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 was 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 intensities) 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, 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-solvent matrices. The figure on the left below shows results for axial-viewing ICP in organic-solvent based analysis.

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 interference 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.

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

The DMMA is a microelectromechanical system (MEMS) component often employed in consumer electronics (e.g., projectors). DMMDAs 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 (>1kHz). Here, a 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, plasma was imaged onto the surface of a 640 x 680 pixel DMMA (Texas Instruments 0.3WVGA). When a pixel was held in the ON state, that portion of the ICP image was reflected onwards to be focused 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 spectrophotometric 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 illuminate any arbitrary subset of pixels.

New Sources for Spectrochemical Analysis

Flowing Atmospheric-Pressure Afterglow for Ambient Mass Spectrometry

In the HiElFlab 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 hollow 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.

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 a 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 little electric 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, since 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 alkaline metal species. Thus, when an alkaline metal is selected as the replacement species in an SCGD-RIC setup, the system has the potential to be highly sensitive for RIC detection.
DOF resolving power attained with:

Distance-of-Flight Mass Spectrometry (DOFMS)

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. A subsequent generation contains 1696 thin-film-nitride-coated aluminum strips, each of which is 8.5 μm wide and spaced on 12.5 μm centers. Each individual detection element (IDE) is wired to its own capacitive trans-impedance amplifier (CTIA) and sample and hold amplifier (S/H/A), 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 pV range. Furthermore, multiple capacitors can be placed in the feedback loop to in individually select the gain of each IDE. A detailed treatment 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.

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 device. 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_f, as described for DOFMS, but only those ions detected at or near t_f will be in focus. Any narrow portion of the mass spectrum can be selected to be detected at t_f 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).

Schlieren Imaging

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 Hiettje 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) that 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).