portable spectrometer (Spectrotest—$40,000) can test for any 8 of 24 elements simultaneously. The lightest instrument (ARL's) weighs 265 pounds, while the heaviest (Baird's) weighs 395 pounds. All are mounted on wheeled carts.

An alternative to optical emission spectroscopy is x-ray fluorescence analysis. As with optical instruments, large x-ray fluorescence spectrometers are in widespread use in the metals industries for monitoring the composition of alloys in various stages of production. But smaller, less expensive, portable (or semiportable) machines are available that can be used for metal sorting and alloy identification in storage yards or in the field. One advantage of x-ray machines is that they can analyze a wider variety of materials than the optical instruments, including powders, liquids, and samples with highly irregular surfaces. But a disadvantage is that the truly portable instruments are capable of analyzing for only one element at a time and thus are much slower at sorting out alloys with complex compositions.

The grandfather of portable x-ray fluorescence analyzers is made by the Pitchford Scientific Instruments Division of the Hankison Corporation. The Portaspec was introduced 14 years ago. It consists of a tungsten x-ray tube, a lithium fluoride wavelength dispersive analyzing crystal, and a proportional counter detector, all in a probe unit that weighs 18 pounds. A separate power supply unit weighs 55 pounds and is connected to the probe by a 9-foot-long cable. The Portaspec can detect the presence of elements from titanium (atomic number 26) through uranium (atomic number 92) in the periodic table. A meter on the probe unit indicates the intensity of x-ray fluorescence detected and thereby the concentration of each element. Its price is $12,000.

If 73 pounds is too much to carry around, an even more portable x-ray fluorescence analyzer that weighs only 19 pounds was introduced at the Pittsburgh Conference by Columbia Scientific Industries Corp. It can be operated on batteries alone for up to 12 hours. The CSI 740 Compact Materials Analyzer does not use an x-ray tube but a radioactive isotope as the x-ray source, thus overcoming the need for a large, high-voltage power supply. Iron-53, curium-244, cadmium-109, and americium-241 are examples of isotope x-ray sources.

The system uses a gas-filled proportional counter detector operated in an energy dispersive mode, so that several elements can be determined from one exposure. Although the instrument has a microcomputer to store calibration data for up to 32 elements, the microcomputer is only able to process data in groups of four elements. Moreover, there is only one display panel, so all results must be shown sequentially. There are three probe units, which between them cover the elements of the periodic table from aluminum through uranium for liquid, powder, and solid samples. The CSI 740 costs $19,000 with one probe and just over $20,000 with all three probes.

For those who need to determine the concentrations of only one to three elements, the PGT-100 from Princeton Gamma-Tech may do the trick. Rather than a microcomputer, the instrument has analog electronics that are tuned at the factory to process x-ray fluorescence pulses specific to the selected elements. A triple display panel shows the concentrations of all three elements simultaneously. With a hand-held probe, the PGT-100 weighs 40 pounds and its price is about $10,000.

For more analytical capability, the chemist must give up portability. The most sophisticated x-ray fluorescence analyzers that might still be used for alloy sorting and identification, shown by the Kevex Corporation and Princeton Gamma-Tech at the Pittsburgh Conference, might be described at best as semiportable. The Kevex Analyst 6600, for example, has an optional hand-held, liquid nitrogen-cooled, lithium-drifted silicon detector, but the x-ray tube housing and the electronics unit have to be fixed in place, though they need not be in the same location.

A microcomputer in the Kevex instrument gives it several capabilities. It can do quantitative analysis for up to 18 elements in unknown samples; it can identify up to 170 alloys whose compositions are stored in memory; and it can accept or reject unknowns on the basis of the percentages of up to 18 elements in a given alloy. Operation is simple; instructions on a cathode-ray tube (CRT) screen prompt the operator. Results of all modes of analysis are also displayed on the screen. Time for one run can be as short as 5 seconds. First exhibited at the Pittsburgh Conference last year, the Analyst 6600 costs about $50,000.

Princeton Gamma-Tech's PGT-800, introduced this year as a competitor to the Analyst 6600, costs $40,000.

—Arthur L. Robinson

IC Versatility Promotes Competition

Ion Chromatography is a rapid and sensitive technique for separating and analyzing complex solutions of ionic species. The technique is only 5 years old, but already it is the method of choice for analyzing a variety of organic and inorganic ions in wastewaters, process waters, air samples, biological fluids, food products, and a large number of other materials. It has become so popular, in fact, that some companies are now trying to find ways to achieve comparable analytical success without infringing on the basic patents that cover it.

Ion Chromatography (IC) is a variant of conventional ion exchange chromatography. In ion exchange, a polymeric resin bearing either anionic or cationic functional groups is enclosed in a column and used to separate ions of the opposite charge. A cation resin, for example, bears sulfonate moieties whose attraction for cations in the sample is proportional to the acidity of the cations. When the column is eluted with an acidic electrolyte, the cations that are bound most weakly are eluted first, those bound most strongly are eluted last, and the others are eluted somewhere in between.

Ion exchange is very effective for separating most types of ions—provided the sample can be detected as it leaves the column. Most organic ions and some complex inorganics can be detected spectrophotometrically or by changes in the refractive index of the eluent, but not most simple ionic species, such as halides and metal ions. Ideally, such ions could be detected most efficiently by measuring their electrical conductivity, but the large conductivity of the eluent generally overwhelms any signal arising from the sample. IC provides a way sharply to reduce this background conductivity.

IC was first reported in 1975 by Hamish Small, Timothy S. Stevens, and William C. Bauman of the Dow Chemical Company. They developed both a new separator resin and a unique detection system. Conventional ion exchange res-

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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.

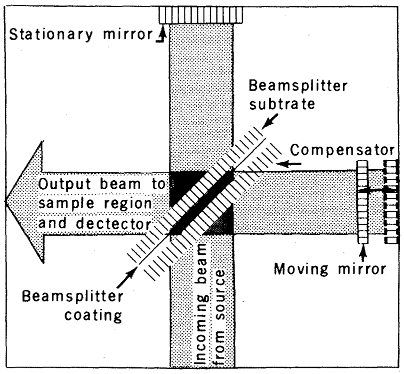
There are three major limitations to IC. Ions with ionization constants (*p*K values) higher than 7 have poor detection limits, even though they can be separated by IC. Cyanide, silicate, and phenates are among the ions that can be detected at trace concentrations only with great difficulty. Certain 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

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.

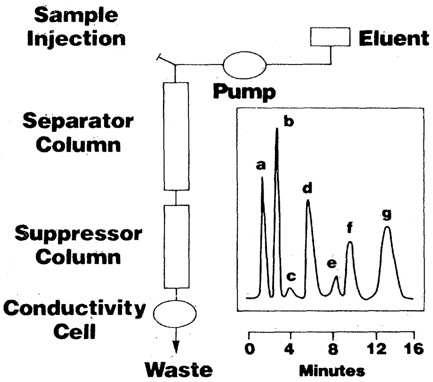


The Analect Transept interferometer differs from the Michelson interferometer on three major points: (i) path length scanning is accomplished by a moving wedge of transparent (refractive) material rather than a moving mirror; (ii) the interferometer filters. The technique has proved much faster than, and equally as accurate as, colorimetric methods. Mulik and his colleagues have also shown that ambient concentrations of sulfur dioxide in air can be monitored by IC if the air is passed through a solution that traps and oxidizes the pollutant. Other investigators have used IC to monitor environmental concentrations of ammonia, fluoride, arsenate, phosphate, and other ions.

Frank Meserole of Radian Corporation in Austin, Texas, has shown that IC can be used to monitor the concentration of both sulfite and sulfate in flue gas desulfurization samples taken from coal-fired power plants with limestone scrubbers and in sulfuric acid mists in gas streams. Daniel Haynes of Stanford Research Institute has used the technique to monitor formic acid vapor in industrial plants and Phillip R. McCullough and J. W. Worley of Monsanto Corp. have shown that it can be used to monitor chloroacetyl chloride vapor. Many investigators have used IC to measure the concentration of pollutants in rain and snow. In recognition of this utility EPA has sponsored a symposium on the applications of IC to analysis of environmental pollutants in each of the last 2 years and is planning future symposia.

IC is also useful in water pollution analysis, although it is not yet recognized by EPA as a standard method. Frank C. Smith, Jr., of Dionex, for instance, has shown that the technique can be used for analysis of trace concentrations of nutrients in biopond waters, oxalate, sulfate, and other anions in green and Kraft-black liquors in the pulp and paper industry, and many anions in groundwater. Lee C. Westwood of Ford Motor Company has found that it can be used to monitor the concentration of toxic azide in effluents associated with production of air bags for automobiles; he has also found it useful for analysis of engine coolants. Bernard Wargotz of Bell Laboratories has found that it can be used to monitor the concentration of many ions in wash waters used on electronic components.

Quality control is another arena where IC has proved useful. Richard D. Posner and Alan Schoffman of United States Testing Company, Inc., reported at the Pittsburgh Conference that it can be used to monitor the concentration of various constituents of Portland cement, including sodium, potassium, calcium, and magnesium. Similarly, Jeffrey W. Whittaker and Paul R. Lemke of Pfizer, Inc., reported that IC can be used to monitor concentrations of sulfite and sulfate in sulfate salts of various antibiotics and sodium and potassium in salts of other antibiotics. They also found that IC was better than conventional wet chemical methods for assaying formate concentrations in bulk sodium formate. Investigators at Dionex have also shown that IC can be used to monitor concentrations of fluoride, chloride, sulfate, and hexavalent chromium in electroplating baths.



Schematic diagram of an Ion Chromatograph and a typical chromatogram. In the separator column, the exchange reaction is $\text{resin-}N^+HCO_3^- + Na^+X^- \rightleftharpoons \text{resin-}N^+X^- + Na^+HCO_3^-$*, where X is* F^-, Cl^-, NO_2^-, PO_4^{3-}, Br^-, NO_3^-, *or* SO_4^{-2}*. In the suppressor column there are two reactions:* $\text{resin-}SO_3^-H^+ + Na^+HCO_3^- \rightarrow \text{resin-}SO_3^-Na^+ + H_2CO_3$*, and* $\text{resin-}SO_3^-H^+ + Na^+X^- \rightarrow \text{resin-}SO_3^-Na^+ + H^+X^-$*. The peaks in the chromatogram are (a) 1.4 ppm* F^-*, (b) 2.9 ppm* Cl^-*, (c) 2.9 ppm* NO_2^-*, (d) 14.3 ppm* PO_4^{3-}*, (e) 2.9 ppm* Br^-*, (f) 8.6 ppm* NO_3^-*, and (g) 14.3 ppm* SO_4^{2-}*.*

One other area of interest is energy production. Judith A. Rawa and Julie A. Mosko of Calgon Corporation reported at the conference that IC can be used to characterize water-formed deposits on turbine blades from power plants. Several investigators have shown that IC can be used to monitor part-per-billion concentrations of both anions and cations in deionized water used in steam turbine power plants. Stevens and his colleagues have shown that it can be used for routine monitoring of concentrations of phosphate, chloride, sulfate, and glycolate in boiler blowdown waters. It can also be used to monitor the relative concentrations of nitrite and nitrate in boiler waters where nitrite has been added as an antioxidant.

IC is very good for measuring the concentration of chloride ion in the presence of iodide, a need that has arisen in the nuclear power industry as a result of the incident at Three Mile Island. Other energy uses that have been demonstrated include measurement of various ions in geothermal brines, assay of ions in oil shale extracts and coal-gasification producer waters, quantitation of heteroatoms in coal and crude oil, and quantitation of sulfur in coal and in liquid fuels.

These and a variety of other uses for IC have prompted other companies to take a hard look for ways to circumvent the Dow patents. The first commercial result of this effort is a joint venture of Wescan Instruments, Inc., of Santa Clara, California, and The Separations Group of Hesperia, California. Wescan has developed a stable, sensitive conductivity meter that is capable of detecting very small changes in conductivity, even in the presence of a high background conductivity. The Separations Group has developed an ion exchange resin in which a small number of sulfonate moieties are bonded onto the surface of silicate spheres. This material has an even lower capacity than the Dionex resins, and thus can be eluted with more dilute electrolytes.

In practice, the two components are attached to the user's conventional high-performance liquid chromatograph. A small amount of sample is injected and eluted with a millimolar solution of phthalic acid. No suppressor column is used; the background conductivity is suppressed—"bucked out"—by the detector and only the changes in conductivity caused by passage of the sample through the conductivity cell are observed. Both components are sold by each company. The detector costs $1400 and a typical column costs $240.

The two companies claim that their system reduces the band broadening of sample peaks that results from the use of a suppressor column and eliminates the need for column regeneration. Sensitivity is in the parts-per-million range, but could be improved by concentrating the sample. The companies also say that the system makes it possible to use a variety of eluents not suitable for use with suppressor columns.

On the negative side, the system is suitable for use only with eluents whose *p*H is between 5 and 8; stronger acids or bases degrade the silica substrate. No columns are available yet for cations, but the companies hope to have one on the market within a year. Furthermore, the detector must be calibrated for each cation/anion combination that is measured. The system thus seems most suitable for an inexpensive introduction to ion analysis for conventional anions such as nitrite, phosphate, chloride, bromide, nitrate, sulfate, and carbonate. For more complex applications, though, the Dionex system would still appear to be mandatory.—THOMAS H. MAUGH II