SPECTROSCOPY COMES OUT OF THE LAB

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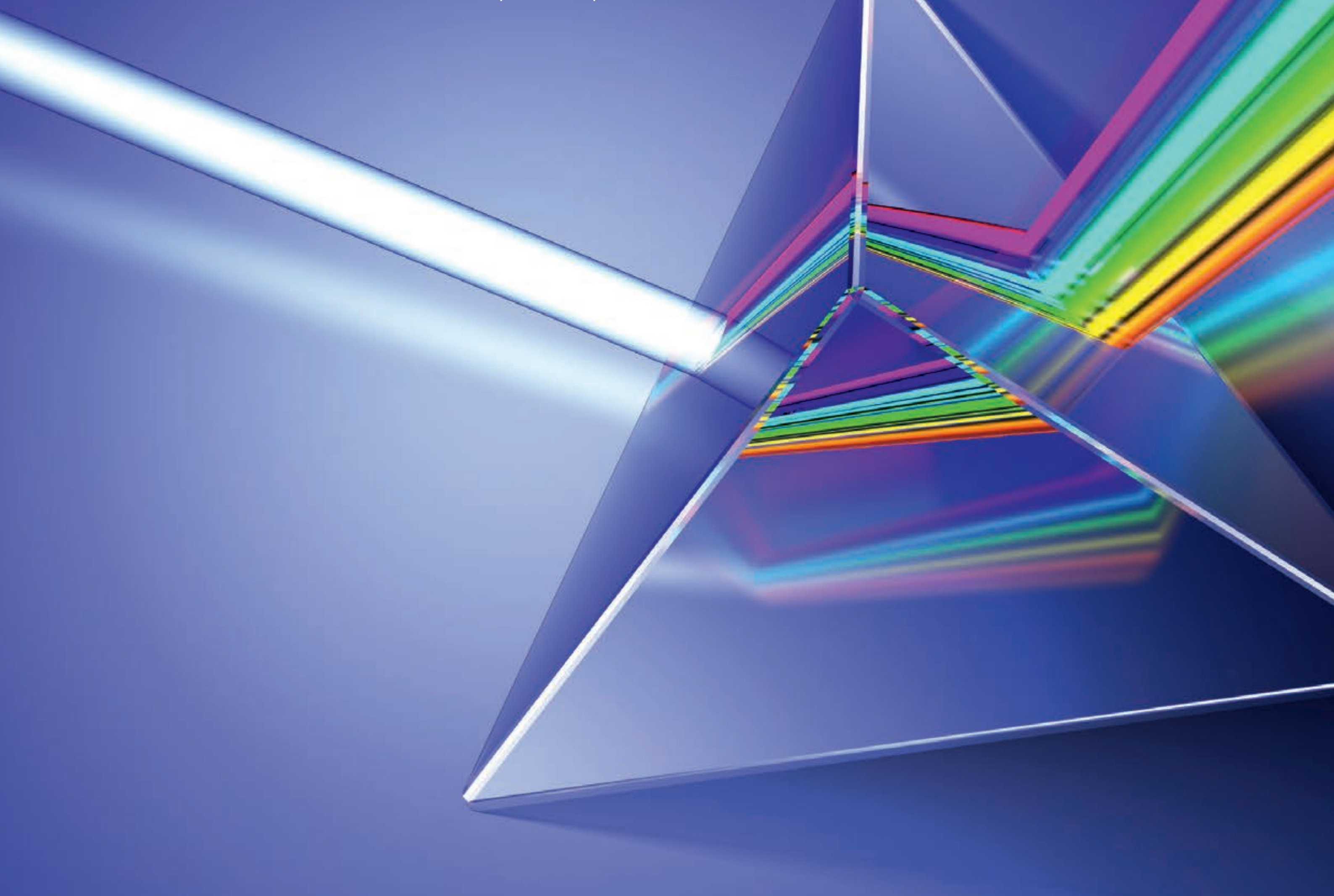
Developments in technologies for building spectroscopes and spectrometers have advanced in leaps and bounds since the first commercial infrared spectroscope was developed in the 1940s and the first FT-IR spectrometer came on the market in 1969. Today, spectrometry is moving out of the lab and into the field and the process plant.



Advances in computers and microchip technology, as well as better and smaller sample handing systems, have now made it possible to use spectrographic measurement in the field with portable instruments and in situ in processing plants. The main advantage is obvious - being able to test solids, liquids or gases in real time, without having to ship samples to laboratories and wait for results, means that action can be taken on the results more quickly or even immediately. In addition, the use of modern microprocessor technology is making it possible to develop portable instruments that can be used by relatively untrained personnel.

Portable instruments

In the development of portable, handheld devices, there have been critical factors that needed to be considered such as weight, size, power consumption, safety, user friendliness, durability and, of course, accuracy of measurement. Consideration of these factors has led to the development of handheld systems using various technologies including microelectromechanical systems or MEMS.

Devices produced using MEMS can be mass manufactured so they are low cost and extremely robust and reliable products. MEMS-based spectrometers are compact devices that are ideal for the construction of handheld tools. The availability of portable spectrometers is a key driver in developing many new applications, in which the measurements can be easily carried out on site without needing to bring the sample to the laboratory. Potential applications for handheld spectrometers come from a broad range of industries and services. Below are some examples.

Raw materials inspection

Many process-driven industries need to test the quality and verify the identity of materials before they are used. Allowing an on-site quality control inspector to test the materials without having to wait for a laboratory to test samples can represent high cost savings for the pharmaceutical, food and beverage, chemical and petrochemical industries.

Fraud identification

Approximately 10% of the pharmaceuticals sold are counterfeit and can be dangerous or ineffective. Handheld analysers permit field inspection and investigation to help expose counterfeits. In fact, this type of portable technology can be very effective in detecting any type of fraudulent material by its chemical signature, another common example being the textile industry, in which cheap synthetics are often passed off as expensive silks.

Forensics

In the field of forensics, speed of detection is important, along with the ability of relatively untrained law enforcement or immigration personnel to be easily able to analyse a substance on the spot and take immediate action. The possibility of immediate white powder analysis allows for narcotics identification and the initial primary detection of the potential presence of explosive residues. Portable instruments based on Raman spectroscopy have also recently been developed for non-intrusive testing for cocaine mixed in bottles of alcohol, with obvious public health, law enforcement and liability benefits.

> IN INDUSTRIAL ENVIRONMENTS, THERE ARE SIGNIFICANT DIFFICULTIES ATTACHED TO THE SAMPLING AND ANALYSIS OF PROCESS FLUIDS AND MATERIALS. WHILE SOME INDUSTRIAL ENVIRONMENTS ARE RELATIVELY BENIGN FOR SAMPLING ... IN MANY CASES ... THE OFTEN HIGH PRESSURES, EXTREME AND RAPID TEMPERATURE CHANGES, AND HIGHLY AGGRESSIVE CHEMISTRIES MEAN THAT SAMPLING IS DIFFICULT AND HIGHLY DANGEROUS, AND VERY OFTEN IMPOSSIBLE.

Medicine

New diagnostic instruments have recently been announced that enable the simple screening of samples for bacterial, fungal and microbial infection. These systems allow accurate, rapid and cost-effective identification through a process in which organisms are identified by the unique spectrum of the major proteins and peptides that constitute their makeup. This has the potential to greatly improve the efficacy and efficiency of microbiology labs.

Environmental pollution

The ability to easily measure air, water and soil contamination are of benefit in many areas. Industrial technology for the in-situ and inline/online measurement of air and wastewater pollution has been available for some time, but the ability to perform manual spot checks with a handheld spectrometer also aids in the independent identification and quantifying of pollutants by environmental inspectors and to cross-check the accuracy of other methods. Monitoring the long-term effects of environmental disasters such as oil spills and chemical leaks is also more effective if handheld instruments are available. The CSIRO, for example, recently announced the development of a handheld IR spectrometer device for measuring petrochemical contamination in soil, silt, sediment and rock, enabling the rapid detection of the presence of contaminants at a site, providing significant cost advantages in terms of reduced testing costs and the avoidance of delays.

In-situ and extractive instruments for industrial environments

Three different forms of spectroscopy are generally used for the analysis of a variety of chemical processes. Near-infrared spectroscopy is the most advanced, and recent advances in robust sample interfacing promise to aid in the expansion of near-IR applications to cover an even greater range of processes. Mid-IR also has a long history but has been restricted to a fairly narrow range of applications, largely due to the limitations of mid-IR optical materials. However, even in this field, recent probe developments combined with mid-IR's ease of calibration promise to expand the use of mid-IR, especially for expensive products involving short run batch processes. The use of Raman spectroscopy for industrial process

Definitions

Spectroscopy was originally the study of the interaction between radiation and matter as a function of wavelength (λ).

Spectrometry is the spectroscopic technique used to assess the concentration or amount of a given chemical (atomic, molecular or ionic) species. In this case, the instrument that performs such measurements is a spectrometer, spectrophotometer or spectrograph.

Spectroscopic methods can be classified on the nature of their interaction - absorption, emission and scattering.

Infrared spectroscopy is a form of absorption spectrometry in which the infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a monochromatic beam, which changes in wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once. Analysis of these absorption characteristics reveals details about the molecular structure of the sample.

NIR spectroscopy is where the near infrared (NIR) range (~800 to 2500 nm), immediately beyond the visible wavelength range, is used. It is especially important for practical applications because of the much greater penetration depth of NIR radiation into the sample than in the case of mid-IR spectroscopy range. It also allows large samples to be measured in each scan and is currently employed for many practical applications as described in the article. Typical applications include pharmaceutical, medical diagnostics (including blood sugar and oximetry), food and agrochemical quality control, as well as combustion research.

Raman spectroscopy uses the inelastic scattering of light to analyse vibrational and rotational modes of molecules. The Raman effect occurs when light impinges on a molecule and interacts with the electron cloud and the bonds of that molecule. Photons excite the molecules from the ground state to a virtual energy state. When the molecules relax they emit photons, and the difference in energy between the original state and this new state leads to a shift in the emitted photon's frequency away from the excitation frequency. Since it is a scattering technique, specimens do not need to be fixed or sectioned. Raman spectra can be collected from a very small volume and water does not generally interfere with Raman spectral analysis. Thus, Raman spectroscopy is suitable for the microscopic examination of minerals, materials such as polymers and ceramics, and cells and proteins.

analysis is relatively new, but given the inherent advantages of Raman for many applications, this branch of molecular spectroscopy is also likely to find more widespread use in industrial processes.

Sampling in hostile environments

In industrial environments, there are significant difficulties attached to the sampling and analysis of process fluids and materials. While some industrial environments are relatively benign for sampling (such as total organic carbon, or TOC, analysis in food industry wastewater monitoring), in many cases, particularly in the chemical and petroleum industries, the often high pressures, extreme and rapid temperature changes, and highly aggressive chemistries mean that sampling is difficult and highly dangerous, and very often impossible. In addition, samples taken from a process may undergo considerable chemical change by the time they can be analysed offline. As a result, in most industries, process materials need to be sampled and analysed within the process itself (in situ), or as close as possible (extractive sampling).

Extractive sampling

Extractive sampling systems for use in liquid analysis usually include two subsystems in addition to the spectrometer itself. A 'fast loop' is used to tap off some of the liquid or gas and must maintain a sufficient flow of sample past the entrance to the analysis system to ensure that the sample reaching the spectrometer at a given time is representative to the actual current conditions in the process stream or vessel. A sample conditioning system is then used to maintain the condition of the sample as close as possible to that existing in the actual process while removing particulate matter or bubbles that might interfere with the analysis. This method is expensive and complex and includes

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a number of different components such as a sample extraction probe, valves, filters and separators, flow meters and controllers, pressure gauges and regulators, and usually a sample pump. Every component in the system is a potential source of maintenance requirements and risk - a particular concern if the stream is hazardous.

In-situ sampling

For in-situ sampling an optical sampling window is inserted into the process reaction vessel or pipeline and the direct test radiation is injected and received back via optic fibres feeding back to a spectrometer outside the system. By removing the need for extraction and sample conditioning, in-situ analysis eliminates a major source of installation cost, maintenance requirements and risk. At the same time, by making the measurement within the reaction vessel or pipeline it improves measurement speed, accuracy and reliability. In-situ sampling has been in use since the 1980s; however, for many years its implementation was limited due to high hardware costs, labour-intensive calibrations, and the limited robustness and reliability of the sample interfacing equipment then available, but recent advances in the design of optical probes and related hardware for spectroscopic sample interfacing have significantly improved its practicality. Over recent years, there have been a number of technical advances including the advent of smaller and more robust instruments, the availability of fibre-optic signal transmission and multiplexing, the development of more robust probes and flow cells using diamond, sapphire or fused silica windows, and the implementation of new forms of analysis such as process diffuse reflectance and Raman spectroscopy.

Conclusion

Spectroscopy has come a long way from the early research of Robert Bunsen and Gustav Kirchhoff, and the large and complex early spectrographic equipment developed in the mid-20th century. While spectrometers of various types are now ubiquitous in laboratories everywhere, modern advances in materials and microchip technology are now making it possible to move spectrometry out of the lab and into the world where it can find a much larger range of application.