The 1983 Pittsburgh Conference: A Special Instrumentation Report

If the 34th annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy were to be described in one word, that word might well be "sober." Admittedly, attendance, the number of exhibitors, and the number of booths were all up again, with attendance breaking the 20,000 mark for the first time to reach 21,728. Gone, however, were the magicians, the man in the alligator suit, and the festive air that permeated last year's exposition. Gone, too, was the rosy optimism of last year that had large instrument companies predicting substantial increases in sales despite the recession. Those large increases never materialized and, in a few product lines, sales even dropped slightly. For the coming year, the companies are expecting only very modest sales increases. There were also few really new instruments at the show. Most companies seemed to be consolidating the advances they had made in recent years. About the only discernible trends were the introduction of color graphics on video display units—a cosmetic addition, albeit a useful one in many cases—the appearance of less expensive models in many product lines, and the presence of more products with a biological orientation. Both the potential and the need for innovation were still present, however, as witnessed by some statistics disclosed by Hewlett-Packard Company. Last year, fully 50 percent of that company's instrument sales were accounted for by products introduced within the past 3 years. Furthermore, the company devoted to research and development a sum equivalent to about 10 percent of total sales, a figure substantially higher than that for U.S. industry as a whole. Comparable figures may vary slightly from company to company within the industry, but they tell much the same story. Gone forever, it would seem, are the days when a Beckman DU or a Spectronic 20 can dominate sales in a particular category year in and year out with no significant changes.

Quadrupoles Appear in New Instruments

The quadrupole is a simple, inexpensive way to separate ions by mass. In recent years, quadrupoles have begun to appear much more frequently, either alone in relatively inexpensive instruments for mass spectroscopy (MS) or as one or more of the segments of an MS/MS instrument that provides both sample separation and identification. At this year's Pittsburgh Conference, there were three new instruments that wed a quadrupole to another instrument to facilitate chemical analysis. Two of the instruments represent important advances in MS technology.

The quadrupole is a simple mass filter constructed by placing four stainless steel rods in close proximity lengthwise to form a passageway for ions. When both a radio-frequency (RF) current and a direct-current (d-c) voltage are applied to the rods, ions passing between them travel in a complicated pathway. For any given combination of RF current and d-c voltage, only ions of one mass-to-charge (m/z) ratio will follow a stable trajectory all the way through the center of the quadrupole; all others will hit the sides of the instrument and be captured. By scanning through various combinations of RF current and d-c voltage, it is possible to produce a conventional mass spectrum. The quadrupole gives results that are nearly as good as those produced by a magnetic sector instrument, but it is smaller and less expensive. It is also much simpler to operate under computer control.

Donald J. Douglas and his colleagues at Sciex Inc. of Thornhill, Ontario, have combined a quadrupole with an inductively coupled plasma (ICP) source to produce a new instrument called the Elan ICP/MS Elemental Analysis System. The ICP is a source that has sparked new interest in atomic emission spectroscopy (AES), which identifies elements by their optical emissions after they have been excited in the plasma (*Science*, 24 Mar. 1978, p. 1324). In the ICP, argon flows through a cylindrical quartz "torch," the end of which sits inside an induction coil. An RF current through the coil creates the plasma by accelerating argon to high energies; it also confines the plasma. A second argon stream carries a nebulized sample into the plasma, where the high temperatures (6000 to 10,000 K) ionize the individual atoms. In AES, light emitted by the excited ions is measured photometrically. Douglas's group in Thornhill, however, has found a proprietary way to channel the ions into a quadrupole detector.

Much of the first work on ICP/MS was conducted by Stan Houk and Allen Gray of Iowa State University. They used a small orifice, 0.003 inch in diameter, to allow some of the ionized atoms to escape the plasma and enter the quadrupole. Since the length of the orifice must be less than its diameter, they used a very thin sheet of platinum foil to separate the plasma from the MS vacuum system, which meant they had to work at low pressures. But the small orifice plugged up frequently and the thin foil could not withstand the heat from the plasma.

Douglas was able to get around this problem by making use of a cryogenic pumping system developed at Sciex. They use an orifice ten times as large, 0.03 inches in diameter, so they can use a much thicker metal foil that will withstand the heat better; they can also work at atmospheric pressure. A mechanical pumping system is used to withdraw about 10^{-4} of the atoms in the plasma through the orifice into the interface; the cryogenic pump then pumps a small fraction of the gas in the interface into the spectrometer; a supersonic expansion nozzle cools the ions to about 14 K before they enter the quadrupole.

The foremost advantage of ICP/MS compared to ICP/AES, says Douglas, is simplicity. Optical spectra contain many different emission lines for each element, so that the spectrum is complex and there is a great deal of overlap between elements. There are also what is known as matrix effects, in which the signal from elements such as calcium or aluminum mask the signals from other elements. In ICP/MS, there is only one peak for each atom, corresponding to its *m/z* value. (Multiply charged ions would produce additional peaks, but these are produced only in very small quantities.) An *m/z* peak is produced for each isotope of each element, so there is some overlap in the spectra, but there is at least one *m/z* value for each element that is unique and that can be used for quantitation. "Mother Nature was kind to us," says Gordon Rosenblatt of Sciex, "in that there is no overlap for any of the elements that have only one isotope."

The multiplicity of spectral lines is, in fact, a benefit, since it makes it possible to quantify the concentration of an element by isotopic dilution. If one were trying to determine the concentration of copper, for example, one would spike part of the sample with a known amount of copper-65. By comparing the ratio of copper-65 to copper-63 in the sample with the new ratio in the spiked sample, it is possible to determine the absolute concentration of copper in the original specimen.

The Elan system can analyze more than 90 percent of the elements in the periodic table, says Rosenblatt, at minimum concentrations ranging from 0.5 to 10 parts per billion. Halogens and sulfur, which often present problems in AES, can be analyzed as negative ions. The instrument has a dynamic range of 10^6—that is, it can measure concentrations varying by as much as six orders of magnitude without dilution—compared to a range of 10^4 for ICP/AES. It costs about $155,000, which is more than an ICP/AES that performs analyses sequentially but less than a premium instrument that performs many analyses simultaneously.

Hewlett-Packard Company introduced a quadrupole-based mass-selective detector, called the HP 5970A, for use in capillary gas chromatography (GC). GC/MS systems have, of course, been around for quite awhile, with perhaps three-fourths of them incorporating quadrupoles. What Hewlett-Packard has done in this case, however, is to strip the quadrupole down to its most simple form so that it can be marketed at a price ($35,000) that is about half that of the next cheapest MS system for GC.

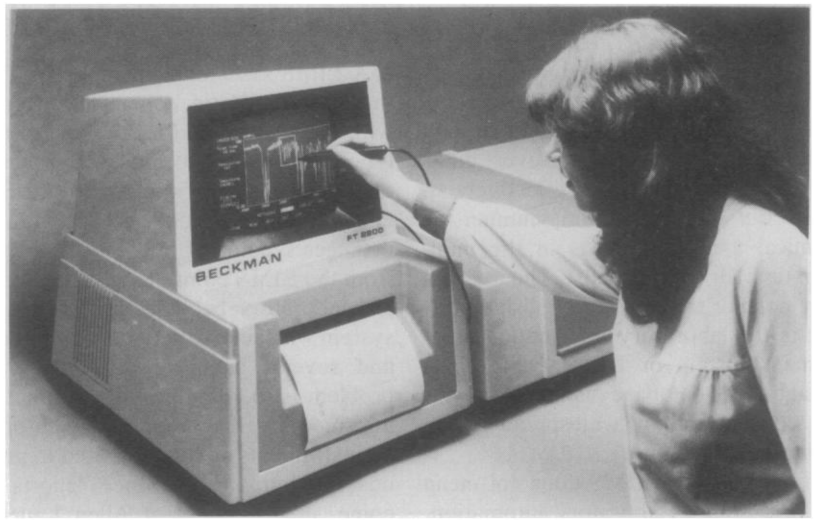
One way simplicity is achieved is by using only an electron impact ionization system; larger systems typically have several ionization systems. The HP 5970A also uses an air-cooled turbomolecular pump to pump off helium carrier gas while ions of interest are focused into the spectrometer by a lens system. Because of this feature, and the fact that the module is designed to be used only with capillary GC's, expensive and complicated interfaces between the GC and the quadrupole are unnecessary. For wide-bore, fused-silica capillary columns, a so-called open-split interface is used; in essence, the inlet tube is split in two by a Y fitting and flow into the spectrometer is limited by a restriction. For narrow-bore columns, the flow is fed directly into the spectrometer.

A mass-sensitive detector gives the chromatographer several options. Obviously, it is possible to obtain a mass spectrum of each peak that is eluted, giving positive identification in most cases. It is also possible to monitor any given *m/z* ratio to produce a chromatogram. As many as six different *m/z* ratios can be monitored to determine when a specific substance is eluted. Operation of the spectrometer and data acquisition and manipulation are controlled by a built-in microprocessor. The company predicts that the system will find applications in methods development, drug and pesticide analyses, and for rapid identification of drugs in overdose cases, among others.

Many of the same markets have been targeted by Finnigan MAT for its new "Ion Trap Detector" or ITD. The unusual ITD was developed by George C. Stafford and Paul E. Kelley of Finnigan MAT, working with John Todd of the University of Kent in England. Many of the details are proprietary, but the basic concept is rather simple. The gas stream from the GC is introduced directly into the doughnut-shaped quadrupole by a heated transfer tube. An electron beam enters from the top of the chamber and ionizes sample molecules inside the quadrupole so that no lenses are required. Carrier gas is again pumped off with a turbomolecular pump.

The ITD differs from a conventional quadrupole in that the ions are all trapped inside the quadrupole chamber, where they trace three-dimensional Lissajous figures. One of the problems with developing the ion trap is regulating these paths accurately so that ions do not collide to form new products or collide with the walls of the chamber. When a sufficient number of ions are collected, the containment field is relaxed so that the ions are released sequentially through the bottom of the chamber, where they are counted by a conventional pulse-counting system. The inventors claim that the mass sensitivity of this system is greater than that of a conventional quadrupole, but not as great as that of a magnetic sector instrument.

Like the HP 5970A, the ITD can look at the entire mass range from *m/z* 10 to 650; if can also monitor as many as 16 *m/z* ratios simultaneously. The instrument costs only $21,000, but it is controlled and the data is processed by an IBM Personal Computer, which must be purchased separately at a price of about $5000.—**Thomas H. Maugh II**



The year of the gadget, part 1

Beckman Instruments' Series FT-1000 and FT-2000 Fourier-transform infrared spectrophotometers feature an interactive light pen that is used to control all of the functions of the instruments. A menu of choices is displayed on the screen and the user selects one by touching it with the light pen. Prices of the instruments vary from $25,000 to $80,000.