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The Electroreduction and Photometric Detection of Low-Level Uranium in Aqueous Purex Solutions

D. T. Bostick
J. E. Strain

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THE ELECTROREDUCTION AND PHOTOMETRIC DETECTION OF LOW-LEVEL URANIUM IN AQUEOUS PUREX SOLUTIONS

D. T. Bostick and J. E. Strain
Analytical Chemistry Division

Date Published - April 1983

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HIGHLIGHTS

During proper operation of the Purex process for the recovery of uranium and plutonium from spent reactor fuel, there are only trace levels of uranium in the aqueous waste. In the event of an upset in the extraction columns the aqueous waste stream would give the first indication of breakthrough. From the standpoint of process control it would be desirable to have an in-line, real-time sensor for uranium in the aqueous waste stream. It was toward this end that this investigation was undertaken.

The measurement technique that seems to provide the most sensitive method without addition of reagents appears to be the electrochemical reduction of UO_2^{+2} to U(IV) followed by spectral measurement. The electrochemical reduction to U(IV) increases the sensitivity by a factor of three to five and shifts the measurement wavelength to a spectral area (647 nm and 1075 nm) unaffected by fission products. Using the proposed analysis sequence it is possible to determine uranium at a level of 0.2 g/L in the presence of relatively high spectral background.

This report details the electrochemical reduction of U(VI) in nitric acid solutions (0.5 M to 2.0 M) with platinum-vitreous carbon electrodes and examines the spectral behavior of U(IV) as a function of nitric acid concentration.

1. INTRODUCTION

The photometric analysis of uranium in aqueous Purex streams is accomplished by measuring uranyl absorbance at the 416 and/or 426 nm absorption bands (1). If the length of the optical path is optimized for the uranium concentration in the stream, the photometric method is accurate to within a few percent. The accuracy of the photometric procedure will, however, deteriorate if the process solution contains optically absorbing contaminants or optically dispersive suspended solids. Dispersion of the light source radiation by suspended particles produces an elevated optical background which creates a positive bias in the uranium analysis. Because this background is essentially flat over a small wavelength range, a reference wavelength, at which the analyte does not absorb, can be used to compensate for the bias. In the case of the uranyl ion (Fig. 1A), a wavelength longer than 530 nm can be used to correct for sample turbidity.

Procedures for estimating and eliminating interferences produced by contaminants absorbing at the same wavelengths as uranium are not quite so direct. Uranium concentration in Purex solutions can be overestimated due to colored ions originating from stainless steel corrosion or by nuclear fission. Table 1 lists the major cations produced by either source, as well as their respective molar absorption coefficients at 416, 647 and 1075 nm (2,3). Not included in this tabulation are the zirconium and molybdenum fission products which can exist in a variety of soluble and insoluble polymeric forms. These two types of contaminates will elevate the optical background slightly at uranyl wavelengths by both light dispersion and optical absorption.

The concentration of these colored cations is great enough in the HAW Purex streams (4) to produce a background absorbance at 416 nm which is equivalent to greater than 50 g/L U (Fig. 2A). In aqueous solutions downstream from the HA extraction column, the optical interference of the contaminating ions is not quite so severe because their individual concentrations are rarely greater than 100 ppm. Aqueous raffinate streams typically exhibit a background absorbance at 416 nm which is equivalent to a few gram per liter UO_2^{2+} (Fig. 2B). This low level of interference would mandate a correction for only optical dispersion in the measurement of

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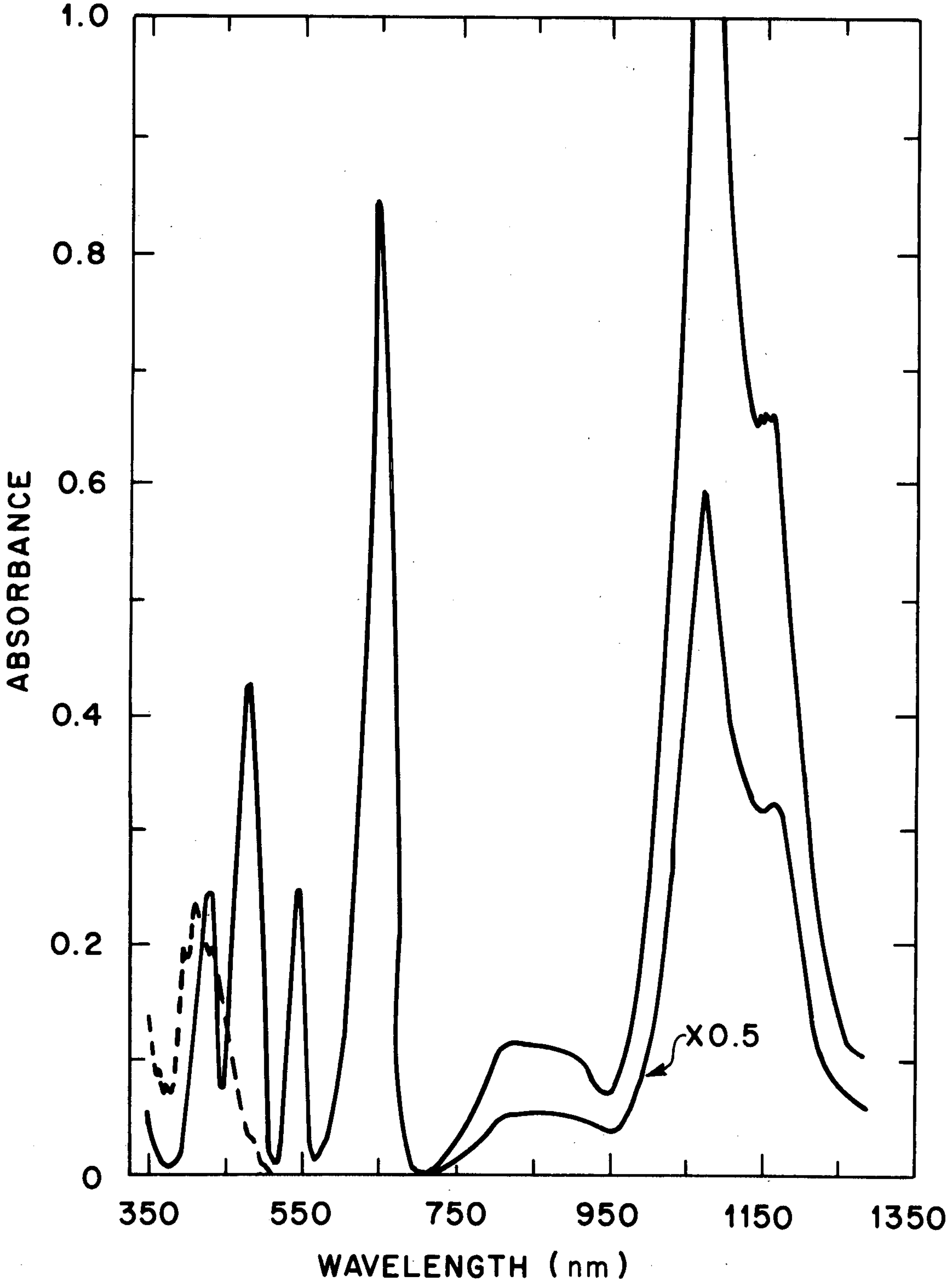

Fig. 1. Superposition of U(VI) and U(IV) spectra: (a) 6.4 g/L U(VI) and (b) 6.4 g/L U(IV) in 1.3 M HNO_3.

Table 1. Molar Absorption Coefficients for Uranium and Main Purex Process Stream Contaminants*

Cation	Wavelength (nm) 416	647	1075_4
UO_2^{2+}	8.57	0	0
U(IV)	2.62	29.5	42.8
Stainless Steel Corrosion Products:			
Ni(II)	2.52	1.82	2.05
Co(II)	0.59	0.29	0.71
Fe(III)	0.61	0	0
Cr(III)	2.24	1.20	0.68
Mn(II)	0.66	0.55	0.11
Fission Products:			
Rh (III)	77.2	0	0
Ru(III)	50.5	0	0

*Molar Absorption coefficients in units of $\underline{M}^{-1}$ cm^{-1}, measured in 1.5 $\underline{M}$ HNO_3 media.

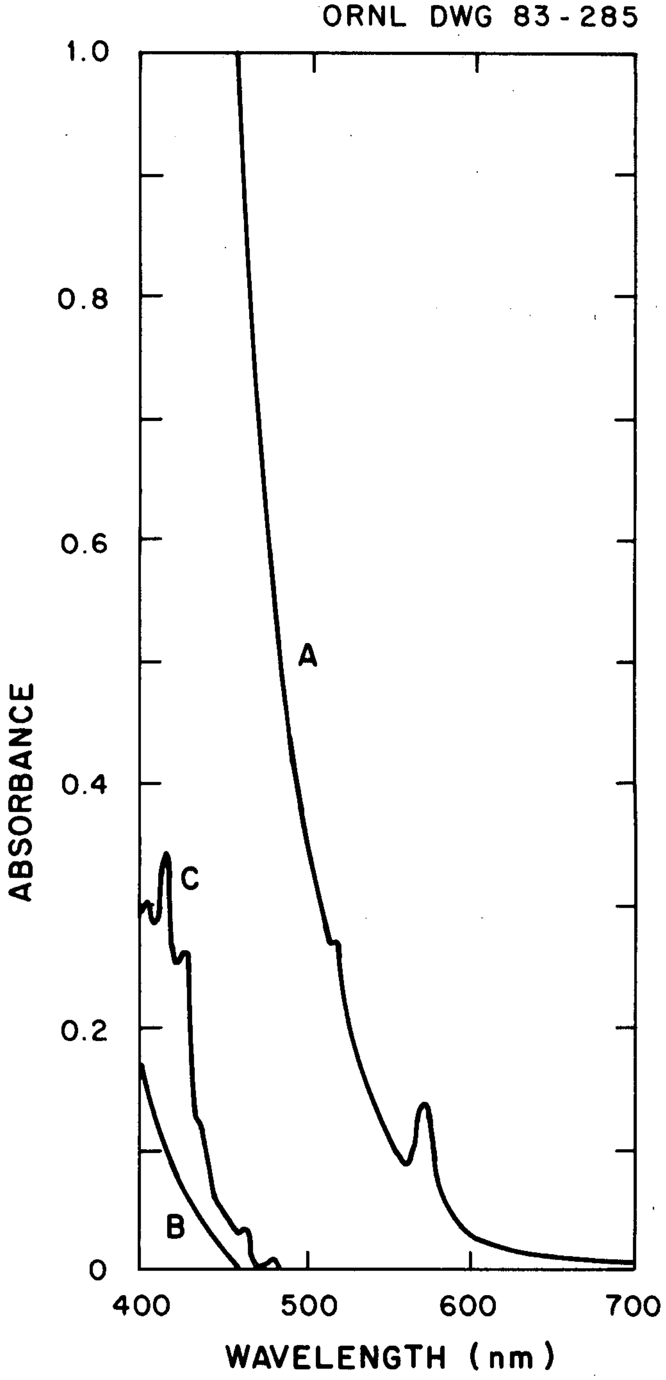

Fig. 2. Visible scan of Purex process impurities: (a) prepared sample of fission products at concentrations present in HAW solution during LWR fuel reprocessing, (b) aqueous raffinate process sample off a secondary extraction column used for uranium waste recovery, all U has been removed from the sample and (c) 10.78 g/L U standard in 0.1 M HNO_3.

uranium in concentrated product streams. In solutions containing less than 20 g/L U, the optically absorbing cations significantly alter the analytical results and therefore correction for both impurity dispersion and absorbance is required to obtain the desired accuracy.

To this end, a measurement scheme has been proposed that both increases the sensitivity of the photometric analysis of U and, at the same time, monitors and corrects for an optically absorbing and dispersive background. One can conclude from Table 1 and Figure 2 that cationic absorbance decreases at longer wavelengths. The major absorption bands in the visible spectra of U(IV) (Fig. 1B) occur at wavelengths longer than the UO_2^{2+} ion, i.e., 428, 480, 547, 647 and 1075 nm. By determining the uranium concentration in solution based on U (IV) absorbance at either 647 or 1075 nm, analytical sensitivity would be improved by a factor of 3 or 5, respectively, and be less affected by process impurities. The smaller optical background observed at the U(IV) wavelength could be measured directly by the following scheme: 1) measure the total optical background at the U(IV) absorption band, 2) electrochemically reduce the UO_2^{2+} ion, 3) measure U(IV) absorbance at the same wavelength and correct this value by subtracting the background absorbance previously recorded. The resulting analysis should provide an indication of solution uranium concentration independent of suspended solids or absorbing stream impurities.

This report defines the conditions necessary for the complete reduction of the uranyl ion and reviews the spectral behavior of U(IV) in typical aqueous Purex waste streams. From the electrochemical and spectral behavior it is possible to estimate the analytical accuracy that can be realized from the proposed in-line measurement scheme.

2. REAGENTS AND EQUIPMENT

Uranium standards were prepared from solid $UO_2(NO_3)_2 \cdot 6H_2O$, purchased from Alfa Products Corporation. The total uranium concentration in the dissolved standards was determined by potentiometric titration using the Davies-Gray procedure (5). U(IV) concentration in reduced samples was measured titrimetrically using standard ceric sulfate (6).

A Cyclic Voltammeter Model 02943B, designed by Mueller and Jones (7), was used to control the reduction potential between the working and counter electrodes during uranium electrolysis. Electrode materials investigated included: fine platinum gauze, 1.4 mm O.D. platinum rod, gold foil, 6 mm diameter vitreous carbon prepared using the technique of Gupta (8), reticulated vitreous carbon (RVC) sponge having an average pore size of 0.01 in., purchased from Fluorocarbon (Anaheim, CA), and pyrolytic graphite.

A Cary 14 recording spectrometer was used to scan uranium solutions contained in a 1 cm quartz cell. All absorbance measurements were made versus a water blank.

3. RESULTS

Uranium concentration is monitored in aqueous waste streams to minimize process losses of the heavy metal. The analytical technique used for this measurement must be accurate and rapid so that process parameters may be altered immediately if high levels of uranium are detected in the raffinate solutions. Conditions were therefore defined for the complete and rapid reduction of uranyl ion in nitric acid solution. The following parameters that affect the rate of electrochemical reduction were investigated: electrode material, electrode surface preparation, electrode size, solution acidity and uranium concentration. The spectral characteristics of U(IV) were also studied as a function of heavy metal and HNO_3 concentrations to assure accuracy of the photometric uranium measurement. The results of these studies are summarized below.

3.1 Electrode Material

The cathodic reduction of uranyl ion has been studied polarographically using a dropping mercury electrode. The reduction is a two step process where U(VI) is first reduced to U(V),

$$UO_2^{2+} + e^- \rightarrow UO_2^+$$

and this species disproportionates by the following reaction:

$$2\ UO_2^+ \rightarrow UO_2^{2+} + U^{4+}$$

This reduction of U(V) to U(IV) involves the breaking of oxygen bonds and is therefore acid dependent. If the pH is less than 1.0, a condition met by aqueous Purex raffinate streams, the rate of U(V) disproportionation is great enough to allow uranyl reduction to be described as a single irreversible half reaction:

$$2\ UO_2^{2+} + 4\ H^+ + 2\ e^- \rightarrow U^{4+} + 2\ H_2O$$

The reduction potential for this reaction is near zero when measured versus a standard calomel electrode (9).

A dropping mercury electrode cannot be conveniently used as the electroactive surface in on-line or in-line process instrumentation. Previous uranium electrolysis has been performed at gold (10) or platinum (11) surfaces; these solid materials are more suitable for stationary electrodes in process monitors. Glassy carbon is also commonly used as an electrode and has recently been useful in the electrochemical detection of Purex process reagents (12). Pyrolitic graphite is an attractive electrode material because of its relatively low cost, its compatability with dilute nitric acid and, like glassy carbon, nitrate ions are not reducible at its surface. Each of these solid materials was used as both cathode and anode in a stirred 30 mL glass reduction vessel. Because uranyl reduction is an irreversible reaction, both electrodes were placed directly in the reduction vessel rather than isolating the anode from the electrolyzed solution by a salt bridge. The four electrode materials were compared on the basis of the time required to obtain maximum reduction of 75 mg U(VI), the maximum percent of U(VI) reduced, and the potential difference maintained between the electrodes by the cyclic voltammeter. The efficiency of each solid electrode material is summarized in Table 2.

The use of gold electrodes, in the form of a 1 cm by 3 cm foil, resulted in approximately 25% reduction of the uranyl ion when the potential between the anode and cathode was less than, or equal to, 2.2 V. Maximum reduction of the uranium samples occurs within 10 minutes and reoxidation of U(IV) by oxidants generated at the anode is not observed. Nitrite formation, commonly encountered at the cathode surface from the catalytic reduction of nitrate ion in the presence of uranyl (13) was not observed. The low reduction efficiency may be due to an oxide layer that forms on the surface of the anode during sample reduction decreasing its effective surface area.

Glassy carbon electrodes, in the form of polished 6 mm diameter rods, resulted in a 10% reduction of the UO_2^{+2} ion in 30 minutes of electrolysis at potential difference of 2.2 V. The amount of reduction observed is commensurate with the small electrode area (28 mm^2) and the low current observed.

Table 2. Reduction Efficiency of Electrode Materials

Electrode Material	% U(VI) Reduced	Reduction Time	Electrode Potential Difference
Solid Electrodes			
Gold Foil	25	10 m	2.2V
Vitreous Carbon Rod	10	30 m	2.2 V
Pyrolytic Graphite Rod	50	10 m	2.25V
Platinum Rod	4	10 m	4 V
Porous Electrodes			
Platinum Gauze	35	20 m	4 V
RVC	14	10 m	4 V
Mixed Electrode Systems			
Pt Gauze cathode & RVC anode	9	10 m	4 V
RVC cathode & Pt Gauze anode	50	10 m	4 V
RVC cathode & Pt rod anode	100	10 m	4 V

Pyrolytic graphite electrodes, having a surface area of 3.6 cm^2, reduced 50% of the uranyl ion within 10 minutes if the electrode potential difference was maintained at 2.25 V. The reduction was characterized by considerable gas evolution at the anode surface and disintegration of the graphite surface.

Platinum rod electrodes were least efficient in reducing uranyl ion. Two platinum rods, each with an estimated surface area of 15 mm^2, required an electrode potential difference greater than 2.5 V before any U(IV) was observed. Only 4% of the uranium was reduced after a ten minute electrolysis time at a 4V potential.

Porous electrode materials were investigated in an effort to increase the electroactive surface area and, thereby, increase the uranium reduction efficiency. A maximum of 35% U(IV) was produced in 30 minutes using two platinum gauze electrodes, each having an estimated surface area of 470 mm^2.

Recently, a reticulated vitreous carbon (RVC) sponge was introduced as a high-surface area electrode material (14). RVC is a glass-like carbon with a porous structure having a surface area of about 65 cm^2/cm^3. The RVC is structurally rigid but is easily machined into any desired electrode configuration. Uranium reduction was performed using two 2.5 x 2.0 x 0.3 cm RVC rectangles suspended parallel to each other in the reduction vessel. Electrical contact leads were made by wrapping platinum gauge around a corner of each electrode. Uranium reduction, using identical RVC electrodes, was limited to 14%. However, when the anode was replaced by either platinum gauze or rod, the reduction efficiency increased dramatically. Total uranium reduction can be achieved in less than ten minutes using an RVC cathode, a platinum rod anode and continuous sample solution mixing.

3.2 Characteristics of the RVC-Platinum Electrode System

The reduction time required to prepare a 100% U(IV) sample must be minimized for process control considerations. Several experimental parameters can be adjusted to speed sample reduction. A passivated platinum anode surface can retard uranyl reduction. If the electrode system is allowed to run through an initial sample reduction, as indicated in Fig. 3A, the platinum surface is sufficiently cleaned by water oxidation

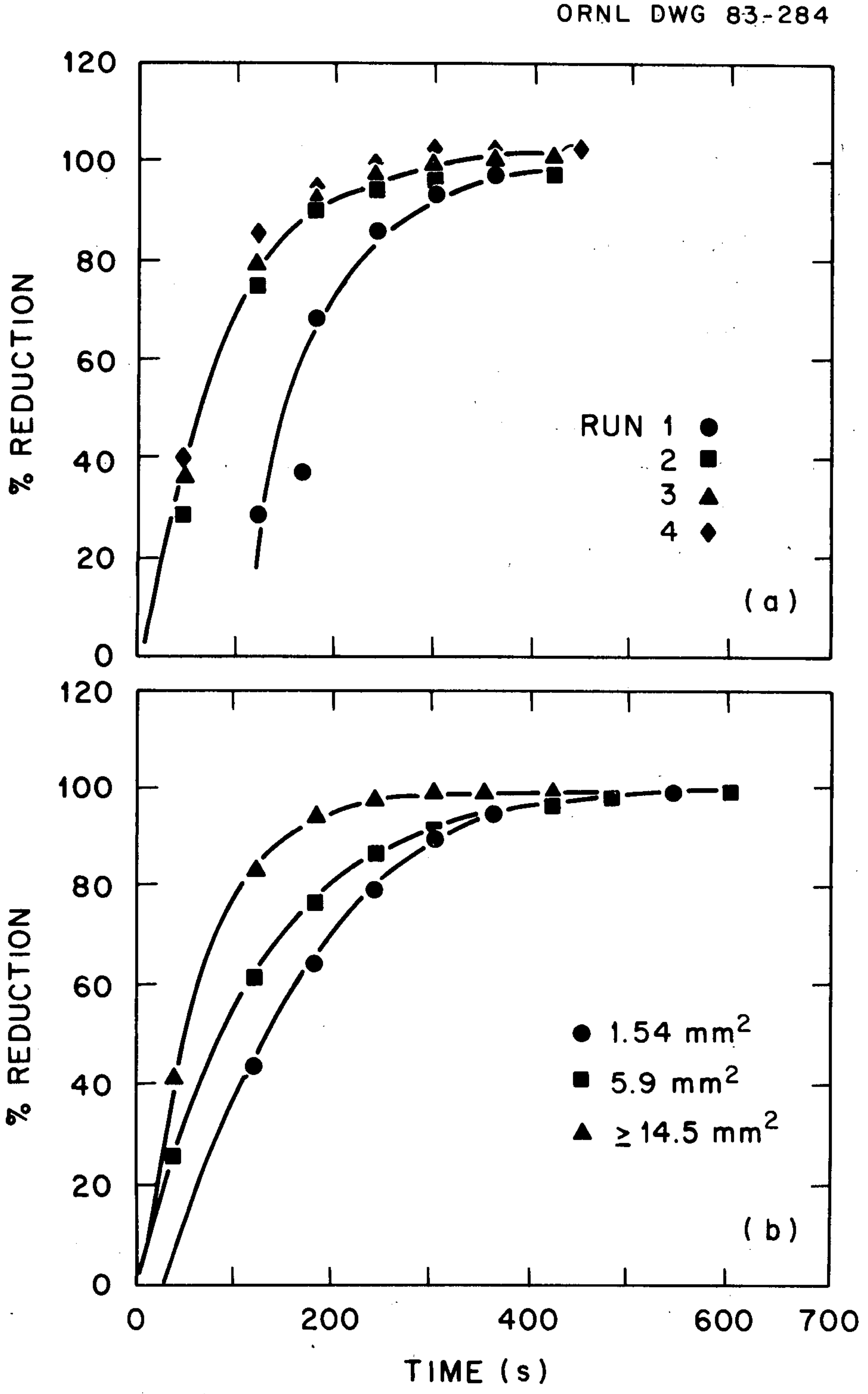

Fig. 3. Experimental parameters affecting reduction efficiency (15 ml of 1.2 g/L U(VI), 1.66 M HNO_3, 4 V potential difference between 0.25 cm^3 RVC cathode and 15 mm^2 platinum cathode): (a) reduction efficiency versus reduction run number and (b) reduction efficiency versus platinum electrode area.

at the electrode, that subsequent samples proceed at maximum rate. Alternatively, a fresh platinum surface can be generated by voltametric cycling of the electrode between the hydrogen and oxygen overpotentials.

The area of the platinum anode also controls the rate of uranyl reduction. Using the 0.15 cm^3 rectangular RVC cathode, greater than 15 mm^2 platinum is required to obtain the maximum rate of U(IV) formation (Fig. 3B). This area was found to be independent of uranyl concentration up to 20 g/L and acidities greater than 0.2 M HNO_3. Below 0.2 M HNO_3 uranyl ion is reduced to UO_2, which forms as a fine green-black precipitate. Under optimum electrode conditions, uranyl ion in solution is totally reduced within five minutes and greater than 95% reduction is achieved in 3 minutes.

3.3 Spectral Characteristics of Reduced Uranium

The accuracy of the proposed spectro-electrochemical determination of uranium is dependent on the total reduction of uranyl ion, as well as on the accurate photometric measurement of U(IV) concentration produced. The optical behavior of U(IV) has been reviewed by several investigators (2, 15). The absorbance at all U(IV) absorption bands was found to be linearly proportional to U(IV) concentration if the maximum absorbance of the sample did not exceed one absorbance unit at any given wavelength. The molar absorptivity of U(IV) at a wavelength of 647 nm is such that 1.0 absorbance unit corresponds to 7.2 g/L and 0.02 absorbance units corresponds to 0.14 g/L in a 1 cm path length optical cell. U(IV) exists in a variety of forms in weak nitric acid solutions, including the uncomplexed ion, mono-, di- and tri-nitrate species. Therefore, U(IV) absorbance is dependent upon the strength of the complexing agent, nitrate ion. Figure 4 summarizes the observed influence of nitrate ion on the molar absorption coefficient of U(IV). Because the effect is significant, accurate photometric measurement of U(IV) must be made with the knowledge of stream nitrate concentration or, as has been demonstrated previously (1), made using two U(IV) wavelengths. A dual wavelength calculation would measure U(IV) essentially independent of nitric acid and simultaneously provide an estimate of nitrate ion concentration.

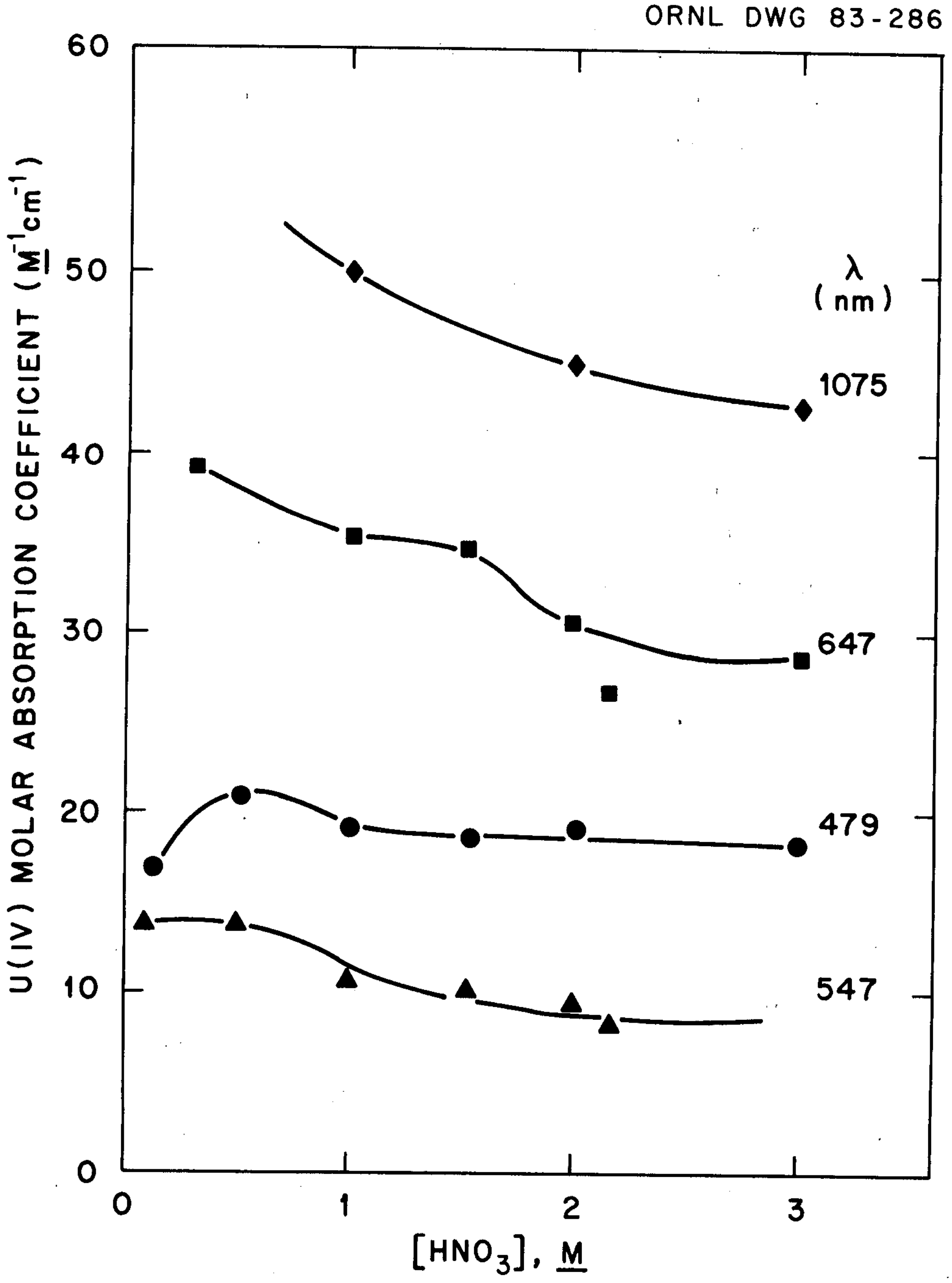

Fig. 4. Effect of nitric acid on U(IV) absorptivity

A multiwavelength photometer has recently been developed to monitor five wavelengths simultaneously (16), and could be applied to the analysis of U(IV) in nitric acid waste solutions. By monitoring 416, 427, 580, 647 and 1075 nm absorbance, the photometer could provide an initial estimate of U(VI) concentration, monitor sample turbidity at a 580 nm blank wavelength, and measure colored background absorbance at the wavelengths where U(IV) absorbs. Once reduction is initiated, the photometer would provide a time base to monitor the production of U(IV), corrected for nitrate concentration, and thus provide reduction rate information. Maximum U(IV) absorbance would signify total sample reduction and permit calculation of total uranium concentration in the sample solution based on this absorbance. If a 5-10 minute analysis time is too great for process control requirements, uranium determination need not be based on a totally reduced sample. Alternatively, the reaction rate information from a partially reduced sample can be used to predict the final total U(IV) absorbance. Such an approach has been developed for the coulometric analysis of uranium (17) and has since been applied to the photometric analysis of reduced species (18). Conceivably, total U(IV) concentration can be determined with as little as a 30% reduced sample, which is equivalent to an analysis time of no greater than 2 minutes.

3.4 Electroreduction and Photometric Detection of Uranium in Aqueous Purex Waste Solutions

The accuracy of the proposed electrochemical measurement of uranium in Purex solutions is dependent upon the fact that process contaminants cannot prevent the electroreduction of the uranyl ion. Additionally, the absorbance of the contaminants at U(IV) wavelengths must not change during sample reduction. Two process solutions were obtained to check these assumptions. The most contaminated aqueous stream in the Purex process is the HAW raffinate, containing all fission products and some stainless steel corrosion products. A non-radioactive, prepared HAW solution was electrolyzed for ten minutes in the RVC-platinum rod electrode system to simulate uranyl reduction in this type of process sample. No significant spectral changes were observed after reduction, however, U(IV) was not formed in the same solution spiked with 1 g/L U(VI), even after a thirty minute reduction period. Addition of a chemical reducing agent to contaminated solutions has previously been suggested (9) to maintain uranium in the reduced state, once U(IV) was formed. Hydroxylamine nitrate (HAN) and hydrazine nitrate (HYN) reductants are available as process reagents in many Purex facilities, and therefore could be used for this purpose. The spiked HAW sample was made 0.5 M in HAN and 0.1 M in HYN and subsequently reduced. At least 25% of the uranyl ion was reduced, however the background absorbance at the 647 nm U(IV) absorption maxima increased ten fold. Although this combination of chemical reductants did not significantly aid uranium measurement in HAW solutions, perhaps an appropriately selected reductant can be found to maintain uranium in the reduced state without altering the chemical composition of solution contaminants.

An aqueous raffinate sample from a secondary extraction column was obtained from the Y-12 uranium recovery facility. This sample contains little or no fission product contamination and represents the majority of aqueous raffinate solutions in a typical Purex process. The original uranium in the Y-12 solution was removed by successive extraction with a tributylphosphate/kerosene organic wash. The solution was then electrolyzed before and after a known amount of uranium was added. Figure 5 shows the visible spectra of the solution before and after electrolysis. The superposition of the two spectra indicate that the background absorbance of U(IV) wavelengths does not change with electrolysis, although no uranyl ion was reduced. HYN was subsequently added to the raffinate sample to prevent reoxidation of U(IV) during electrolysis. Addition of the reducing agent immediately eliminated the optical background at uranyl wavelengths such that an accurate measurement of sample uranium concentration could be made based on U(VI) absorbance at 416 nm and 426 nm. Once the solution was electrolyzed, all uranium was completely reduced in the presence of HYN, so that heavy metal determination could also be based on U(IV) absorbance at 647 mm.

4. CONCLUSION

Uranium measurement in aqueous Purex process streams can be performed directly by the photometric detection of the uranyl ion at concentrations of $\geq$ 1 g/L. If the stream is relatively concentrated and free from impurities, measurement accuracies better than 5% can be obtained.

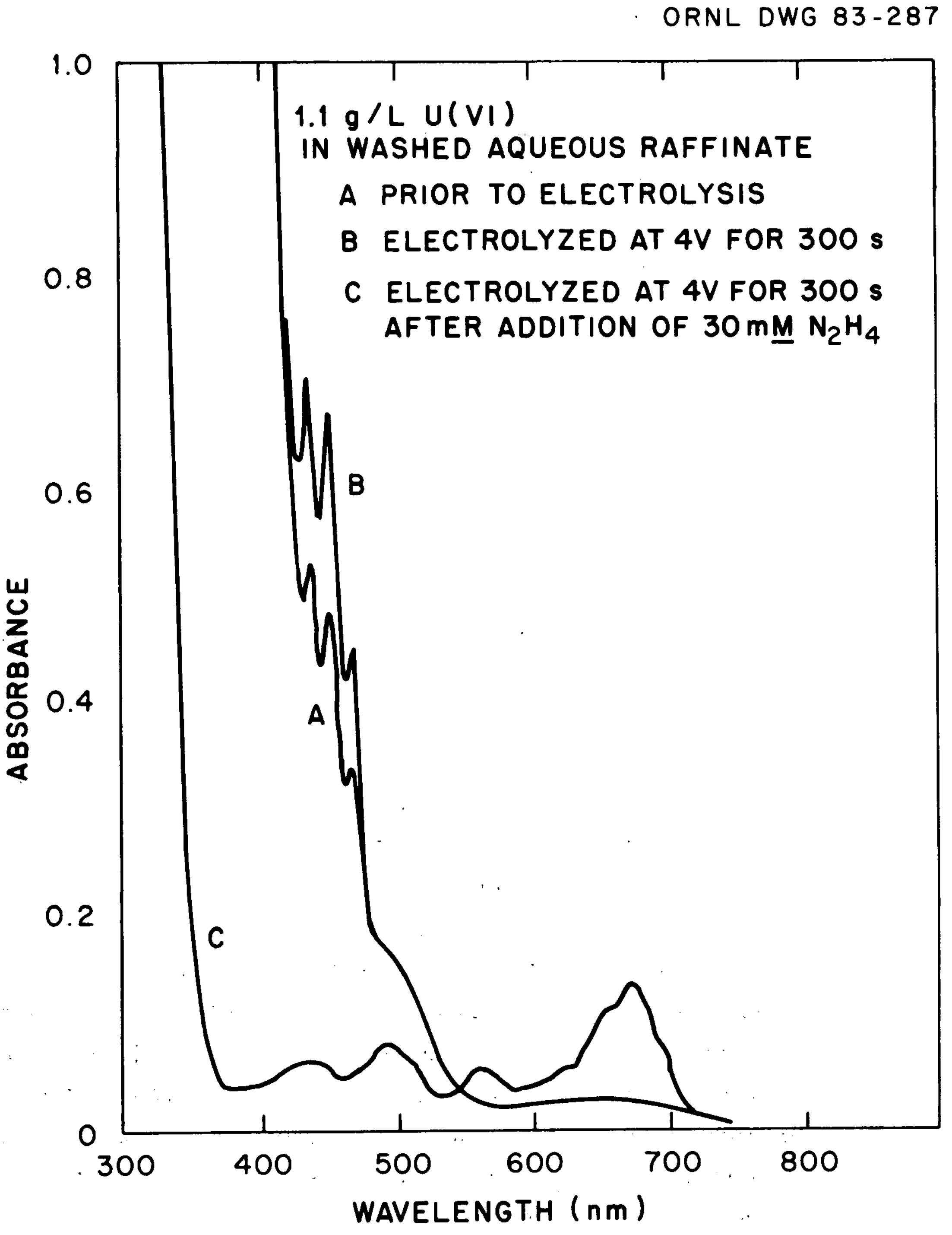

Fig. 5. Effect of hydrazine on uranium reduction 1.1 g/L U(VI) in washed aqueous raffinate: (a) prior to electrolysis, (b) electrolyzed at 4V for 300 s and (c) electrolyzed at 4V for 300 s after addition of 30 m$\underline{M}$ N_2H_4.

Many of the process impurities, including fission and stainless steel corrosion products, absorb at the uranyl wavelengths, producing a positive bias in the uranium determination. Except for a few sharp absorption bands, these same impurities produce little or no optical absorbance at wavelengths longer than 600 nm. The most sensitive absorption bands for U(IV) also occur at wavelengths longer than 600 nm and are three to five times stronger than uranyl absorption maxima. Uranium analysis would therefore be more accurate and more sensitive if the uranyl ion were reduced and the measurement based on U(IV) absorbance. A measurement of background optical absorbance at the U(IV) wavelengths before and after sample reduction could be used to correct for solution impurities. Measurement of uranium at a concentration of $\geq$ 0.2 g/L should be possible.

The U(VI)-U(IV) reduction couple is ideally suited for Purex solutions. The half reaction is irreversible so that both anode and cathode can be placed in the same reduction vessel, simplifying instrumental needs. Total uranyl reduction can be achieved with an RVC cathode, which is inexpensive, easily machineable and has a very high electroactive surface area. The platinum rod anode need only be cycled between the hydrogen and oxygen overpotentials at instrument start-up to prepare the electrode surface. Complete reduction of 15 ml samples can be achieved in five minutes for solutions containing up to 20 g/l U and greater than 0.2 $\underline{M}$ HNO_3.

The photometric determination of reduced uranium is relatively uncomplicated since the absorbance at all of the U(IV) absorbance maxima are linearly related to the uranium concentration. The U(IV) absorption coefficients are, however, nitrate ion dependent so that a dual wavelength calculation is necessary to compensate for variation in nitrate concentration. The recently developed multiwavelength photometer (16) is capable of making the above measurements and has the timing and computational ability to make predictive uranium calculations based on kinetic data. This predictive ability will decrease the time required for a complete uranium measurement to less than two minutes.

In highly contaminated solutions, impurities oxidized at the anode may subsequently reoxidize U(IV) and prevent total uranyl reduction. In some cases, an appropriate chemical reductant, already available in the Purex facility, can be added to the sample solution to preserve the reduced uranium state. If the raffinate sample from the Y-12 secondary extraction column is representative of other solutions, addition of a chemical reductant to a sample may decrease the optical background sufficiently so that the metal determination can be made directly, using U(VI) absorption measurement. As a final note, in situations where no chemical reductant can be found to retard U(IV) reoxidation, the anode might be isolated from the sample using a salt bridge. Although the instrumentation would be slightly more complicated, solution contaminants would not be oxidized and therefore would not interfere with uranyl reduction.

The proposed electroreduction of uranium would provide an in-line heavy metal monitor which is more sensitive, essentially non-destructive, reagentless or requiring only process-available reductants, rapid and free from optical interference from both optically dispersive and absorbing species.

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