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**Feasibility Study for the
Oxidation of Am(III) by
Photolysis**

H. A. Friedman

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CHEMICAL TECHNOLOGY DIVISION

FEASIBILITY STUDY FOR THE OXIDATION OF Am(III) BY PHOTOLYSIS

H. A. Friedman

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FEASIBILITY STUDY FOR THE OXIDATION OF Am(III) BY PHOTOLYSIS

H. A. Friedman

ABSTRACT

The results of a literature survey indicate that Am(III) may be light sensitive because it is characteristically similar to neptunium and plutonium. The redox potentials of americium are greater than the other two elements (which will probably make it more difficult to photolyze), and it does not absorb appreciable uv above 240 nm. A lamp whose emission is in the far uv region, a Suprasil quartz spectrophotometric-photolysis cell, and possibly an inert-atmosphere containment jacket would be needed to photolyze Am(III) in the glove box.

1. INTRODUCTION

A literature survey was undertaken to determine the likelihood of the oxidation of Am(III) to a higher valence state by photolysis for possible use in the separation processes of Am from Cm and to determine the feasibility of its investigation at Oak Ridge National Laboratory (ORNL). These separation processes¹ depend on the Am being at a higher oxidation state than the Cm, which occurs only in the three-valence state. Photooxidation was the only process considered because the purpose of the photolysis was to have Am and Cm at different valence states.

Americium is very similar to Np and Pu. Each exists in the three-, four-, five-, and six-valence states and the stability of some valences is dependent on the acid concentrations. Each of the ions is known to form complexes with many solvent anions. Only ^{241}Am and ^{243}Am have half-lives long enough for this type of investigation. Although ^{243}Am is not as radioactive as ^{241}Am and should offer fewer problems, it is rarer and more difficult to obtain;* therefore, ^{241}Am was considered for this investigation because it is more abundant and is the isotope that would be mixed with the Cm.

* Both ^{243}Am and ^{241}Am can be purchased as AmO_2 from Isotope Sales at ORNL.

2. CHEMISTRY OF AMERICIUM

Spectrophotometry and ion exchange have been used to characterize the complexing of the three-valence species of Np, Pu, and Am.² Each element exhibited strong absorption at a characteristic wavelength when complexed with Cl^- or Br^- . The stability of the complexes increased with increasing atomic number of the actinide, and the chloride complexes were more stable than the bromide. The results correlate well with those for U(III). These potentials are believed to be based on a standard hydrogen electrode, although this was not stated in the literature.^{1,3,4}

Evidence exists for the formation of AmClO_4^{2+} and $\text{Am}(\text{pTS})^{2+}$ (americium *p*-toluenesulfonate) as weak ion pairs from solvent extraction data, and the order of interaction is $\text{pTS}^- > \text{ClO}_4^- > \text{BF}_4^-$.⁵ The redox potentials for Am, Np, and Pu are shown in Tables 1 through 5. Redox, disproportionation, and radiation reactions and kinetic data of and for Am (also Pu, Np, and U) are also given in a report by T. W. Newton.⁶ The tables show that the oxidation-reduction potentials for Am are greater than those for either Pu or Np. The characteristics of Am, Np, and Pu are similar and the latter two elements can be photolyzed; therefore, Am may possibly be photolyzed, but it will probably be more difficult because of the larger redox potentials.

Americium dioxide can be dissolved in 1 M HClO_4 ,⁷ and Am(III) is the common valence in the solution.⁸ Americium(IV), because of the high value of +2.4 V for the standard potential of the Am(IV) to Am(III) couple, is not stable in most mineral acid solutions.¹ However, pure Am(IV) can be prepared by anodic oxidation of Am(III) in 10 to 15 M H_3PO_4 .⁹ Americium hydroxide $[\text{Am}(\text{OH})_4]$ is stable in concentrated solutions of NH_4F , RbF , and CsF .⁶ Americium(V) disproportionates in highly acidic solutions, is slower in 3 M HClO_4 than in 6 M HClO_4 ,¹⁰ and is reduced by autoreduction, especially ^{241}Am . Americium(VI) can be prepared in acid solutions, but autoreduction makes it unstable. Reference 1, which gives very good descriptions of the methods of preparation of the different valence states, indicates that oxidation by electrolysis proceeded in strong acid solution [6 M HClO_4], whereas oxidation by an oxidizing agent (peroxydisulfate) proceeded to completion only in acids below 0.5 M.

Table 1. Electrode potentials of americium (volts)^{a,b}1 M HClO₄ 1 M OH⁻

Phosphoric acid

^aSource: see ref.1.^b1969 International Union of Pure and Applied Chemistry sign convention.^cValues are determined by difference.

Table 2. Standard and formal redox potentials of pairs of neptunium ions^a

Electrode process	Standard potentials (V)	Formal potentials in 1 M HClO ₄ (V)
$\text{Np} = \text{Np}^{3+} + 3\text{e}^-$	-1.856	-1.83
$2\text{Np} + 3\text{H}_2\text{O} = \text{Np}_2\text{O}_3$	-1.420	
$\text{Np}_2\text{O}_3 + \text{H}_2\text{O} = 2\text{NpO}_2 + 2\text{H}^+ + 2\text{e}^-$	-0.962	
$\text{Np}_2\text{O}_3 + 5\text{H}_2\text{O} = 2\text{Np}(\text{OH})_4 + 2\text{H}^+ + 2\text{e}^-$	-0.928	
$\text{Np}^{3+} = \text{Np}^{4+} + \text{e}^-$	-0.152	0.155
$\text{Np}^{3+} + 2\text{H}_2\text{O} = \text{NpO}_2 + 4\text{H}^+ + \text{e}^-$	0.337	
$\text{Np}^{3+} + 4\text{H}_2\text{O} = \text{Np}(\text{OH})_4 + 4\text{H}^+ + \text{e}^-$	0.391	
$\text{Np}^{3+} + 2\text{H}_2\text{O} = \text{NpO}_2^+ + 4\text{H}^+ + 2\text{e}^-$	0.451	0.447
$\text{Np}(\text{OH})_4 = \text{NpO}_2^+ + 2\text{H}_2\text{O} + \text{e}^-$	0.530	
$\text{NpO}_2 = \text{NpO}_2^+ + \text{e}^-$	0.564	
$\text{Np}^{4+} + 2\text{H}_2\text{O} = \text{NpO}_2^+ + 4\text{H}^+ + \text{e}^-$	0.749	0.739
$\text{NpO}_2 = \text{NpO}_2^{2+} + \text{e}^-$	1.149	0.137
$2\text{Np}(\text{OH})_4 = \text{Np}_2\text{O}_5 + 3\text{H}_2\text{O} + 2\text{H}^+ + 2\text{e}^-$	1.219	
$2\text{NpO}_2 + \text{H}_2\text{O} = \text{Np}_2\text{O}_5 + 2\text{H}^+ + 2\text{e}^-$	1.253	
$\text{Np}_2\text{O}_5 + \text{H}_2\text{O} = 2\text{NpO}_3 + 2\text{H}^+ + \text{e}^-$	1.310	
$\text{NpO}_2 + \text{H}_2\text{O} = \text{NpO}_3 + 2\text{H}^+ + \text{e}^-$	1.998	
$\text{Np}^{3+} + 2\text{H}_2\text{O} = \text{NpO}_2^{2+} + 4\text{H}^+ + 3\text{e}^-$		0.667
$\text{Np}^{4+} + 2\text{H}_2\text{O} = \text{NpO}_2^{2+} + 4\text{H}^+ + 2\text{e}^-$		0.938

^aSource: see ref. 3.

Table 3. Redox potentials of neptunium (volts at 25°C)^a1.0 M HClO₄

-0.477

1.0 M HCl

-0.437

1.0 M H₂SO₄ 1.02 M HNO₃

1.0 M NaOH

^aSource: see ref. 3.

Table 4. Formal potentials for plutonium couples in various 1 M solutions^a

	HClO ₄	HCl	HNO ₃	H ₂ SO ₄
Pu(III)–Pu(IV)	-0.982	-0.970	-0.92	-0.74
Pu(IV)–Pu(VI)	-1.043	-1.052	-1.05	-1.2 - 1.4
Pu(III)–Pu(VI)	-1.028	-1.024	-1.04	
Pu(V)–Pu(VI)	-0.92	-0.912		

^aSource: ref. 4.Table 5. Redox potentials of plutonium^a

<u>Acid solution</u>				
Pu	$\frac{2.03}{\text{Pu}^{3+}}$	$\frac{-0.97}{\text{Pu}^{4+}}$	$\frac{-1.15}{\text{PuO}_2^{+}}$	$\frac{-0.93}{\text{PuO}_2^{2+}}$
			-1.04	
<u>Basic solution</u>				
Pu	$\frac{2.42}{\text{Pu(OH)}_3}$	$\frac{0.95}{\text{Pu(OH)}_4}$	$\frac{-0.70}{\text{PuO}_2\text{OH}}$	$\frac{-0.26}{\text{PuO}_2(\text{OH})_2}$
			-0.51	

^aSource: ref. 4.

The valence states of ^{241}Am higher than (III) are not stable in mineral acid solutions because of autoreduction. The rate of reduction of the (VI) state amounts to $\sim 4\%/h$, and the rate of reduction of the (V) state is $\sim 2\%/h$.¹¹ Americium(VI) is reduced almost completely to Am(V) before Am(V) is reduced to Am(III).

The rate of reduction of Am(VI) to Am(V) is faster than that caused solely by H_2O_2 from radiolysis.¹¹ Both H_2O_2 and radical ions probably cause this reduction. There was no H_2O_2 as long as Am(VI) was present.

After all the Am(VI) is reduced to Am(V), H_2O_2 forms in an amount that would have occurred from the radiolysis of H_2O . Hydrogen peroxide is not consumed by the reduction of Am(V); therefore, Am(V) is not reduced by the H_2O_2 but by the HO_2 radicals produced by radiolysis. Although Am(V) is reduced by HO_2 radicals, it is also oxidized to Am(VI) by OH radicals.¹¹

3. EXPERIMENTAL PREREQUISITES

Before a species can photolyze, the substance must absorb light energy at the wavelength of the emitting lamp. The larger the extinction coefficient for the species to be photolyzed at the wavelength of the lamp supplying the light, the more energy is absorbed, and other factors being equal, the better the chance for photolysis. Based on the data in Fig. 1,¹² an extinction coefficient of 20 at 254 nm could be calculated for Am(III) in 0.1 M HClO_4 if all the absorbance was due to Am(III). However, Stephanou et al.¹³ claim that most of the absorbance was caused by H_2O_2 , because the profile of the base line was that of H_2O_2 and increased with time; they suggested that the true extinction coefficient for Am(III) in 0.1 M HClO_4 should be ~ 1.3 , a very low value.

A concentration of $\sim 4 \times 10^{-3}$ moles/L H_2O_2 would be necessary to explain the assigned absorbance in a 5-cm cell (~ 1.18 at 250 nm and 0.111 at 300 nm) as the cause for the increase in the base line.^{12,13,*} The radiation from ^{241}Am will produce $\sim 1.4 \times 10^{-2}$ mole of H_2O_2 per hour

* Extinction coefficients of $58.86 \text{ L mole}^{-1} \text{ cm}^{-1}$ at 250 nm and $5.35 \text{ L mole}^{-1} \text{ cm}^{-1}$ were calculated for H_2O_2 .¹² The concentration of H_2O_2 , calculated from absorbances at both 250 and 300 nm and using the appropriate extinction coefficient,¹¹ was 4×10^{-3}

Fig. 1. Ultraviolet absorption spectrum (246 to 350 nm) of 0.124 mole/L Am(III) in 0.1 M HClO₄ (5-cm cell). Source: see ref. 12.

per mole of Am,^{14,15,*} or 1.74×10^{-4} mole per liter of H₂O₂ per hour in a 1.24×10^{-2} M solution. It would thus take approximately 23 h for the concentration of H₂O₂ to increase to 4×10^{-3} mole/L, assuming the reported values in the literature are correct.

Part of the absorbance attributed to H₂O₂ could be that of Am(III), but the length of time the Am was in solution before the spectrum was scanned was not reported; however, the extinction coefficient for Am(III) increases sharply below 240 nm (Fig. 2).¹³ Based on this literature survey, a shorter wavelength than 240 nm would have a better chance of photolyzing the Am(III) than would a 254-nm lamp.

*Americium-241 produces 5.55×10^{23} eV per mole of Am per hour.¹⁴ The g factor for H₂O₂ formation is approximately 1.5 molecules of H₂O₂ per 100 eV, which will vary with temperature, acid type, and concentration.¹⁵

Fig. 2. Absorption spectrum of 8.54×10^{-3} mole/L Am(III) in 0.1 M HClO₄ (5-cm cell). Source: see ref. 12.

The strong complexing of Am with Cl⁻ and Br⁻ both increases and shifts the absorbance to longer wavelengths, the amounts being dependent on the anion concentration.² The Am-Cl complex in 9.9 M LiCl has an extinction coefficient of ~ 250 at 254 nm. The absorbance for the bromide complex in this region was not determined because of the strong absorbance of Br⁻. Although the Am complex has a high extinction coefficient at the appropriate wavelength, by assuming the data are correct it is anticipated that the strong complex, which stabilizes the Am(III), could prevent its photolysis. Even if Am could be photolyzed in this medium, the method would probably not be practical for a separation process because of the large amounts of LiCl that would eventually need disposal.

The best possibility for successful photolization of Am(III) would probably be in very dilute perchlorate (~ 0.1 M) with a wavelength < 240 nm, at which Am(III) begins to have appreciable absorption. The Am(III) forms almost no complexes in dilute perchlorate,¹ but it will complex with NO₃⁻,¹⁶ SO₄⁻²,¹⁶ Cl⁻,² and Br⁻,² and PO₄⁻³,¹⁷ hampering the photolysis. The lower acidity is desirable because (1) Am is more easily oxidized when the higher valence states are more stable; (2) the quantum efficiencies

for Pu and Np,^{18,*} which are similar elements to Am, are in reverse ratio to the acidity; and (3) Am(III) has been oxidized by gamma radiation in a low-acid solution.¹⁹ In perchlorate solutions with pH 3 to 6 in the presence of excess N_2O , $\text{S}_2\text{O}_8^{2-}$ ions, or XeO_3 , Am(III) is oxidized to Am(V) and (VI) by gamma radiation from a ^{60}Co source.¹⁹ The medium will probably need a pH of >2.5 and a strong oxidizing agent before Am(III) will photolyze.

The H_2O_2 formed from the radiolysis of H_2O should not be a problem because, at a wavelength of 310 nm and a quantum yield of 7,²⁰ it would be destroyed by photolysis.

4. LIGHT SOURCES

Several types of lamps are available for photolysis in the far uv region. The most practical light source would possibly be an excimer laser operating at 193 nm (ArF)[†] or 248 nm (KrF). This would provide optimal rectilinear propagation of the radiation from a source located some distance from the experimental system containing the Am.

Resonance lamps, containing either Xe or Kr plus He to give maximum intensity and operated by microwave power, will emit lines from 116 to 174 nm depending on the gas used in the discharge tube.²¹ The maximum intensity, measured by actinometry of CO_2 , was 1×10^{15} quanta/s for any of these lamps, an intensity of approximately 1/100 of the lamps now being used.

Another light source is the low-pressure mercury or "resonance" lamp (similar to one we are presently using) which produces radiation rich in 254-nm light. If Suprasil quartz is used instead of regular quartz, it is also rich in 184.9-nm radiation.²² Approximately 40% of the radiation intensity from the coil would be 185-nm radiation.^{**}

*The Am(III) was 14.5 times more concentrated in the sample used to obtain the absorbance for Fig. 1 than in the sample for Fig. 2; therefore, the absorbance for wavelengths ~ 240 nm for Fig. 2 would be very great in relationship to the bands in Fig. 1.

[†]Laser is available from Tachisto, Inc., 13 Highland Circle, Needham, MA 02194.

**Coil is available from UV Products, 5100 Walnut Avenue, San Gabriel, CA 91776.

5. SPECTROPHOTOMETRIC-PHOTOLYSIS CELL

If the lamp is in the glove box, a redesigned cell would be needed, in addition to a containment shell for the cell and light. The cell would need to be constructed of Suprasil, which would pass light in the far uv region, rather than quartz. The containment shell would contain an inert gas to prevent the absorption of radiation by O_2 and photolysis to form O_3 , an undesirable gas in the glove box. Photolysis of O_2 will occur at ~ 1 atm in the 130- to 190-nm range at a quantum yield of 2, and the product would be O_3 .²²

6. DETECTION SYSTEM

The concentration of the various Am species in solution can be determined once the extinction coefficients are known. The values for the extinction coefficients and the dimensions of the spectrophotometric-photolysis cell will also be factors in determining the concentration of Am for the solution being photolyzed.

The absorption spectra with extinction coefficients for Am(III), (V), and (VI) in $HClO_4$ have been reported.^{8,14,23-27} Table 6 contains the extinction coefficients for Am(III), (V), and (VI) in 0.1 and 1 *N* $HClO_4$.

7. RADIOACTIVITY

The activity of ^{241}Am is high. The activity per gram of ^{241}Am (60-keV gamma radiation) would be 1.5 R/h at 0.3 m and 41.4 R/h at 0.05 m, assuming the sample is a powder (the radiation would be less if Am was in a solution).²⁸

Although the low-energy gamma activity of ^{241}Am is relatively high for unshielded glove-box operations, it can probably be handled safely in small samples. A 5-cm circulating cell that holds 15 ml of solution (such as the one now in use at ORNL), with a concentration 5.6×10^{-3} *M* Am [the concentration at which the absorbance of Am(III) at 811 nm would be 1.8], would contain 20.24 mg of Am. A powdered sample containing 20.24 mg of ^{241}Am would have an activity of 0.84 R/h at 0.05 m (less in liquid) and 0.023 R/h at 0.3 m. In addition to being able to handle

Table 6. Extinction coefficients for Am(III), (V), and (VI)
in 0.1 and 1 M HClO₄

Oxidation state	Acidity (mole/L)	Wavelength (nm)						
		715 ^a	718 ^b	719 ^c	811 ^b	816 ^c	995 ^c	996 ^c
Am(III)	0.1				64.4			
	1.0			0.03		69.2		0.6
Am(V)	0.1	59.3	59.6					
	1.0			62.5		1.5		3.0
Am(VI)	0.1						63.8	
	1.0			8		1.5		83.3

^aSource: refs. 12 and 28.

^bSource: ref. 24.

^cSource: ref. 27.

individual samples more safely than a stock solution, in which a much larger amount of Am would be concentrated, the effect of the radiolysis product, H₂O₂, would also be reduced.

8. CONCLUSIONS

Americium(III) may photolyze, and the element can probably be handled safely, with caution, in unshielded glove boxes (with the use of lead containers for storage); however, a light source that emits light below 240 nm will probably be needed in addition to Suprasil quartz sample cells, a containment jacket around the sample, and light if the light is in the glove box. These conclusions are based on the following:

1. Americium, which has the characteristics of Pu and Np, may photolyze, but probably not as well as either Pu and Np, because the redox potentials are greater for this element. The redox potentials are 1.69 for Am(III) to Am(V), 1.04 for Pu(IV) to Pu(VI), and 0.74 for Np(IV) to Np(V).¹

2. The probability of photolyzing Am(III) with 254- or 300-nm light would be small since the extinction coefficient at both wavelengths is about 1.²³ A very small percentage of the light would be absorbed by the sample at these wavelengths. The chances of photolysis of Am(III) <240 nm would be better because the extinction coefficient increases dramatically below this wavelength.¹²
3. Lasers may be the best way to achieve the desired wavelength.
4. Lamps are available which operate by microwave power that emits lines from 116 to 174 nm depending upon the gas in the resonance lamp,²¹ but the output of these lamps produces no more than 0.01 the intensity of the lamps now being used.
5. Low-pressure mercury lamps (similar to the 254-nm light source in use at ORNL), made from Suprasil quartz, emit radiation that is rich in 185-nm light.²²
6. The photolysis of oxygen studied at wavelengths between 155 and 175 nm had a quantum yield of 2.²² The light coil and sample cell would probably have to be surrounded by an oxygen-free atmosphere to prevent loss of radiation in the air and formation of O₃ (O₃ is not desirable in glove boxes).
7. The formation of H₂O₂ caused by the activity of ²⁴¹Am probably would not interfere with the photolysis because H₂O₂ is photolyzed in the uv region. At a wavelength of 310 nm the quantum efficiency is 7.²⁰
8. A new Suprasil quartz sample cell would probably be needed to pass light in the far uv region; this might also require a change in design if a containment shell is necessary to exclude O₂ from the light.
9. The extinction coefficients of Am(III), (V), and (VI) needed to calculate the concentrations of the specimens are reported in the literature.^{12,23,26,27} These species are the only ones found in acid solutions.

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