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### Title

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# Detection and Quantification of Pu(III, IV, V, and VI) Using a 1.0-meter Liquid Core Waveguide

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## Abstract

Detection and quantification of the aquo ions of Pu in 1 M HClO<sub>4</sub> was carried out using a 1-meter liquid core waveguide (LCW) coupled to a fiber optic UV-Vis spectrometer. Detection limits of  $7 \times 10^{-7}$  M for Pu(VI),  $1.6 \times 10^{-5}$  M for Pu(V),  $5 \times 10^{-6}$  M for Pu(IV) and  $8 \times 10^{-6}$  M for Pu(III) were achieved. The limits of detection represent increases of 18 to 33 times those achievable using a conventional 1-cm path length. Because of the much lower detection limits of the LCW, routine identification of the oxidation states in dilute Pu solutions can be made.

**Keywords:** plutonium, absorption spectroscopy, liquid core waveguide

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## Introduction

Several U.S. Department of Energy sites have been contaminated with radionuclides due to nuclear weapons and power production. Nuclides present at contaminated sites include isotopes of Cs, Sr, Tc, U, Np, and Pu. Initiatives to study the transport of these elements and to develop remediation strategies for these contaminated sites have focused on both laboratory and field scale investigations of these complex environmental systems. For reliable transport models and remediation strategies to be developed both in the field and on the bench, chemical information regarding the oxidation state, speciation, and quantity of the nuclide must be known.

In the case of plutonium, the oxidation-reduction chemistry in aquatic and environmental systems is extremely complex. Plutonium possesses four oxidation states that are stable [ $\text{Pu}^{3+}$ ,  $\text{Pu}^{4+}$ ,  $\text{Pu(V)O}_2^+$ ,  $\text{Pu(VI)O}_2^{2+}$ ] and can co-exist in near-neutral aqueous solution [1]. Because the chemical properties such as solubility and speciation and consequently transport properties of each oxidation state vary widely a reliable method for the quantification of the oxidation states must be available.

Existing methods for detecting and quantifying the oxidation states of plutonium require the use of organic extracting agents (HDEHP, TTA, PMBP) coupled with radioactive counting of the extraction phases [2]. These series of extractions must be performed rapidly and in parallel to provide accurate measurement of the oxidation state distributions. Uncertainty due to perturbation of the existing redox equilibrium in the aqueous phase as a result of these extraction routines is unclear. While providing excellent limits of detection ( $\sim 10^{-11}$  M, depending on the chosen isotope)

these methods produce waste that is often difficult and costly to dispose of and require several sequential processes that can be time consuming for routine analysis.

Colorimetric methods for detecting plutonium at low concentration, such as complexation with a chromotropic dye such as chlorophosphonazo-III or arsenazo-III lack specificity for oxidation states and are often subject to interferences from other metal ions and electrolyte ions [3,4].

The unique spectra of the plutonium aquo ions provides the information regarding oxidation state, and often times speciation information [5,6]. However, the low molar absorption coefficients of the plutonium absorption bands ( $2 - 550 \text{ M}^{-1} \text{ cm}^{-1}$ ) make spectrophotometry with traditional 1 or 10 cm cuvettes inadequate for studies at dilute concentrations [5,7].

Direct detection of the plutonium oxidation states in solution can be achieved through the use of laser photoacoustic spectroscopy. This method uses a tunable laser system to scan through the wavelengths of interest and the signal is detected using a piezoelectric transducer [8]. Neu et. al. showed that the photoacoustic methods provide comparable results versus liquid-liquid extraction [8]. To their disadvantage, laser based photoacoustic methods require the use and maintenance of expensive and complex equipment.

More recent work by Kuczewski et al. describes the coupling of capillary electrophoresis to ICP-MS [9]. This CE-ICP-MS system allows for the separation of actinides along the CE column and detection with the ICP-MS. The limits of detection for this system were reported as  $0.2 \mu\text{M}$  for a single oxidation state of an

actinide [9]. While providing a limit of detection superior to UV-VIS spectroscopy, this method requires the use of expensive ICP-MS and CE systems.

Development of liquid core waveguides (LCW) has allowed for the use of extremely long path lengths with minimal sample volumes, and rapid sampling times [10]. Cells of this type have been used in the analysis of trace iron, nitrate and other analytes of interest [10,11,12]. The LCWs provide lower limits of detection because of the increase in path length as described by the Beer-Lambert law.

In this paper we report the use of a 1.0 meter LCW coupled to a fiber optic spectrometer for the detection and quantification of all four valences of plutonium at acidic pH. Results are presented from samples in 1 M perchloric acid (Pu III, IV, VI) and at 0.001 M perchloric acid (Pu V). Considerable enhancements in detection were achieved and are discussed.

## **Experimental**

A liquid core waveguide (LPC-1) with an effective path length of 1.0 meter was used and connected to a UV-Vis-NIR fiber optic spectrometer (ST-2000) using a tungsten halogen light source (LS-1), all received from Ocean Optics Inc. The LCW consists of a Teflon AF-2400 capillary with a fill volume of 250 microliters coupled to the light source and spectrometer through T-shaped junctions constructed of PEEK [10]. The incident fiber carrying the light intersects the Teflon capillary at an angle of less than 19 degrees to allow for total internal reflection of the incident light in the LCW. Construction and design are discussed in detail by Waterbury, Yao, and Byrne [10].

The filling port to the LCW was connected to a mini peristaltic pump (VWR Scientific Products) using platinum cured silicone tubing with an inner diameter of 0.078 inches (VWR Scientific Products). The cell was continuously pumped during sample measurement at a flow rate of 5 mL/min. The tubing was cleaned with concentrated perchloric acid before sampling. No degradation in spectral quality or reproducibility was observed with washing the cell with either concentrated nitric or perchloric acid. Five spectra were collected and averaged for each sample. The absorption maxima were recorded at one common wavelength for each absorption band. Background measurements were made using a blank sample of 1 M HClO<sub>4</sub> or 0.001 M HClO<sub>4</sub> where appropriate. Limits of detection were determined using an absorbance value calculated at three times the standard deviation of the noise.

### **Plutonium Preparation**

A stock solution of <sup>239</sup>Pu was purified by anion exchange chromatography using a Dowex anion exchange resin in the nitrate form conditioned using 7.0 M HNO<sub>3</sub>. The column was loaded with Pu(NO<sub>3</sub>)<sub>6</sub><sup>2-</sup> in concentrated nitric acid. The ion exchange column was subsequently washed with several column volumes of 7.0 M nitric acid and the plutonium eluted as Pu(IV) by washing with 0.36 M hydrochloric acid. An alpha spectrum taken of the stock solution showed no indication of <sup>241</sup>Am from the decay of <sup>241</sup>Pu.

Solutions of Pu(VI) were prepared by first fuming the plutonium stock solution with concentrated nitric acid to remove any organic material that may be present as a safety precaution for the following steps with perchloric acid.

*CAUTION! Small quantities of organic materials present in concentrated and hot*

*perchloric acid may cause explosive compounds to be formed.* After several repetitions with the nitric acid, concentrated perchloric acid (70% Double Distilled from VYCOR, G.F. Smith) was added to the stock solution and boiled at 190° C for three hours to oxidize the plutonium to Pu(VI). Manipulation of Pu was performed inside of a glovebox at a pressure lower than that of the laboratory to prevent contamination. All steps with the nitric and perchloric acid were performed in specially designed glassware to prevent the accumulation of hot perchlorate and nitrate vapors inside the glovebox, and to prevent the formation of explosive perchlorates.

Solutions of Pu(III), and Pu(IV) in 1 M HClO<sub>4</sub> were prepared electrochemically from the Pu(VI) stock solution using a three electrode cell consisting of Pt-mesh working electrode and a Pt counter electrode separated from the cell by a VYCOR frit, and an Ag/AgCl reference electrode following the methods described by Cohen [13]. Oxidation state purities of the concentrated stock solutions were checked using spectrophotometry. Solutions of Pu(V) were prepared by first diluting the Pu(VI) solution to 0.5 mM in 0.001 M HClO<sub>4</sub> and re-adjusting the pH to 3.0 during electrolysis using 0.1 M NaOH. Working at pH 3.0 and dilute Pu concentration is necessary to slow the disproportionation of Pu(V) to Pu(IV) and Pu(VI) [1,13].

Dilutions of the Pu(VI), IV, and III stock solutions were made in 1 M HClO<sub>4</sub> with the exception of the Pu(V) which was studied at pH 3. Concentrations of the Pu samples ranged between 100 and 0.1 micromolar in volumes of 1 mL. Concentrations of the stock solutions and dilutions of the Pu samples were

determined by liquid scintillation counting using a Perkin Elmer Guardian 1414 liquid scintillation counter with  $\alpha/\beta$  discrimination and Ecolume scintillation cocktail (ICN).

## Results and Discussion

Representative spectra of each of the oxidation states of plutonium acquired with the LCW are presented in Figure 1. These spectra agree well with the spectra presented by Cohen [5]. The molar absorption coefficients and limits of detection of the major absorption bands measured using the 1-meter LCW are presented in Table 1 with literature values of the molar absorption coefficients for comparison taken from Silva and Nitsche [7]. A complete listing of the absorption bands and calculated molar absorption coefficients are listed in Table 2.

The spectrum of Pu(III) in 1 M perchloric acid is presented in Figure 1. Several absorption bands are present in this spectrum. The molar absorption coefficients for these absorption bands were calculated using a standard Beer's Law plots. The resulting molar absorption coefficients for all absorption bands are presented in Table 2 along with the results from the linear regression analysis. The data are in good agreement with the literature values, Table 1, and the resulting  $R^2$  values for the regression analyses show good linearity. The measured molar absorption coefficient for the absorption band at 600 nm is  $33.8 \pm 0.2 \text{ M}^{-1} \text{ cm}^{-1}$  and corresponds to a detection limit for Pu(III) of  $8.0 \times 10^{-6} \text{ M}$ , an increase of approximately 30 times the detection limit in the 1-cm cell.

The Pu(IV) absorption spectrum in 1 M perchloric acid is presented in Figure 1 and is characteristic of those presented previously by Cohen [5]. This spectrum



however does not show an increasing baseline attributed to the formation of Pu(IV) colloidal species [1]. Because the Pu(IV) hydrolyzes near pH 1 care must be taken to keep the solution sufficiently acidic to prevent hydrolysis and subsequent colloid formation. The Pu(IV) spectra presented in this study show no evidence of Pu(IV) colloidal species in the absorption spectra and the resulting increase in absorption due to scattering processes. The molar absorption coefficient for the signature absorption band of Pu(IV) at 470 nm was determined to be  $49.0 \pm 0.4 \text{ M}^{-1} \text{ cm}^{-1}$ . This molar absorption coefficient was used to calculate a limit of detection of  $5.0 \times 10^{-6} \text{ M}$  for Pu(IV), an increase of 30 times that measured for the 1-cm cuvette.

The Pu(VI) ion, exists as the dioxo-cation  $\text{PuO}_2^{2+}$  and has a characteristic absorption band at 830 nm. In a 1-cm cuvette, this molar absorption coefficient for this band was determined to be  $550 \text{ M}^{-1} \text{ cm}^{-1}$  by Cohen [5] and later reported by Silva and Nitsche [7]. Using this molar absorption coefficient, we calculated a limit of detection of  $12.4 \times 10^{-6} \text{ M}$  in a 1-cm cuvette, Table 1. The measured molar absorption coefficient and corresponding limit of detection were measured to be  $288 \pm 10.0 \text{ M}^{-1} \text{ cm}^{-1}$  and  $7.0 \times 10^{-7} \text{ M}$  using standard Beer's Law plots, Table 2. The disagreement between our measured molar absorption coefficient and that measured by Cohen and Silva and Nitsche is due to the limited spectral bandwidth of our spectrometer. This band at 830 nm is also well outside the transmission window for the LCW (400 to 700 nm) using aqueous media, and the resulting limit of detection is higher than would be expected if this band were to occur inside the transmission window of water. The increased noise above 700 nm is due to the overtones of the water absorption bands in the visible and near infrared [14,15]. Only with long path

lengths do these overtones become significant and the resulting increase in the background above 700 nm is attributed to them.

The spectrum of the Pu(V) aquo ion shows characteristic features of Pu(VI) (831 nm) from incomplete reduction of the starting Pu(VI) solution. This contamination of the spectrum is due to the difficulty of preparing pure oxidation states of Pu(V) and the instability of Pu(V) solutions with respect to disproportionation [1] and was not evident in the 1-cm cell measurements made at the end of the reduction. Using our calculated molar absorption coefficient for Pu(VI) it is estimated that the Pu(VI) contamination is approximately 6 % of the total plutonium in solution. The measured molar absorption coefficient for the major absorption band of Pu(V) is  $17.2 \pm 0.2 \text{ M}^{-1} \text{ cm}^{-1}$  and is in fair agreement with previously reported values. This molar absorption coefficient corresponds to a limit of detection of  $16.0 \times 10^{-6} \text{ M}$ . The poor linearity of the band at 518 nm is probably due to the overlap of this band with the Pu(VI) absorption bands in this region.

The incomplete enhancement in the limit of detection (100 times) can be attributed to the increase in the noise using the 1.0 meter cell. Limits of detection were calculated at three times the standard deviation of the background. In the case of the 18-fold increase seen in the Pu(VI) samples, the lack of quantitative enhancement in the limit of detection is attributed to both the increase in noise noticed with the LCW and the lack of transparency of the cell in the near infrared region.

## **Conclusions**

Molar absorption coefficients for each of the characteristic absorption bands were measured and standard plots were made. Linear regression analyses were performed on the data for each of the major absorption bands and the resulting calculated molar absorption coefficients are presented along with literature values for 1-cm cuvettes from Silva and Nitsche [7] in Table 1. The measured molar absorption coefficients using the LCW for each of the oxidation states of Pu are in good agreement with literature values for 1 cm cuvettes. The use of LCW provides enhancements in detection limits on the order of 30 times lower than those achievable with a conventional 1 cm cuvette.

Use of the liquid core waveguide for the identification of plutonium oxidation states in aqueous solution provides a rapid, non-destructive method of analysis. While the 1-meter LCW does not provide the sensitivity that liquid-liquid extraction coupled with radioactive counting provides, it does eliminate the generation of mixed radioactive-organic wastes and may be a viable option for routine oxidation state identification for laboratory scale studies.

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Table 1. Comparison of calculated molar absorptivities and limits of detection for 1 cm and 1 m cells.

Pu Ion	Abs. Wavelength (nm)	Molar Absorptivity <sup>1</sup> (M <sup>-1</sup> cm <sup>-1</sup> )	Limit of Detection <sup>2</sup> 1.0 cm cell	Limit of Detection 1.0 m cell
III	600	33.8 (38)	236 μM	8 μM
IV	470	49.0 (55)	158 μM	5 μM
V	568	18.8 (19)	518 μM	16 μM
VI	830	288 (550)	12.4 μM	0.7 μM

<sup>1</sup> Values in parentheses taken from Silva and Nitsche [7]. <sup>2</sup> Limits of detection calculated using the molar absorptivities reported by Silva and Nitsche [7].

Table 2. Calculated molar absorptivities for all major absorption bands for Pu ions.

Ion	Wavelength (nm)	Molar Absorptivity ( $M^{-1}cm^{-1}$ ) errors at $3\sigma$	$R^2$ value
Pu(III)	557	$33.8 \pm 0.1$	0.9999
	600	$33.8 \pm 0.2$	0.9997
	664	$16.3 \pm 0.1$	0.9997
Pu(IV)	470	$49.0 \pm 0.4$	0.9996
	505	$11.9 \pm 0.1$	0.9995
	555	$14.6 \pm 0.1$	0.9995
	652	$36.5 \pm 0.2$	0.9998
	726	$15.6 \pm 0.1$	0.9996
Pu(V)	811	$20.9 \pm 0.1$	0.9998
	517	$8.9 \pm 0.9$	0.9153
	568	$18.8 \pm 1.5$	0.9351
Pu(VI)	831	$287.9 \pm 10.0$	0.9946

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## Figure Captions

Figure 1. Representative absorption spectra of Pu ions in 1 M perchloric acid A.) Pu III, B.) Pu IV, C.) Pu V (0.001 M HClO<sub>4</sub>), D.) Pu VI.

