The 1980 Pittsburgh Conference: A Special Instrumentation Report

Flower power may be as strong in the 1980's as it was in the 1960's. The 31st annual Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy this year left Cleveland, its home for the past 12 years, and moved to Atlantic City, largely because of a continuing conflict in scheduling with the Cleveland Flower Show. The conference organizers have not yet made a commitment for the site of next year's show, but it now seems to be a toss-up between Atlantic City and Atlanta, with Atlanta nearly a sure bet for the following year. Pittsburgh is not in the running because it does not have adequate facilities. The meeting itself, meanwhile, was saturated with the circus atmosphere of Atlantic City: light airplanes towed banners reading "Nuts to Nernst!" and the like along the boardwalk; slot machines, drawings, and other contests popped up in a significant fraction of the booths; and meeting attendees were apparently as ready to drop their money in the instrument booths as other Atlantic City visitors were to drop theirs in the busy casinos. Because of the large amount of demolition and new casino construction near the convention center, there were many complaints about the lack of nearby hotel rooms and good restaurants for the 16,032 registered participants; what rooms and meals were available were very expensive. If they couldn't find a place to go for lunch or dinner, though, the participants then had more time to visit the 1056 booths (114 more than 1979) occupied by 458 exhibitors (89 more than last year). Many of the exhibitors were foreign companies trying to increase their share of the affluent American market and, in fact, many of the most sophisticated, most expensive high-performance instruments were manufactured abroad. The proportion of foreign participants also seemed to increase, although final figures are not yet available. Among the newcomers were a delegation of five scientists from the People's Republic of China; a delegation from the U.S.S.R. canceled its scheduled visit, however, presumably because of the Afghanistan problem. On the floor, there appeared to be a large number of cosmetic changes in instruments, changes attributed by one manufacturer to an increased importance of subjective factors—above and beyond performance—in the evaluation of instruments. One manufacturer's representative even admitted candidly that his company had changed the color of its instrument cabinets from the traditional but cold blue and gray to warmer "earth tones" because of the increasing number of women with purchasing power in laboratories. Microprocessor controls, real-time data-handling systems, and other software were also more abundant this year, and manufacturers seemed to be placing an increased emphasis on service capabilities. On the whole, it seems unlikely that anyone who attended the Pittsburgh Conference this year could have crapped out.

Options for Preparative and Analytical HPLC

"Divide and conquer" would be an apt description of high-performance liquid chromatography (HPLC). In HPLC a solution containing two or more compounds is first separated into its constituents by passage under pressure through the chromatographic column. Then the concentrations of the components are determined by means of (usually) an optical technique, such as measurement of refractive indices, optical absorption, or fluorescence emission. In analytical work, chemists tend to be more interested in the identification of the components and the determination of their concentrations. The separation part of the process is thus a necessary part but not the main object of the exercise. A second kind of HPLC is called preparative or, simply, prep LC. The objective of prep LC is the isolation of substantial quantities of one or more of the constituents for subsequent use in some other analytical technique, in preparing intermediates for organic syntheses, in producing chemically pure standard materials, and so forth. The Pittsburgh Conference had several new instruments for both types of liquid chromatography.

The newest prep LC instrument was from the Du Pont Company. Du Pont calls its machine a high-performance preparative liquid chromatography (HPPLC) system, presumably because it is in many respects an analytical system scaled up to handle larger quantities of material and therefore retains many of the properties of an analytical system, high resolution in particular. Resolution is determined in part by the width of peaks in the chromatogram. Peak width is measured by a parameter called the number of theoretical plates per meter; Du Pont's HPPLC system is claimed to have a value of 32,000 plates per meter.

The penalty for maintaining a high resolution, admits David McClemens of Du Pont, is that the rate at which material can be separated (throughput) is reduced, since the two factors tend to be inversely related. The HPPLC system can process separations ranging from a few milligrams to several grams in a single run of a half hour or less. The normal mode of operation would be to develop a separation method (choice of column packing material and solvents) on an analytical system. Then, since the two types of instruments are so similar, the same method can be used on the HPPLC system. Throughput is determined by how widely spaced the peaks in the chromatogram are and the desired purity. Throughput can be adjusted upwards by increasing the amount of sample loaded into the column until the peaks just begin to overlap.

How important the relatively low throughput of the Du Pont system is apparently depends on the application. McClemens says that a few milligrams of highly purified material can be worth its weight in gold in some instances and that trace impurities that lower resolution prep LC instruments would never catch can be separated with the HPPLC. The system costs about $15,000 with a fixed wavelength ultraviolet absorbance detector and two chromatographic columns, and $18,900 with a variable wavelength spectrophotometer as the detector.

At the other end of the spectrum of products shown at Atlantic City is the 5-year-old Waters Associates, Inc., PrepLC/System 500, which emphasizes a higher throughput than Du Pont can offer but at the expense of a lower resolution. The Waters philosophy is that the traditional prep LC method of letting gravity force solvent through an open, large-diameter column packed with large particles has too low a resolution, but that the alternative, a scaled-up analytical system would be too expensive because of the need for many large-diameter columns packed with small particles in large-scale separations. Analytical systems use approximately 10-micrometer-diameter particles packed in a column 10 to 25 centimeters long and about 5 millimeters inside diameter, whereas prep LC columns range from 30 centimeters to 1 meter in length and 20 to 80 millimeters in diameter.

Waters' compromise is a unique radially compressed, flexible-walled cartridge packed with large particles (75 micrometers in diameter). The compression removes voids and channels that degrade resolution but does not reduce throughput when a moderate [600 pounds per square inch (psi) versus 4500 in Du Pont's HPPLC system] pressure is applied. To increase resolution, Waters has made provision for recycling the solution through the cartridge several times. On each pass through the system, only that part of each component that lies in the leading edge or trailing edge of overlapping peaks is collected, thus ensuring purity. The PrepLC/System 500A (the current model), including a refractive-index detector, a built-in chart recorder, and a compression chamber holding two cartridges, costs $15,900.

An alternative to radial compression is axial compression, and this approach has been taken by the J-Y Optical Systems Division of Instruments SA, Inc., a French company. J-Y Optical manufactures three prep LC systems. The Prep 100 is about as old as the Waters PrepLC/System 500, while two newer instruments, the Prep 10 and the Miniprep LC, were introduced at the Pittsburgh Conference last year. Joseph Giglio of J-Y Optical says that the axial compression method permits simultaneously achieving high resolution and high throughputs. The Prep 100, for example, is said to be able to separate more than 10 grams per run while maintaining a column efficiency of 7,000 to 15,000 plates per meter, while the Miniprep LC is designed for samples of less than 1 gram and has a column efficiency of about 35,000 plates per meter.

Lid of oven chamber on Du Pont's new HPPLC system is raised to show the column in place. Sample is injected through the port above the operator's hand. [Source: Du Pont]

Another advantage of axial compression, says Giglio, is low cost because any commercial packing material can be used without buying expensive cartridges or columns. The J-Y Optical systems use a column with a piston at the bottom. Packing is first made into a slurry with the solvent and then is loaded into the column, where the piston compresses it. Next the sample is injected into the column and forced through by up to 170 psi pressure from a nitrogen gas cylinder. Prices range from $11,200 for the Miniprep LC to $14,900 for the Prep 100, not including detectors. An even larger system for separating 100's or 1000's of grams may also be available soon, according to Giglio.

A fourth option is the use of centrifugal force to drive solvent through packing material, which is what Hitachi Scientific Instruments has done in its 1-year-old CLC-5 Centrifugal Chromotograph. As explained by Edward Dixon of Hitachi, the "column" is actually a 30-centimeter-diameter stainless steel disk, a thin porous spacer, and a tempered glass disk. To pack the column a slurry of packing material and solvent is introduced into a port on the axis of the disk assembly, and the centrifugal force generated when the disk spins about its axis does the rest in 5 minutes or less. Separation is accomplished in a similar way as centrifugal force drives the sample from an injection port on the axis of the disk assembly through the packing and out the edge of the assembly through the porous spacer into a collector. Hitachi claims an effective column efficiency of 500 plates, which is comparable to that of the Waters PrepLC/System 500, and an ability to separate up to 10 grams of material at exceptionally rapid rates, perhaps ten times faster than other prep LC systems. Hitachi charges about $7,000 for the system, including a fixed wavelength ultraviolet absorbance detector.

Finally, for those who may wish to convert existing HPLC analytical systems into prep LC systems, Whatman, Inc., offered a new chromatographic column, the Magnum 20. The Magnum 20, which has a column efficiency of 25,000 plates per meter, is being sold for $1,500, fully tested and guaranteed.

Several HPLC manufacturers introduced analytical instruments with ternary gradient elution capabilities, thus joining Spectra-Physics, which pioneered the technique 3 years ago. Gradient elution refers to the use of a solvent whose composition is continuously varied during a chromatography run. The reason for wanting to vary solvent composition is to get adequate separation of sample constituents in minimum time. One solvent composition is used to elute the first component, a different composition for the second, and so on. Binary gradient elution, in which two solvents are mixed, has been available for some time. Now it looks as though most manufacturers will be adding the ability to mix three solvents, although the usefulness of ternary mixing has yet to be fully established in the chromatography literature. The virtue claimed for ternary mixing is that there is one more variable to adjust in optimizing a separation method, thus there is more flexibility and some separations difficult to do with two-solvent mixing are made easier. The counterargument, made mostly by representatives of companies not yet offering the ternary mixing option, is that there are in fact relatively few jobs requiring this capability and, therefore, the added complexity of the instrument is not justified.

Companies introducing a ternary mixing option at this year's Pittsburgh Conference were Beckman Instruments, Inc., Micromeritics Instrument Corporation, Tracor Instruments, and Varian Associates. As mentioned, Spectra-Physics has offered this capability for the last 3 years.

Although HPLC sometimes seems close to being a universal technique for analysis of chemical compounds, in one respect it is profoundly deficient. HPLC is great for separating and measuring the concentrations of constituents in a sample, but it has little ability to identify unknowns. Practitioners of another chromatographic technique, gas chromatography, have remedied this deficiency admirably by mating gas chromatographs with mass spectrometers or infrared spectrophotometers in the form of GC/MS and GC/IR instruments. This year at the Pittsburgh Conference, Hewlett-Packard followed up on a hint dropped at last year's meeting by introducing a liquid chromatography/mass spectrometry interface. The Finnigan Corporation actually was first out of the gate with an LC/MS interface; it exhibited its device for the first time last year. A third company, VG Micromass, offered an LC/MS interface but did not exhibit one.

One problem that has prevented effective LC/MS coupling in the past is finding a way to introduce the liquid effluent from an HPLC into the vacuum of a mass spectrometer ionization source. The technique adopted by Hewlett-Packard was adapted from a method developed by Michael Baldwin and Frederick McLafferty of Cornell University in 1973. The interface consists of a long tubular probe whose tip is inserted into an inlet in the mass spectrometer. A needle valve controls the fraction of the HPLC effluent that flows through the probe into a chemical ionization chamber. Solvents in the effluent are used to form the reactant ions necessary for the chemical ionization of the sample constituents. A liquid nitrogen-cooled copper cold trap acts as a cryopump to maintain vacuum in the face of the large pressure increase that would otherwise occur upon vaporization of the liquid effluent.

The interface is an option for the company's top-of-the-line HP 5985B GC/MS system and can be used with any HPLC system meeting certain flow and flow stability requirements. Cost of the device is about $11,500 on a new GC/MS and $20,000 as a retrofit on instruments in the field.

The approach taken by Finnigan and VG Micromass to solve the vacuum/liquid problem is to use a moving belt. Effluent from the HPLC is dropped on the belt, which passes through an infrared heating chamber to remove the solvent. The belt then moves through a two-stage pumping chamber before depositing the sample into either an electron or chemical ionization source, where it is flash heated. The technique is adopted from that described in 1976 by Bill McFadden, H. L. Schwartz, and Stanley Evans of Finnigan. Advantages claimed for the moving belt technique are the ability to take both electron and chemical ionization spectra. Moreover, according to G. L. Kearns of VG Micromass, the moving belt interface can be mated with both high-voltage magnetic and lower-voltage quadrupole mass spectrometers. Finally, the moving belt approach permits processing 30 to 40 samples per hour, as compared to perhaps 3 to 4 with the Hewlett-Packard method.

The Finnigan and VG Micromass LC/MS interfaces, which will operate with most commercial HPLC instruments, are priced at $19,000 and $30,000 respectively.—ARTHUR L. ROBINSON

Portable Elemental Analyzers Pushed

"It's alright to gamble in Atlantic City but not in the steel yard" might have been the motto of several manufacturers exhibiting optical emission and x-ray fluorescence elemental analyzers at the Pittsburgh Conference. It is not exactly a comforting thought, but steel companies, for example, do not always know what alloys are being stored where in their yards. One alloy may look pretty much like another, but if the wrong alloy were shipped by mistake, and the error went undetected, the results could be catastrophic.

The traditional method of sorting alloys is the spark test in which an experienced metallurgist visually notes the characteristics of sparks (the trajectories of the sparks, for example) emitted when the metal is struck by a high-speed grinding wheel to identify the alloy. Folklore has it that these people were so valuable that they demanded and got high salaries and valuable fringe benefits, just as today's superstars of sports do. If rather subjective, the visual spark test method can be expensive. One steel company needed 300 man-hours to sort out 12,000 pieces that had become mixed up.

Spark emission spectrometers make the testing faster and more quantitative. While such instruments are well known in the various metals industries, what is new are small, portable instruments that can be dragged around salvage, shipping, and storage yards for onsite testing without the need to saw off samples for removal to a laboratory spectrometer. The penalty for portability is that the sensitivity and resolution possible with large and expensive spectrometers is missing. Nonetheless, the capabilities of the portable instruments are quite adequate for alloy sorting and identification. And the price (about $40,000) is small enough that the instruments pay for themselves in a few months to a year, manufacturers claim.

Three portable spark emission spectrometers were shown at the Pittsburgh Conference by Applied Research Laboratories (a division of Bausch & Lomb), the Baird Corporation, and Technics. Baird's machine was shown last year; the other two were exhibited for the first time. All three work in much the same way. A spark source located in a pistol-like probe vaporizes a small quantity of metal at the surface of the sample being analyzed. Atomic emission lines from the vaporized metal are collected by a light pipe in the probe and channeled through a 10-meter-long optical fiber cable to a lens which focuses the light on the primary slit of a direct reading spectrometer. Direct reading means that several exit or secondary slits are located at fixed positions corresponding to wavelengths emitted by the elements to be detected. A diffraction grating disperses the incoming light so that any lines belonging to the elements to be detected are directed toward the proper secondary slit. In this way several elements can be detected simultaneously.

A reference standard is needed to tell the instrument the composition of the alloy being sought, and dials on the front panel of the spectrometer are used to set the range of allowed variations in the percentage of each element. Accept (green) and reject (red) lights on the probe flash on to indicate if the sample tested has the right composition. Testing takes 10 seconds or less. ARL's machine (Quantotest 36000—$36,000) can analyze up to 10 elements. To add new elements requires exchanging the spectrometer optics, which can be done in 10 minutes. Baird's instrument (Spectromobile—$40,000) has a spectrometer with 24 exit slits, but only 5 of these can be monitored at one time. Similarly, Technics'

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