrometers

## Simultaneous, Multichannel Array Detector



A multi-channel Faraday-strip array detector, termed the focal plane camera (FPC), has been constructed as a joint project among the University of Arizona, Pacific Northwest National Laboratory, and Indiana University. The current generation contains 1696 titanium-nitride-coated aluminum strips, each of which is 8.5  $\mu\text{m}$  wide and spaced on 12.5  $\mu\text{m}$  centers. Each individual detection element (IDEL) is wired to its own capacitive trans-impedance amplifier (CTIA) and sample and hold amplifier (SaHA), which allows truly simultaneous detection. The circuit (shown above) has several important characteristics. First, the output voltage of the amplifier is inversely proportional to the capacitance in the feedback loop of the operational amplifier. With this device, capacitors on the order of 8 fF are used, resulting in output voltages for a single ion in the  $\mu\text{V}$  range. Furthermore, multiple capacitors can be placed in the feedback loop in order to individually select the gain of each IDEL. A final advantage of this design is the ability to non-destructively read out each channel multiple times, which allows any read noise associated with the device to be greatly reduced. The goal is to collect the entire atomic mass spectrum continuously with high resolution.

## Distance-of-Flight Mass Spectrometry (DOFMS)



a) Phosphor screen-MCP detector assembly used for DOFMS is shown. The phosphor screen is visible as a white plate. b) The DOF detector is pictured from a side-on view: ions travel into the image between the bottom two stainless steel plates. A voltage pulse is applied to the bottom plate; the top plate is cut out in the center and is grounded. c) This image shows the DOFMS detector with the DOF lines of copper and zinc isotopes from a brass sample.

### Phosphor screen-MCP Detection Assembly

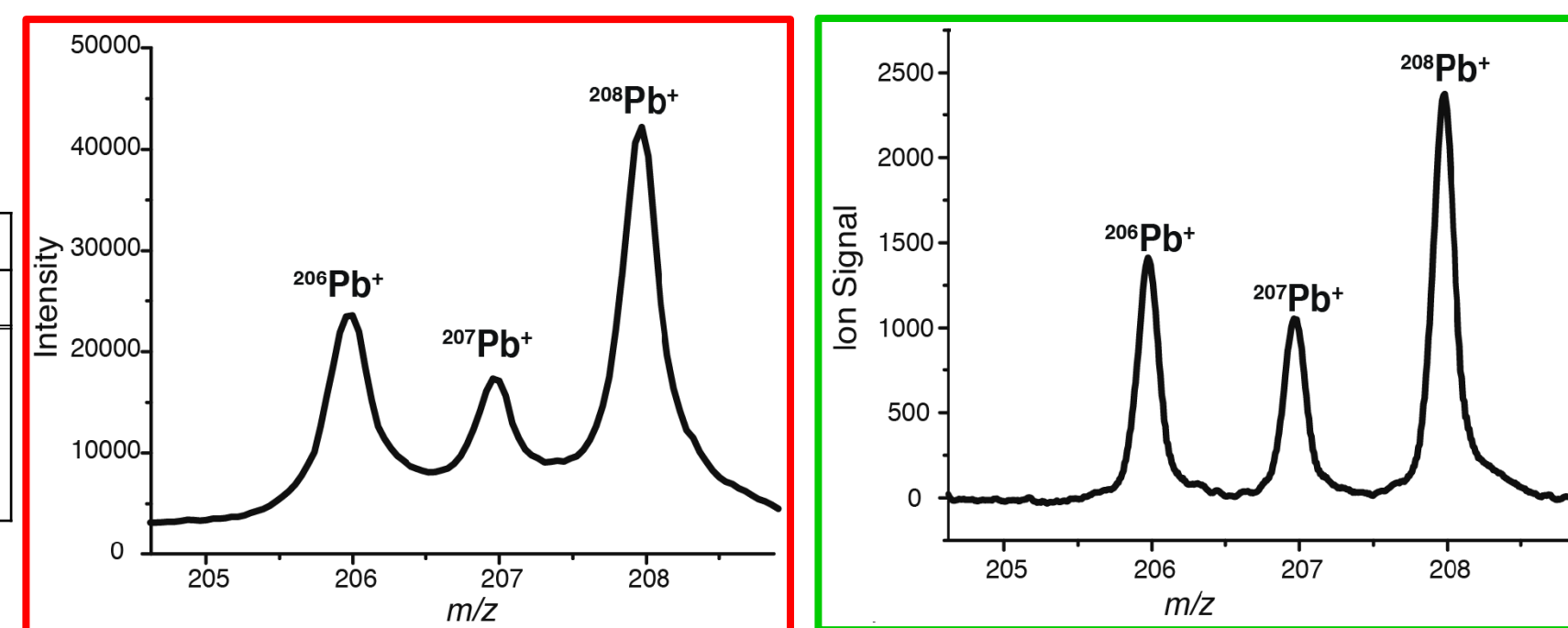
### DOFMS Schematic Diagram

We are currently developing a new type of mass analyzer for distance-of-flight mass spectrometry (DOFMS). In contrast to traditional time-of-flight mass spectrometers (TOFMS), which measure the time required for each  $m/z$  to traverse a known distance, DOFMS focuses ions at different locations along a detector surface based on  $m/z$ . A constant momentum acceleration (CMA) pulse is used to extract ions that are subsequently mass-separated in a field-free region and energy-focused in a linear-field reflectron. At the energy focus time ( $t_{ef}$ ), mass-separated ions are pushed onto a spatially sensitive detector surface to evaluate the distance the ions have travelled during the time period following CMA extraction. The distance of flight is inversely proportional to  $m/z$ . The DOFMS is architecturally simple, has an unlimited  $m/z$  range, has greater detection efficiency than TOFMS, and does not require fast electronics or timing circuits.

Two types of detectors have been utilized for DOFMS: a phosphor screen-microchannel plate assembly that images DOF mass spectra at the detection time (above left) and the FPC detector described above. The operation of the DOFMS is the same for each detector and it is possible to detect ions simultaneously with both detectors (above right). Below is a table of representative mass resolutions for each detector when operated with a glow discharge ionization source and two corresponding mass spectra for lead.

DOF resolving power attained with:

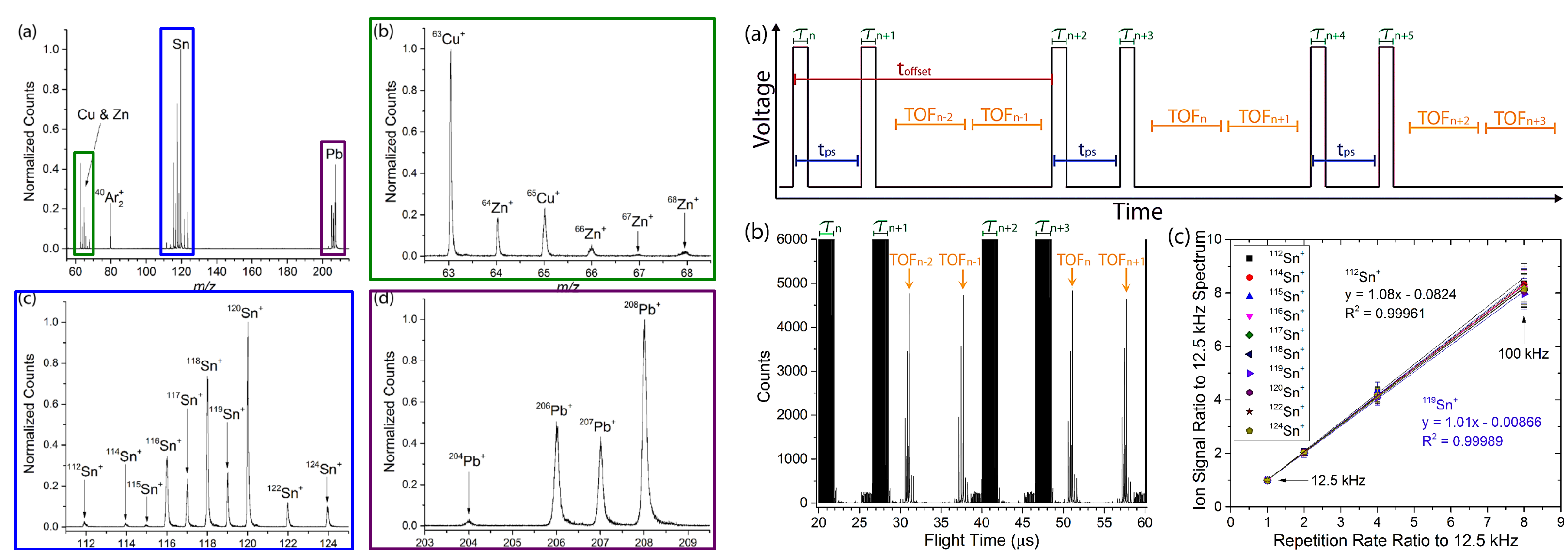
Isotope	MCP/Phosphor Detector		FPC Detector	
	$\Delta d$ (FWHM)	R (FWHM)	$\Delta d$ (FWHM)	R (FWHM)
$^{63}\text{Cu}$	620 $\mu\text{m}$	580	250 $\mu\text{m}$	1100
$^{120}\text{Sn}$	920 $\mu\text{m}$	380	325 $\mu\text{m}$	1040
$^{208}\text{Pb}$	700 $\mu\text{m}$	510	270 $\mu\text{m}$	1030



## Zoom-Time-of-Flight Mass Spectrometry (Zoom-TOFMS)

Zoom-TOF mass spectrometry is a new approach to time-of-flight mass spectrometry (TOFMS) that makes use of both conventional, constant-energy acceleration (CEA), and constant-momentum acceleration (CMA); with CMA-TOFMS used as a zoom mode. Constant-momentum acceleration is an attractive complement to CEA-TOFMS because it can provide superior mass resolution, albeit over a limited mass range. Improved resolution is achieved by focusing ions onto the TOF detector at  $t_{ef}$ , as described for DOFMS, but only those ions detected at or near  $t_{ef}$  will be in focus. Any narrow portion of the mass spectrum can be selected to be detected at  $t_{ef}$  and it is, therefore, possible to improve both mass resolution and instrument sensitivity through mass-range isolation and higher repetition rates.

The zoom-TOFMS concept has been tested on a 43-cm orthogonal-acceleration TOFMS system with a linear-field reflectron and a glow discharge ionization source. Mass resolution improvement of 1.4-1.6x is typical when comparing CEA- and CMA-TOFMS (below left). The narrow target mass range in CMA mode can also be isolated and the instrument can be operated at up to 100 kHz (below right).



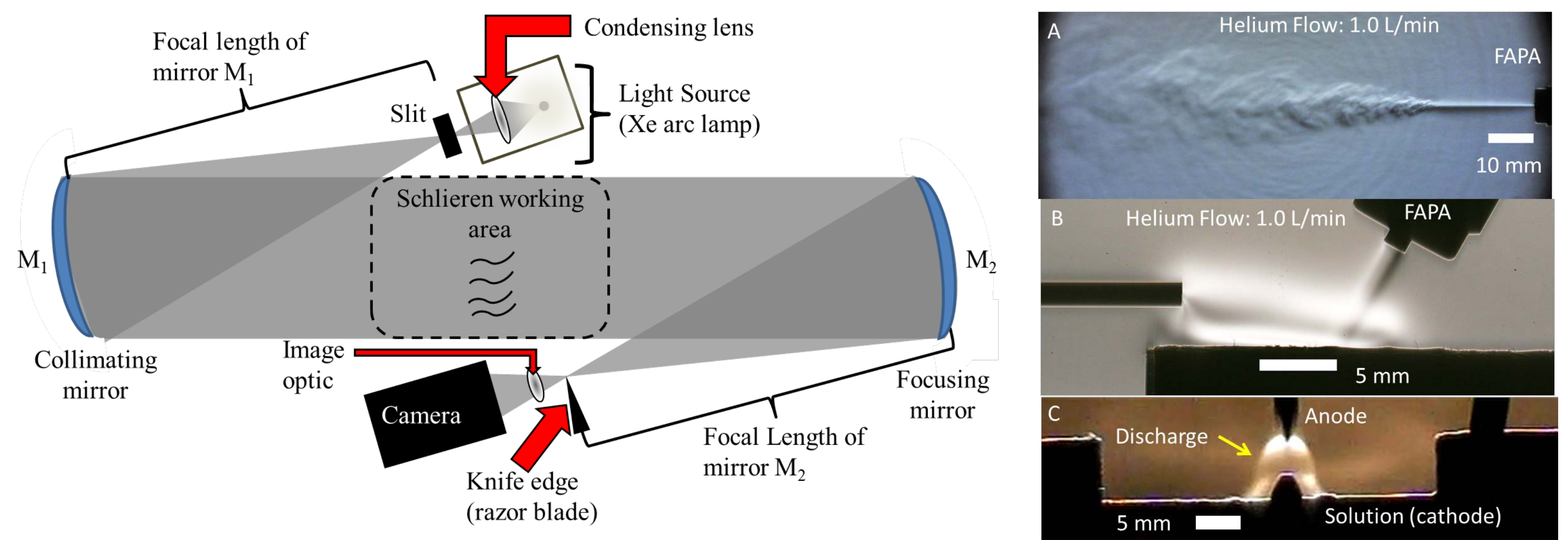
Above left: Results of a GD-zoom-TOFMS analysis of a copper sample with a solder plug. Part a is a CEA-TOF mass spectrum that shows all sample components with similar resolving power (FWHM, approximately 1330). Parts b-d show mass spectra from three individual CMA-TOFMS (zoom) experiments conducted to determine the isotopes of copper and zinc, tin, and lead in the GD sample. In each of the CMA-TOFMS experiments the  $RP_{FWHM}$  observed for the target mass was improved compared to the CEA-TOFMS spectrum in part a by an average of 1.45x.

Above right: Timing diagram for (a) and outcome of (b-c) increasing the repetition rate in a CMA-TOFMS experiment. A timing diagram in shown in part a for the acceleration pulse duration ( $t_{acc}$ ), the detection time (TOF), burst-mode acceleration-pulse spacing ( $t_{off}$ ), and offset time between bursts ( $t_{offset}$ ). Part b shows the CMA-TOFMS spectrum for the detection of singly charged tin isotopes when a repetition rate of 100 kHz is used. Part c shows a linear increase in integrated peak area for each of the tin isotopes as  $t_{offset}$  was lowered from 160 to 20  $\mu\text{s}$  (12.5 to 100 kHz average repetition rate).

# Spectrochemical Imaging Techniques

## Schlieren Imaging: an old dog learning new tricks

Schlieren imaging is an optical technique used for visualizing small changes in refractive index. The technique originated with observations of candle flames by Hooke in 1665. This technique has primarily found usage for flow visualization within fluid mechanics problems. However, there are numerous applications for this technique within the Hieftje laboratory. A schematic diagram of the schlieren imaging system can be seen below (left). Light from an arc lamp is defined by a slit before collimation by a focusing mirror, a second mirror focuses the light back to the original slit on a beam stop (razor blade) which produces an even darkening of the light field. Changes in refractive index within the schlieren working area manifest as areas of enhancement or attenuation of light in the camera. Several applications of the schlieren source to plasma sources in the lab are shown below (right).

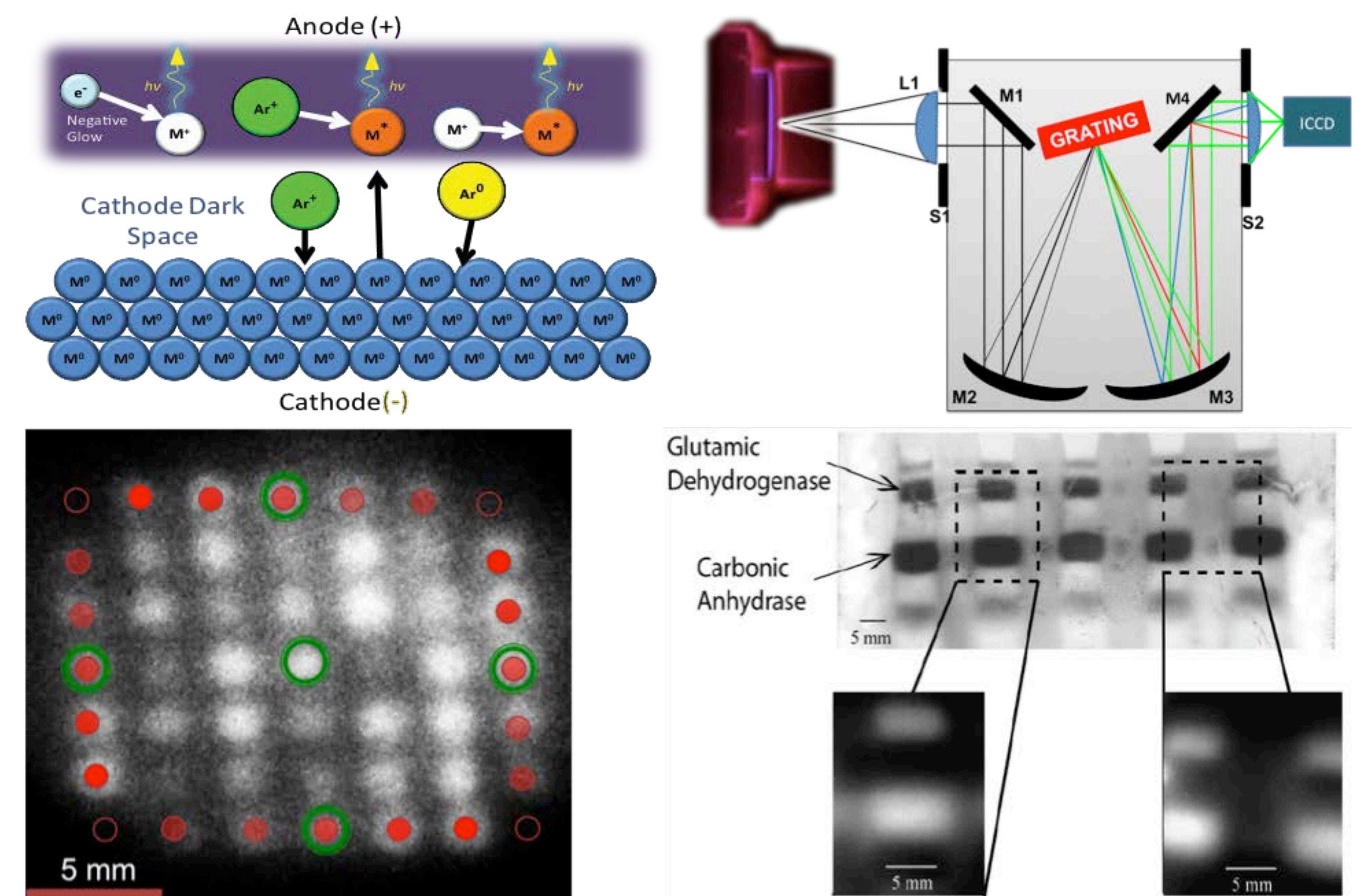


Above left: Laboratory setup for the Schlieren imaging system.

Above right: Schlieren images of A) Pin-to-capillary FAPA source showing transition to turbulent flow, B) FAPA source impinging on a surface at 60 degrees and C) Solution-cathode glow discharge which shows "mushroom" forming around discharge

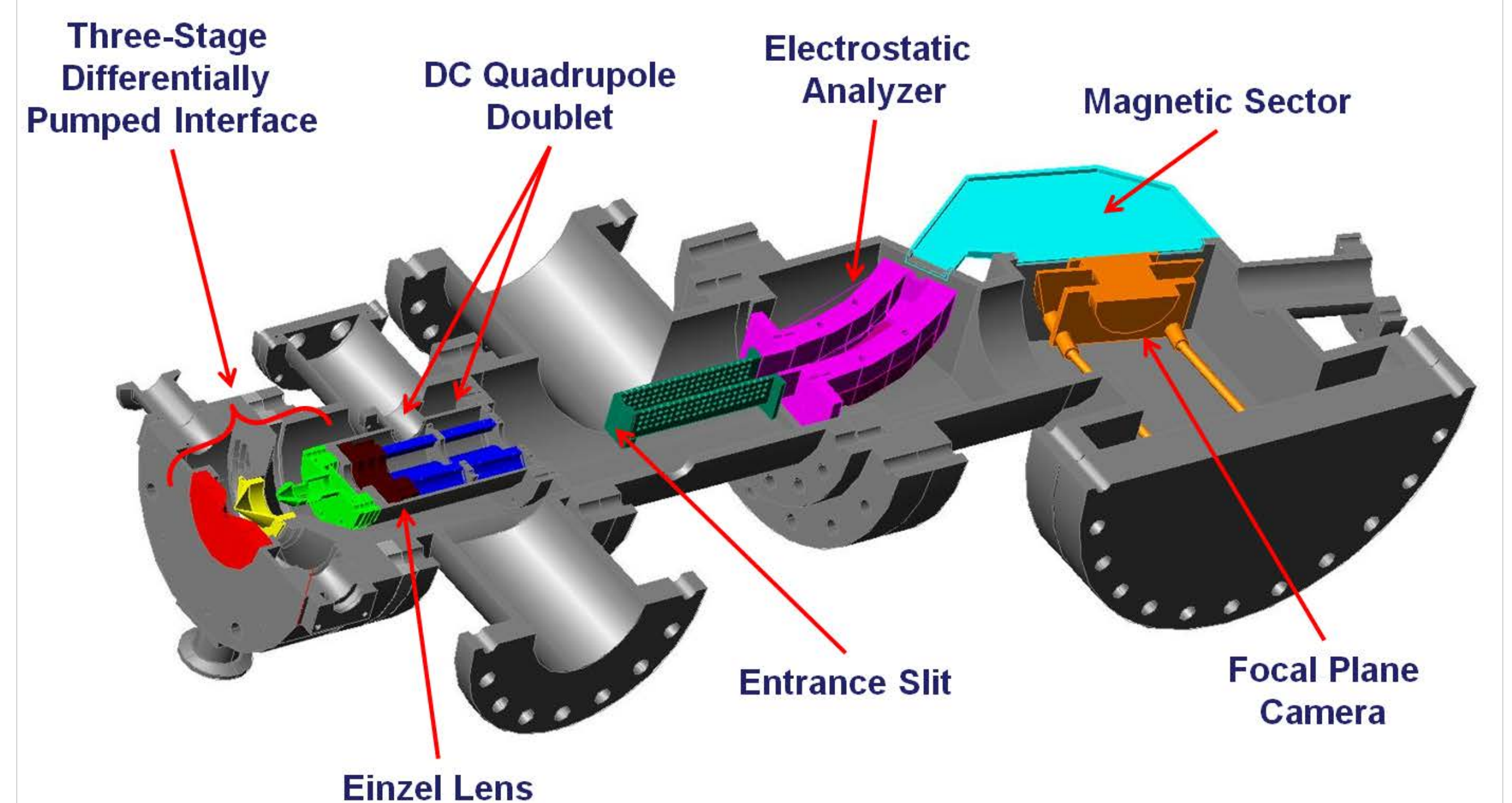
## Glow Discharge Imaging Spectrometry

Glow discharge optical emission spectrometry typically is used for bulk and depth analyses in situations where a degree of spatial homogeneity in the sample is assumed. We have devised ways to spatially resolve the emission from glow discharge sources in a manner that is representative of the elemental surface concentration of a sample. Current work is focused on the application of glow discharge imaging technology to emission measurements from silver-stained protein blots (obtaining higher sensitivity than traditional techniques) and measurements of liquid samples that have been deposited onto a surface with an inkjet printer (allowing dozens of parallel measurements of liquid samples and a concentration step for an extended dynamic range). Another goal for the glow discharge imaging project to couple the lateral elemental distribution information obtained for a sample to the precise depth profiling information. Pairing these technologies would enable three-dimensional profiling of surface samples.



Clockwise from top left: A glow discharge operates by sputtering away the surface of a solid sample when a kilovolt potential is applied between the anode and cathode, a monochromatic imaging spectrometer can be used to generate a 1-nm bandpass of spatially resolved optical emission from the glow discharge, a silver-stained protein blot can be characterized by silver emission from the glow discharge, and an array of samples can be printed on a surface and analyzed with a glow discharge.

## Miniature Mattauch-Herzog Geometry Mass Spectrograph



A miniature Mattauch-Herzog mass spectrograph (MHMS) has been constructed. This instrument, though small in size, has the ability to simultaneously and continuously disperse and focus all  $m/z$  values within the atomic range in two convenient  $m/z$  windows. Previously, the MHMS has been coupled to a variety of atomic ionization sources, including the inductively coupled plasma (ICP), glow discharge (GD), and microwave plasma torch (MPT). Molecular species as well as positive and negative ions have been detected with the MHMS through the use of the flowing atmospheric pressure afterglow (FAPA) source. Furthermore, the MHMS has been used with single channel ion detectors, such as the secondary electron multiplier (SEM), and multi-channel detectors, such as the electro-optic imaging detector (EOID). More recently, a Faraday-strip array detector has been coupled to the MHMS, enabling simultaneous  $m/z$  measurements with figures of merit that rival or exceed those of the well-established SEM. Current efforts with the MHMS are focused on adding a collision/reaction cell or a collision-based interface to remove unwanted ions and/or reduce the energy spread of the ion beam.