Chemical Sensing in Process Analysis

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Summary. Improvements in process control, which determine production efficiency and product quality, are critically dependent upon on-line process analysis. The technology of the required instrumentation will be substantially expanded by advances in sensing devices. In the future, the hardware will consist of sensor arrays and miniaturized instruments fabricated by microlithography and silicon micromachining. Chemometrics will be extensively used in software to provide error detection, self-calibration, and correction as well as multivariate data analysis for the determination of anticipated and unanticipated species. A number of examples of monolithically fabricated sensors now exist and more will be forthcoming as the new paradigms and new tools are widely adopted. A trend toward not only on-line but even in-product sensors is becoming discernible.

In the chemical and petroleum industries, it is widely recognized that investments in on-line process analysis provide very high rates of return. As a result, in a single modern petroleum refinery, for example, there may be more than $100 million worth of process control instrumentation. Moreover, increasing competitiveness in world markets, a steady decline of traditional feedstocks, and growing pressures to improve product quality and operating efficiency will combine to ensure that demands for more sophisticated and versatile process analysis and control instrumentation do not diminish (*1*).

Considering obvious needs for chemical analysis in a chemical processing plant, a scientist not familiar with this industry might at first be surprised to learn that the vast majority of on-line measurements are made by pressure, temperature, density, and refractive index transducers and that the sophisticated chemical instrumentation which has revolutionized scientific research in so many disciplines is largely confined to a central laboratory. In fact, very few chemical processing lines employ sophisticated chemical sensors on line because the technological constraints imposed by the extreme reliability requirements and the hostile nature of the plant environment are forbidding. Even infrequent instrumentation failures are intolerable when one is dealing with a process stream valued at $500,000 an hour and concerned about its possible safety implications for a $500-million plant. Typically, more than 99 percent reliability is required in environments that have extreme and rapidly varying temperatures, high levels of noise and vibration, substantial chemical exposures, and "dirty" samples. Furthermore, instruments are expected to remain accurate over prolonged periods, without calibration or even frequent inspection and maintenance. In current practice, industrial process control meets these requirements through highly conservative design. Thus, simple physical sensors are overwhelmingly favored.

Nevertheless, it is possible to obtain data on chemical composition from physical sensors. Such information is gleaned by inference, as years of (costly) experience in small-scale pilot plants have taught process engineers the correlation between process stream compositions and pressure, temperature, and other physical measurements at various points. Severe problems arise from the economic limitation on the number of points sampled, and are dealt with in the same way.

While this practice has certainly bypassed some of the difficulties of designing process analytical instruments, there are some unpleasant side effects. The cost and delay of the pilot plant learning process are the least of these. A more serious problem is that such experience-dependent interpretation is progressively less reliable the farther a plant process deviates from normal conditions. In the limit, analysis will fail completely when it is most needed. Interpreting the behavior of a plant that is out of control then becomes a guessing game with high stakes; an example is Three Mile Island.

Thus, in many cases process engineers have been forced to put more sophisticated instrumentation on line to provide chemical information in detail. For the most part, because of the well-founded attitude of conservatism discussed above, they have favored techniques that are simple or that have been in general use for a long time. This is evident from Table 1, where types of instrumental analysis are listed under widespread, occasional, or potential utilization in process control. A comparison of this current list with one representing the laboratory instrumentation state of the art of 30 years ago would show a striking resemblance.

Furthermore, the power of many of the process instruments is less than that of their laboratory counterparts, as quite different design principles are used to make the instruments robust, stable, and affordable. Figure 1 shows the differences between a laboratory infrared spectrometer, based on the Fourier transform technique, and a process control infrared photometer, based on a microphonic gas cell detector combining the functions of spectral separation and signal transduction (*2*, *3*). In the process sensor, the analytical power of scanning a complete spectrum has been forfeited in favor of ruggedness and reliability.

Clearly, then, there is a need for process analysis that is well beyond the current state of the art. This has led to the establishment of a new subdiscipline in academic analytical chemistry: process analytical chemistry, which can be defined as the use of sophisticated analytical procedures and instrumentation on line as an integrated part of an automated chemical process. In order to make progress in this field, a systems approach must be taken. Interdisciplinary interaction between process engineers, analytical chemists, instrumentation designers, and computer scientists will be required. Although the major emphasis in this article will be on instru-

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mentation and chemometrics, the remaining areas of sampling and use of chemical data in optimization and control are of equal importance to this discipline.

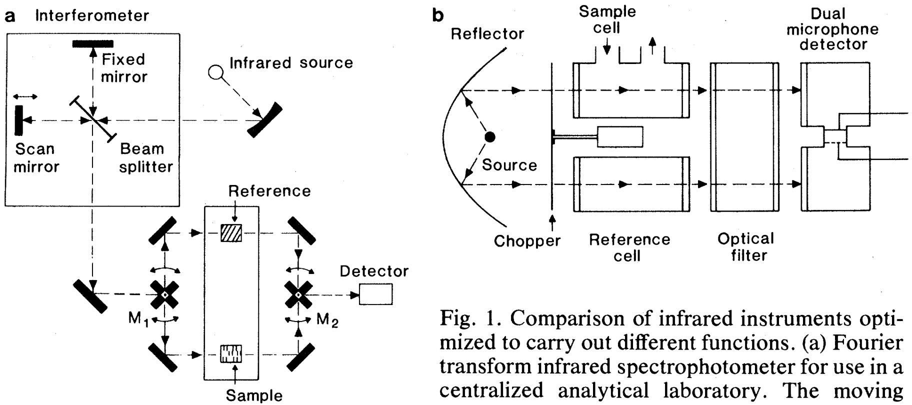

Fig. 1. Comparison of infrared instruments optimized to carry out different functions. (a) Fourier transform infrared spectrophotometer for use in a centralized analytical laboratory. The moving mirror of the Michelson interferometer is mounted on air bearings and its position is controlled and sensed to better than 1 μm. (b) Nondispersive filter infrared spectrophotometer optimized for process control. There is no mechanical scanning or delicate optical alignment in this device.

Rationale for Chemical Sensors in Process Analysis

Analytical instrumentation, including its process control variants, is increasingly dominated by the products of the microelectronic revolution. As electronics exerts an ever larger influence on instrument technology, it has also come to account for most of the hardware content. This trend is growing as built-in microcomputers become the rule rather than the exception. This not only adds to the electronic content of the system, but allows the remainder of the system to be simplified as machine intelligence and processing power are substituted for intrinsic sophistication in the detection and transduction front end (*4*).

In process control itself, distributed digital control systems now define the state of the art in industrial control technology. The system begins with a widely distributed set of dedicated, programmable controllers at the lower level of a hierarchy. Here, considerable fault detection and redundancy are built in. Work performed at this level of the hierarchy is then coordinated by a set of successively higher level computers, connected by an extensive communications network. Finally, this network is integrated into the management information system of the corporation.

The overwhelming economics of scale of microcircuitry, which has promoted this proliferation, also forces considerable standardization on electronic subsystems. The overall trend is toward generalized instruments containing one or several sensors that transduce the quantity to be measured to an electronic output (directly or through an intermediate optical or mechanical interaction), and a fairly standardized electronics-computer system that provides the desired output (*5*), as seen in Fig. 2.

In this context, progress in instrumentation can be achieved through the evolution of newer and better sensors and more and more universal electronics support systems. At the same time, the sensors themselves will become simpler as more sophisticated and "expert" algorithms become available. Eventually, the sensors will become a component rather than a subsystem. Economically, this is advantageous as commonality in electronics brings not only economics of scale in production but also economics of use, as many sensors may share one electronic system. There is even a potential for positive feedback, as reductions in the cost of sensors and electronics allow an increased number of monitoring points and further economics of scale in the sensor itself.

Clearly, the reliability of modern electronics is adequate even for the requirements of process control instrumentation. Also, automatic recalibration and self-verification routines are possible and provide the answer to the stability requirements of such an instrument. The bottleneck lies in the design of the sensor itself, and here a number of shortcuts are possible. When an instrument is a combination of electronics and a sensor, it is desirable to design as many functions as possible out of the sensor and into the data processing. We no longer require linearity in a sensor, but merely a monotonic response. We may use internal standardization in lieu of reproducibility, redundancy in lieu of the very difficult last increment of reliability, correction based on internal or external information in lieu of insensitivity to perturbation, and so on. In the limit, a merely fair performance is enough if it is repeatable, well understood, and coupled with a high enough signal-to-noise ratio to allow the data-processing algorithms to proceed with a reasonable chance of success (*6*).

Existing Types of Process Chemical Sensors

The evolution of analytical instruments toward a combination of low-cost sensor front ends on a microcomputer is still far from complete. In reviewing current sensor technology we will therefore exclude many techniques whose use requires a full-scale laboratory instrument, such as a gas chromatograph–mass spectrometer (GC-MS), which would be of limited adaptability for on-line processing.

Chemical sensors can be based on physical, chemical, or transport properties of the sample. Among physical sensors, optical detectors have a long history of use, but have been limited by cost and reliability to such relatively simple forms as filter absorption photometers in

Table 1. On-line instrument utilization in process control.

Widespread	Occasional	Potential
Temperature	Wet-chemical processor	Chemiluminscence
Pressure	Chemical tape systems	Microwave absorption
Flow	Specific-ion electrodes	Optical emission
Density	Fluorometry	X-ray fluorescence
Refractive index	Infrared absorption (scanning)	Raman
Ultraviolet-visible colorimetry	Mass spectrometers	Infrared emission
Infrared absorption (filter)	Ultraviolet spectrometry	Nuclear magnetic resonance
Gas chromatography	Gamma-ray absorption	Near-infrared reflectance
Indicator tags	Dielectrometry	Acoustic emission
*p*H electrodes	Magnetometry	Chemresistor
Acoustic velocity	Particle counters	Piezobalances
Amperometry	Viscosity	Acoustic attenuation
	Liquid chromatography	Turbulent flow
		Array chromatography
		Electrophoresis

the ultraviolet-visible region (*7*) and gas correlation instruments such as those shown in Fig. 1 (*3*). Advanced devices include circular variable filter spectrometers (*8*) and correlation spectrometers which have vibrating masks in the focal plane of a grating (*9*) or correlate the outputs of a limited number of arbitrary bandpasses (*10*) or random (*11*) filters. Extremely simple instruments of this type can give a very large fraction of the capabilities of fully equipped, costly laboratory spectrometers. Other developments in this area include a "planar" integrated spectrometer, which may eventually provide the functions of a laboratory spectrophotometer in a single microsensor (*12*).

Absorption measurements are predominantly made in the ultraviolet and visible optical regions, where they are heavily dependent on colorimetric reagents, and the mid-infrared, where they are limited by current sampling problems to mainly gaseous streams. However, near-infrared spectroscopy, which combines the universality of infrared with the more permissive sampling characteristics of the visible region (*13*), has benefited from advanced computer methods and has become a major contender in this area (*14*).

Ionizing radiation has been used in the factory as an absorption sensor for material thickness measurements (*15*) and, less frequently, as an x-ray fluorescence sensor for selected elements (*16*). Here new possibilities include two-channel sensors using different radiation energies to give some compositional selectivity, and abridged compound-specific x-ray diffractometers of potentially adequate simplicity.

Use of electromagnetic sensors has been dominated by various forms of dielectrometers, which give data on the dielectric constant and dielectric losses over increasingly wide frequency ranges (*17*). Here, the strong frequency dependence of microwave dielectrometry can greatly improve discrimination (*18*). The spatial averaging and mapping ability of microwave dielectrometry will eventually prove of value for solid-bed analysis (*19*). Microwave spectroscopy, on the other hand, is a superior procedure for specific analysis of polar gases and, through advances in microwave integrated circuits, can now be implemented with a simple sensor device (*20*).

Acoustic measurements have a particularly long history as process sensors. One of the first on-line sensors, which was built in the 1910's to measure the H/N ratio in NH_3 synthesis process streams, used frequency comparisons between an organ pipe carrying the process stream and a tuning fork. Acoustic velocity (*21*) and attenuation (*22*) measurements are commonly used, and acoustic emission, which is now employed to spot-check critical machinery, could eventually be used for routine surveillance.

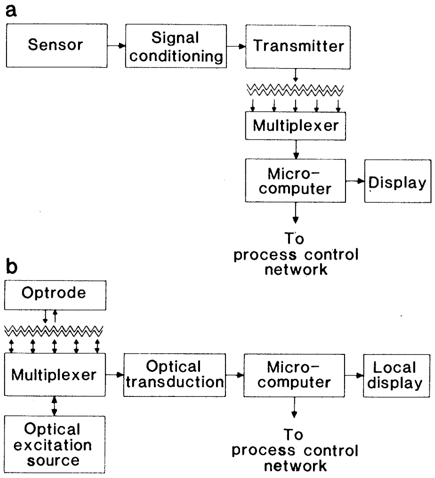

Fig. 2. Idealized process instruments based on microsensors and standardized electronics and computer system. (a) System based on an array of microelectronic sensors, each of which requires signal conditioning. (b) System based on an array of optical sensors with excitation and detection functions remotely located.

Most physical property sensors are based on measurements of temperature, pressure, density, level, or flow. Less commonly, measurements are made of viscosity, turbulence (represented by the variance of a local flow measurement), or thermal diffusivity [an adaptation of the common gas chromatographic thermal conductivity detector for gas monitoring or scale buildup measurements (*23*)]. Other possibilities include on-line sensing of mechanical effects of sample stream composition and direct real-time measurements of various types of surface effects.

Recently, chemical sensors, particularly electrochemical devices, have received a major share of the attention in sensor development. This is because of the inherent simplicity of obtaining a direct electrical readout and the opportunities for using integrated circuit technology for sensor (or sensor array) manufacture (*24*). The most obvious approach here is to scale down *p*H or specific-ion electrode technology, which has already made inroads into process control (*25*), into the microcircuit domain, and to overcome the problems of small signals by integrating the electrode into the gate of a field-effect transistor (*26*) (Fig. 3a). Such essentially potentiometric sensors can be built for the gas phase as well (*27*), and their use for specific gas detection is quite common. Related microelectronic sensors use the impedance variation of a *p-n* junction–metal oxide semiconductor capacitor when the gate surface interacts with the solution ions (*28*), or the changes in reverse bias voltage of a Schottky diode when its metal layer absorbs a vapor that affects its work function.

Conductometric sensors are another broad family of electrochemical devices, ranging from simple conductivity meters for inorganic dissolved solids in water to gas sensors based on conductivity changes of an exposed heated semiconductive oxide (*29*) (Fig. 3b). A more advanced system, the chemresistor (*30*), detects resistivity changes in a thin-film organic semiconductor due to vapor absorption.

The selectivity of all of the sensors discussed above leaves much to be desired, but can be greatly enhanced by chemometric computations on data from arrays of detectors with different partial selectivities (*31*). In many situations, only modest selectivity is required in the first place (for instance, combustible gas monitoring or organic chloride vapor detection). In these cases the selectivity of the available detectors is quite adequate, and often even less selective ones, such as the flame ionization or electron capture sensors familiar from gas chromatography (GC) technology, can be used.

Selective chemical transformation is often an intermediate step on the way to an optical or electrochemical readout, and is usually achieved with an immobilized, preferably reversible, chemical reagent (*32*). Freestanding chemical sensors are the sole components of many dosimeter tags and usually involve irreversible color-forming reactions (*33*). These latter have been widely used for personal protection, but deserve equal consideration as equipment monitors, local leak detectors, reactor bed exhaustion detectors, and so on. Complex chemical processes can take place in multilayer films, as first shown in Polaroid film, and the application of such films in clinical chemistry has been impressively successful (*34*). This technology can be directly transferred to process control, often without developing additional sensor types, as the side reactions and interferences of sensors originally developed for clinical use can be exploited (*35*).

A special category of chemical analyzers, sequential processing systems involving complex wet-chemical reactions followed by physical sensors, have become very popular in clinical analysis (*36*). These do not seem to be likely candidates for reduction to low-cost sensors. However, a variant of this technology, flow injection analysis (*37*), benefits from favorable scaling laws that allow instrumentation to be shrunk to the dimensions of a printed circuit board (*38*).

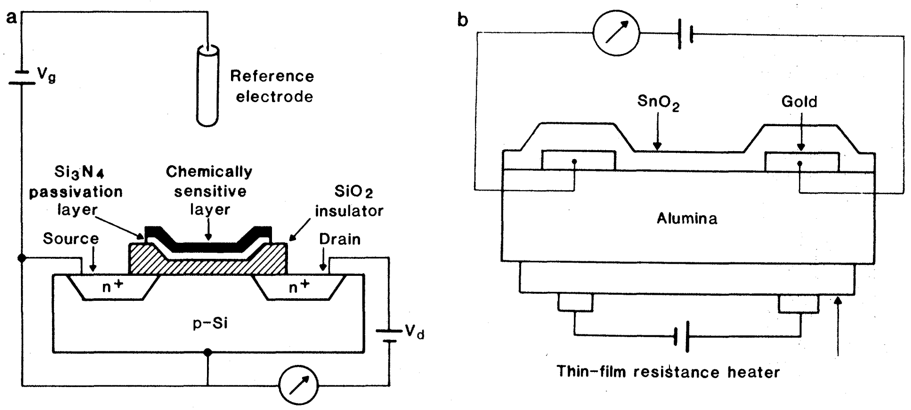

Fig. 3. Electrochemical microsensors fabricated by microlithography. (a) Chemically sensitive field-effect transistor. (b) Thin-film oxide gas sensor.

Biological sensors can be described as an extension of chemical ones, using reagents of exquisite selectivity (and, unfortunately, delicacy). For the ultimate in selective chemistry, immunochemistry, sensors based on optical (*39*) or electrical (*40*) readout are being developed. Enzymatic reagents, however, are more generally usable with the smaller molecules common in process chemistry, and their lower sensitivity and selectivity is rarely a disadvantage for process control applications (*41*), where again they are normally coupled to an optical or electrical readout. Ingenious but somewhat fragile sensors have even been developed which use immobilized bacteria or their organelles as chemical reagents coupled to a potentiometric electrode (*42*).

The fact that real samples are frequently mixtures of many components strongly suggests using chromatographic sensors with their built-in separating ability. The complexity of such devices has limited their use somewhat, and only GC is employed on line with some frequency (*43*). The technological tour de force of miniaturizing and integrating a gas chromatograph into a silicon chip is a dramatic example of the technique's potential for further development (*44*). In such chromatographic sensors, however, the increase in separating power is coupled with a loss of recognition reliability, as the identification of peaks by retention time only is somewhat risky (*45*). Clearly, a hyphenated system such as a low cost GC-MS sensor would provide nearly the ultimate performance (in fact, such a miniature GC-MS, but not a cheap one, now sits on Mars with Viking). More down-to-earth, multicolumn micro gas chromatographs have become available (*46*) and greatly alleviate the problem of selectivity. Liquid chromatography (LC) is making its way into process analysis, which will benefit from the growing popularity of micro-LC (*47*). Electrophoresis seems even farther from the factory floor, but help may come from the new technology of capillary column electrophoresis (*48*).

The techniques of GC, LC, capillary electrophoresis, and flow injection analysis are undergoing a convergent evolution in design, so that it is possible to begin to conceptualize a universal chemical analysis microlaboratory in which the functions of sample acquisition, processing, reaction, separation, detection and analysis are combined in a module no larger than a shoe box. Such a system, with a modular design and interchangeable components, could be used in a variety of situations for a variety of analyses.

A particularly simple chemical sensor is the piezobalance, a vibrating quartz crystal coated with a selectively absorbing thin layer whose absorption changes the crystal's oscillating frequency (*49*). Since frequency can be measured very accurately, subnanogram quantities of chemicals can be detected with very simple equipment. The lack of selectivity of these sensors has recently been circumvented by multicrystal sensors with an array of layers, whose response pattern, as seen in Fig. 4, is characteristic although that of an individual layer is not (*31*). Surface acoustic wave sensors, a closely related technology, may provide similar behavior with even higher sensitivity (*50*).

Mass spectrometers, which have already been used in the factory, will evolve toward a sensor-type technology and with widespread use as the potentially less expensive technology of ion traps (*51*) matures. An offshoot of MS, plasma spectroscopy (*52*), may be easier to adapt to the process environment, as it is not dependent on high-vacuum techniques.

Diffusion and extraction have generally been used as sample preparation steps for sensors, and advances in membrane technology may greatly increase the potential of existing sensors.

Sensor Limitations: The Lessons of Chemometrics

At this point, the reader might be tempted to conclude that in the near future the task of a process chemist will be simply to devise a list of analytes to be monitored and then choose a set of highly selective sensors, each optimized to detect the target substance free of interference from all others. However, this straightforward and relatively simple strategy has a major drawback: when the process line fails because of the presence or inadvertent production of unanticipated chemicals, the array of preselected detectors may tell us very little. At the same time, despite enormous efforts to achieve selectivity by use of membrane technology and selective chemical reactants and absorptive surfaces, it remains true that these sensors are highly prone to interferences. In fact, the number of publications introducing new laboratory sensors is far exceeded by the number of publications describing analytical interferences and what to do about them.

Yet this very susceptibility to interference can be exploited to increase the selectivity of the system. Chemometrics (*53, 54*), the science of chemical data analysis, tells us that with a perfectly selective single-parameter detector, only quantitation of the specific component is possible. However, with an array of sensors, each of which can respond differentially to at least two of the components in a mixture, far more analytical information can be obtained. In the first place, if the components are linearly additive and are all known, that is, calibration data are available, for them, then they can all be quantitatively determined simultaneously (*55*). Even if a variable number of unknowns are present, the quantity of each of the known components can be expressed as an upper limit (*55*). For qualitative analysis, the differentiating power of multiple arrays of sensors increases rapidly as the number of sensors and the number of output levels of each sensor grow (*45*). Therefore, a relatively nonselective sensor is desirable, provided it is a member of an array of nonselective sensors, each of which exhibits a different response to each of the different types of molecules to be detected and quantitated.

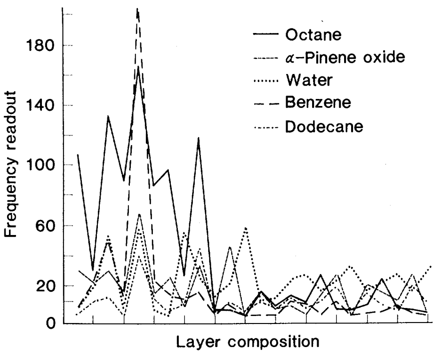

Fig. 4. Response of correlation piezobalance microsensor. Each chemical vapor has a different affinity for each of the various sensing layers; the response profile over the layers constitute a unique fingerprint for each chemical entity.

But according to chemometrics it is possible to extract even more information from multiple measurements by using pattern recognition strategies and learning algorithms (*56*). An excellent example of this is the use of near-infrared reflectance spectroscopy to perform compositional analysis of agricultural products (*57*). Optical absorptions in the near-infrared (from 0.7 to 2.5 μm in wavelength) arise mainly from overtone and combination vibrations of OH, NH, and CH groups. The measurements may often be made directly on granular or powder samples. The data for each sample consist of a series of precise diffuse reflectance intensity values at a number of arbitrary or near-arbitrary wavelengths. Calibration is carried out by multiple regression analysis, using a learning set of at least 30 and preferably more known samples which have been independently chemically analyzed. Despite a high degree of spectral overlap, weak transitions, and a marked degree of background variation, excellent quantitation and good reproducibility are obtained. The method has been extensively studied in the wheat-growing industry and has almost totally supplanted the more classical, time-consuming chemical methods for determination of starch, protein, and water (*58*).

Near-infrared spectroscopy is also commonly used to determine components, such as ash, which do not have transitions in this spectral range. Apparently, the presence of these components alters the spectra of the detectable components in a reproducible fashion. In addition, the techniques can be used to measure properties of a sample which cannot be directly determined by chemical analysis. For example, animal feeds have been quantitated for "in vitro metabolizable energy" and "digestibility" (*59*), and endosperm "texture" and "resistance to grinding" have been determined (*60*) by using near-infrared spectroscopy and suitable training sets.

Chemometrics also shows the benefit of instrumentation that produces multidimensional data which can be represented in the form of a tensor product of vectors, where each vector represents a response to a specific variable (*45*). Two examples of this type of data are fluorescence intensity measurements as a function of both excitation and emission wavelengths (*61*) and GC-MS data (*62*). For such data sets extremely powerful data reduction strategies are possible: (i) where all of the components are known, quantitation is obviously possible (*55*); (ii) where none of the components are known, it is nevertheless possible to obtain a lower bound for the number of components present, and in favorable cases, where the number is low, to obtain the spectra of each (*63, 64*); and (iii) it is also feasible to quantitate the known components in the presence of a variable background of unknowns by the technique of rank annihilation (*65*).

Trends in Process Control Sensors

The same technologies and economic driving forces that were the basis for the microelectronics revolution are providing the impetus for a similar revolution in chemical sensor design. The key to this development is the adaptation of microlithography and chemical etching to produce two- and three-dimensional entities that can serve as the components of chemical sensors. This includes not only electronic and signal-conditioning elements but also transducers (thermistors, photodiodes, and so on), electro-optics (light-emitting diodes, light guides, interference filters), and mechanical devices (valves, nozzles, diaphragms). The techniques used to form the necessary structures collectively form the basis of "silicon micromachining." Some 20 years ago, a classical lecture by R. P. Feynman entitled "There is plenty of room at the bottom" pointed out the possibility of microscale engineering (*66*). In such microengineered devices, scaling laws allow new levels of ruggedness, shock and acceleration resistance, thermal uniformity, and response speed. In addition, there are cost savings in manufacturing as well as reductions in weight, volume, and power consumption. Thus, such micromachining provides new trade-offs between complexity, cost, and reliability which will allow increased sophistication in the instrument. Finally, scaling laws dramatically change the relative importance of different physiochemical interactions in microdevices, allowing novel design principles, measurement methods, and capabilities.

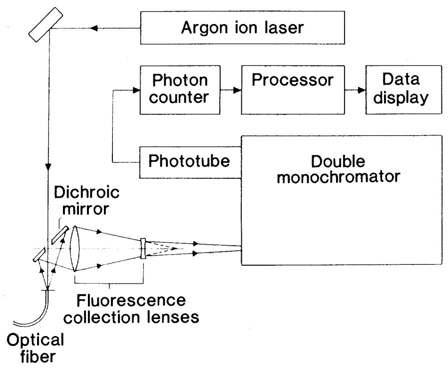

Fig. 5. Readout instrument for remote spectrometric analysis over optical fibers.

Nature is also a source of inspiration for advances in sensor design, having evolved some sophisticated "low-cost" microsensors during the past billion years. The simpler sensors of the insect world (*67*) are already well enough understood to provide design suggestions for sensor development research. An example is the antenna of the gypsy moth, which is capable of detecting individual molecules of the female's pheromone against a background 15 to 20 orders of magnitude greater. This is achieved by a combination of diffusive sampling, two-dimensional chromatography, and receptor sites. Many advances in sensor technology may eventually begin with detailed studies of insect physiology.

A different direction in improving process control analysis technology is to make the sensor physically separate from the readout system. In such a remote measurement system, the sensor is the major system component installed in the factory, with a single common readout and data system installed back at the control panel. Since the time constant of most sensors is typically of the order of a second, while the time interval between measurement updates at the factory is typically at least a few minutes (limited by the production process time constants), hundreds of points can be monitored from one central location.

This not only achieves savings in the overall cost, by limiting the per-station cost to that of a small, simply installed sensor with minimal support, the connections, and a small share of the readout, it also places most of the system out of the aggressive factory environment, in a location where instrument adjustment, servicing, maintenance, and replacement can be accomplished at low cost. Furthermore, with affordable redundancy these can be achieved without significant downtime. In this case, it is important to minimize the fraction of the system at the distal end, by making the sensor simple, and putting as much of its support as possible back at the control panel.

To reduce the distal portion of the system, electro-optical technology has distinct advantages for sensor development (*68*). Inexpensive, low-loss miniature fiber-optic light guides allow the construction of a sensor that has no electrical components at the sensing end. Instead, the probe light is generated remotely and conveyed to the sensor end by a light guide, where it interacts with a chemical probe by absorption, scattering, or fluorescence. The light, which is now encoded with chemical information, is then returned by the same or a second light guide to an optoelectronic transducer, which creates the desired electrical signal (Fig. 5).

Today's optical "conductors" (long-range communications fiber optics) are equivalent in performance not to an electrical conductor but to an electrical superconductor. This allows long-distance connections over very small cables, which can often be installed in existing facilities without exorbitant conduit costs. Since insulation against ambient noise in optical systems is nearly perfect, the system does not even require a distal preamplifier or electrical power supply (*69*). Figure 2b shows such an optical sensor for multipoint sensing from a central readout.

In practice, this technology is usually combined with the use of specific immobilized reagents in the sample interface or "optrode" to ensure the desired sensitivity and specificity (*68, 70*). More than 15 types of such optrodes have been developed by immobilizing different types of reagents at the fiber tip, including ones for temperature, *p*H, Cl_2, I_2, Fe^{3+}, UO_2^{2+}, Pu, HCHO, NH_3, O_2, and $CHCl_3$; many more are possible and are under development. Current optrodes use mainly ultraviolet and visible absorption and fluorescence, but near-infrared optrodes are promising for many applications (*71, 72*).

Once the restraints on sensor proliferation set by reliability and cost have been weakened, new criteria arise for choosing what to measure. Clearly, large amounts of data are now optimal. We want not only measurements that are complete enough to reduce inferential interpretation and reduce the pilot plant effort, but also overdetermination to ensure reliability against both sensor failure and unexpected variations in the process, as well as some flexibility in the operating behavior of the plant. At this point, chemical sensor networks are not only a way to improve plant process control analysis and reduce its cost, but also a powerful way to increase the efficiency, quality, and versatility of the production process itself.

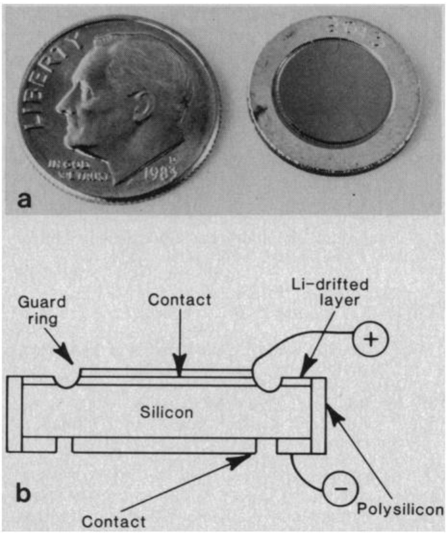

Fig. 6. Temperature history microsensor. This device passively records the entire thermal history (temperature-time curve) of a device or location for readout on demand.

Beyond Process Control

Thus far, we have only considered the processing of raw materials into chemicals. We need to realize that these chemicals will, in many cases, be further processed into various kinds of manufactured items. These two- or three-dimensional entities, varying in size from computer microcircuits to large commercial aircraft, must in many cases be manufactured to exacting chemical standards, with means provided for chemically monitoring their production and for final inspection and quality assurance in a chemical sense. In this endeavor we wish to know not only the chemical composition of an entity, but the spatial relations of the chemically distinct components. Ideally, the results of such an analysis would be displayed as a "chemical image" on a computer graphics terminal with each analyte encoded as a different color and the amount of each as a different intensity.

In the ultraviolet-visible optical region, analysis is greatly facilitated by high-speed laser scanners and optical imaging devices. Their use for analytical chemistry with spatial resolution has been reviewed (*73*). Unfortunately, the ultraviolet-visible region of the spectrum is seldom suitable for inspection of the interior of an object, and the ultraviolet region is limited for solid-state analysis of industrial products. X-ray and nuclear magnetic resonance devices, employing the tomographic principle, have recently been used for this purpose with great success (*74*). Optical imaging technologies are readily adapted to x-ray viewing with scintillators or image converters (*75*). Simplified, high-speed tomographic techniques can be employed for on-line inspection of regular objects, as only a few cameras would be sufficient to define the object's geometry. On-line nuclear magnetic resonance tomography seems much farther in the future.

Another aspect of process analytical chemistry that is ripe for development is in-product sensors. Technical requirements and user preference have forced the automotive industry to manufacture automobiles with a multitude of built-in sensors, reporting to either the human operator or to internal control loops in the system. Surprisingly, the vast majority of industrial products of comparable value are devoid of even the most elementary internal sensing capability. There are two reasons for this. One is technological inertia, but the main one is economic. Until recently, in-product sensors were possible only within the economies of scale of the automobile industry. The proliferation of microsensors will soon change this, and in the process will change quality control from a statistical assurance by the manufacturers to a "here and now" verification by the user.

Examples of this trend already exist. In-product sensors that are becoming available range from simple thermoluminescent radiation dosimeter tags (*76*) to color indicator tags for chemical exposure (*77*), jolt sensors for transport of delicate items, paints indicating maximum temperature (*78*), and steadily more sophisticated indicators of appropriate refrigeration temperatures for perishable goods (*79*).

Growth is evident in the sophistication and capability of these devices. The temperature microsensor, shown in Fig. 6, which measures (retroactively) the complete time-temperature history of a part with a passive, unattended sensor (*31*), and the microdryer, a microdevice that both removes humidity from an enclosure and indicates its residual level, are examples of this trend. Many of the sensors described above for process use are simple, rugged, and inexpensive enough to merit use as installed indicators in a product.

Conclusions

Microengineering, remote measurement techniques, and chemometrics together provide the tools with which to engineer a new generation of chemical sensors that will be ideally suited for process analytical chemistry. We look forward to a movement of analytical chemistry from the laboratory onto the factory floor. In addition, we foresee the extension of these concepts to the analysis of manufactured products and the use of in-place sensors.

These developments may benefit the laboratory scientist as well. As the articles in this issue attest, laboratory analytical instruments are generally large, complex pieces of equipment. Over the past 10 years there has been a tendency in large scientific institutions to establish a centralized analytical facility where sophisticated instrumentation is maintained at the state of the art, the economics and efficiency of time-sharing use are attained, and an expert staff is available for consultation. Thus, the situation for analytical instrumentation resembles that of computing a decade ago, when computer centers offered the only cost-effective access to computing for scientists. Just as personal computers revolutionized computing, in situ instruments have the same potential to broaden the scope of analytical chemistry. In analysis, as in computation, there is a trend toward distributed power, and this will ultimately return to the end user the oversight of product quality and performance.

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