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ANALYTICAL METHOD
FOR IN - LINE PLUTONIUM ANALYSES

Pu
by

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August 1961

MASTER

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ABSTRACT

Laboratory studies demonstrated the feasibility of a colorimetric method for the in-line analysis of plutonium(III) and plutonium(IV) in the Purex process. Negligible interference was caused by normal variations in the concentration of nitric acid, nitrous acid, or ferric sulfate.

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ANALYTICAL METHOD FOR IN-LINE PLUTONIUM ANALYSES

INTRODUCTION

In the process for separating uranium and plutonium from spent reactor fuels at the Savannah River Plant, an in-line analysis for plutonium was needed to aid in avoiding the accumulation of a critical mass due to reflux of plutonium within a mixer-settler.

This study was undertaken to determine the feasibility of using a colorimetric method for the in-line analysis of plutonium at concentrations of 0.1 to 0.6 mg/ml in the Purex process. For protection from an excursion, a precision of 10-20% was adequate because critical limits exceeded process limits by a factor of two to three. The practicability of a colorimeter as an in-line instrument had been demonstrated previously in the satisfactory operation of a unit designed for the analysis of uranium.⁽¹⁾

The purpose of the experimental work described in this report was to measure, in a colorimetric method for plutonium, the interferences that occur with changes in the process conditions. Much information was available in the literature^(2,3,4,5) on the absorption spectra of plutonium and on the effect of different reagents and temperatures. This information was used without further experimental work when it was directly applicable to the problem. The experimental work involved primarily plant samples and various dilutions of the plant samples, in order to reproduce plant conditions as closely as possible.

SUMMARY

A colorimetric method was shown to be feasible for the in-line analysis of plutonium in the Purex process. The colorimetric determination of plutonium over the concentration range of 0.1 to 0.6 mg/ml was made directly on samples of process streams without the addition of reagents. The method was insensitive to changes in composition of process solutions that contained Pu(III). The absorbance of Pu(IV) in aqueous solutions was dependent on the concentration of nitric acid; however, the degree of dependence was not sufficient to limit the application of the method. The optimum wavelengths were determined for the measurement of Pu(III) and Pu(IV) in solution. From these data and the absorptivities the proper optical filters and dimensions for absorption cells were determinable for the design of an in-line instrument.

DISCUSSION

Absorption spectra were obtained for two solutions from the Purex process. One solution was the plutonium product solution, 1BP, from the 1B bank, and the other was the feed solution, 2AF, for the second plutonium cycle. A typical composition of these solutions is given in Table I.

TABLE I

Composition of Purex Solutions

<u>2AF Feed Solution Containing Pu(IV)</u>	<u>1BP Product Solution Containing Pu(III)</u>
4.0M Nitric acid	1.26M Nitric acid
0.016M Ferric sulfate	0.04M Ferrous sulfamate
0.1M Nitrite	0.60 mg Pu/ml
0.23 mg Pu/ml	

The absorption spectra were obtained in order to define the optimum wavelengths for measuring Pu(III) and Pu(IV) in aqueous solution. Absorption spectra were measured also for solutions of Pu(IV) in Purex solvent (30% tributyl phosphate-"Ultrasene"*) prepared in the laboratory. From these data it is possible to choose the proper optical filters and to specify approximate dimensions for the absorption cell for each system. The effect of changes in sample composition on the colorimetric plutonium analysis was determined to establish the accuracy of the method for plant operation.

EXPERIMENTAL PROCEDURE

The absorption spectra for plutonium in Purex solvent were determined from solutions prepared in the laboratory. The 2AF solution was contacted with an equal volume of the solvent so that the plutonium was extracted into the organic phase. This organic solution was then diluted with fresh solvent to provide different concentrations of plutonium and nitric acid. The plutonium concentration was determined for each solution by alpha counting.

To determine the effect of changes in composition of plant solutions, known amounts of the concentrated reagents were added to the plant solutions to give the desired concentrations. The absorbance of the solution was then measured at the specified wavelengths to determine the extent of the interference in the plutonium analysis. In addition, the absorbancies of the individual reagents were measured at the wavelengths of interest.

The absorption curves were made with a "Cary" recording spectrophotometer, and the absorbancies at the selected wavelengths were measured from the curves. Five-centimeter absorption cells were used for all of the measurements and the spectra were recorded against distilled water as a reference.

*Product of Atlantic Refining Co.

RESULTS

The absorption spectra for the two plant solutions and for Pu(IV) in Purex solvent are shown in Figure 1. The spectrum of the feed solution, 2AF, shows the characteristic absorption peaks of Pu(IV) with the principal peak at 478 m μ ; as shown in Figure 1c, the Pu(IV) peak is shifted to 492 m μ when the plutonium is present in the Purex solvent. The spectrum of the product solution, 1BP, shows the characteristic absorption peaks of Pu(III). The pertinent data from these spectra are summarized in Table II.

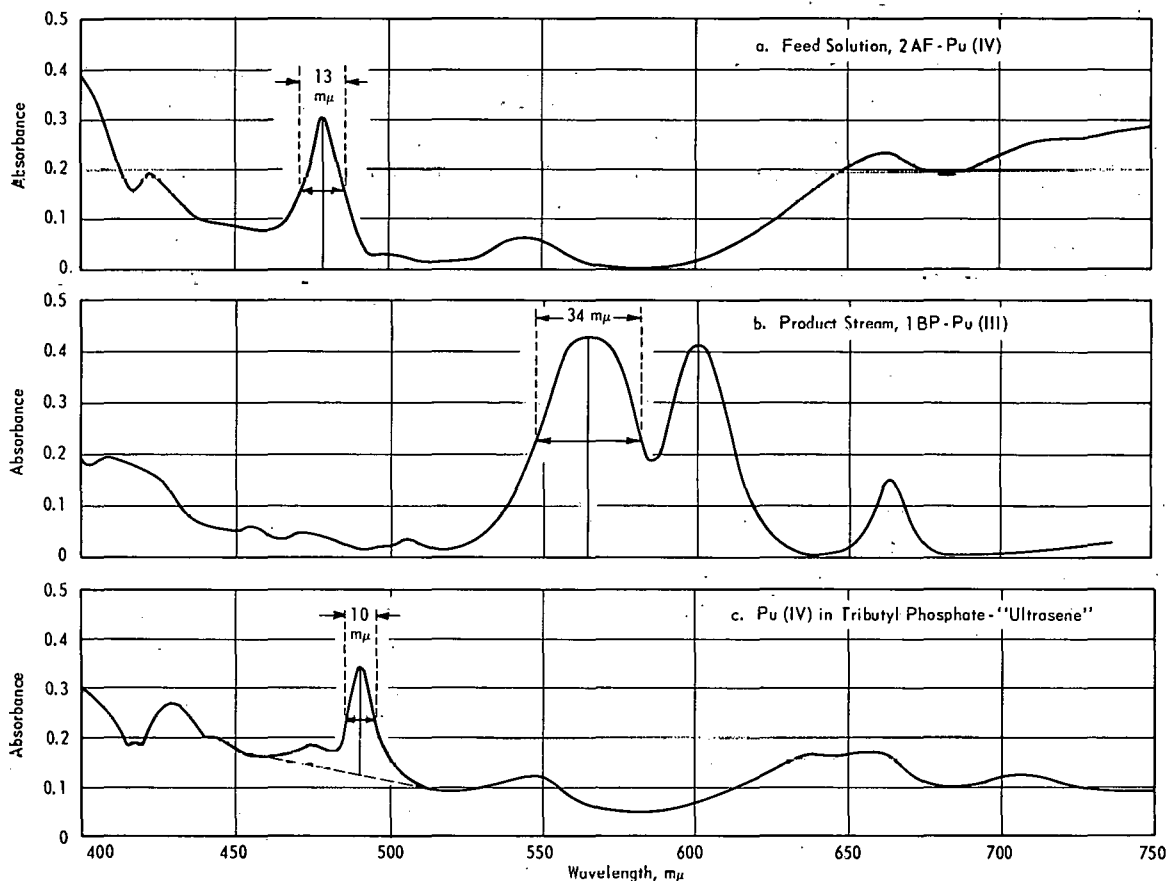


FIG. 1 ABSORPTION SPECTRA

TABLE II

Absorbance Data for Plutonium in
Aqueous and Organic Solutions

Solution	Wavelength, m μ	Absorbance	Width of half-height, m μ	Molar Absorptivity (ϵ)
2AF Feed Containing Pu(IV)	478	0.31	13	64
1BP Product Containing Pu(III)	564	0.43	34	37
Solvent Containing Pu(IV) (0.17 mg/ml)	492	0.35(a)	10	42

(a) Includes absorbance of 0.2 for solvent vs. water.

These data show that the sensitivity of the colorimetric method is adequate for the analysis of plutonium in Purex process streams. The optimum wavelengths for measurement of each valence state of plutonium are given in Table II and the optical filter for the colorimeter should be chosen for these wavelengths. In addition, the bandpass of the filters should be selected in accordance with the width of the absorption peak so that the maximum sensitivity is obtained. The molar absorptivities found for plutonium are in agreement with those reported in the literature.^(2,3)

The results for the 2AF feed solution show that the absorbance of Pu(IV) at 478 m μ was dependent upon the concentration of nitric acid or sulfate ion. The change in absorbance is due to the formation of complex ions^(2,4,5). The sulfate ion forms a more stable complex with Pu(IV) than does nitrate ion; hence the absorbance is changed significantly by low concentrations of sulfate in solution. A colorimeter that serves as a criticality monitor in the 2AF stream would not be limited by these changes in the absorbance of plutonium.

In the product solution, 1BP, the absorbance of Pu(III) was not changed significantly by variations in the composition of the solution. Therefore, in the 1BP stream the colorimetric method is applicable for criticality control.

Absorption spectra were obtained for the individual constituents of the process solutions. The data given in Table III show that these materials do not give a significant absorption at the wavelengths of interest and, therefore, should not interfere in the plutonium analysis. The absorbance of the solvent remains constant from 400 m μ to 575 m μ . The solvent was plant-grade material, and no information was obtained on the effect of impurities on the absorbance of the solvent at 478 m μ .

TABLE III

Absorbance Data for Constituents of Plant Solutions

Constituent	Molar Absorptivity			
	Experimental		Literature	
	478 m μ	564 m μ	476 m μ	564 m μ
Fe ₂ (SO ₄) ₃ in 1M HNO ₃	0.03	0.02	-	-
Fe(NH ₂ SO ₃) ₂	-	-	0.2	0.1
30% TBP - "Ultrasene"	0.2(a)	0.2(a)	-	-

(a) Absorbance units for 5-cm cell measured against water.

The effect of variations in the concentration of the constituents of each process solution on the absorbance of plutonium was studied and the results are given in Table IV. The range of concentrations was greater than any encountered in normal plant operation.

TABLE IV

Molar Absorptivity of Plutonium as a
Function of Solution Composition

<u>Feed Solution Containing Pu(IV)</u>				
Pu, mg/ml	HNO ₃ , M	NaNO ₂ , M	Fe ₂ (SO ₄) ₃ , M	ε
0.23	4.0	0.10	0.016	64
0.20	3.5	0.08	0.130	53
0.20	3.5	0.08	0.013	64
0.20	5.9	0.08	0.013	45
0.19	3.3	0.12	0.013	63

<u>Product Solution Containing Pu(III)</u>				
Pu, mg/ml	HNO ₃ , M	Fe(NH ₂ SO ₃) ₂ , M	Fe ₂ (SO ₄) ₃ , M	ε
0.60	1.26	0.04	0	37
0.52	1.21	0.15	0.12	37
0.52	1.22	0.03	0	35
0.52	3.65	0.03	0	37
0.45	5.35	0.03	0	37

Solvent Containing Pu(IV)

Pu, mg/ml	HNO ₃ , M	ε
0.17	0.7	42
0.12	0.5	41

The absorbance of Pu(IV) in the TBP solvent is less than that for Pu(IV) in nitric acid solution, and changes in the concentration of nitric acid in the solvent do not produce large changes in the absorbance of Pu(IV). Therefore, the colorimetric method is suited for the analysis of plutonium in solvent streams.

APPLICATION

The data developed as a result of this study were applied by the Applied Physics Division in the design of a colorimeter for measurement of the plutonium content of streams of the Purex process⁽⁶⁾. The instrument was never applied as a criticality monitor of the mixer-settler operation; a neutron monitor was designed instead to meet that requirement.^(7,8) However, the instrument has been applied in the B-Line operation for the analysis of individual samples for criticality control purposes.

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