$40,000 instruments. They are conventionally used to subtract the light fluoresced by the solvent the sample is dissolved in from the light fluoresced by the sample, thus correcting for fluorescence of the solvent. Last year, however, Perkin-Elmer Corporation in Norwalk, Connecticut, came out with a medium-priced double-beam spectrofluorometer and this year Farrand Optical Company in Valhalla, New York, introduced a similar instrument. According to Louis Capasso of Farrand, his company was stimulated to produce its new instrument by the Coast Guard's demands.

Instrument designers have long been plagued by the problem of correcting fluorescence spectra for instrument-based distortions. If these corrections are not made, data from one instrument are not comparable to data from another. And, although corrected spectra have been available for a decade, the corrections have not always been perfectly reliable nor available on medium-priced instruments. All the instrument companies that exhibited at the Pittsburgh Conference are now offering fully corrected spectra on medium-priced instruments. This year, however, Perkin-Elmer introduced a new way to correct spectra on their medium-priced instruments. This company is correcting their spectrofluorometer's distortions with a microprocessor (see accompanying article). The Perkin-Elmer double-beam spectrofluorometer can, as an option, be hooked up to a microprocessor. This use of microprocessor enables Perkin-Elmer to increase the ease of operation of their instrument and the reliability of their corrections but does not increase the cost of their instrument.

Donald Helman of the American Instrument Company reported at one of the oil spill symposiums that another kind of correction often proves important in fluorescence spectroscopy—correction for the light absorbed by the solvent in which the sample is dissolved. Since many solvents absorb light of the same wavelength as light absorbed by the sample, measurements of the amount of light directed at the sample do not always indicate how much light is available for it to absorb. This problem occurs, for example, when fluorescence of oils is measured. Oils are usually dissolved in cyclohexane which, like the oils, absorbs light in the ultraviolet region of the spectrum. To correct for this effect, American Instrument Company introduced this year a medium-priced instrument in which the light absorbed by the solvent is measured and subtracted from the light recorded as being available for absorption by the sample.

Since fluorescence spectroscopy is as much as 1000 times as sensitive as the more widely used technique of ultraviolet absorption (in which only the light absorbed is measured to determine how much of a given compound is present), its increasing popularity among analytical chemists is not unexpected. Now that new applications of fluorescence spectroscopy are being reported and now that manufacturers have begun introducing features on their $20,000 instruments that were previously available only on $40,000 instruments, industry representatives agree that the recent trend toward the use of fluorescence spectroscopy is likely to continue.—GINA BARI KOLATA

Surface Analysis: Multiple Techniques for Monolayers

If anything characterized the Pittsburgh Conference, it was the smell of money. Although forbidden by conference rules to make sales on the exhibition hall floor, instrument makers aggressively showed their wares, and many company representatives claimed to have the kind of solid leads to sales that have been lacking in earlier Pittsburgh Conferences. Instrumentation for the analysis of solid surfaces was no exception, despite the fact that little in the way of anything new was offered.

It is a cliché to point out that the advent of ultrahigh vacuum techniques two decades ago has enabled researchers to invent a panoply of electron, ion, and x-ray spectroscopic techniques capable of characterizing solid surfaces, and in fact has led to the establishment of the discipline of surface science. Nonetheless, apart from the fundamental research laboratories, the use of these so-called clean surface methods has only been slowly appreciated. Thus, in the past, manufacturers have had to sell the very idea of surface science to a skeptical audience before they could tout the advantages of their own instruments.

John Yates, Jr., of the National Bureau of Standards (NBS), Gaithersburg, Maryland, has completed a survey of some 104 academic, government, and industry laboratories. This study turned up about 60 experimental techniques that investigators use to study surfaces. Many of these, of course, are not restricted to surface analysis, and, of those that are, only a few are widely used and thus are of interest to commercial manufacturers.

The makers of instruments of commercial importance have concentrated on techniques that involve measuring the kinetic energies of electrons emitted from the surface of a solid subjected to either electron beams or to x-ray or ultraviolet radiation. Auger electron spectroscopy (AES) has been the workhorse of these electron spectroscopies, partly because identification of chemical elements (except hydrogen and helium) on solid surfaces can be obtained by technicians with relatively inexpensive equipment ($50,000 and up).

Auger electrons are secondary electrons ejected from a solid when a beam of electrons with energies of several thousand electron volts first knocks out an inner shell electron, creating an electron vacancy (hole) which is quickly filled by a less tightly bound electron. The energy lost by the latter electron is imparted to a second outer electron which becomes the Auger electron and whose kinetic energy (5 to 2000 ev) is the difference between the energy imparted to it and its binding energy. This energy difference is unique to each element and thus provides the means of chemical identification. Auger electrons are readily scattered by atoms in the solid as they travel toward the surface, and therefore only those electrons created within the first 3 to 30 angstroms from the surface (1 to 10 monolayers) escape with the characteristic energy and are measured.

By focusing a beam of inert gas ions onto the solid surface, researchers can systematically etch away the surface. In addition to merely cleaning contaminants from the surface, such sputter-etching provides a way to observe the concentration of one or more elements with depth, because the peak in the Auger spectrum characteristic of each element can be monitored as a function of etching time. The height of each Auger peak is presumed to be proportional to the concentration of a given element.

In the last 2 years, instrument makers have developed scanning Auger systems in which the electron beam can be focused to a diameter of about 5 micrometers and scanned across the surface much as in a scanning electron microscope (SEM). This scanning capability in conjunction with ion beam etching means that three-dimensional elemental analysis is available to an investigator. Two manufacturers (Physical Electronics Industries, Inc., Edina, Minnesota, and Varian Palo Alto Vacuum Division, Palo Alto, California) had displays on scanning AES systems at this year's Pittsburgh Conference, although neither was being shown for the first time.

Scanning AES systems can provide several kinds of information in addition to the elemental analysis and depth profiling provided by normal AES. Measurement of the electric current to the sample due to absorption of the electron beam (the specimen current) during scanning gives rise to an image like that from a conventional SEM, but with a lower spatial resolution. So-called Auger images indicate where on the surface a particular element exists and are obtained by setting the electron energy analyzer to accept only electrons with energies corresponding to that element while scanning the area of the surface being imaged. The relative concentration of a given element at different points along a line on the surface can be obtained by measuring the magnitude of the Auger peak for that element while scanning along the line.

Other manufacturers are following a different approach to scanning AES by adding an electron energy analyzer to a SEM in order to obtain a submicrometer spatial resolution. There is, however, a substantial difference between the two cases. Being surface specific, AES and the other surface spectroscopies are tremendously sensitive to surface contamination. Some researchers can recount cases where they found contaminants in their spectra that were traced to a colleague's experiment on the other side of the laboratory with a material sufficiently volatile that some atoms drifted across the room to the sample under investigation. Although they image the surface of an object, SEM's are not as critically sensitive to impurities in most cases and thus vacuums obtainable with oil diffusion pumps [only 10^{-4} to 10^{-5} pascal (1 pascal = 7.53×10^{-3} torr)] have been good enough.

Unfortunately, at 10^{-4} pascal up to a monolayer of adsorbed gas can form each second, so that hydrocarbons from the diffusion pump oil quickly cover a sample's surface. Thus, makers of SEM's have had to redesign their instruments to incorporate an ultrahigh vacuum of 10^{-8} pascal or better in order to carry out AES. Ultrahigh vacuum has also permitted the use of a field emission electron gun with a concomitant fivefold increase in the obtainable spatial resolution. At very small beam diameters, a field emission electron source can be 1000 times brighter than the traditional tungsten or lanthanum hexaboride hot filament source. Spatial resolution is not the only consideration. For example, as the beam diameter decreases, the number of electrons in the beam and hence the Auger signal also decreases, and it takes longer to analyze a given surface area without losing accuracy. And maintenance of an ultrahigh vacuum becomes more crucial than ever.

At the Pittsburgh Conference, Coates and Welter Instrument Corporation, Sunnyvale, California, Etec Corporation, Hayward, California, and VG Scientific Ltd., Sussex, England, all offered high-resolution scanning AES systems based on SEM's, with VG claiming a 500-

Pittsburgh Highlights

Small Companies Are Big Successes

It was hard to miss the splashy exhibits of the large instrument manufacturers at the Pittsburgh Conference. The Perkin-Elmer Corporation, for example, spread their display over 20 booths and a seminar room, and they sent 43 representatives to the conference. Nestled among displays of such giants were the one-booth displays, complete with hand-lettered black and white signs, of the small companies. Although unobtrusive, the small companies cannot be overlooked. They constitute a significant fraction of the exhibitors at the conference and, in most cases, offer products available from no other companies.

The task of founding a small company and attracting sufficient business to make the company profitable would seemingly be difficult in even the best economic times. Yet, according to Harold Sweeney of Koppers, Inc., of Monroeville, Pennsylvania, who helps each year to organize the Pittsburgh Conference, very few small companies go under and new ones are continually being formed. Most that exhibit one year and not the next fail to do so because they have been absorbed by large companies. Several small companies present at the conference last year, however, decided not to exhibit this year because they now have so much business they can fill no new orders.

Most founders of small companies start out by working for large companies, then get ideas for the development of unique products and strike out on their own. This means that small companies often turn out to be the source of new concepts in research instrumentation. For example, Laser Analytics, Inc., of Lexington, Massachusetts, makes the world's only infrared spectrometer with a laser light source—a development that gives their machine a spectral resolution at least two orders of magnitude better than that of instruments that use conventional sources of infrared light. Philip Goetz of the Pen Kem Company of Croton-on-Hudson, New York, points out that his 12-person company makes the first commercially available instrument for measuring zeta potentials. Although the company was incorporated only 4 years ago, they have already sold hundreds of instruments to customers in 16 countries.

Vincent Coates who, by himself, runs Nanometrics, Inc., of Chatsworth, California—a company that advertises the "world's first computerized microspectrophotometer and accessories"—has more experience than most in founding small companies. After working for a large company for 22 years, he and a partner started their own company. The company did very well and soon grew until it consisted of 75 people, whereupon Coates and his associate sold it to a large company and Coates founded Nanometrics. With this experience Coates has developed some theories to explain why small instrument companies are so often successful.

Coates attributes the ease with which small instrument companies become established to the fact that research instrumentation is one of the few areas in which a small company can develop a product just as well as a large company. Makers of most research instruments are not hindered by federal regulations, such as those that force pharmaceutical firms to employ extensive tests to demonstrate the safety and efficacy of their products. Nor must makers of research instruments produce large numbers of their product before they can become profitable, as must automobile manufacturers, for example. Thus research instrumentation remains an open field for a person with a good idea and small companies continue to proliferate.—G.B.K.

angstrom resolution in the scanning Auger mode. (The spatial resolution in the scanning AES mode is always poorer than in the SEM mode because the incorporation of the electron energy analyzer necessitates placing the sample farther from the aperture of the electron focusing optics.) The price of this fine a resolution, however, is high. Between $175,000 and $250,000 is charged by VG for their scanning Auger system, as opposed to a little more than $80,000 for the basic Varian apparatus.

Surface scientists working in fundamental research laboratories have known for years that no single surface analysis technique can completely characterize a surface. Hence, they have tended to build experimental apparatuses much in the way of a hi-fi enthusiast by assembling a system from components. Their ultrahigh vacuum systems often contain a half dozen or more ports, each of which can incorporate the necessary source and detector for a different spectroscopic technique. The advantage of such multipurpose vacuum systems is that many techniques can be used with full confidence that the sample surface will not have been contaminated in the time it takes to switch from one measurement tool to another. And the cost of a separate vacuum system for each technique is avoided.

As an example where combining techniques is useful, AES, which is easy to use for identifying elements present on a surface, yields information on chemical bonding only with much effort on the part of the researcher. Electron spectroscopy for chemical analysis (ESCA), which is also known as x-ray photoelectron spectroscopy (XPS), contains this information in a much more accessible form than does AES in most cases. X-rays incident on a solid surface knock out inner shell electrons from surface atoms. Those electrons close enough to the surface to escape without loss of energy are collected and the energy is analyzed just as in AES. But in ESCA, the kinetic energies of the photoelectrons depend on both the identity of the surface element and its chemical bonding state. Because x-rays do less damage to surfaces, ESCA can also be used on delicate materials, such as polymers, where AES is inappropriate.

But ESCA is not the general-purpose technique that AES is. Because ESCA peaks are often narrower than AES peaks, a more sophisticated energy analyzer is required than for AES. Partly for this reason and partly because of the higher cost of x-ray sources as compared to electron guns, ESCA apparatuses are usually more expensive. (DuPont Instruments, Wilmington, Delaware, however, exhibited an ESCA system designed for industrial quality control, the base price of which is about $55,000, comparable to a basic AES system.) Moreover, a highly skilled operator is needed for ESCA. Finally, because x-rays cannot easily be focused and moved around in the way electron beams can, ESCA cannot be used in a high spatial resolution, scanning mode.

Offered at the Pittsburgh Conference were versions of combined ESCA-AES spectrometers by AEI Scientific Apparatus Ltd., Manchester, England, GCA/McPherson Instrument, Physical Electronics Industries, Inc., and VG Scientific Instruments Ltd. The GCA/McPherson and VG spectrometers also include ultraviolet sources in addi-

Pittsburgh Highlights

Lasers Finally Making It in Commercial Instruments

Lasers have found many uses in the laboratories of talented chemists who are able to construct their own instruments. Few commercial spectrometers, however, have been equipped with them—except for Raman spectrometers, where laser light sources are imperative for reasonable sensitivity. But this year instruments incorporating lasers were present in substantial numbers.

Not all the instruments use lasers as a light source for spectroscopy. Fourier transform infrared spectrometers displayed at the Pittsburgh Conference, for example, contain helium : neon or similar lasers as an internal reference standard for accuracy in wavelength determination. A laser microprobe displayed by Jarrell-Ash of Waltham, Massachusetts, employs laser energy from a xenon-pumped neodymium glass laser to vaporize very small (about 25 micrometers in diameter) portions of a sample for elemental analysis. The vaporized sample is excited to emission by an electrical discharge and the emission spectrum is analyzed in a conventional spectrograph. The $60,000 system requires no sample preparation, and the analysis is nondestructive.

A laser-illuminated instrument for measuring zeta potential—the effective negative charge on the surface of a colloidal particle—was exhibited by the Pen Kem Company of Croton-on-Hudson, New York. The instrument has a rotating prism used in conjunction with a microscope to measure the rate of migration of such particles in an electrophoresis cell. Use of a helium : neon laser in the $8500 Laser Zee Meter gives an order-of-magnitude increase in sensitivity, the company claims; the laser source also transmits less heat to the sample so that thermal convection is minimized. Spectrex Corporation of Redwood City, California, displayed a $6900 instrument in which a scanning helium : neon laser counts the number of particles in fluids. The instrument is unique in that the sample does not have to be pumped through a chamber or orifice for counting, as is the case with conventional particle counters.

Three other new instruments incorporate a laser as a light source for spectroscopy. Chromatix, Inc., of Mountain View, California, demonstrated a low-angle light scattering photometer based on a helium : neon laser. This application is similar to Raman spectroscopy in that measurement of scattered or reflected light requires a light source of very high intensity. The light source in the $19,500 instrument can be collimated into a very narrow beam, furthermore, to reduce light scattering by dust and air bubbles. Molectron Corporation of Sunnyvale, California, uses a nitrogen-pumped tunable dye laser in conjunction with a specially designed photometer to perform spectroscopy in the ultraviolet region (from 215 to 750 micrometers). The $12,000 instruments incorporating lasers were as easy to use as a conventional spectrometer, but gives an increase of 100,000-fold in average power from the light source.

The most technologically advanced instrument is an infrared spectrometer, produced by Laser Analytics, Inc., of Lexington, Massachusetts; it is the first commercial spectrometer to incorporate a tunable diode laser. Because of the laser, the $19,500 instrument provides a spectral resolution 10,000 times better than that of conventional infrared spectrometers.

Laser spectrometers are obviously still specialty instruments. But the growing number of such instruments is heartening to the many chemists who think that the laser is the instrument light source of the future.—T.H.M.

tion to x-ray, so that ultraviolet photoelectron spectroscopy (UPS) can be done. The AEI and VG instruments are probably the best examples of the hi-fi syndrome among the instruments shown, having eight and nine ports respectively and offering almost any combination of experimental techniques desired. Prices range from about $110,000 for the GGA/McPherson system to more than $350,000 for the most complex AEI machine.

In the last 3 years there has been an increasing interest in the use of ions, rather than electrons, to probe solid surfaces. A major feature of probing with ions is that the ion does not penetrate the surface into the bulk, unlike electrons or photons, so that these techniques are highly surface specific. The ion techniques necessarily remove the surface atoms with which they collide. so that the methods are inherently able to do depth profiling. On the other hand, it is not possible to re-examine a surface once it has been ion etched.

Secondary ion mass spectrometry (SIMS) is probably the most popular of the ion techniques. In SIMS, a beam of energetic gas ions sputter positive and negative ions, as well as neutral atoms, from the sample surface. These secondary ions are collected and analyzed with a mass spectrometer. Advantages of SIMS include its high sensitivity (to parts per billion in optimum cases), its ability to detect hydrogen, and its ability to distinguish isotopes.

Researchers usually consider SIMS to be a secondary technique to be used in conjunction with AES, ESCA, or some other. A major disadvantage is the extreme variability in the secondary ion yield (number of ions removed per incident ion), which can extend over some five orders of magnitude, thus making quantitative analysis very difficult. The wide range of yields derives from the complex interactions between surface atoms and the incident ion, which are strongly dependent on neighboring atoms. In fact, an oxygen stream is usually directed at the point on the surface where sputtering occurs, because oxygen enhances the ion yield greatly.

Extranuclear Laboratories, Inc., Pittsburgh, Pennsylvania, 3M Company, St. Paul, Minnesota, Physical Electronics Industries, Inc., and VG Scientific Instruments Ltd. advertised SIMS instruments with quadrupole mass spectrometers and ion beam diameters about 100 micrometers or more at the Pittsburgh Conference this year. In addition, Cameca Instruments, Inc., Courbevoie, France, and Applied Research Laboratories, Sunland, California, had information available about a more sophisticated instrument using a magnetic mass spectrometer called an ion microprobe mass analyzer, which they and AEI Scientific Apparatus Ltd. had introduced 3 years ago. These machines have a quite high spatial resolution (of the order of 2 micrometers) but are much more expensive than SIMS ($350,000 as compared to between $50,000 and $130,000 for a complete quadrupole SIMS system). An attachment for adding SIMS to an existing vacuum system costs $25,000.

A technique that some researchers see as a future competitor to AES as a workhorse surface analysis tool is ion scattering spectrometry (ISS). In this method, the same ions from the ion beam used in SIMS (the two methods can be used simultaneously) recoil from the solid surface. The energy of the reflected ions depends on the scattering angle and on the masses of the incident ion and the atom from which it scatters.

Analyzing Scattered Ions

Some researchers think that because of the relative simplicity of the surface interaction, there is a good possibility that ISS may become the most quantitative of the surface analysis spectroscopies. There is only one peak in the energy spectrum for each different surface element, and the method gives easily interpretable spectra. Disadvantages include the rather large (100 micrometers or larger) diameter of the ion beam, so that high resolution scanning is not yet possible. There is also a significant problem with overlap of peaks due to different elements, so that the possibility exists of losing elements present in low concentrations, because the peaks in the ISS spectra are not sharp.

So far, only the 3M Company is selling a commercial version of the ISS instrument (for $50,000 or $70,000 for ISS and SIMS together). The sensitivity of the ISS instrument offered by 3M this year is 100 times greater than that of earlier models because of an improved ion energy analyzer.

All of the surface spectroscopy instruments have either standard or optional data analysis modules. These modules are essentially hardwired (nonprogrammable) computers for such functions as data averaging, background subtraction, computing derivatives or integrals of spectra, and normalizing spectra. Multiplexers permit following several elemental peaks at once over a period of time. These instruments are usually completely digital and therefore compatible with computers, so that on-line, automated operation by a computer is possible. At least two companies, GCA/McPherson and VG Scientific, offer minicomputers for completely automated operation of their spectrometers.

A persistent problem with all these methods of surface analysis is that they are not quantitative. They are useful for identifying elements and in some cases their chemical states, and even for gauging relative concentrations between different samples. But obtaining absolute concentrations is another story. Although figures of 10 or 20 percent are sometimes quoted for the relative accuracy of concentrations determined by these techniques, even these uncertainties can only be obtained when standard reference materials quite close in composition to the unknown exist.

Recently, for example, members of an American Society of Testing Materials (ASTM) Committee D-32 on catalysts sponsored a study in which 12 laboratories carried out ESCA measurements on certain powder materials used in catalysts and 7 laboratories did similar experiments using AES. According to Ted Madey of NBS, who organized the study, the spread between the results of the different laboratories was much greater than the accuracy of any individual measurement. The results on catalysts are probably indicative of the situation in many materials.

Recognizing the need for improved accuracy in surface analysis, ASTM is forming a new committee on surface analysis (to be Committee E-43) which will become a full fledged ASTM committee this spring after 2 years of organization while in subcommittee status. ASTM committees draw up standard procedures and methods which if approved then become available to all interested parties. Adherence to the standards is strictly voluntary, however.

In 1972, only one company exhibited a surface spectroscopic instrument at the Pittsburgh Conference. This year there were 12, together with about 9 more who presented surface related instrumentation, such as SEM's and surface area measuring devices. Cedric Powell of NBS pointed out that, although perhaps one half of existing surface spectroscopic instruments are already used in practical, problem solving laboratories, the surface has still barely been scratched as compared to possible applications. Now it looks like both the money and the interest are there for surface science to penetrate even further into the practical worlds of metallurgy, catalysis, and many others.

—ARTHUR L. ROBINSON