Remote Spectrometry with Fiber Optics

The ability of quartz cables to carry an optical signal may engender the next revolution in spectrometry

"Many chemical samples are too hot, too cold, too radioactive, too corrosive, or too otherwise nasty to get close to for an analysis," says Tomas Hirschfeld of the Lawrence Livermore Laboratory. "Some samples, like an underground nuclear explosion or underground gasification of coal, you can't get close to. Last, but not least, there are those situations in industry where you have a hundred spots you want sampled on a near-continuous basis." A new way to handle these situations, he continues, "comes to us courtesy of Ma Bell, who has spent a billion dollars in the last few years developing fiber-optic communications, in the process giving us the ability to send out light a mile or so in a fiber optic cable, have it interact with a sample, and have an echo come back that can tell us what is going on in that sample."

It may not be possible yet to analyze a sample a mile away, and there are still no commercial spectrophotometers in which fiber optics are used for sampling. But a revolution in spectrometry may be just over the horizon. There is now one commercial instrument that can monitor temperatures remotely by means of fiber optics, and two others may be near commercialization. A prototype fiber-optic spectrophotometer for measuring the concentrations of uranium and plutonium in reprocessing solutions is already in operation at the Oak Ridge National Laboratory (ORNL), and systems are being planned for some nuclear installations. Lawrence Livermore, moreover, is negotiating with six instrument companies for the manufacture of fiber-optic systems specific for various chemicals.

The key to all of this activity is the fiber-optic cable, originally developed at Bell Laboratories but now manufactured by several other companies. In such a cable, a core of quartz or other optical material is surrounded by a transparent material of lower refractive index. Such cables transmit light by internal reflection: light rays strike the interface between core and covering at a shallow angle and are reflected back with virtually no loss. The primary limiting factor is the absorption of light by the cable itself. Using a laser source and near-infrared light, a signal can be transmitted as much as 50 kilometers. With ultraviolet radiation from a conventional tungsten-halogen source, the maximum range might be less than 1000 meters. Optical fibers are beginning to be widely used for transmitting computer data and telephone conversations, and a great deal of technology has been developed for splicing cables, connecting them to light sources and receivers, and interconnecting multiple cables. This technology has greatly simplified the job of developing fiber optics for remote spectrometry.

The first commercial fiber-optic instrument is a temperature probe developed by Kenneth Wickersheim of Luxtron, Inc., Mountain View, California. Wickersheim observed that the intensities of individual emission lines of certain rare-earth phosphors, such as europium-doped gadolinium oxysulfide or lanthanum oxysulfide, change with temperature at different rates. By measuring the ratio of the intensities of two different lines, it is possible to measure temperatures accurately between −30° and +240°C. This is achieved by placing a small amount of the phosphor on the tip of a quartz fiber and enclosing it in black teflon, both to protect the phosphor and to keep light out. This assembly has been given the generic name "optrode" (the optical analog of an electrode).

> Monitoring groundwater contamination with fiber optics could save $500,000 per site.

Ultraviolet light is focused into the other end of the cable to stimulate the phosphor, and the resultant phosphorescence is carried to a detector through the same cable. A microprocessor measures the intensities and calculates the temperature. Because the optrode is entirely glass and plastic, it is (like most proposed sensors) immune to microwaves and electromagnetic interference.

A fiber-optic sensor useful for higher temperatures was reported in September by Ray Dils of the National Bureau of Standards. Working with the Saphikon division of Tyco Corporation, Dils developed single-crystal aluminum oxide fibers as long as 30 centimeters. A cavity at one end is coated with thin films of iridium and aluminum oxide to create a classical blackbody cavity. When the tip is inserted into a hot gas stream, the iridium cavity emits an intense light that is transmitted to a detector by the fiber. The intensity of the light, measured at 0.6 and 0.7 micrometers, is proportional to the temperature.

The system is accurate to 0.05 percent over a temperature range of approximately 670° to 2000°C—more than 500°C above the temperatures that can be measured with conventional thermocouples. The device is also about eight times as fast as a thermocouple.

A third approach to temperature measurement was reported by Gerald B. Brandt of the Westinghouse Research and Development Center at the recent meeting* of the American Chemical Society (ACS). Brandt and his colleagues hope to use the inherent blackbody radiation of the quartz fiber itself to detect hot spots in electrical equipment, chemical reaction vessels, and nuclear reactors. When any section of a fiber is heated, it emits weak infrared radiation. "Nature has been kind to us," Brandt says, because the radiation increases rapidly at the temperatures of interest.

Detectors at both ends of the fiber measure the intensity of the radiation at two wavelengths to determine the temperature. The ratio of the intensities at the two ends tells where on the fiber the hot spot is occurring. If two fibers are used, the three-dimensional location of the hot spot can be determined. In the laboratory Brandt has successfully used the technique to measure temperatures between 135° and 700°C.

Debra Bostick, J. Edward Strain, and David McCue of ORNL have been developing remote instrumentation for monitoring uranium reprocessing operations. They use a modified visible-ultraviolet spectrophotometer connected to a remote cell by two fibers, each about 20 meters long. Conventional lenses are used to focus light from the first fiber into a narrow beam through the cell and to collect transmitted light for return to the spectrophotometer through the second fiber. A rotating filter selects appropriate wavelengths for independent detection of uranium, plutonium(III), and plutonium(IV) ions, as well as for a background reading. The spectrophotometer readings are then used to calculate abso-

*Held 12 to 17 September, Kansas City, Missouri.

0036-8075/82/1126-0875$01.00/0

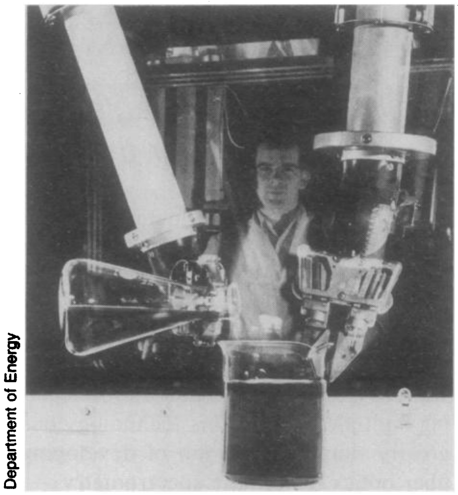
lute concentrations in a conventional manner.

At ORNL one such system is now being used to ensure that above-normal amounts of these radioactive species are not present in a uranium-depleted waste stream of a reprocessing facility. The device can monitor three separate sample cells independently. Similar installations are being considered for other facilities. Bostick predicts that the technology will be very useful in the future for monitoring compliance with international agreements regulating reprocessing facilities. The chief problem with the system is deterioration of the cables' light-carrying ability caused by damage from gamma radiation. This damage limits the useful life of the cables to less than 3 years if they are unshielded.

Perhaps the most varied work has been conducted by Hirschfeld, who also reported his results at the ACS meeting. He has chosen to use fluorescence spectroscopy because it requires only one cable. This not only reduces the cost of the system but also eliminates the sensitivity of alignment of two fibers at the remote cell. Light is provided by a laser source and detection by a Raman spectrometer, which, he says, is "orders of magnitude more efficient than a fluorimeter." A Raman emission line of the fiber is used as an internal standard. Hirschfeld calls this approach remote fiber fluorimetry, or RFF.

Hirschfeld and Terry Deaton, who is now on the staff at the U.S. Air Force Academy, have used three main types of optrodes. The simplest is just the bare end of the optical fiber inserted into the sample or a fluorescence cuvette; this is used mostly if the sample is highly fluorescent. If greater sensitivity is required, they use a small sapphire ball to focus incoming light at a point about 0.5 millimeter into the sample; this ensures that weak fluorescence is concentrated near the fiber. They have also constructed a membrane optrode in which the sample flows into a small chamber, where it is interrogated by the light beam. This optrode allows more control of the sample environment, which is often important because fluorescence can be environmentally sensitive.

Using this setup, the two investigators have successfully performed RFF with fibers as long as 1280 meters. Light transmission begins deteriorating at 800 meters, however, and work at longer distances requires great care. In most of their experiments, they have generally used cable lengths of 200 meters. They have also developed some simple but effective switching devices that make it possible to use one fluorimeter with many optrodes. This device should make the technique particularly valuable in refineries and chemical processing plants where a large number of spectrophotometers are required to monitor operations, often in harsh environments. A typical refinery, for example, has about $100 million worth of instrumentation, says Hirschfeld; on the average, there is about $3 worth of process control instrumentation for every $1 worth of laboratory instrumentation. Use of a centralized spectrophotometer connected to many remote optrodes could not only reduce the cost of instrumentation significantly but would also allow the instrument to be installed away from the harsh environment of the plant.


Department of Energy

On its way out

Remote handling of samples can be minimized by remote spectrometry.

The U.S. Environmental Protection Agency is now studying RFF for monitoring groundwater near hazardous waste dumps. Groundwater does not normally fluoresce, whereas contaminated water typically does. It should thus be possible to detect leakage from a dump merely by observing fluorescence in surrounding water. The chief advantage is cost. Withdrawing samples of groundwater for laboratory analysis typically requires drilling a 10-centimeter hole down to the aquifer, whereas remote sensing with fiber optics requires only a 1.2 centimeter hole. At a typical site, the savings in drilling costs, Hirschfeld says, can be as much as $500,000.

Not all chemicals of interest fluoresce, of course; most, in fact, do not. This problem can be overcome, Hirschfeld says, by making chemically specific optrodes with standard reagents that do fluoresce. A year's worth of reagent can be attached to the optrode in a small reservoir as with chemically specific electrodes. Orion Laboratories of Cambridge recently began selling accessories to construct such optrodes.

Many reagents have variable fluorescence that can be used to quantify an unknown sample. The dye rose bengal, for example, fluoresces in the absence of oxygen, but phosphoresces in its presence; it can thus be used as a specific oxygen sensor. The fluorescence of rubrene is quenched by molecular iodine. Silver fluoresceinate can be used as a probe for chloride ion, while uranyl ions can be used as a probe for iron. Hirschfeld has also developed probes specific for plutonium, sulfate, various organics, temperature, pressure, and pH.

Because uranyl ions fluoresce and plutonium can be detected indirectly, RFF could also be used in uranium reprocessing plants. Robert A. Malstrom and his colleagues at the DuPont Company's Savannah River Laboratory are working with Hirschfeld to develop this technique. He told the ACS meeting, however, that the fluorescence is very sensitive to the concentrations of phosphoric acid and nitric acid in the solution, as well as to the pH, and that these limitations must still be overcome.

Many other applications are also possible. Another group at Westinghouse, headed by Kenneth B. Steinbruegge, is developing fiber-optic systems for measuring voltages, current flow, and other electromagnetic phenomena. In one typical application, polarized light is passed through a magnetooptic current sensor; the Faraday effect induced in the sensor by the current rotates the plane of polarization of the light. Measurement of the rotation yields an accurate measure of current flow.

Stanley Kronenberg of the U.S. Army Electronics Technology and Devices Laboratory in Fort Monmouth, New Jersey, reported at the ACS meeting on leuko dyes that are sensitive to ionizing radiation. Color changes in the dye can be monitored remotely to indicate the intensity of radiation. Elias Snitzer and his colleagues at the United Technologies Research Center also reported that strain can be measured by monitoring the cross-talk—leakage of light—between two cores enclosed in the same sheathing. And finally, Brandt notes, the U.S. Navy is attempting to use fiber optics to detect submarines. Quartz fibers are relatively insensitive to sound waves, he says, but the amplification in a 10-kilometer loop makes it "the most sensitive microphone known." Unfortunately, he concludes, such loops are also sensitive to temperature changes, a major factor that has delayed their use as hydrophones.—**Thomas H. Maugh II**