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MASTER

DIFFERENTIAL COLORIMETRY FOR NUCLEAR
PROCESS STREAMS

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ABSTRACT

An in-line process differential colorimeter, with automatic check system, has been developed with the capability of analyzing Pu(IV) in the range of 0.1 to 2.5 grams per liter. The instrument measures the difference in light transmittance at two wavelengths, 580 and 660 nanometers. These wavelengths are a characteristic of Pu(IV), and the difference in transmittance is a measure of the plutonium concentration.

INTRODUCTION

In-line colorimeters have been used to measure the plutonium concentration in anion column effluents throughout various AEC installations (1,2). Early colorimeters utilized a single wavelength (660 nanometers) for the detection of Pu(IV) in these streams. These units operated satisfactorily as long as clean Pu(IV) solutions passed through the flow cell. Periodically, column degradation products passed through the flow cell and the readings obtained were no longer a true measure of the Pu(IV) concentration. Chromium(III) has been found in the process streams and since its absorbance lies in the same spectral range as Pu(IV), erroneous indications were obtained from single beam colorimeters.

Spectrophotometric analyses of Pu(IV) solutions have shown a quantitative peak-valley relationship at 580 nanometers and 660 nanometers (See Figure 1). This information led to further investigations for measuring the transmittance of solutions at these two wavelengths. Proper electronic circuitry was used to differentiate the transmittances at the two wavelengths and thus indicate the Pu(IV) concentration.

SPECTRAL RESPONSE OF $Pu(IV)$ SHOWING THE 580
AND 660 NANOMETERS PEAK-VALLEY RELATIONSHIP

FIGURE 1

DRAWN JLM	THE DOW CHEMICAL COMPANY ROCKY PLATS DIVISION DENVER, COLORADO	
CHECKED		
O. K.		
DATE 6-10-66	SPECTRAL RESPONSE OF $Pu(IV)$	A. E. C. CONTRACT AT (20-1)-1106
SCALE		

THE INSTRUMENT

The differential colorimeter described in this paper consists of four major components: the flow cell, the detector unit, the electronic console, and the check-out system.

Flow Cell

The flow cell consists of a specially designed stainless-steel cylinder, with a rectangular slot perpendicular to the cylindrical axis, through which the solution flows (See Figure 2). A beam of light produced by a G. E. No. 253X prefocused lamp intercepts the solution path through two Pyrex glass windows. The purpose of the Pyrex glass windows is to contain the stream solution and thus eliminate contamination of the component parts.

The lamp is mounted at one end of the cylinder in a special light housing assembly which permits the adjusting of the light beam. The other end of the cylinder has an orifice through which the light beam leaves the flow cell after having passed through the stream solution. The detector cell assembly mounts at this end of the flow cell. Therefore maintenance is easily accomplished by removing the detector assembly from the flow cell.

Detector Unit

The detector unit as shown in Figure 3 consists of a beam divider, two interference filters, two cadmium-sulfide (CdS) photocells, and the necessary wiring.

FIGURE 2

DRAWN JLM	THE DOW CHEMICAL COMPANY ROCKY PLATS DIVISION DENVER, COLORADO	
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O.K.	SKETCH OF THE FLOW CELL ASSEMBLY	
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The beam divider splits the light emerging from the flow cell. Half of the light is passed through the 660 nanometer filter onto a cadmium-sulfide photocell, and the other half is passed through a 580 nanometer filter onto another CdS photocell. The filters have a bandpass of about ± 10 nanometers around the desired wavelengths.

A light attenuator provides a physical means for balancing the light intensity on the two photocells when water-clear liquid (acid solution) is in the cell. This is necessary since the photocell responses are not equal nor is the light beam equally split by the beam divider.

All of the components constituting the detector unit are mounted in a 4-1/2 by 4-1/2 by 2-1/2 inch box. The material used in the construction of this box was 1/4 inch Micarta which, because of its insulating properties, will not conduct any heat to the CdS photocells and affect their leakage current. Care must be taken to insure that the box is light tight; otherwise excessive background current may be registered on the readout meter with a consequent loss in sensitivity.

The Electronic Console

The electronic console contains part of the bridge circuit, the power supply, and the readout meter. These circuits are shown in Figure 4. The CdS photocells located in the detector unit are in effect photo-resistive devices, that is, their internal resistance changes in accordance with light intensities striking the sensitive surface of the photocells. Each photocell constitutes one arm of the bridge with two equal value resistors as the other two arms. A zero adjustment is provided by the potentiometer on the negative side of the bridge.

FIGURE 3

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CHECKED		
O.K.		
DATE 6-10-66	A.E.C. CONTRACT AT (20-1)-1106	
SCALE	DETECTOR CELL ASSEMBLY	

A 100-microampere meter detects unbalanced currents in the bridge which arise from the different light intensities on the photocells. Thus the meter indicates the difference in the absorption of the process solution at 580 and 660 nanometers, respectively. The greater the Pu(IV) concentration in the process solution, the greater the meter reading providing that other solution components have an equal light absorption at the 580 and 660 millimicron wavelengths.

A recorder output has been installed in series with each photocell. This output circuit is designed to deliver 10 millivolts when the flow cell is filled with a water clear solution (maximum light transmittance). As light absorbing material passes through the cell, the recorder signal drops. This produces an indication of the amount of light absorption in each individual photocell. These readings are used to monitor the transmittance of the solution at the specified wavelengths.

Check-Out System

The automatic check system consists of a voltage following amplifier, integrated micrologic circuits, and transistor drivers for associated relays and indicator lamps.

The purpose of this check-out system is to provide an alarm as soon as a malfunction develops in the colorimeter. This close monitoring of the instrument eliminates the possibility of "control runaway" when the colorimeter is used for process control applications.

FIGURE 4

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ROCKY PLATE DIVISION
DENVER, COLORADO

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The power supply required to drive the bridge circuit, the check system, and furnish power to the light source consists of a step-down transformer, a capacitor, six diode rectifiers, three zener regulating diodes, one transistor, and three voltage dropping resistors. The combined action of the filter capacitor and the zener diodes provide sufficient regulation to the bridge and logic circuits so that the meter and recorder output readings are free of fluctuations and instability.

EXPERIMENTAL

Proper calibration of the differential colorimeter required that several sample solutions be drawn from the process stream. These samples were relatively free from particulate matter and their plutonium concentration was in the range of 0.1 to 2.5 grams per liter. Each sample was placed in the flow cell and the differential readings, as well as the individual 580 and 660 nanometer readings, were recorded. These samples were then analyzed by the control laboratory for plutonium concentration using two methods, X-ray and radio-assay. Table I shows the values reported by the laboratory and the readings which were obtained from the differential colorimeter. Figure 5 shows the standard curve obtained from these values.

To determine the stability of the system, a second set of samples was tested four months later. The results obtained are also presented in Table I along with the plutonium concentration values reported by the control laboratory.

FIGURE 5

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COLORIMETER STANDARD CURVE

The precision of the laboratory analyses and the differential colorimeter was tested using duplicates of each sample. Table II shows the results of these tests.

Even though there was a long interval between the two sets of data presented in Table I, the readings obtained all fell within the 90% confidence limit. During this period of time no maintenance was required on the instrument.

TABLE I

COLORIMETER STANDARDIZATION DATA

Control Laboratory Analyses (Pu Concentration - g/l)	Colorimeter Readings (% Transmittance)		
	580	660	Differential
	Nanometers	Nanometers	
0.19	99	97	2.0
0.34	98	94	5.0
0.58	96	89	10.0
1.07	92	76	20.0
2.08	88	66	30.0
2.36	85	56	36.0

These data were recorded from a second set of samples four months later.

0.34	98	96	3.5
0.30	98	92.5	6.5
0.36	98	90	8.0
0.73	98	86	13.0
0.94	98	80.5	17.5
1.47	99	74.5	25.0
1.96	99	68	31.0
2.72	99	56	45.0

TABLE II

COMPARISON OF RESULTS OBTAINED WITH THE
DIFFERENTIAL COLORIMETER AND THE CONTROL
LABORATORY ON DUPLICATE SAMPLES

Laboratory Analyses (g/l)		Differential Colorimeter Reading	
0.34	0.22	3.5	2.5
0.30	0.31	6.5	6.5
0.36	0.37	8.0	7.0
0.73	0.71	13.0	13.0
0.94	0.89	17.5	17.0
1.47	1.38	25.0	23.5
1.96	1.67	31.0	29.5

CONCLUSION

The differential colorimeter described in this paper has been successfully used toward automation of an ion exchange facility at Rocky Flats.

The split beam approach is more sensitive than the single beam colorimeter, and it is more immune to other interfering substances which absorb light at the same wavelength as Pu(IV).

The instrument is capable of detecting the concentration of Pu(IV) in nitric acid solution, providing that other components in the solution have equal light absorbance at the two wavelengths of operation, 580 and 660 nanometers. Occasionally other interfering ions, such as chromium(III), can result in erroneous readings on the differential colorimeter. In these cases, it is advisable to check the Pu(IV) solutions for spectral purity and insure that the solutions do not contain large amounts of NO_3^- ion which will cause a plutonium complex formation. The experimental work performed at Rocky Flats indicates that best results are obtained when the solution hydrogen ion concentration is between 1.0 and 7.0 N.

Plutonium solution concentrations in the range of 1 to 20 grams per liter have also been tested with the differential colorimeter. These tests were successful, but it was necessary to decrease the flow cell path length in order to increase the sensitivity of the instrument.

A differential colorimeter for detecting low level solutions around 10^{-2} grams per liter was also developed, but the sensitivity of the instrument was not sufficient to reach this level of detection even with a long cell path.