

NOTICE  
 This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

## SEARCH FOR PLUTONIUM FLUORESCENCE\*

M. A. Lyster,<sup>†</sup> R. L. Fellows\*\* and J. P. Young<sup>††</sup>

Transuranium Research Laboratory, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37830, USA

## ABSTRACT

The possible fluorescence of aqueous Pu in its various oxidation states at room temperature has been investigated, over the wavelength range of 300 to 800 nm. For each oxidation state, absorption spectral measurements were made of the experimental solutions, both before and after fluorometric study, to confirm that the desired oxidation state of Pu was studied. No emissions were observed for aqueous solutions of plutonium in any of its oxidation states of (III), (IV), (V), (VI) or (VII). Prior to this work there have been only two published reports of plutonium fluorescence, and these dealt with fluorescence in the solid state.

A reaction of thenoyltrifluoroacetone (TTA) with Pu(VI) was found to yield a fluorescent, organic product which might serve as a basis for a fluorometric determination of Pu(VI). In a slightly basic solution, pH 7-8, Pu(VI) will oxidize TTA within a matter of seconds to yield a product that exhibits an emission peak at 550 nm with a shoulder at 500 nm. At the same pH in the absence of Pu, TTA is oxidized slowly, in a matter of days, to yield the product. Since the oxidation is rapid with Pu(VI), a fluorometric determination of Pu(VI) is possible using a standard calibration curve. It has also been demonstrated that Pu(VI) is reduced to Pu(IV) in the reaction with TTA. The method is therefore ideally suited to the fluorometric determination of Pu(VI) even in the presence of Pu(IV), and with the incorporation of photon counting techniques, the determination could be quite sensitive.

## INTRODUCTION

Because of a growing concern about possible plutonium spills and leakage into environmental areas, the need to gain further knowledge of the behavior of extremely dilute aqueous solutions of plutonium is evident. One of the most important properties that must be determined is the oxidation state of the plutonium in these solutions. This investigation deals with the possibility of using fluorescence techniques to determine the oxidation state of plutonium in aqueous solutions.

There have been only two published reports of plutonium fluorescence. B. B. Cunningham and coworkers reported that Pu<sup>3+</sup> doped into LaCl<sub>3</sub> fluoresces

\* Research sponsored by the U. S. Energy Research and Development Administration under contracts with Union Carbide Corporation and University of Tennessee (Knoxville).

† Albion College; Great Lakes Colleges Association - Oak Ridge Science Semester participant, Fall 1974.

\*\* Department of Chemistry, University of Tennessee, Knoxville, Tenn. 37916, USA.

†† Analytical Chemistry Division

in the 500 nm region when cooled to 77°K [1].

R. D. McLaughlin and coworkers studied the fluorescence of Pu doped CaF<sub>2</sub> crystals at 77°K. Fluorescence peaks were found at 1.78 microns and 1.95 microns. These peaks were attributed to Pu<sup>3+</sup> and Pu<sup>4+</sup> respectively [2].

Instrumental constraints limited this work to the 200-800 nm region. In this investigation, aqueous solutions of plutonium in the oxidation states +3, +4, +5, +6 and +7 were studied. The isotope <sup>242</sup>Pu was used to minimize radiation effects.

#### EXPERIMENTAL

All fluorescence data were obtained with an Aminco-Bowman Spectrophotofluorometer with xenon arc source. Spectra was recorded on an Aminco-Bowman x-y recorder. The sensitivity of the Aminco-Bowman Spectrophotofluorometer was established with solutions of Eu<sup>3+</sup> TTA (TTA = thenoyltrifluoroacetone). Eu(TTA)<sub>3</sub> complex was dissolved in an acetone-water mixture (3:1 by volume) which was 10<sup>-3</sup> M in TTA. All dilutions were made with the same acetone-water-TTA solution to inhibit the dissociation of Eu(TTA)<sub>3</sub> complex. The Eu<sup>3+</sup> fluorescence was detected down to a Eu<sup>3+</sup> concentration of 10<sup>-11</sup> M.

All plutonium oxidation states studied were identified by absorption spectra taken with a recording Cary Spectrophotometer, model 14M. The spectra were checked against previously reported spectra of plutonium solutions [3]. Absorption spectra were taken of each sample, before and after fluorescence spectra were taken, to ensure that the plutonium oxidation state was known and stable, during each study. All spectra (fluorescence and absorption) were taken with the samples in quartz cuvettes.

The stock solution of plutonium was made from 136.6 mg of <sup>242</sup>PuO<sub>2</sub>. The <sup>242</sup>PuO<sub>2</sub> was dissolved with a mixture of 7 ml of concentrated HNO<sub>3</sub> and 1 ml of 0.01 N HF. To remove the HF, the solution was taken to dryness and the residue was re-dissolved in a mixture of 3 ml of concentrated HNO<sub>3</sub> and 0.5 ml of concentrated HClO<sub>4</sub>. This solution was taken to dryness and the residue was finally dissolved with 2 N HNO<sub>3</sub> to a volume of 50 ml. The final stock solution was about 1.0 x 10<sup>-2</sup> M in Pu<sup>6+</sup>.

Following are the procedures used to obtain the plutonium oxidation states, to be studied, from the Pu<sup>6+</sup> stock solution:

Pu<sup>7+</sup> - 0.5 ml of the Pu<sup>6+</sup> stock solution was added to 4 ml of 18 M KOH. Then 1.5 ml of 1 M KBrO was added. The solution was heated at 80°C for 1.5 hours. The solution turned from a yellow to a green-black in color. The solution was stable for about one week before appreciable reduction back to Pu<sup>6+</sup> [4].

Pu<sup>6+</sup> - For Pu<sup>6+</sup> in acidic media the Pu<sup>6+</sup> stock solution was used as is. For Pu<sup>6+</sup> in alkaline media 1 ml of Pu<sup>6+</sup> stock solution was added to 4 ml of 18 M KOH.

Pu<sup>5+</sup> - To 2 ml of the Pu<sup>6+</sup> stock solution 1.25 ml of 3 M KOH and 0.75 ml of 0.1 M KI were added. The reaction proceeded immediately upon the addition of the KI at room temperature. The I<sub>2</sub> that was formed was extracted with CCl<sub>4</sub> [5].

Pu<sup>4+</sup> - 1.5 ml of the Pu<sup>6+</sup> stock solution was added to 1 ml of concentrated HNO<sub>3</sub> and 0.75 ml of concentrated HI was added. The reaction proceeded immediately upon the addition of the HI at room temperature. The I<sub>2</sub> that was formed was extracted with CCl<sub>4</sub> [5].

Pu<sup>3+</sup> - To 2 ml of the Pu<sup>6+</sup> stock solution 20 mg of ascorbic acid was added. The reaction took about five minutes to completion at room temperature. This solu-

tion was stable for about four days before appreciable oxidation to  $\text{Pu}^{4+}$  [5].

An attempt to make a  $\text{Pu}^{6+}$ -TTA complex was made as follows:

To 1 ml of the  $\text{Pu}^{6+}$  stock solution 0.5 ml of a 0.1 M TTA in acetone solution and 0.5 ml of acetone were added. At this point no apparent reaction had resulted so concentrated  $\text{NH}_4\text{OH}$  was added until the solution was just basic to pH paper (about 0.25 ml). When the solution became basic a vigorous reaction resulted turning the solution orange and forming a green-brown powdery precipitate. The supernatant liquid was collected for spectral studies. The precipitate was collected and 2 ml of benzene was added to dissolve the precipitate. Some of the precipitate dissolved yielding a slightly green solution. The remaining precipitate was dissolved in 2 ml of 2 N  $\text{HNO}_3$ . The benzene and  $\text{HNO}_3$  solutions of the precipitate were saved for spectral studies.

Fluorescence and absorption spectra were taken of the following samples:  $\text{Pu}^{3+}$ ,  $\text{Pu}^{4+}$ ,  $\text{Pu}^{5+}$ , and  $\text{Pu}^{6+}$  in acidic media,  $\text{Pu}^{6+}$  and  $\text{Pu}^{7+}$  in alkaline media and the three solutions obtained from the  $\text{Pu}^{6+}$ -TTA complexation in alkaline solution, (supernatant liquid, benzene solution-with dissolved precipitate,  $\text{HNO}_3$  solution-with dissolved precipitate).

#### DISCUSSION AND RESULTS

The acidic solutions of  $\text{Pu}^{3+}$ ,  $\text{Pu}^{4+}$ ,  $\text{Pu}^{5+}$ ,  $\text{Pu}^{6+}$  and the alkaline solutions of  $\text{Pu}^{6+}$  and  $\text{Pu}^{7+}$  showed no fluorescence due to plutonium in the range of 200-800 nm at room temperature. The excitation wavelength range was 200-800 nm. These results are for the scanning range, excitation range and solution conditions indicated and do not eliminate the possibility of plutonium fluorescence under other experimental conditions or wavelength ranges.

It was found that the fluorescence intensity of the  $\text{Eu}^{3+}$  in the  $\text{Eu}(\text{TTA})_3$  complex was about 1,000 times the fluorescence intensity of the uncomplexed  $\text{Eu}^{3+}$ . Because of this result and the fact that a  $\text{Pu}^{6+}$ -TTA complex had been used for extraction purposes [6] the  $\text{Pu}^{6+}$ -TTA complexation was attempted. Absorption spectra from the three solutions obtained from the attempted complexation (supernatant liquid, benzene solution-with dissolved precipitate and  $\text{HNO}_3$  solution-with dissolved precipitate) demonstrated that the  $\text{Pu}^{6+}$  had been reduced to  $\text{Pu}^{4+}$ . From the supernatant liquid a fluorescence spectrum was obtained (Fig. 1), with peaks at 500 and 550 nm.

Studies run on alkaline TTA solutions containing no metal ion and containing either  $\text{Sm}^{3+}$  or  $\text{Gd}^{3+}$  indicate that the fluorescence peaks at 500 and 550 nm were due to a TTA oxidation product. The two fluorescence peaks were also seen in the spectra of 2-4 day old alkaline TTA solutions both with and without a metal ion present but were not seen in acidic solutions of TTA. An analytical method for  $\text{Pu}^{6+}$  determination could be based upon this reaction.

Because the  $\text{Pu}^{6+}$ -TTA reaction proceeds to completion very rapidly (within seconds) in alkaline solution, it is also possible that this same procedure could be used for  $\text{Pu}^{5+}$  and  $\text{Pu}^{7+}$  determination.

#### ACKNOWLEDGEMENTS

The authors would like to thank J. H. Oliver for preparing the  $\text{Pu}^{6+}$  stock solution.

#### REFERENCES

1. B. B. Cunningham, D. M. Gruen, John G. Conway and Ralph D. McLaughlin, *J. Chem. Phys.*, 24 (1956) 1275.
2. R. McLaughlin, R. White, N. Edelstein and John G. Conway, *J. Chem. Phys.*, 16 (1968) 967.
3. J. M. Cleveland, *The Chemistry of Plutonium*, pp. 13-19, Gordon and Breach, Science Publishers, Inc., New York, 1970.
4. Yu. A. Komkov, V. P. Peretrukin, N. N. Krot, and A. D. Gel'man, *Soviet Radiochemistry*, 11 (1969) 398.
5. J. M. Cleveland, *loc. cit.*, pp. 49-51.
6. A. M. Poskanzer and B. M. Foreman, Jr., *J. Inorg. Nucl. Chem.*, 16 (1961) 323.

ORNL - DWG. 75 - 9398

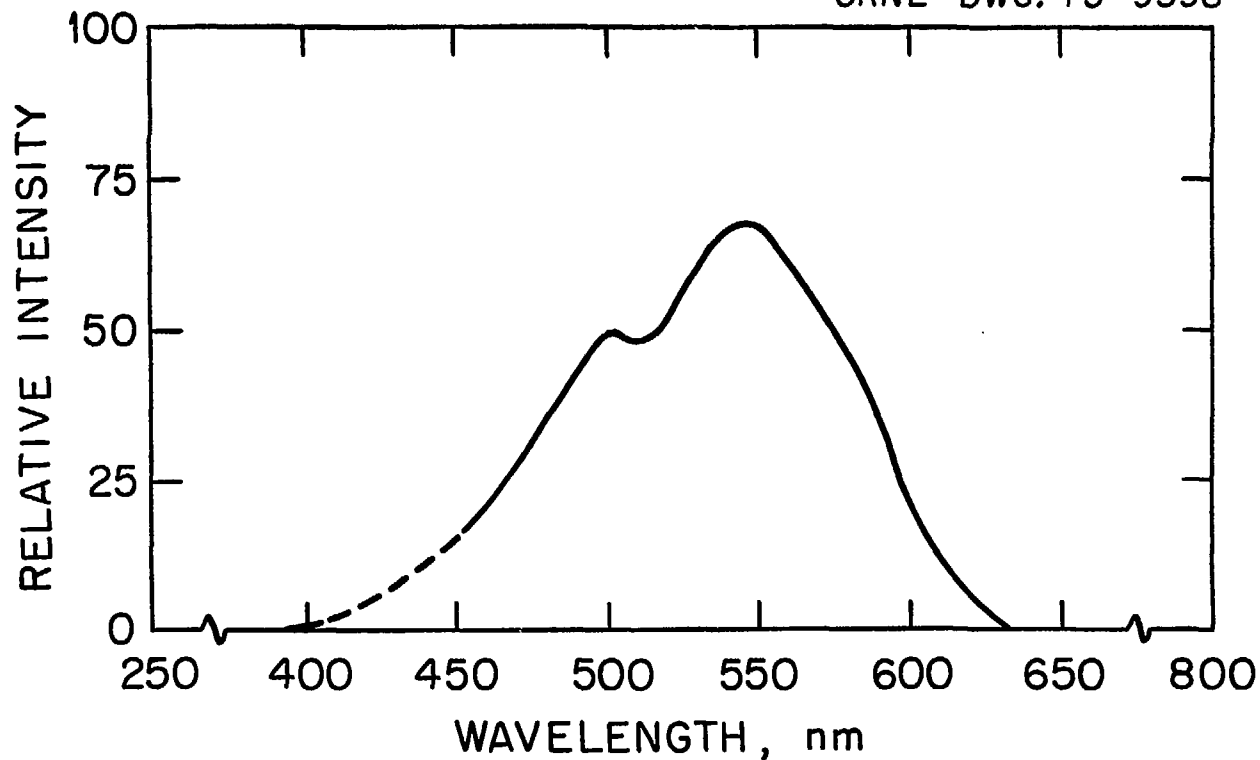


Figure 1. Fluorescence spectrum from Pu<sup>6+</sup>-TTA solution. The fluorescence peaks observed from the supernatant liquid were obtained from the Pu<sup>6+</sup>-TTA redox reaction and are due to a TTA oxidation product. The dashed line indicates the wavelength region of the excitation source.