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ONLINE FIBER-OPTIC SPECTROPHOTOMETRY (U)

by

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ABSTRACT

The Savannah River Plant operates two radio-chemical separations areas to recover uranium and plutonium from nuclear reactor fuel and target assemblies. Chemical processes in these areas are controlled based on laboratory analysis of samples extracted from the process. While analytical results from the laboratory are reliable, the process of pulling samples, transporting them to the laboratory, analyzing them, and then reporting results is time consuming and potentially exposes many workers to highly radioactive solutions. To improve the timeliness of chemical information and reduce personnel radiation exposure, the Savannah River Laboratory has developed online absorption spectrophotometers.

Absorption spectrophotometers are rugged instruments which can provide precise, detailed information about chemical states and concentrations. However the technique is susceptible to interference from other optically absorbing species and changes in analyte absorbance due different matrixes. Also it is difficult and expensive to interface absorption spectrophotometers to SRP's radioactive processes. SRL has developed an online fiber optic spectrophotometer which substantially solves these problems by combining three new technologies, fiber optics, diode array spectrophotometers, and multivariate data analysis.

The analyzer monitors the uranium and nitrate concentration of seven aqueous process streams in a uranium purification process. The analyzer remotely controls the sampling of each process stream and monitors the relative flow rate through each sampler. Spectrophotometric data from the analyzer is processed by multivariate data analysis to give both uranium and nitrate concentrations as well as an indication of the quality of the data. The precision and sensitivity of the instrument is 0.5 milliabsorbance units which translates to 20 ppm uranyl and 4 ppm plutonium. The accuracy of the PLS models is better than 2% of reading for concentrations above 1 gram per liter.

INTRODUCTION

Information about chemical state and concentration of compounds in process solutions is essential for safe and efficient operation of chemical plants. The degree of control, safety, and efficiency in chemical processes generally depends on both the accuracy and time response of the measurement system used to deduce the chemical information. Online analyses provide rapid time response but are typically not as accurate or selective as laboratory analyses performed on samples extracted from processes. For online analytical methods to be most effective, they must be as accurate and selective as laboratory methods but completely automated and highly reliable. Automation should not only include instrument control but also data reduction and analysis and results validation.

Absorption spectrophotometry is one of the techniques which has long been recognized as adaptable for online chemical analysis. The technique is simple, relatively easy to interface to processes, and can be selective and sensitive for analytes which absorb light. Commercially available filter photometer systems provide reliable high-precision online data. These systems typically monitor two optical frequencies, one coincident with analyte absorption and the other at a point of no absorption. These instruments automatically account for spectral baseline shifts, but are severely affected by interfering chromophores and changes in analyte absorptivity due to varying matrix conditions. These problems are so severe that in general the high-precision data of filter photometer instruments cannot be converted to high accuracy analyte concentrations. More sophisticated spectrophotometer systems which collect multiple channels of data can correct for some of these effects but until recently have been too complicated and delicate to operate in process environments. The objective of this work was to develop a rugged, reliable spectrophotometer system which could be remotely located from the harsh process environment.

Previous work has demonstrated that remote online photometric measurements can be made over optical fibers. Six commercial two wavelength filter photometers have been modified with fiberoptic cables to monitor the elution of neptunium and plutonium from anion exchange columns at the Savannah River Plant (SRP).[1] Researchers at Oak Ridge National Laboratory developed a fiberoptic photometer based on a rotating filter wheel to monitor the concentration of uranium and plutonium in process streams.[2] Workers in France have developed similar analyzers using industrial photometers with as many as five measurement wavelengths. A multiplexed analyzer has also been developed by the French using optical fibers and a commercial diode array spectrophotometer.[3-4] This analyzer can monitor up to four sample locations in series acquiring data over the 400-800 nm range.

Diode array instruments have many advantages over filter photometers and conventional scanning spectrophotometers for process analysis. They have the fast data acquisition of filter instruments and the multiwavelength information of scanning instruments. In addition they are inherently rugged because they have no moving parts. This paper describes a multiplexed fiber optic spectrophotometer system, based upon a diode array spectrophotometer, which has been installed in a radiochemical separations facility at SRP.

EXPERIMENTAL

Analyzer System Description

A schematic diagram of the analyzer system is shown in Figure 1. Light from a xenon arc lamp is focused into a fiber-optic cable connected to the linear translation stage. The stage is positioned to align the lamp fiber with one of the fixed fibers which directs the light to a measurement cell. Light returns from the measurement cell along another fiber to the multiplexer where it is coupled to the fiber leading to the spectrophotometer. Spectra produced by the spectrophotometer are analyzed by an IBM AT-compatible computer.

The analyzer system was installed on the Second Uranium Cycle purification process shown schematically in Figure 2. In this process, uranium from dissolved reactor fuel tubes is separated from fission products by solvent extraction. Uranium and nitric acid (nitrate) concentrations must be known at several points in the process to ensure maximum uranium decontamination and to maintain nuclear safety. The analyzer system was installed in the process control room and optical fibers were run to the sample aisle where air-lift samplers for process tanks are located. Maximum distance between the analyzer and the samplers is 100 meters. The analyzer is connected to nine sets of optical fibers. Seven pairs of the fibers are connected to the seven numbered process tanks shown in Figure 2. One pair of fibers is connected to a standard measurement cell also located in the sample aisle. Different uranyl nitrate standards in sealed cuvettes are used to check the calibration and assess instrument performance. The last set of fibers is used as an external reference. Each measurement cell was flushed with water and the absorbance of the cell was measured relative to the reference fiber. This "cell spectrum", unique for each measurement cell, was then stored in memory. All measurements of process solutions are made relative to the reference fiber. The net absorbance of the species in solution is calculated by subtracting the cell spectrum from the collected absorption spectrum.

Spectrophotometer Description

A DuPont Instruments Diode Array Process Analyzer was used for this work (DuPont Instruments, Wilmington, DE). This prototype analyzer is essentially a Hewlett-Packard model 8452 diode array spectrophotometer (Hewlett-Packard Co., Palo Alto, CA) which has been interfaced to optical fibers and repackaged in a rugged enclosure.

The 8452 is a single-beam spectrophotometer that uses a deuterium lamp, fixed concave holographic grating, and 328-element photodiode array to cover the 190-820 nm spectral region. For long distance measurements over optical fibers, the deuterium lamp was replaced by a high brightness xenon arc lamp.

Fiber-Optic Coupler Description

A very simple fiber-optic coupler was developed to interface the spectrophotometer to optical fibers. The lens mounted in front of the spectrograph entrance slit was removed and a fiber-optic coupler was mounted in its place. The coupler consisted of a piece of aluminum machined to fit in front of the entrance slit. The aluminum piece was drilled and tapped for an SMA short threaded bushing (OFTI, Nutting Lake, MA, part# 2210) which held the optical fiber. The distance between the end of the optical fiber and the slit was minimized (<1 mm) to achieve the highest possible coupling efficiency.

External Lamp Description

For long distance (>50 feet) remote measurements over optical fibers, an external light source was used with the spectrophotometer. The light transmission system consisted of a 75-watt xenon arc lamp (Hamamatsu Corp., Bridgewater, NJ, part# L2194), xenon lamp power supply (Hamamatsu part# C2177-01), lamp housing (Oriel Corp., Stratford, CT, part# 66057), lamp adapter (Oriel part# 66150), iris diaphragm (Oriel part# 6203), and fiber-optic adapter (Oriel part# 77800). The stability of the xenon lamp was as good as the internal deuterium lamp and its high brightness allowed us to make precise online measurements at distances of up to 100 meters. To reduce the effect of solarization on the optical fibers, the shutter from the spectrophotometer was moved to the external lamp housing so that light was passed through the fibers only when a measurement was being made.

Multiplexer Description

The fiber-optic multiplexer, shown in Figure 3, is based on a stepper-motor-controlled linear translation stage.The multiplexer consists of a heavy duty, stepper-motor-driven stage (Aerotech, Inc., Pittsburgh, PA, part# ATS204-50SMB2-HM), stepper motor controller (Aerotech, Unidex I), and custom fiber-optic mounting brackets. One bracket mounts to the base of the stepper motor stage and holds twenty-two SMA short threaded bushings (OFTI) in a side-by-side arrangement. Up to eleven pairs of optical fibers, corresponding to eleven sample locations, are attached to these bushings. The other bracket mounts to the movable stage and holds two, SMA, short-threaded bushings (OFTI) in a side-by-side arrangement. One bushing holds the fiber coming from the light source, the other holds the fiber going to the spectrophotometer. Thus, the eleven pairs of multiplexed fibers are in fixed positions and only a single pair of fibers moves between them. The small spacing (1mm) between the ends of the stationary fibers and the ends of the moving fibers yields small transmission losses (2dB) at each fiber-to-fiber junction.

Measurement Cell Description

The measurement cells used in this work were of two types: (1) screw-cap quartz cuvettes (Spectrocell, Oreland, PA, part# R-2010-T), and (2) custom process flow cells based on Swagelok fittings. Both types of measurement cells required collimated light from the optical fibers. Collimation was achieved through the use of a lens mounted in a Swagelok reducer fitting (Figure 4). The lens was made from a fused silica rod 9.85 mm in diameter, 10.0 mm long, with a 15-mm focal length lens ground onto one end (Atlantic Industrial Optics, Georgetown, DE). This lens was epoxied into the end of a 1/4" to 1/2" stainless steel reducer. The screw-cap cuvettes held uranyl nitrate standard solutions which were used as inline standards to verify the accuracy of the analyzer system. The cuvettes were mounted in an acrylic block which also held the lens assemblies.

The process flow cells were simply Swagelok 1/2" unions, crosses, and tees. The union flow cell had a 1/4" stainless steel inlet and outlet tube welded to it. By drilling out the inner diameter of the union, pathlengths as small as 1.5 mm were attained. The cross flow cells (26-mm pathlength) were used in two different configurations. In the first configuration, two arms of the cross were used for the inlet and outlet, and the lens assemblies were mounted in the other two arms. In the second configuration, 1/2" inlet and outlet tubes were welded to the cross body. One set of arms was used for the lens assemblies while the other set was used for viewing windows. Flat, polished fused silica rods held in place with Teflon (Du Pont) ferrules permitted viewing into the stream being measured. For the installation described in this paper, 1/2" tees with a 26-mm pathlength were used.

Optical Fiber Description

The optical fiber used in this work was Quartz et Silice PCS 600W (Quartz Products, Plainfield, NJ). This is a polymer-clad silica (PCS) fiber which has a high hydroxyl content (300 ppm OH) for good UV response and good radiation resistance. Nominal fiber measurements are 600-micrometer core diameter, 750-micrometer cladding diameter, and 1060-micrometer ETFE buffer diameter. The 600-micrometer core diameter was chosen as a good compromise between fiber flexibility and light-carrying capacity. In addition, this size slightly overfilled the 50 x 500 micrometer entrance slit to the Hewlett-Packard spectrograph. A 1060 micrometer core diameter fiber was much stiffer and did not increase coupling efficiency significantly.

The PCS 600W fiber was purchased in cable form (Applied Photonic Devices, Danielson, CT) which consisted of a Belden #226101 Bitlite tight tube configuration with Kevlar (Du Pont) strength members and a PVC jacket.This configuration provided excellent physical and chemical protection for the optical fiber.

Two types of stainless steel fiber-optic terminations were used, SMA (905 style) connectors (OFTI, Nutting Lake, MA, part# SMA-5630-2551) at the instrument interface, and custom designed connectors at the measurement cells. The custom connectors were made from 1/4" stainless steel stock and were designed to connect to the Swagelok-based lens assemblies.

Sampler Interface Description

Due to the radioactive nature of the materials being processed, process tanks are remotely located in a heavily shielded concrete "canyon". Sampling of the material in these tanks is accomplished by an air lift sampler which uses the vacuum created by an air jet to pull solution from the tank. Air is bled into the pickup tube to assist in raising the solution 35 feet to the sample aisle.

The four valves used to operate the sampler are controlled by the analyzer computer through a remote electronics interface (Opto 22, Huntington Beach, CA) over an RS422 communications link. A large stainless steel box encloses the Opto 22 modules which communicate between the computer and the electric solenoid valves located in a smaller enclosure. A manual switch box is included to allow the sample aisle operator to manually pull a sample.

Due to the two-phase (air/liquid) nature of the solution being sampled, a sampler interface incorporating a degasser was required to introduce a bubble-free stream into the flow cell. Figure 5 shows the fiber-optic sampler interface which is composed of a sample probe for manual sampling, a 1/2" Swagelok tee measurement cell, and a 1/4" Swagelok tee containing an internal jet for sample mixing. Slugs of air and liquid first flow through the sample vial on the probe and then are jetted through the 1/4" tee into the 1/2" measurement tee. A small volume of solution is retained in the measurement tee and the rest of the air/liquid mixture flows around the outside of the jet in the 1/4" tee back into the process tank. Slugs of liquid cause good mixing and once the bubbles have dispersed, accurate and precise measurements may be made on the retained volume in the measurement tee.

Industrial Computer Description

An IBM 7552 industrial computer (IBM Corp., Boca Raton, FL, IBM AT compatible) was chosen for its ability to operate reliably in process environments which are typically hot and dusty, with noisy electrical power and high levels of electromagnetic interference. The computer is equipped with the MS-DOS 3.2 operating system, 10-megabyte hard disk, 1.2-megabyte flexible disk, 1 megabyte of memory, RS-232 and RS-422 serial communications ports, and an

IEEE-488 parallel communication port. The computer controls the spectrophotometer through the IEEE-488 interface and the multiplexer through the RS-232 interface. The computer controls sampling valves in the process through Opto 22 modules located at each sampler location. The valve control modules are connected to the computer via the RS-422 interface. All control software for the instrument is written in Microsoft QuickBASIC version 4.0 and linked to the IEEE-488 library with the MS-DOS linker.

The instrument control software can measure and adjust optical throughput of sample cells, flush sample cells with water and collect blank spectra, collect calibration spectra for analysis by multivariate data reduction programs, and monitor the sample cells connected to the system.

Multivariate Software

Models of the absorption characteristics of our chemical systems were built using the SRL Multiple Variable Analysis computer program (SRLMVA) developed by the authors. This program computes models of analyte concentration based on correlations between known concentrations and measured absorption spectra. Available models include Partial Least Squares (PLS), Principle Component Regression (PCR), Classical Least Squares (CLS), and Multiple Linear Regression (MLR) analyses.[5] The program assumes that the known concentrations are linearly related to input data.
A discussion of uranium and plutonium data reduction methods is found in reference 6.

DISCUSSION

Optical performance of the fiber-optic process spectrophotometer was comparable to the commercial Hewlett-Packard 8452: peak-to-peak noise between 350 and 800 nm was +/- 0.0004AU, sensitivity and precision was less than 0.001AU, and imprecision due to the multiplexer was less than the optical noise. Multiplexer switching time was less than 1 second for adjacent points.

The multiplexer was connected to a reference optical fiber, a standard cell filled with a known uranium standard, and seven air-lift tank samplers. Typically the spectrophotometer measured each of these positions sequentially. After a reference spectrum was acquired, a blank was remeasured to test the reference and establish the instrument noise level. If the calculated uranyl concentration for the blank was above the noise limit (12 ppm), the reference was reacquired. Next the standard was measured. If the computed uranyl and nitrate concentrations were outside set limits (1% for uranyl and 0.2 M for nitrate) a warning was printed.

Uranium and nitrate data from the inline uranyl nitrate standard are shown in Figures 6-7. For uranium, the long-term (24 hour) precision (two sigma) was < 0.5% and the short-term precision was <

0.1%. For nitrate, the numbers were comparable. The slowly varying character of the signal was probably due to temperature fluctuations in the sample aisle and control room which affect the shape of the uranyl nitrate spectrum.

After the blank and standard positions were measured, each of the process locations was monitored. Rapid acquisition and averaging methods were necessary to ensure that only valid data from flowing streams were used to calculate concentrations. At each multiplexer position, fifteen one-tenth second spectra were collected. If the baseline offset of a spectrum was less than a cutoff value, the spectrum was included in the calculation of the average and variance spectra. The magnitude of the variance spectrum was indicative of flow through the process measurement cells. Disturbances in a flowing stream caused fluctuating baseline offsets which were typically 10 to 100 times the variance of static solutions. If the variance at a process location was less than 5 times the variance at the standard, the operators were warned that the sampler may be plugged.

Online data from the uranyl nitrate product hold tank are shown in Figure 8. Initially, the concentration of uranium in the sampler was about 1.5 g/L. From the data variance, it was known that the sampler was off so this residual uranium was due to incomplete flushing of the sampler with water. The rest of the data plot shows the sampler turned on to pull a sample, flushed with water and turned off, and later turned on and left on. The uranium concentration in the flow cell came to equilibrium with the concentration in the tank in less than five minutes. Short-term and long-term precision were comparable to the values for the inline standard.

Accuracy of the online data was determined by comparison to laboratory measurement of manual samples, Table 1. The laboratory measurements were made using a diode array spectrophotometer and a PLS model of the uranyl nitrate system. Accuracy of the laboratory method was +/- 2%. From Table 1, the online and laboratory results generally agree to within the accuracy of the laboratory method. So, the accuracy of the online spectrophotometer was at least +/- 2%.

CONCLUSIONS

Fiber-optic diode array spectrophotometers and multivariate data analysis can provide accurate and reliable online measurements comparable to high-quality laboratory analytical methods. High-precision diode array spectrophotometers can be reliably adapted to harsh process environments. Fiber optics provide a simple and cost-effective means of connecting a single spectrophotometer system to multiple points in a process. Multivariate data analysis methods allow conversion of high-precision absorption spectra to high-accuracy concentrations.

Just as important as accuracy and precision, this system allows the analytical chemist to program some of his judgement into the instrument. Online blank and standard solutions provide real time measures of system noise and calibration, rapid data collection allows real time sample verification, and PLS residuals are indicative of uncalibrated interferences and matrix effects.

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Table 1. Comparison of Results - Uranyl Nitrate Tanks

Tank	Laboratory Result (g/L)	Online Result (g/L)
Feed Adjust	5.29	5.34
	5.36	5.43
	5.24	5.30
Product Hold	6.44	6.45
	6.55	6.42
	6.57	6.50
	6.69	6.63
	6.84	6.85
	6.47	6.32

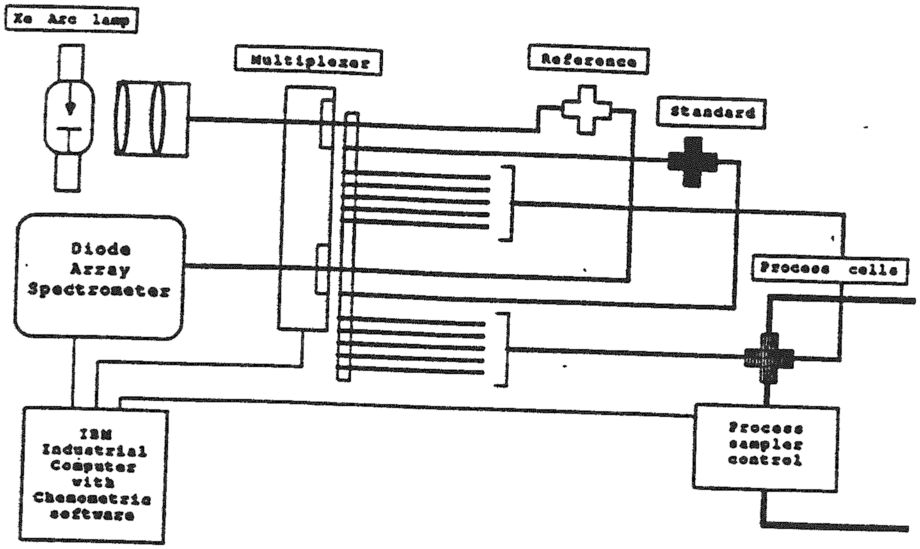

FIGURE 1. Fiber-Optic Spectrophotometer Schematic

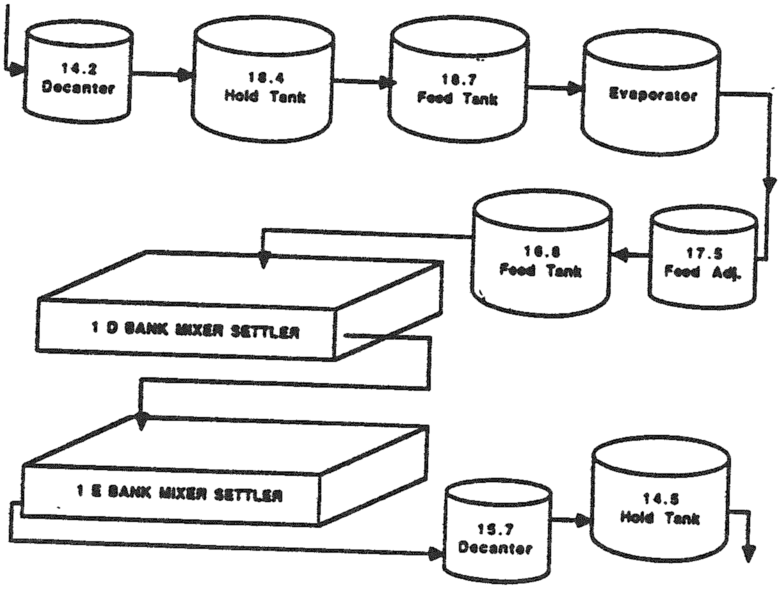

FIGURE 2. Second Uranium Cycle Process

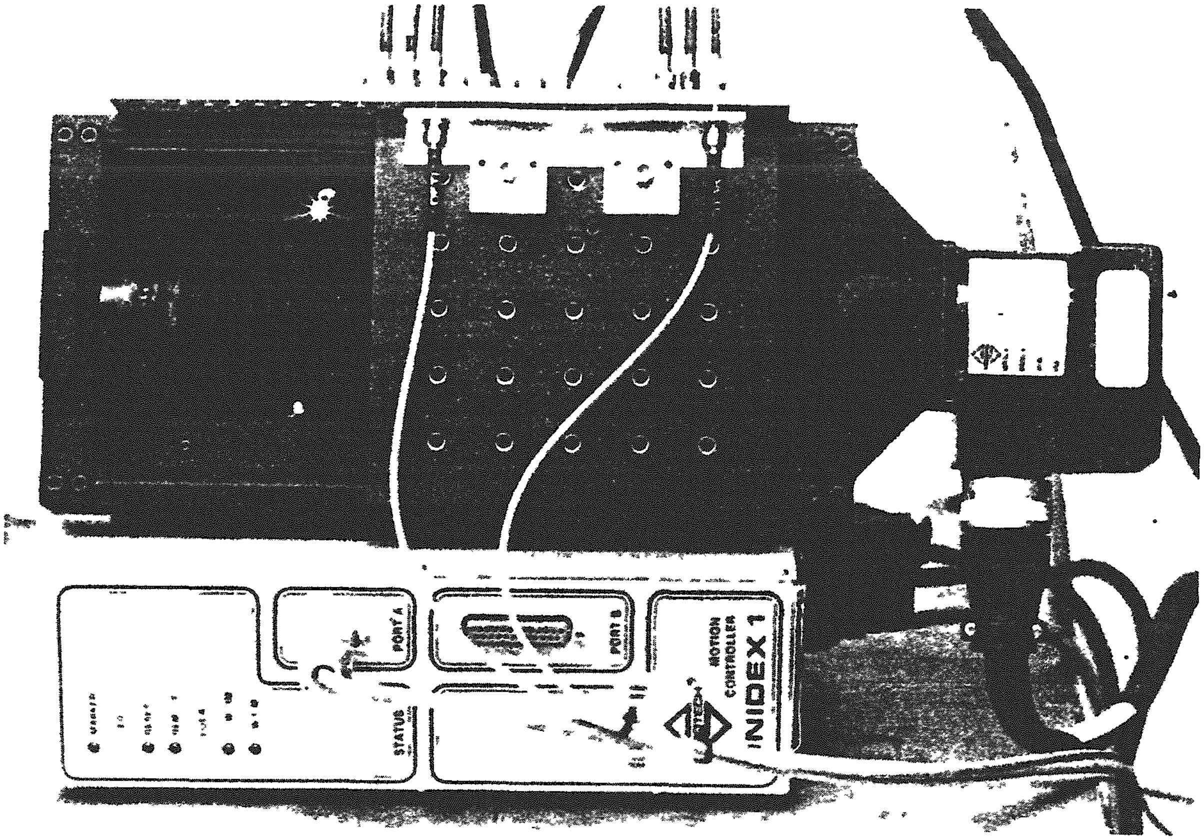

FIGURE 3 Fiber-optic Multiplexer

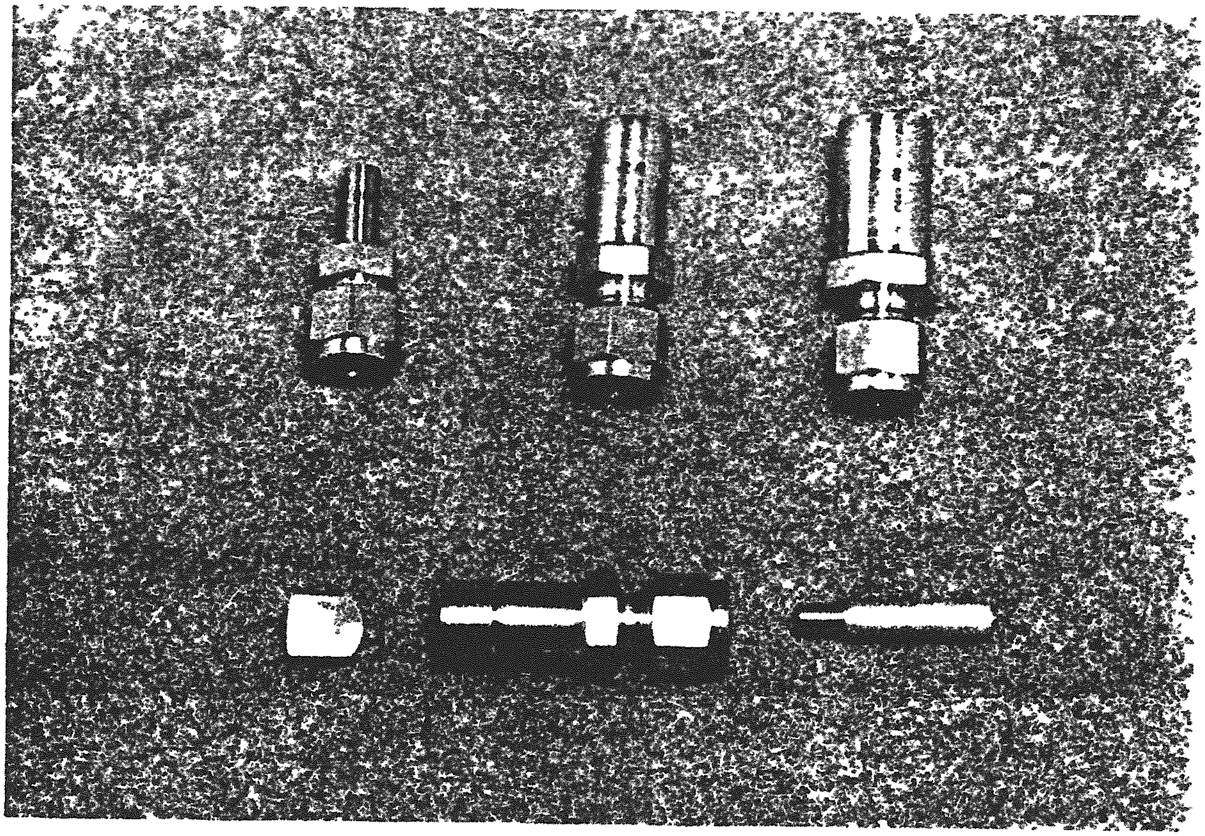

FIGURE 4 Lens Mounting in Swagelok™ Reducer

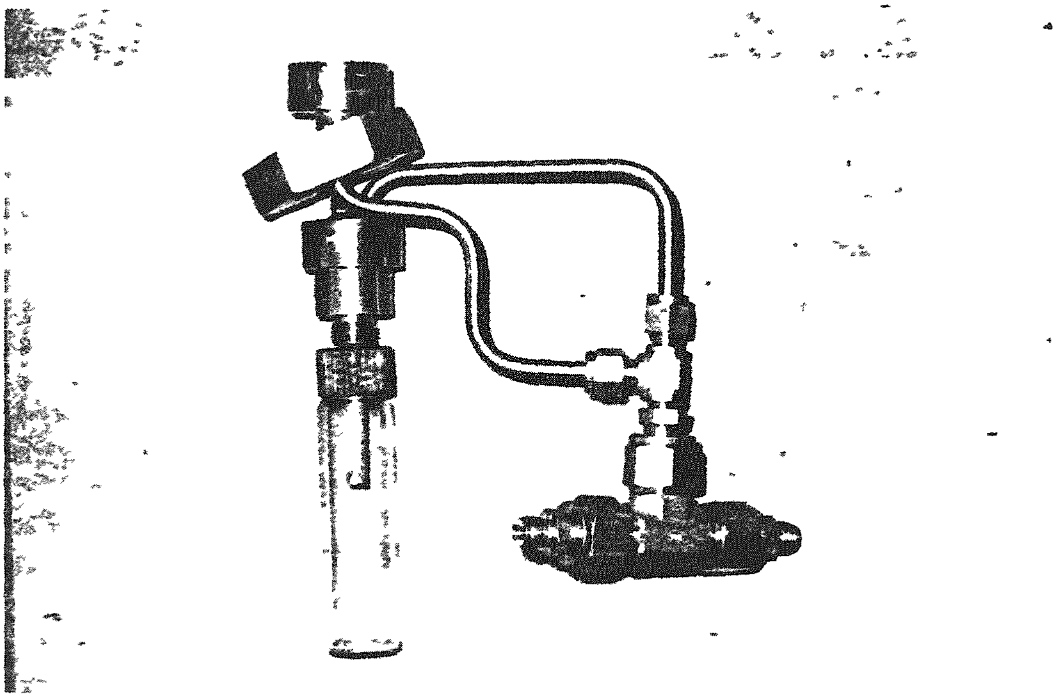

FIGURE 5 Sampler Interface Containing Sample Probe

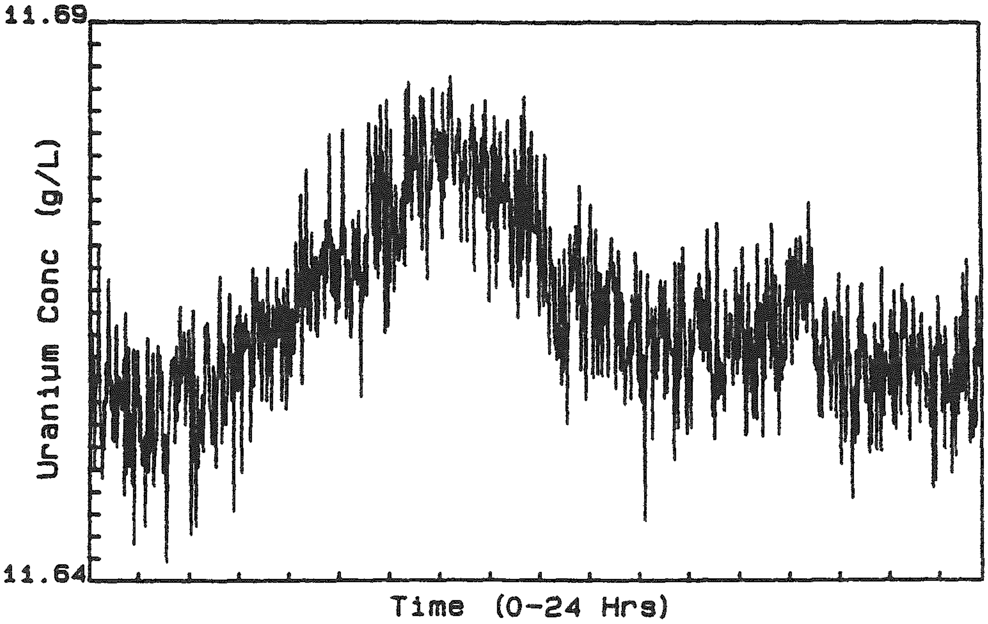

FIGURE 6 Uranyl Concentration of Inline Standard

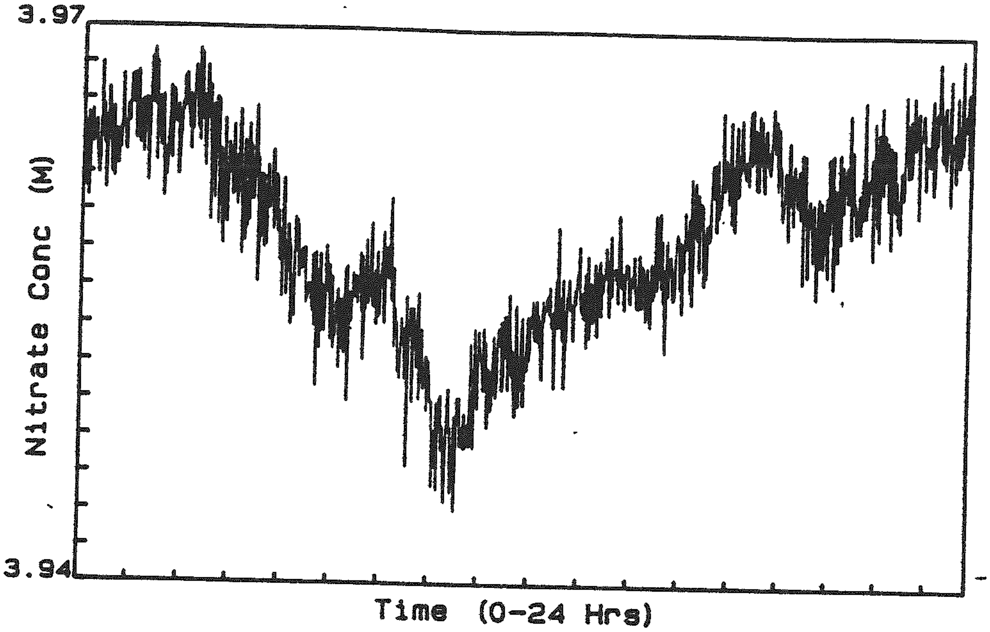

FIGURE 7 Nitrate Concentration of Inline Standard

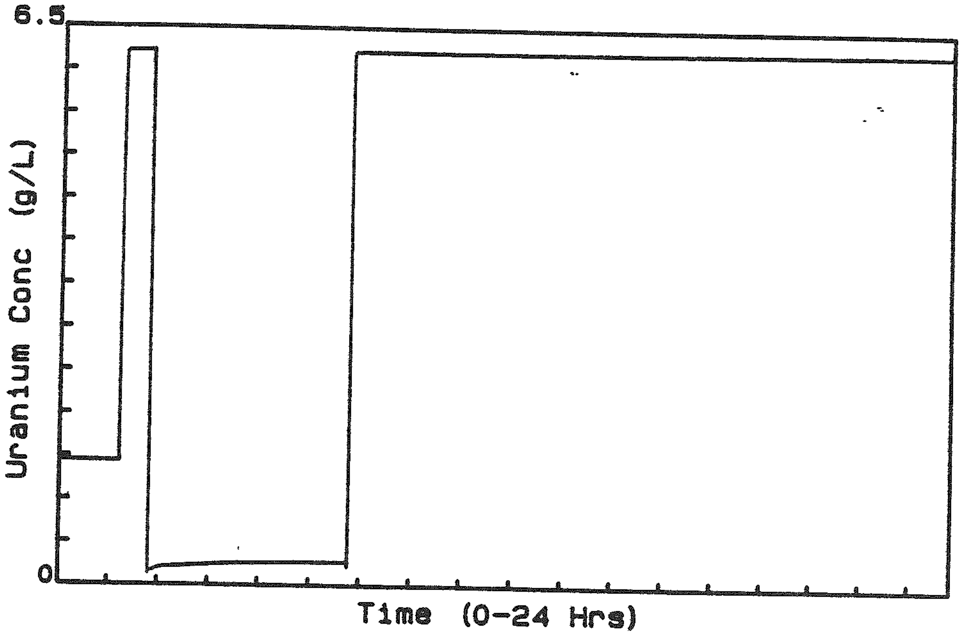

FIGURE 8 Uranyl Concentration of Product Hold Tank