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AN IN-LINE MULTIWAVELENGTH PHOTOMETER FOR THE DETERMINATION OF HEAVY-METAL CONCENTRATIONS*

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DISCLAIMER

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ABSTRACT

An in-line photometer has been developed for continuous monitoring of uranium and plutonium concentrations in high radiation environments of nuclear fuel reprocessing plants. The instrument is equipped with multiple narrow band interference filters to monitor sample transmission in the 400-to 800-nm range. The filters are mounted in a rotating filter wheel which is located in front of a stationary tungsten halide light source. The monochromatic light from the respective optical filters is transmitted through a fiber optic cable of up to 10 m in length to the in-line sample flow cell located within the reprocessing area. A similar length of cable returns the optical signal to the photometer where the light intensity is detected with a photomultiplier tube, amplified, and processed with an LSI-11 computer system. The combined use of a rotating filter wheel and fiber optic cables provides a nearly simultaneous multiwavelength, multielement analysis directly in the reprocessing stream, while isolating the radiation-sensitive optical and electronic components in accessible, protected locations.

This report will describe the design and operation of the individual components of the prototype photometer. The performance of the photometer as an in-line monitor for the determination of heavy metal concentration in both aqueous and organic process solutions will also be discussed.

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INTRODUCTION

The reprocessing of nuclear fuels requires real time information regarding the oxidation state and concentration of uranium and plutonium throughout the recycling procedure. Such information allows the operator to continuously adjust process parameters to optimize the quality and yield of the heavy metal products. In-line densitometers and flow meters have routinely been used to monitor heavy metal concentrations, based on the average density or flow rate expected in a given stream.[1] Because these detectors respond only to a bulk property of the stream, the operator acquires little accurate information regarding the purity or oxidation state of the uranium or plutonium in the process stream. In-line alpha monitors have been used to obtain a degree of analytical selectivity, provided that there is no significant background radiation present and that the isotopic composition of the nuclear fuel is established prior to reprocessing.[2] Again, the oxidation state of the heavy metals cannot be ascertained with this instrumentation. Filter photometers have occasionally been used to follow process stream composition. The optical transmission at a selected wavelength is dependent upon the concentration of a given heavy metal in a specific oxidation state.

Present in-line photometers have mainly been applied to the determination of U(VI) concentration.[3-7] A dual-wavelength optical package is used to monitor uranyl transmission at 416 nm and to correct for stream turbidity at a wavelength where uranium does not absorb. The performance of these dual-channel photometers is limited by several factors. The operating life of the photometric monitor is dependent upon the vulnerability of the optical and electronic components to the radiation environment in and about the monitored stream. In addition, uranium cannot be determined in process streams containing a mixture of heavy metals since plutonium also absorbs at uranyl absorption maxima. Uranyl transmission at 416 nm is also affected by nitrate concentration in aqueous streams, which often results in errors as great as 15-20% in the estimation of U(VI) concentration.[4] Recent studies suggest that the effect of nitrate ion can be eliminated if the analysis is based on the absorbance at two U(VI) wavelength maxima.[8] However, present photometers are not designed to accommodate the use of the extra optical filters.

An in-line photometer has recently been developed which overcomes the above limitations. The photometer uses a rapidly rotating filter wheel, containing multiple optical filters, to monitor the transmission of a stream containing U(VI), Pu(III), Pu(IV), and Pu(VI) species. The monitor is equipped with fiber optic cables to transmit the monochromatic light from the photometer into and out of the hazardous areas of the reprocessing facility. Such a monitor design provides a nearly simultaneous multiwavelength, multielement analysis directly in the reprocessing stream while isolating the radiation sensitive optical and electronic components in accessible, protected locations.

This report will describe the design and operation of the prototype photometer. Photometric results will be compared with uranium analyses obtained by standard techniques to estimate the accuracy and precision of the multiple filter instrument.

DESCRIPTION OF THE SYSTEM

Instrument Components

The prototype photometer has three major components: the in-line flow cell, the out-of-cell optical head, and the data system (Figure 1). The in-line flow cell is a stainless steel block containing only optical components whose material and design are suitable for long-term exposure to high gamma fields (Figure 2). These include single strand quartz fiber optic light pipes to transmit the monochromatic light into and out of the process cell, front surface mirrors to collimate the light beam and to direct it through high purity sapphire windows, which interface directly with the process stream.

The out-of-cell optical head contains a) a tungsten halide incandescence source maintained at 2900°C, b) collimating and focusing optics, c) a filter wheel containing multiple narrow-band interference filters, selected in accordance with the process chemistry to be measured, d) a photomultiplier tube and e) a mechanical commutator to alternate the monochromatic light between the reference and sample light paths. The reference light path is constructed of a single strand optical fiber similar to the optical transmission path into the processing area. Its purpose is to provide a reference signal to automatically correct for changes in the narrow-band filters, spectral and intensity shifts in the radiant energy source and spectral drift in the photomultiplier tube. The transmission data is collected and processed with an LSI-11 computer system.

Instrument Operation

High intensity white light from the quartz halide source is collimated and directed towards a motor driven wheel carrying an array of selected narrow-band (5 nm, FWHM) interference filters. As each filter enters the beam of white light, monochromatic light from the filter is transmitted by the fiber

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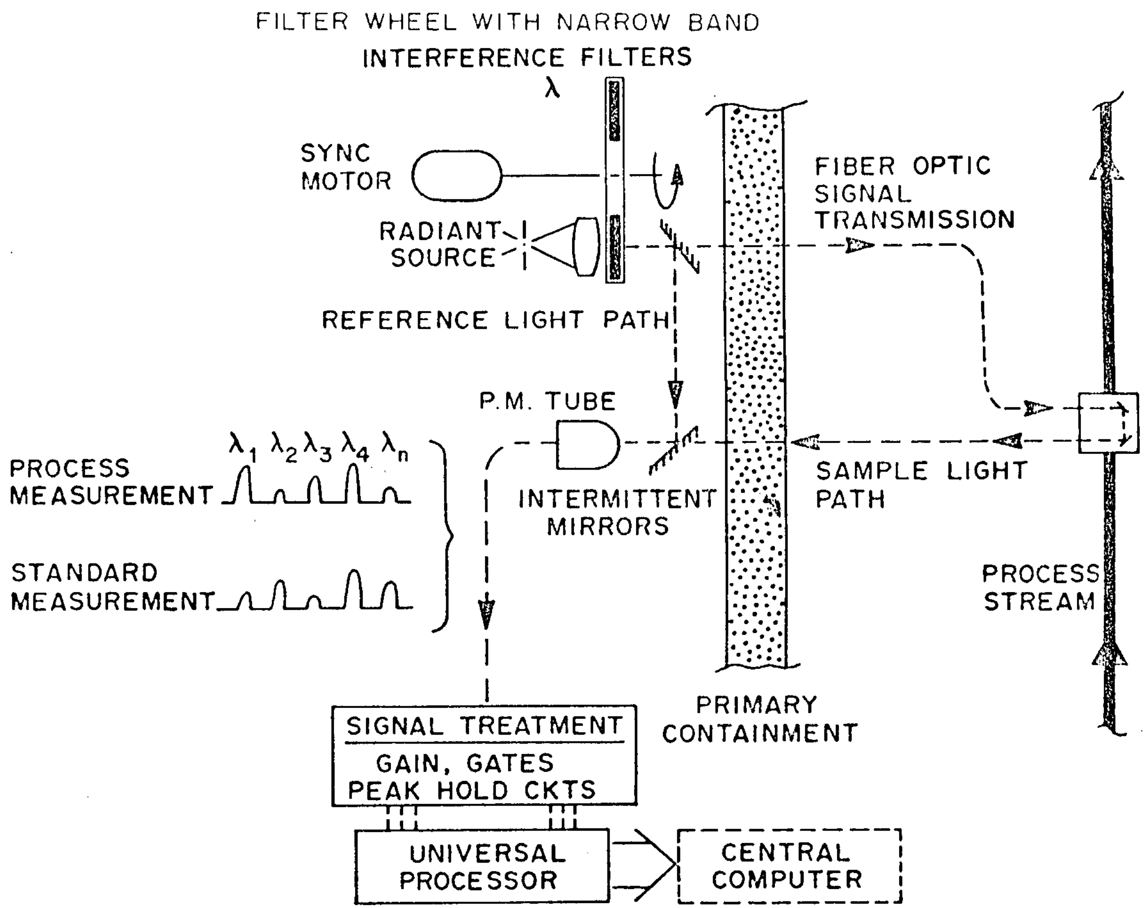
THE MULTI-WAVELENGTH PHOTOMETER UTILIZES MINIMUM IN-CELL HARDWARE



IN-LINE PHOTOMETER

Figure 1

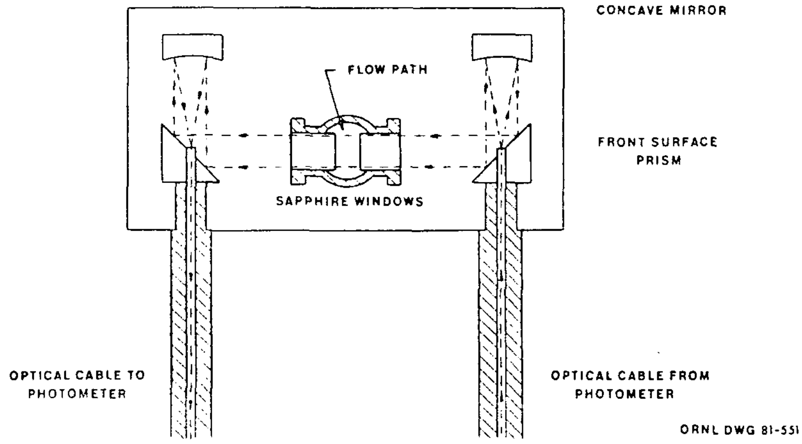


Figure 2. In-line flow cell

optic light pipe into the process flow cell. The monochromatic light is attenuated in accordance with the chemistry of the process stream and is returned via the light pipe to the photomultiplier tube. Subsequently, the monochromatic light from the same filter is optically switched through the reference optical path. In this way, two electronic signals are generated for each wavelength selected, one for the process measurement and one for standardization.

The amplitudes of the signals received by the photomultiplier are held by peak hold electronic circuits. Automatic gain control is applied to the photomultiplier bias in order to assure that each set of filter signals has the optimum gain coefficient. The set of reference signals are compared to stored information in the dedicated mini-computer and correction factors are established for each wavelength. These correction factors are applied to the attenuated signals from the process flow cell. The corrected sample transmission signals are in turn submited to a heavy metal concentration algorithm previously programmed into the computer. The computer outputs the concentration of one or more process stream constituents in units of grams per liter. The entire cycle repeats every six seconds. The system output is available for process management or as a control signal to optimize the performance of the plant.

INSTRUMENT PERFORMANCE

The prototype photometer, to date, has been evaluated as an instrument for monitoring uranium in both aqueous and 30% tributylphosphate/dodecane organic samples. Uranium transmission was observed at 416, 426, 476, 495 and 530 nm, using a 1.3 mm path length flow cell. The 416 and 426 nm filters monitored uranium concentration; the 530 nm filter was used for sample background corrections. The remaining filters will be used to follow Pu(IV) concentration in future studies.

System Reproducibility and Linearity

Absorbance values at each wavelength are calculated from the average of data compiled from six revolutions of the filter wheel. With sequential sampling of a given sample, the reproducibility in the calculated absorbance was estimated to be ±0.004. The day-to-day variation in the measurement of sample absorbance varied by ±0.006. The absorbance at both 416 and 426 nm is linearly correlated with uranium from 0.05-1.10 ODU, which corresponds to a linear detection range of 10-210 g/l U in aqueous samples and 5-100 g/l U in organic solutions.

Instrument Accuracy

A series of blind organic and aqueous uranium standards were analyzed using the photometer and results compared with those obtained by standard methods and instrumentation. The standard analytical techniques included a) the Davies-Gray titrimetric procedure,[9] coulometry,[10] x-ray fluorescence,[11] and colorimetric analysis using a Cary-14 spectrophotometer.[8] All of the results were assembled into a correlation study to compare the accuracy of the different measurement techniques. The average error observed by each technique is presented in Table 1. The prototype photometer behaves comparably with standard procedures in both aqueous and organic media. The relative standard error observed between the true concentration of uranium and that determined by the photometer is ±2.9% and ±3.4% for aqueous and organic samples, respectively.

CONCLUSION

The design and performance of the described prototype photometer indicates an accurate in-line analysis of the oxidation state and concentration of a heavy metal can be made directly in a complex process stream, while locating the bulk of the instrumentation off-line. Such a design protects the radiation sensitive optical and electronic components, as well as locates the mechanical moving parts in easily accessible locations. This feature simplifies instrument maintenance,

Table I. Uranium Correlation Study

ORGANIC URANIUM ANALYSIS

U Present (g/1)	U Found (g/1)		
	Photometer	Cary	XRF
9.75	7.99	10.1	9.15
15.24	13.3	14.8	14.6
19.72	18.0	19.1	19.4
29.00	30.1	32.1	29.1
30.15	28.4	29.4	26.7
39.77	37.4	37.9	38.3
49.40	47.8	47.2	47.9
55.28	53.4	52.5	54.1
60.30	58.5	57.0	60.7
64.26	61.7	60.9	61.7
70.28	62.9	66.3	62.9
74.99	70.7	71.5	70.7
84.13	79.5	85.0	79.5
Average Absolute Error (g/1):			
	2.2	2.0	1.9

AQUEOUS URANIUM ANALYSIS

U Present (g/1)	U Found (g/1)		
	Photometer	Cary	Standard Methods
20.33	16.5	20.5	20.15 (Coul.)
30.98	30.4	31.7	
47.77	45.1	46.9	51.0 (XRF)
55.75	59.3	60.2	
59.65	54.6	56.7	62.4
64.82	64.4	64.2	
70.53	67.6	71.0	75.6 (XRF)
75.52	77.3	76.5	
78.63	77.5	79.5	
89.09	83.1	87.1	86.0 (XRF)
74.09	75.7	74.7	
100.9	99.0	102.	99.16 (D-G)
105.7	105.	106.	
137.8	134.	138.	136.2 (D-G)
161.4	161.	155.	159.8 (D-G)
179.4	174.	164.	178.3 (D-G)
200.5	194.	185.	199.2 (D-G)
Average Absolute Error (g/1):			
	2.4	2.9	2.2

Cary = Cary 14 spectrophotometry
Coul. = Coulometry
D-G = Davies-Gray titration
XRF = X-ray fluorescence

replacement and calibration procedures. The rapidly rotating filter wheel permits a multielement determination while simultaneously correcting for stream background absorbance. Signal averaging and discrimination of the absorbance data can be incorporated into computer software to improve sampling reproducibility by correcting for spurious fluctuations in stream composition. The reference fiber optic light path at the same time corrects for fluctuations in light source intensity, and photomultiplier drift, as well as provides an indication of the integrity of the individual optical filters and sample fiber optic light path. The design of the photometer can be modified to incorporate any number of optical filters, extending the application of the fiber optic photometer to in-line photometric analysis other than in fuel reprocessing.

ACKNOWLEDGEMENTS

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