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Author(s): L. F. Walker, D. J. Temer, and D. D. Jackson

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Procedure for Plutonium Determination using Pu(VI) Spectra

by

L. F. Walker, Donald J. Temer, and Darryl D. Jackson

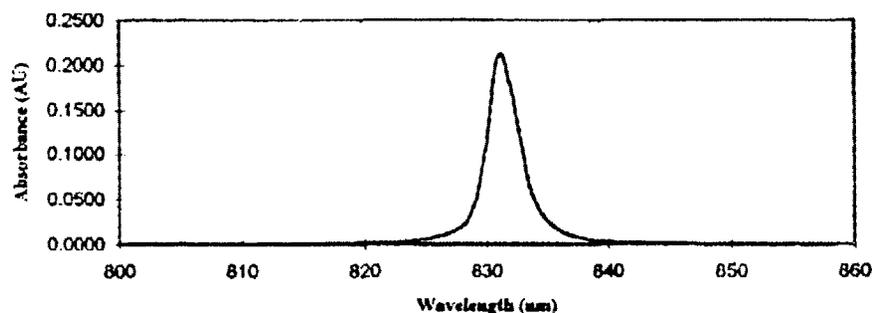
Abstract

This document describes a simple spectrophotometric method for determining total plutonium in nitric acid solutions based on the spectrum of Pu(VI). Plutonium samples in nitric acid are oxidized to Pu(VI) with Ce(IV) and the net absorbance at the 830 nm peak is measured.

Introduction

Plutonium exhibits distinctive spectra in several oxidation states. In the +6 state, it has a very sharp peak at 831 nm and a maximum molar absorptivity of 500 (1). Because of these two features, it has been used by several laboratories to quantitate plutonium (2-5). Ozone, argentic oxide, perchloric acid, and cerium(IV) have been used to quantitatively oxidize plutonium to the +6 oxidation state. We have chosen cerium(IV) because of its rapid response, ease of handling, and stability in the system. With cerium oxidation, our quantitation of total plutonium as Pu(VI) in a 2M HNO₃ system is similar to that used by Savage and Cook (5). An example spectrum is shown below.

Pu(VI) Spectrum
0.1 mg Pu/ml



This method applies to plutonium nitrate solutions with plutonium concentrations >1 g/l. It is ideal for production lines utilizing nitric acid dissolution of plutonium containing materials and for nitrate waste streams. The precision is 0.2% for high purity streams with plutonium concentrations >50 g/l and is typically better than 1.0% even for streams with plutonium concentration as low as 1 g/l containing large quantities of impurities. The method is tolerant of many impurities including Al, Fe, Na, Mg, Ni, Cr, Zn, Mo, F, and PO₄ at levels exceeding the plutonium content itself (6). The keys to success using this method are in the precision of the sampling and instrumentation

Sampling

This method is designed for use with plutonium samples in nitric acid. Determine the volume of sample to take using the table in the Appendix and the estimated plutonium concentration. The sample volume should not exceed 1 ml and should contain 1 to 10 mg of plutonium. We recommend using calibrated microliter pipettes. The precision of the assay can be no better than that of the sampling. Use of a single pipette for dispensing both samples and standards will avoid the bias between pipettes and is encouraged. Because the absorbance is very sensitive to the nitric acid concentration, the acidity of the sample must be determined and adjusted if it is significantly different than the nominal 2.0 M of the assay system. Changing the overall nitric acid concentration by as little as 0.02 M can affect the measured absorbance by 0.1%. The contribution to the assay for not adjusting the nitric acid concentration in the extreme case of a sampling volume of 1 ml at an acidity of 16M can be as large as 1%. Adjustments are made by adding water to the assay flask to compensate for the acidity and size of the sample aliquant. The table in the Appendix gives suggested adjustments for various sample concentrations and acidities.

Standards

A plutonium solution in 2M HNO₃ at approximately 5 mg Pu/ml is made by dissolving three grams of high purity plutonium oxide with the nitric acid sealed reflux system (7). The solution is transferred to a beaker and fumed to near dryness, redissolved in 2M HNO₃ and fumed to near dry again. The plutonium nitrate is finally transferred to a clean 500 ml volumetric and made to volume with 2M HNO₃. The resulting solution is assayed for plutonium using coulometric assay to verify the concentration of the solution. Since changes in temperature will affect the volume, and therefore the sampling when volumetric sampling is used, the density is measured and the temperature noted for reference so corrections can be applied if needed. The plutonium stock solution prepared in this manner is stable for >1 yr. If the stock solution has not been used for an extended period, as a precaution, we recommend verification of the plutonium concentration before use. Three grams of plutonium oxide is enough for about 70 calibration curves. Since volumetric sampling is sensitive to temperature changes, all samples and standards should be taken within a close time frame to eliminate variation between sampling conditions of samples and standards. Weighed aliquants can be used but are more time consuming and offer little improvement in precision over properly dispensed volume aliquants. Standards are pipetted into flasks delivering plutonium at five or more levels from 2 to 10 mg per flask in the optimum range (the range may be extended at the expense of precision). A calibrated automatic pipette works well for this purpose.

Instrumentation - Guided Wave Model 260

The Guided Wave Model 260 is a high resolution, high precision, UV/Vis/NIR, fiber optic instrument. The operation conditions are discussed in detail in a report evaluating an earlier model of this instrument (8). A brief list of key components and parameters using the Model 260 are given here:

Fibers - 2m x 500um from source to cell
2m x 300um from cell to detector
Parameters - Source - Tungsten Halogen Lamp
Filter - 495 nm Cut Off
Grating - 800 lines/mm
Detector - Si
Range - 800-860 nm
Step - 0.1 nm
Dwell - 0 dark cycles before reading after grating movement
Rate - 5 points per wavelength
Average - 3 scans per sample
Cell - 1cm path, 80ul micro flow cell, thermostated to $\pm 0.1^{\circ}\text{C}$
Peripherals - Autosampler
Peristaltic pump

Reagents and Supplies

HNO_3 - 2M made from reagent grade chemicals. As discussed earlier, the method is sensitive to variations in nitric acid concentration, so this reagent is made in large batches to ensure that the nitric acid concentration is constant for all samples and standards in an assay.

Cerium(Ce) solution - 1M ceric ammonium nitrate made in water. Centrifuge this reagent using a clinical centrifuge (10 min at full speed) to remove particulates.

Note: Distilled or deionized water must be used for all reagents.

Pipette - We use a Rainin automatic pipette. The pipette must be calibrated for all volume settings that are used in an assay. Replicate doses at a single setting can be used as follows:

If the standard stock solution is 4 mg Pu/ml, then five standards, A- E, over the calibration range from 2 mg Pu/flask to 10 mg Pu/flask can be prepared using a calibrated 500 ul pipette. For standards use A=1x500, B=2x500, C=3x500, D=4x500, and E=5x500 ul for the calibration standards. Then for samples use the same 500 ul setting and replicate doses as needed. The calibration at 500 ul is needed to measure the exact amount of plutonium in a single dose of the standard. For our purposes, precision of 0.1% or better is required.

Flasks - 50 ml, calibrated, glass volumetric flasks are used for this assay

Method

To standards, samples (adjusted for acidity if needed), and a reagent blank in assay flasks, add 1 ml of freshly centrifuged Ce solution to each flask. Rinse sides of flasks with 2M HNO_3 , dilute to volume, and mix well. The spectrophotometer should be on and exhibit a

stable baseline with water before collecting data. All solutions are fed into the cell by means of a pump in conjunction with an autosampler or an equivalent technique. The volume in the cell is 80 ul but the amount required for a preinse and to fill the lines entering and exiting the cell is dependent on the individual system and is about five milliliters for our instrument configuration. Once the cell is filled with the solution, the flow of solution is stopped before measurement of the spectra. The spectral scan of a single solution takes about four minutes using the operational parameters listed under the Instrumentation section. The reagent blank is introduced into the cell first and the absorbance measured and stored. Standard and sample spectra are measured against the reagent blank spectra. The cell is rinsed with the next sample/standard and filled with the same solution; then a spectrum is taken and the data is stored on disk. The data stored on disk is analyzed after all the sample/standard spectra are taken. With the autosampler, the entire batch of samples and standards can be run unattended. Although ceric oxidation and absorbance measurement are usually done on the same day, the ceric complex is stable for more than two weeks. The solutions can be measured spectrophotometrically days after preparation but it is recommended that the spectra for standards and samples be collected on the same day.

Data Handling

To determine the net absorbance for the prominent Pu(VI) peak, first determine the wavelength of the maximum absorbance in each spectrum. The peak may drift slightly over the course of several hours because of instrumental instability. A baseline value is computed as the average of the two absorbances at 10 nm to each side of the peak. The net absorbance is the maximum absorbance minus the baseline value. This is calculated using a program which reads the spectral files and returns the net maximum absorbance for each standard and sample.

A calibration curve is generated using the net absorbances and the corresponding concentrations of the standards in mg Pu/ml. The curve with the best residual form and correlation for this data is a quadratic form. A linear fit yields residuals that have a parabolic form, indicating a next order fit. Quadratic fits yield a random pattern for the residuals. The precision of the calibration curve is estimated by the average per cent residual when comparing absorbance measured versus absorbance calculated by the calibration curve parameters. Using the parameters generated, a simple calculation yields the concentration of the sample. Then using the volume of sample added to the flask, the concentration of the original sample is readily available as shown below. An example of calibration data is also shown.

Sample Concentration = $50 * X * CF / \text{Vol of Sample Aliquot}$

where X = Concentration in the assay flask

CF = Calibration Factor for 50ml assay flask

and X is found by solving

$$\text{Absorbance Measured} = a_2X^2 + a_1X + a_0$$

where a's are the calibration coefficients generated by a quadratic fit of the calibration data

Example Calibration Data:

Total mg P / Flask	Pu Concentration* mg/ml	Net Absorbance	% Residual
1.12450	0.022497	0.03260	-0.132
2.24900	0.045018	0.06601	+0.050
3.37349	0.067538	0.09924	+0.082
4.49799	0.090095	0.13220	-0.032
5.62249	0.112657	0.16512	-0.038
6.74699	0.135030	0.19771	+0.006
7.87149	0.157546	0.23029	+0.008

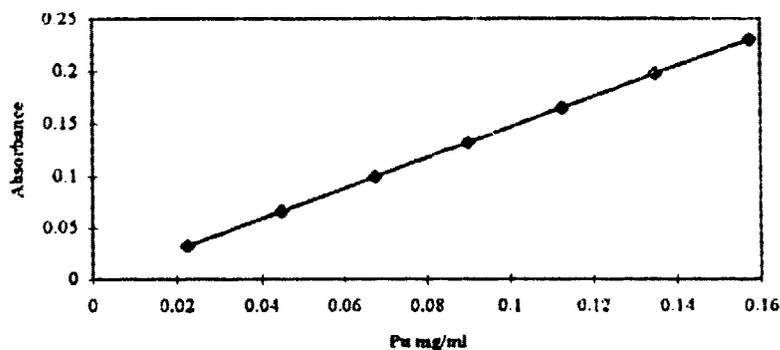
* Flask calibrations are used in determining the Pu concentration in the assay flask.

$$\text{Absorbance} = -0.14867 X^2 + 1.4901X - 0.000805$$

Average absolute percent residual = 0.05%

Notice that since X at mid-range is approximately 0.1 mg/ml, X^2 is 0.01, and the quadratic component is only 1% of the observed absorbance. The quadratic component is not discernible upon visual examination of the calibration curve below.

Calibration Curve



Appendix

Sample Est. Conc. mg Pu/ml	Sample Aliquant ul	Sample Acidity					
		3M	4M	5M	6M	7M	8M
>50	50	<i>25</i>	<i>50</i>	<i>75</i>	<i>100</i>	<i>125</i>	<i>150</i>
15-50	100	<i>50</i>	<i>100</i>	<i>150</i>	<i>200</i>	<i>250</i>	<i>300</i>
5-15	500	<i>250</i>	500	750	1000	1250	1500
1-5	1000	500	1000	1500	2000	2500	3000

Adjustments are made using the table above as a guide to indicate the ul of water to add to the assay flask as indicated in bold type. The amount of water needed is a function of both the nitric acid molarity of the sample and the aliquant size. There is no correction where the numbers are in italic since the change in acidity has a negligible effect on the method.

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