

Sensor and Detector Technology

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Abstract

In the early 1980s, researchers at the then Savannah River Laboratory and later the Savannah River Technology Center began working with fiber optic technologies to use powerful spectroscopic methods for on-line analytical measurements in remote applications. During the past 20 years, these efforts developed fiber optic hardware, sample interfaces, and software integrated with commercially available detectors to form a flexible on-line system for analytical measurements. Methods were developed to analyze solids, liquids, and gases and for physical measurements such as temperature. The system targeted applications in nuclear fuel reprocessing, waste vitrification feed preparation, and weapons surveillance. The advantages were more timely information and reduction in radiation exposure and risks involved with sampling. This technology is in an area of on-going research as more innovative fiber optic probes are developed for measuring new sample types.

The origins of this paper started with developments 20 years ago in fiber optic sensor technology that gained outside recognition with 2 Westinghouse Corporate Signature Awards, an R&D 100 Award, and 16 patents. The scope broadened to include other detector technologies that provided field measurements, particularly the ability to detect and measure radiation. However, the two subjects were too broad for one paper. To do justice to the subject, the author regrettably limited the scope to the original paper.

So, this paper reviews developments in fiber optic technologies by Savannah River Laboratory (SRL)/Savannah River Technology Center (SRTC) researchers that allowed powerful spectroscopic methods, previously confined to the laboratory, to be used for analytical measurements in remote applications. These methods allowed analytical measurements to be made at the point of need rather than relying on time consuming and, in many applications, hazardous sampling followed by laboratory analysis. At the Savannah River Site (SRS), the advantages of these on-line, at-line, or *in situ* analytical methods include reducing personnel radiation exposure and providing timely information to improve control of nuclear materials processing.

Early Attempt at On-line Spectroscopy—Fiber Fluorimetry

In the early 1980s, a vision emerged of automatic control of the SRS reactor fuel and target reprocessing plants, the H Canyon and F Canyon, and the associated product finishing plants, the HB and FB Lines. Computerized distributed control systems were installed, which prompted on-line delivery of analytical information such as chemical compositions as well as traditional pressure, temperature, and flow data. To have significant impact on operations, analytical methods that measured the critical chemical components as accurately and precisely as laboratory instruments would have to be developed, with ruggedness and speed to

provide near real-time information. Early attempts to develop on-line analytical systems for the more important constituents, primarily plutonium and uranium, involved investigating fiber fluorimetry. In this technique, laser light was delivered through an optical fiber to a process location. The quantifiable uranium emission was collected by the fiber and returned to a diode array detector. Such a system was demonstrated in the Savannah River Laboratory and included an in-house designed multiplexer, which allowed several sample points to be measured sequentially by cycling the instrument light output and signal input fibers to fiber pairs connected to different sample points. However, the detection limit of 200 ppm in 0.5M nitric acid and 10% uncer-

tainty was insufficient for process control. In addition, the system was not cost-effective to install in the plant since it could only measure uranium.

Though never installed in the plant, the fiber fluorimetry system pioneered three important features needed to practically apply laboratory spectroscopic methods to process or on-line use:

- Using fiber optic cables to remove the instrumentation from the harsh environment (heat, moisture, radiation) of the sample interface
- Using multiplexing to spread the cost of expensive instrumentation over several sample points
- Using the diode array spectrophotometer.

The diode array, which involved no moving parts, simultaneously measured a breadth of wavelengths by projecting the wavelengths of a diffracted light signal onto an array of light-sensitive diodes. The conventional scanning photometric detectors had to rotate a diffracted light signal over a single detector, which made them slow, sensitive to environmental factors, and maintenance problems. The attributes of speed and ruggedness made the diode array spectrometer ideal to use in process areas and for near real-time measurement.

Absorption Spectrophotometry

SRTC scientists recognized that absorption spectrophotometry, in which light is passed through a sample and chemical components are identified and quantified by the extent to which different wavelengths of light are absorbed, could be a powerful analytical tool and more universally applicable than the laser-induced emission-based fluorimetry. However, since many chemicals absorb light at the same wavelength, laboratory applications of absorption spectrophotometry relied upon sample preparation steps to chemically separate the different components before measurement. Since complex feed preparation steps are difficult and time consuming, if not impossible in process usage, applications of spectrophotometry in the

process were limited to colorimeters that used one, or possibly up to five, wavelengths to measure specific chemical components in simple chemical systems. If components in a multiple component sample, which most process samples are, had absorptions in the same area of the spectrum, these instruments could not tell them apart. The diode array detector could quickly gather absorption data over a wide range of wavelengths, making it possible to separate components by comparing their absorptions in many wavelengths. However, the volume of data generated by these full spectral measurements and the complicated overlapping absorptions of different chemicals in mixtures made quantifying individual chemical components impractical.

Chemometrics

Also in the early 1980s, SRL became a member of the Center for Process Analytical Chemistry (CPAC) at the University of Washington. CPAC was and still is a member-sponsored research center dedicated to moving analytical chemistry from the laboratory to the shop floor and process environment. CPAC was premier in developing a discipline that became known as chemometrics, the application of what are called multivariate mathematical techniques to complicated data to reduce it to useful information. Chemometrics was applied to sorting complicated spectral information such as that generated in absorption spectrophotometry, to allow individual chemical component concentration measurement. To use chemometrics, one must know what chemicals will be in the mixture he intends to measure and over what range of concentrations each will vary. With this knowledge, a series of calibration solutions is made that bounds all expected chemical components and concentrations. A mathematical model is made from the spectral data obtained by measuring the calibration set. Once the model is made, the mathematics can be used to predict component concentrations from sample spectra. With even the computers available in the 1980s, the analysis was done quickly and within a relatively small instrument package. In

addition, since the chemometric model identifies components by comparing the measured spectra with the known contributions of each component to the model, it also recognizes the presence of components that were not included in the model. Although chemometrics cannot identify these unknown constituents, it raises a flag that something unanticipated is in the sample and allows further investigation. The diagnostic capability of a chemometric model-based measurement makes it a robust method.

SRL researchers were the first to practically apply chemometrics. They first wrote in-house software that incorporated the data processing and model building routines necessary to use chemometrics. In cooperation with Laboratories Department personnel in the 772-F process control laboratory, they mated the software to diode array spectrophotometers to use in laboratory measurements of plutonium and uranium. These instruments were much faster and simpler to operate for these process control measurements than the previous nuclear counting and emission-based laboratory methods. Complete measurements could be made in seconds rather than hours with better accuracy and precision. The diode array spectrometer system could take complete spectra every 0.2 seconds. The software could be set up to average spectra over whatever time was desired, usually a few seconds, to remove anomalies and provide statistically sound results. With spectrometer manufacturer hardware updates and software improvements for operator ease, these instruments have been successful for the past 15 years.

Fiber Optic Hardware

Reliable fiber optic hardware had to be developed to extend the use of these instruments outside of the laboratory. SRL researchers developed reliable means of coupling fiber optic cables to instrumentation with minimum loss of light using standard SMA connectors. They also developed techniques to couple the fibers to sample cells using lens assemblies to efficiently collect and focus the incident and signal

light. Lens assemblies and fiber optic connectors provided to the Los Alamos National Laboratory (LANL) were used to develop a fiber optic high-acid analyzer that was recognized as one of the year's top 100 technological developments by R&D 100 magazine at the beginning of the 1990s. These fiber optic developments permitted separating the sample cell from the instrument for use in radioactive gloveboxes in the HB-Line analytical facility and in heavily shielded cells such as in Building 772-F. Samples collected in optically clear vials called cuvetts could be placed between the fiber optic lenses in a sample holder within the radioactive containment. The spectrophotometer measured the plutonium or uranium concentration outside the containment.

In the next step, researchers incorporated these basic couplings and lenses into standard swagelok fittings to develop leak-tight flow-through sample cells of various sizes and designs that would directly measure a flowing sample or process stream. With the development of these process sample interfaces, absorption spectrophotometry became a viable tool for on-line analytical measurements. These fiber optic on-line systems were first applied in SRL for real-time analytical information on experiments that simulated the operation of the H- and F-Canyon solvent extraction cycles for plutonium and uranium recovery. These systems eliminated the delays of taking samples, sending the samples to the laboratory for analysis, and eliminated the risks of handling radioactive samples. Since the information was essentially available immediately, it could be used to make changes in the experimental parameters such as flow rates and temperatures as the experiment progressed. In other words, the fast analytical information allowed near real-time process control, which was the ultimate goal.

The system described above, consisting of fiber optic flow cells for sample interface, fiber optic cables and couplings, reliable multiplexers, fast and rugged diode array spectrophotometers, and chemometric software, formed a powerful

tool with potential for on-line analysis of process solutions in the H and F Canyons. The remaining need was to get the process solutions to the flow cells. By design, the canyon process solutions were contained in vessels and piping behind thick concrete shielding walls. The only access to these solutions was through the individual vessel samplers in the sample aisles in the inhabited part of the canyon, several feet above the process tanks. These samplers were used to obtain samples in small vials, which were transported to the 772-F laboratory for analysis. The samplers operated by pulling a vacuum on a pipe submerged in the vessel while at the same time bubbling air into the submerged end of the pipe. The liquid sample lifted the pipe to the sampler in liquid slugs between air bubbles and collected in the vials. Development work included automating the samplers operation and engineering a fiber optic flow-through sample cell that could be installed on the samplers while still allowing the sample vial to be used in the normal manner. The diode array spectrophotometer speed proved essential for this application because the instrument had to obtain and average several spectra between air bubbles. Otherwise the bubbles interfered with the light transmission through the solution and introduced excessive noise into the signal.

Fiber Optic Uses in Reprocessing Applications

With all the pieces of the on-line spectrophotometer system in place, a system was installed to measure uranium and nitrate in seven tanks of the H-Canyon 2nd Uranium Cycle in 1989. The system operated for a time until most H-Canyon processes shut down after reactor operations were stopped. A similar system was designed and built for the Uranium Solidification Facility that was planned to solidify enriched uranium recovered in the H-Canyon operations for return shipment to the Oak Ridge enrichment facilities. However, Department of Energy policy decisions cancelled operation of the facility before the system was

installed. The H-Canyon 2nd Uranium Cycle system is being refurbished at this writing for use with restart of the cycle in December 1999.

After the initial successful demonstration of the system in the 2nd Uranium Cycle, work expanded to using the system to measure other H-Canyon process tanks, primarily those in the "hot canyon". Unlike the 2nd Uranium cycle vessels that handle solutions with the bulk of the radioactive fission products removed, the "hot canyon" vessels handle highly radioactive solutions that pose higher risks for manual sampling and analysis, making on-line analysis more valuable. This goal of a "hot canyon" spectrophotometer system was never realized primarily because of the difficulty of engineering a retrofit fiber optic flow cell for the "hot canyon" samplers, complicated by heavy shielding and remote operating devices. One "hot canyon" sampler was adapted for fiber optics, but the difficulties of retrofitting in high radiation fields with the ever-present risk of high contamination was too costly to continue the program, considering the uncertain future of the "hot canyon" operations.

The Flexible Fiber Optic Spectrophotometer System and Probe Development

We recognized that the fiber optic spectrophotometer system as employed in H Canyon was essentially a modular system for performing spectroscopy over fiber optics and was not limited to absorption measurements in liquids. The components could be exchanged to meet the measurement need. Different light sources, types of fibers, and detectors could be interchanged depending on what measurement was desired and into which area of the electromagnetic spectrum the signal fell. The H-Canyon system used a deuterium light source, 600-micrometer-diameter core silica fibers, and a diode array spectrometer targeted for signal light wavelengths in the visible portion of the spectrum, from 300 to 820 nanometers (nm). For analytes that absorbed light with shorter

wavelengths, in the 190-to-300 nm or ultraviolet (UV) region, a xenon arc light source could be used with a slightly extended range diode array spectrometer for a detector. Measurements of solids could also be made by delivering light from a tungsten-halogen source through a probe in contact or close proximity to the solid and collecting the scattered or reflected near infrared light (in the micrometer wavelength range) back through the probe and separate fiber to the detector. Either a conventional scanning spectrometer or an acousto-optical-tunable filter (AOTF) with an indium-gallium arsenide array could serve as a detector.

A special fiber optic probe development by SRTC researchers made it possible to perform fiber optic Raman measurement. In the Raman effect, light at a specific wavelength, such as provided by a laser, when interacting with certain molecules, will be scattered off the molecule at a different wavelength than the incident light. The shift in wavelength from the incident to the scattered light is very specific to the molecule interacting, which makes Raman measurements highly selective and free from interferences. However, only about one in a million photon interactions with the molecule will undergo this effect, which means the Raman signal is weak. One way to enhance the Raman signal is to use a powerful laser. However, large lasers are expensive, take up space, require cooling, and, in general, are not practical for on-line use in the process environment. The other way to enhance the Raman signal is to collect the scattered light more efficiently. The SRTC-designed probe performed this function by combining seven fibers into a single probe. A center fiber was used to deliver the laser light, six surrounding fibers collected the scattered light signal, and returned it to a charge-coupled device (CCD) for detection. The patented SRTC design beveled the collection fiber tips at a specific angle to optimize light collection. It also included replaceable optical filters to remove unwanted light and prevent fluorescence in the signal cable, which could mask the relatively weak Raman signal.

In the 1990s, the flexibility of the spectrophotometer system was exploited by developing more and more probes, such as the fiber optic Raman probe, and sample cells to measure different types of samples. Some of the most important were probes that used a mirror for absorption measurements. These probes combined the light source fiber and signal fiber into the same probe. In the standard absorbance or transmission cell arrangement, the light from the source fiber was passed through the sample solution in a "X" shaped sample flow cell and into the signal fiber. In the mirror probe, the incident light was focused by the end lens through the sample solution, reflected off a polished metal mirror back through the sample solution, lens, and into the signal cable. This arrangement was ideal to use as a dip probe that could be submerged in tanks. Further enhancements of this concept included making the mirror moveable so it could be brought against the lens to take a blank spectra. The blank spectra could then be subtracted from the sample spectra to correct for any film formation on the lens or mirror surfaces. This self-referencing feature added to the already powerful diagnostic capabilities of the system inherent in the software model's ability to detect unanticipated constituents and to use standards and blanks as measurement positions in the multiplexer cycle. Stepper motor-driven mirror probes were also developed that allowed a variety of sample path lengths to be used in situations where the analyte concentration varied over a broad range.

The applications of the fiber optic spectrometer system mentioned thus far have been either measurements in solution or of solids. Cells were also developed for gas-phase absorbance measurements. The in-tank precipitation (ITP) process, which was planned as the means of removing the bulk of the radioactivity from the SRS high-level waste tanks for vitrification in the Defense Waste Processing Facility (DWPF), introduced the possibility that flammable benzene could be evolved from process solutions. To analyze for benzene in waste solutions, a sample cell was developed in which air was

bubbled through a liquid sample and cycled through a 10-centimeter tube with fiber optic cables at either end. In this way, absorption measurements of benzene vapor were made in the UV. When the measurements reached steady state, indicating equilibrium of the benzene in the vapor with that in solution, the solution benzene content could be determined. A system of measuring benzene in solution at 30 parts per million was installed in the DWPF laboratory. The method was also incorporated into an on-line system for measuring both benzene and nitrite in the Late Wash Facility, which was to perform the final feed preparation step on ITP material moved from the waste tank farm to DWPF.

Sol Gel Indicator Probes, Physical Measurements, and Other End Effect Probes

The most useful absorption spectroscopic information is found in the visible portion of the spectrum and slightly into the UV. In the long wavelength or infrared region of the spectrum, spectral features for components in solution are masked by the broad and intense absorption of water. In the UV region, the fiber optic cables absorb the light, which reduces the distance the sample interface can be removed from the detector to a few feet as opposed to hundreds or thousands of feet for the visible. Although many chemical compounds absorb light in the visible and near UV portion of the spectrum, many do not. One advantage of the Raman probe is that it allows measuring some chemical species in the visible that do not absorb light in the visible. Another way to measure a chemical species in the visible that has no absorption in the visible (no color) is to react it with an indicator that will produce a product that does absorb in the visible. The use of phenolphthalein indicator to determine pH, which is the concentration of colorless hydrogen ions in solution, by turning red is a simple example. Obviously for on-line use it is highly desirable not to use liquid indicators that

require mixing with the sample, waste disposal, and constant addition of the indicator.

SRTC researchers developed a new class of solid materials called sol gel indicators that react with specific chemical species to produce a visible absorbance without the complications of liquid reagents. A sol gel can be thought of as a type of glass formed at low temperature. Since the sol gel does not have to be heated to high temperatures to form its glass properties, it is possible to incorporate organic indicator molecules (most indicators are organic) into them that would be destroyed by the heat of normal glass making. Although the sol gel is a solid, the pore size of the glass matrix can be tailored by manipulating the formation parameters. The indicator molecule is trapped in the gel but the desired species to be measured can still flow through the pores to reach and react with the indicator. The sol gel indicator concept is ideal to use with the fiber optic system since it is a light transmitting solid that can be coated on the mirrored probe lens for submerging in process tanks. Producing a useable sol gel indicator is dependent first on finding an indicator that will react with the analyte of interest. Then the pore size of the gel must be carefully controlled to allow the analyte to reach and react with the trapped indicator (and to dissipate when the concentration of the analyte decreases in the solution) quickly without the indicator leaching out. SRTC researchers demonstrated sol gel indicators for measuring pH, chromium, and uranium.

Just as chemical components can be measured by the changes they cause in light spectra, a physical phenomenon that causes a change in light spectra can also be measured by fiber optic spectrophotometry. While working on one application for spectrophotometric measurement, researchers noticed a cyclical change in the collected spectra from day to day in a long-term test. They ultimately correlated this change with the change in temperature of the fiber optic cables from day to night. This observation led to developing a fiber optic

temperature probe based on the temperature-induced change in absorbance spectra of a neodymium doped glass bead at the end of a fiber optic cable. This simple sensor won an award as one of the top 100 technological developments of 1995 as determined by R&D 100 magazine. This sensor can measure temperature over the range of -200°C to 600°C (limited by the softening point of the glass) with accuracy of $\pm 0.5^{\circ}\text{C}$, resolution of 0.1°C , and 0.2°C repeatability. The outstanding feature of the sensor is that it is non-electrical and non-metallic, which means it can be used in applications where electrical or radio frequency interference is a problem or in explosive atmospheres where electrical connections are not desired. A multiplexed group of these sensors was used to measure soil temperature during a SRS experiment in which contaminated soil was being remediated by radio frequency heating.

In 1999, SRTC researchers developed a fiber optic temperature sensor based on a different concept. This sensor measures the change in absorbance of a zinc selenide crystal. Unlike the neodymium sensor, which basically exhibits gradual changes in the absorbance intensity (or more accurately light transmission intensity) over a range of wavelengths, the zinc selenide crystal exhibits a sharp increase in light transmission that occurs over a narrow wavelength band. The band of wavelengths at which the step increase in light transmission occurs changes reproducibly with temperature. The zinc selenide sensor has two primary advantages over the neodymium sensor. First, the sharp change in light transmission is easier to detect than the more subtle changes in the neodymium absorbance and is subsequently less dependent on the quality of the light source, spectrometer, and power of the chemometric model for quantitation. Secondly, since the zinc selenide transmission occurs over a small portion of the visible spectrum, it leaves the remainder of the spectrum available for use by the spectrometer for other measurements. Thus the zinc selenide crystal can be incorporated as one layer of a multiple component

sensor in which temperature could be measured along with some other quantity by a single fiber optic probe.

Just as the coating of the fiber optic lens with a sol gel indicator or the use of a crystal or doped glass opens the door to spectrophotometric measurement of quantities that cannot be measured by light interaction directly, the use of active films on the fiber optic probe surface is proving to be a fruitful field of research. In an effort funded by the nuclear weapons complex desire to provide surveillance of warhead components being left for longer durations in the field, SRTC researchers recently developed a fiber optic hydrogen sensor. Fiber optics are ideal for measuring this type because of the lack of a spark source in a potentially explosive atmosphere. This sensor is based on light reflected off a palladium film coated on a fiber optic probe tip. The reflected light spectra change in a manner correlated with the concentration of hydrogen in contact with the palladium. The sensor as demonstrated to date has a lower detection limit for hydrogen of 0.01% in air, reacts in 90 seconds, and returns to baseline in 90 seconds when the hydrogen is removed. At the time of this writing, researchers were still attempting to stabilize the long-term response and repeatability of the sensor at the 0.01% hydrogen level.

To adapt the hydrogen sensor to Site needs, work is underway to find a suitable coating to protect the palladium from the harsh chemical environments of the vapor spaces above the H- and F-Canyon process vessels. A long-standing problem exists of monitoring hydrogen generated in the fuel and target reprocessing plants. Today, these plants are dedicated to stabilizing existing nuclear materials. Operators need assurance that dangerous levels of hydrogen are not accumulating. Air purges are used to ensure hydrogen does not accumulate. However, because of the aggressive nature of gaseous nitrogen compounds generated from the nitric-acid-based processes and the complexity of existing gas analyzers, to date there has been no practical way to continually demonstrate by

measurement that the hydrogen is maintained at acceptable levels. The simple fiber optic hydrogen sensor has that capability since stability at the 0.1% hydrogen in air sensitivity level required for the application should be easily attainable compared to the 0.01% target for the weapons application. The present challenge is to protect the palladium from chemical attack.

Another development that SRTC researchers produced for the same weapons application is an extremely sensitive, all fiber optic moisture sensor. This sensor is based on an emerging technology, surface plasmon resonance (SPR) spectroscopy. Under certain conditions, light energy can be coupled (a resonance can be established) into a stack of ultra-thin metal/dielectric layers. The molecule adsorption onto the exposed dielectric film can cause dramatic shifts in the conditions necessary to establish resonance. The resonance may then be optically monitored as reflectivity change, wavelength of a specific feature, or a reflectivity minimum as a function of the incident light angle, and correlated to the degree of absorption of the analyte on the surface. The SRTC moisture sensor uses silica and gold layers in a proprietary arrangement to measure water absorption onto the surface. The sensor can detect parts per million water vapor from 0 to >100% (condensation onset) relative humidity. This sensor has fast response, high sensitivity, low noise, all optical, and intrinsically safe. Potential SRS applications include plutonium metal processing where moisture is a fire hazard and tritium processing where water can form tritium oxide, an extreme health hazard, since the oxide penetrates contamination protection clothing (plastic suits) much faster than the gas.

The continuing work in fiber optic sensors involves developing new probes useable at the fiber optic cable end to allow light to interact with a sample media, whether liquid, solid, or gas, or to react to some physical phenomenon. The modular fiber optic spectrophotometer system for measuring and interpreting light interaction remains essentially the same. The

software mentioned earlier is the heart of the system and responsible for its versatility and longevity. The software is updated to interface with purchased components. The software flexibility measures different models for each measurement point such that one point represents a temperature, another a chemical concentration in a liquid, while still another measures hydrogen in air. The software integrates measurement models from calibration information, operates the on-line instrument to make the unknown measurements, and has alarm/control outputs to interface with a process control system. Several commercial software packages today do some of the necessary functions such as the chemometric modeling and are being incorporated into the SRTC system as appropriate. However, none has the flexibility and capability to interface with the detectors and the full range of functions that the SRTC software does. The basic SRTC system remains a powerful platform for continuing sensor developments in the future.

Biography

Wayne Jenkins graduated from the Georgia Institute of Technology in 1969 with a Bachelor Degree in chemical engineering. He came to the Savannah River Site in November 1972 after serving in the U.S. Army and working for the Aluminum Company of America as a process engineer in aluminum smelter electrode manufacturing. He began his SRS career as an engineer in the Separations Technology Waste Management organization with responsibilities in radioactive waste tank farm operations. After over six years in Waste Management and two years as an operations supervisor in the Tritium Facilities, he returned to Separations Technology where he served as an area supervisor for the Multi-Purpose Processing Facility and the FB-Line and then as technical supervisor for the F Canyon and Outside Facilities. He joined the Savannah River Laboratory/Savannah River Technology Center in 1988 where he has since managed the Sensors and Analyzer Technology Group in the Analytical Development Section.