ins are in the form of porous beads with functional groups on both the surface and the interior. To be able to elute the sample with a very dilute electrolyte, Small, Stevens, and Bauman developed what is known as a pellicular resin. It has a solid core covered by a thin layer of resin, so that the functional groups are only on the surface. There are also fewer functional groups per unit area, so that the total capacity of the pellicular resin is about 1 percent of the capacity of a conventional resin. The pellicular separator column provides high-efficiency separation of ionic species when the column is

Instrument Highlights

Video—A New Approach to Chart Recorders

There are two approaches to analyzing data. The old way, slow and not always very accurate, is to count squares on chart paper to find peak positions, areas, slopes, and so on. The new way, much faster, is to feed data into a computer and have it spit the results out at you on a CRT screen or on paper. Computers can be expensive, though, and then there is the messy business of programming them to handle your particular data analysis problem (which may not be a standard one solvable with the manufacturer's software). And there is a certain feeling of losing touch with the experiment, at least for incurable old romantics who like to feel that they are the ones doing the work.

A new instrument, shown at the Pittsburgh Conference for the first time this year, called a VideoChart Recorder is aimed at filling the gap between tedious manual analysis and expensive or inflexible computer data handling. The product, made by a company called VideoChart of Yalesville, Connecticut, also puts the researcher back into the experiment and strikes one as so much fun to use that it really should only be operated while wearing an old World War I pilot's cap and a long silk scarf.

The VideoChart Recorder is attached to any instrument in the same way as a normal chart recorder. The incoming data are digitized; up to 4096 data points with five digits of resolution can be stored, which, the manufacturer likes to point out, is equivalent to 20 feet of chart paper with a measurement made every 1/16 inch. A 12-inch video screen displays the recorder data. A cursor called a datum line can be moved from one end of the display to the other. There is a joystick-like control that scans the display past the datum line, adjusts full scale, zooms into selected portions of the display, and selects one or more areas of the display to appear brighter than normal. There is also a calculator keyboard with many of the functions of a scientific calculator.

As one example of how the device might be used, consider two overlapping peaks of a spectrum. The area of interest is highlighted with the brightness control, and the calculator determines the area under the curve. Then, rather than using an artificial scheme such as approximating the area due to the neighboring peak with a trapezoid, one can draw in with the joystick one's own background. The calculator recalculates the area due to the peak of interest, and the display shows the resultant peak with the background removed. Through all these machinations, the original data are not lost, and either original data or output from the VideoChart Recorder, such as a spectrum with background removed, can be sent on to a chart recorder or computer for permanent record.

Cost of the VideoChart Recorder is $4950 (or $4490 with 2048 data points).—A.L.R.

New Tool to Monitor Sulfuric Acid Emissions

The control of sulfuric acid and sulfur dioxide emissions from smokestacks and automobiles is a major concern because of the increasing acidity of rainfall throughout much of the world. That control is complicated by the great difficulty of measuring concentrations of sulfuric acid vapor. Generally, this is accomplished by passing the gas of interest through a trapping solution and then performing a wet chemical analysis. Results obtained by this method, however, are often erratic and indicate only cumulative emissions, not ambient concentrations.

Spectroscopic studies of sulfuric acid vapors have been limited by the conflicting infrared absorption peaks of water vapor and carbon dioxide, both of which are invariably present in exhaust gases. New work by investigators at the U.S. Environmental Protection Agency (EPA) and Laser Analytics, Inc., of Lexington, Massachusetts, suggest that these interferences can be eliminated by taking advantage of the high resolution of a tunable diode infrared laser.

Previous research, says Jimmy C. Pau of EPA, showed that there are several very small "windows" in the infrared absorption spectrum of sulfuric acid where neither carbon dioxide nor water absorb. The new instrument developed by Pau and Edwin Pearson of Laser Analytics has two lasers, one tuned to such a window at 882.90 cm^{-1} and the second tuned to 962.160 cm^{-1}, where none of the three gases absorbs. In practice, the lasers are mounted on one side of a smokestack and their beams focused on a mirror on the opposite side, which reflects the beams to detectors. Comparison of the transmitted intensities of the two beams eliminates interference by particulates and other gases in the stack and provides an accurate measure of the concentration of sulfuric acid.

The prototype model of the instrument was recently tested for 3 days in a stack at the Brayton Point Station operated at Somerset, Massachusetts, by New England Power Service Company. This test, says Pau, "clearly demonstrated the capability of this monitor to provide the needed measurements." Pau hopes to conduct a longer test in the near future. Meanwhile, Laser Analytics is working to make a more rugged version of the instrument that can be introduced commercially. Pau also hopes to develop a second-generation instrument that will monitor ambient concentrations of both sulfuric acid and sulfur dioxide simultaneously. It would then be possible, he says, to have an instantaneous measurement of virtually 100 percent of the sulfur being emitted.

—T.H.M.

(Continued on page 166)

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eluted with a dilute—typically millimolar—solution of sodium hydroxide, carbonate, or bicarbonate for anion separations or nitric acid or phenylenediamine dihydrochloride for cation separations.

The detector developed at Dow has two major components, a suppressor column and a conductivity cell. The suppressor column is filled with a conventional ion exchange resin of the opposite polarity of the separator column and is connected directly to the outlet of the separator column. It performs several functions, the most important of which is conversion of the highly conductive eluent to a form which has low conductivity.

In anion analysis by IC, for example, an aminated cationic separator column is connected to a sulfonated anionic suppressor column. When the sample and eluent pass through the suppressor column, the sodium cation associated with hydroxide or carbonate in the eluent is exchanged for the protons of the suppressor column. Protonation of the eluting anion results in formation of a species—either water or carbonic acid—with low conductance. Against this background of low conductivity, the conductivity of the anionic sample can be readily detected. The suppressor column also converts all the anion species in the sample to their protonated form. This generally enhances their detectability and eliminates the need for individual calibration plots for every possible cation/anion combination.

The size of the suppressor column is a compromise between the need for a large column to provide suppression for a maximum number of analytical runs and the need for a small column to minimize broadening of the sample peaks. In a typical application now, the suppressor column generally contains about ten times as much resin as the separator column. This permits operation of the system for 5 to 10 hours before the suppressor becomes expended and must be regenerated. Regeneration is accomplished by pumping a strong electrolyte (sulfuric acid for an anion suppressor, sodium hydroxide for a cation) through the column to convert the resin back to the active form; the excess regenerant is then flushed out with water. Regeneration typically takes about an hour.

The detector is a highly stable conductivity cell with a very small volume. The complete system, including pellicular resin, suppressor column, and detector, was patented by Dow and the name Ion Chromatography trademarked. The whole system has been licensed to Dionex Corporation of Sunnyvale, California, a company created expressly for the purpose of marketing ion chromatographs. Dionex produces instruments ranging from a basic, single-column system that can perform either anion or cation separations ($16,000) to a dual-column, dual-detector system that is capable of analyzing anions and cations simultaneously ($28,000). There is also a fully automatic, microprocessor controlled system ($30,000).

IC has been refined to allow detection and quantitation of 60 anions and 30 cations, and the number continues to grow. One of the main advantages of IC is its ability to detect the ions at microgram to nanogram levels. This means a part-per-million detection limit if the sample is injected directly onto the column and a part-per-billion limit if a special concentrator column is used. Two other features of IC are its specificity for closely related ions and its capacity for sequential determination of several ionic species in one run, even when the ions are in a very complex matrix. Thus, all four halide ions can be readily separated, nitrite can be separated from nitrate, sulfite from sulfate, and ammonia from other primary amines, including methylamine. Special columns and techniques have been developed to decrease analysis time for many specific ions, including divalent metal ions. Anions can be analyzed even in brine and caustic solutions, generally with no sample preparation other than dilution and filtering to remove solids.

There are three major limitations to IC. Ions with ionization constants (*p*K values) higher than 7 have poor detection limits, even though they can be separated by IC. Cyanide, silicate, and phenates are among the ions that can be detected at trace concentrations only with great difficulty. Certain ions may also undergo irreversible reactions with the suppressor resin; some transition and heavy metal ions, for example, precipitate as hydroxides in the suppressor used for routine cation analysis. And finally, high concentrations of organics may impede the separation. More than 10 percent alcohol in the sample, for example, may cause channeling in the separator, ruining the resin bed. This problem can often be circumvented by diluting the sample with water.

IC has a large number of potential applications in environmental chemistry. James D. Mulik of the Environmental Protection Agency (EPA), for example, has shown that it can be used to determine the concentration of sulfates and nitrates in particulates collected from the atmosphere by high-volume glass fiber

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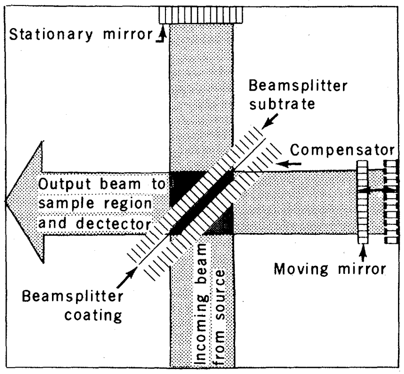
A New Interferometer for Inexpensive FT-IR

A new type of interferometer for performing Fourier-transform infrared (FT-IR) spectroscopy is the basis for an inexpensive new family of instruments, the fX-6000 series from the Analect Instruments division of Laser Precision Corporation. The new design represents the first fundamental change in the interferometer since A. A. Michelson invented it in 1881.

A conventional interferometer consists basically of a beamsplitter, a compensating plate, and a pair of mirrors. The difference in optical path length between the two arms of the interferometer is varied by mechanically scanning one of the mirrors to produce a time-dependent variation in transmitted optical intensity, called the interferogram. If the incoming beam covers, for example, the IR frequency range, the interferogram will then contain the complete IR spectrum of the sample in a coded form. This spectrum can be recovered by performing a mathematical process known as a Fourier transform on the interferogram. Because the entire spectrum is recorded simultaneously by the interferometer, a spectrum is produced much faster than with a conventional IR spectrometer. And since no monochromator is used, the instrument is much more sensitive to small amounts of light. All modern Fourier spectrometers operate in this fashion.



The Analect Transept interferometer differs from the Michelson interferometer on three major points: (i) path length scanning is accomplished by a moving wedge of transparent (refractive) material rather than a moving mirror; (ii) the interferometer

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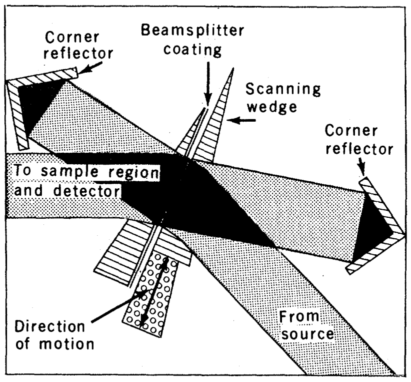
reflectors are cube corners rather than plane mirrors; and (iii) the interferometer arms are not mutually perpendicular.

Use of a refractive scanning wedge amplifies the optical path length change by about an order of magnitude. Because of this increased change, position repeatability of the wedge is not as important as it is for the scanning mirror in the Michelson interferometer. Also, any change in tilt of the wedge produces only a lateral displacement of the beam rather than a change in angular alignment. The corner reflectors return light rays on a path parallel to their direction of incidence, thereby compensating for any dispersive effects resulting from incomplete matching of the fixed and moving wedges. Together, Analect says, these features reduce the criticalness of optical alignment and motion control, making the instrument more rugged and reliable. Because of this ruggedness, the instrument can generally be moved without realignment of the optical system and, when realignment is necessary, it can be performed by untrained personnel.



The fX-6000 spectrometers also use a new multiprocessor data system that reverses the processing order for Fourier transform. Conventional instruments accumulate many interferograms and perform the transform on the coadded product using the instrument's general-purpose central processing unit. The Analect system has a dedicated processor that performs a fast Fourier transform on each interferogram. The spectra thus produced are added by a second processor until the desired signal-to-noise ratio is obtained. A third processor is used for formatting the output. By performing the transform in this method, Analect says, the instrument gives an oscilloscope display of the complete spectrum within 12 seconds, provides periodic updating of the display during coadding, and provides a much greater user flexibility. The complete system has a base price of less than $30,000, less than half the cost of some other FT-IR spectrometers.

—T.H.M.

Fourier Transform Comes to Photoacoustic Spectroscopy

Photoacoustic spectroscopy (PAS) has enjoyed a remarkable surge in popularity since Allan Rosencwaig, then with Bell Laboratories, described a modern version of the technique at the 1975 Pittsburgh Conference (*Science*, 4 April 1975, p. 38). Commercial PAS spectrometers were introduced at the 1977 conference by Gilford Instrument Laboratories and Princeton Applied Research Corporation, and both versions have been steady sellers since. The technique has found many applications for visible and ultraviolet spectroscopy, but has had only limited utility for infrared (IR) spectroscopy because of the low power output of IR sources. Now it appears that this limitation can be overcome by taking advantage of the increased sensitivity to light of Fourier transform (FT-IR) spectrometers.

In PAS, the sample is placed in a specially designed airtight cell equipped with a sensitive microphone. It is then exposed to intermittent (chopped) monochromatic light. If the sample absorbs at the wavelength of the incident light, the light energy is converted to heat energy and the temperature at the surface of the sample fluctuates at the chopping frequency of the light. This temperature fluctuation, in turn, creates a pressure fluctuation in the air of the cell that is detected by the microphone and converted to an electronic signal. By varying the wavelength of the incident light, it is possible to obtain the complete optical absorption spectrum of the sample.

As it happens, an FT-IR spectrometer can be adapted for PAS in a straightforward manner. Mark G. Rockley of Oklahoma State University, for example, built a machined aluminum PAS cell that fits directly in the sample compartment of a Digilab FTS-20 FT-IR spectrometer. A special adaptor focuses the IR beam through a sodium chloride window that seals the PAS sample compartment. Output from the built-in microphone is connected directly to the signal-processing electronics of the spectrometer.

Rockley reported at the Pittsburgh Conference that PAS-IR spectra can be recorded very easily with this configuration, that the technique requires very little sample preparation, and that it can be used for obtaining the IR spectrum of irregularly shaped solids. Among the specimens for which he demonstrated PAS-IR spectra were tobacco leaves, cigarette tobacco, sugar protein, aspirin tablets, polyethylene beads, and coal samples. The spectra were clearly comparable with conventional IR spectra obtained with much more extensive sample preparation. Rockley also found that the technique is very sensitive to oxidative changes on the surface of the specimen—coal, for example—and to gases that have been adsorbed onto the surface of the sample.

The principal limitation of FT-IR-PAS is that it may take several minutes to obtain a spectrum, since 20 to 2000 scans must generally be accumulated. Another minor limitation is that the depth to which the incident light penetrates the surface of the sample, and thus the depth of the sample contributing to the spectrum, depends on the chopping frequency. In ultraviolet and visible PAS spectrometry, only one chopping frequency is used. Because of the nature of the FT-IR spectrometer, however, different chopping frequencies are used in different wavelength regions. Thus, the IR beam may penetrate two to three times as deeply into the specimen at 2000 cm^{-1} as it does at 400 cm^{-1}. For most applications, though, this will not be a problem.

Digilab has constructed a prototype PAS cell for the FTS-20 comparable to Rockley's that it will begin marketing soon. Nicolet Instruments Company has modified a cell from a Gilford PAS spectrometer to fit the Nicolet 7199 FT-IR spectrometer and will also market it soon. Both cells are expected to cost between $3,000 and $4,000, but Rockley says that anyone with a competent machine shop can construct his own for about $600.

—T.H.M.