

Novel Glow Discharges and Spectrometers to Use With Them

Gary M. Hieftje¹, Steven J. Ray¹, Charles G. Barinaga², Elise A. Dennis¹, Carsten Englehard¹,
Christie G. Enke¹, Gerardo Gamez³, Alexander W. G. Graham¹, Volker Hoffmann⁴, David W.
Koppenaar², Jacob T. Shelley¹, Michael Webb⁵

¹Dept. of Chemistry, Indiana University, Bloomington, IN 47405 USA

²Pacific Northwest National Laboratory, 902 Battelle Blvd. MS K8-98, Richland, WA 99352

³Present address: EMPA-Materials Science & Technology, Laboratory For Mechanics Of
Materials & Nanostructures CH-3602 Thun, SWITZERLAND

⁴Leibniz-Institut Für Festkörper- Und Werkstofforschung, Dresden, P.O. Box 27 01 16, Dresden
D-01171 GERMANY

⁵University of North Carolina-Wilmington' 6-1 S. College Road' Wilmington, NC 28403

Glow discharges have enjoyed a long and productive history and have been employed effectively with both mass and optical spectrometry. However, new glow-discharge configurations continue to appear and novel spectrometer systems to exploit them keep being introduced. In this presentation, several of these new alternatives will be described and evaluated.

Two of the newly built glow discharge systems are based on atmospheric-pressure plasmas. At such elevated pressures, the glow-discharge spatial structure persists but is reduced in dimensions. As a result, the negative glow appears as a small disk at the tip of the cathode surface. Because of these small dimensions, the cathode can be sputtered very effectively. Indeed, if the cathode surface is a conductive liquid, the solution surface appears to be disrupted spontaneously in an electrospray mode. Species liberated during this process can then be excited and their emission viewed.

In another atmospheric-pressure configuration, a helium glow discharge can be used to generate reactive species that, in turn, can both desorb and ionize analyte species from solids, liquids, or gases. The resulting mass spectra are extraordinarily simple and therefore easy to interpret. This sort of source has proven valuable in a new field termed ambient mass spectrometry.

In a more conventional arrangement, a pulsed radiofrequency glow discharge can be used to sputter materials from the surface of nonconductive samples. In the particular embodiment to be described here, the sample surface is a blot taken from a two-dimensional gel-based separation of proteins. Because the discharge has a short duration, the location of each protein-containing spot can be identified and the metals associated with the protein determined quantitatively. The same basic configuration can be used for the three-dimensional analysis of conductive or non-conductive solid materials.

In the final system, a glow discharge is used with a completely new kind of mass spectrometer, based on distance-of-flight (DOF) technology. Somewhat similar to time-of-flight mass spectrometry (TOFMS), DOFMS determines the masses and concentrations of particular ions at a specific flight time but at different locations in space. In contrast, TOFMS measures ions at a particular point in space but at different times.

From these examples, it should be clear that glow discharges are not only of historical interest and current importance, but also that they offer tremendous promise for the future of both elemental and molecular spectrometry.