255
8/28/87 JS (2)

(5)

I-31677

DR-0295-X

LBL/SRP-23344
UC-70

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

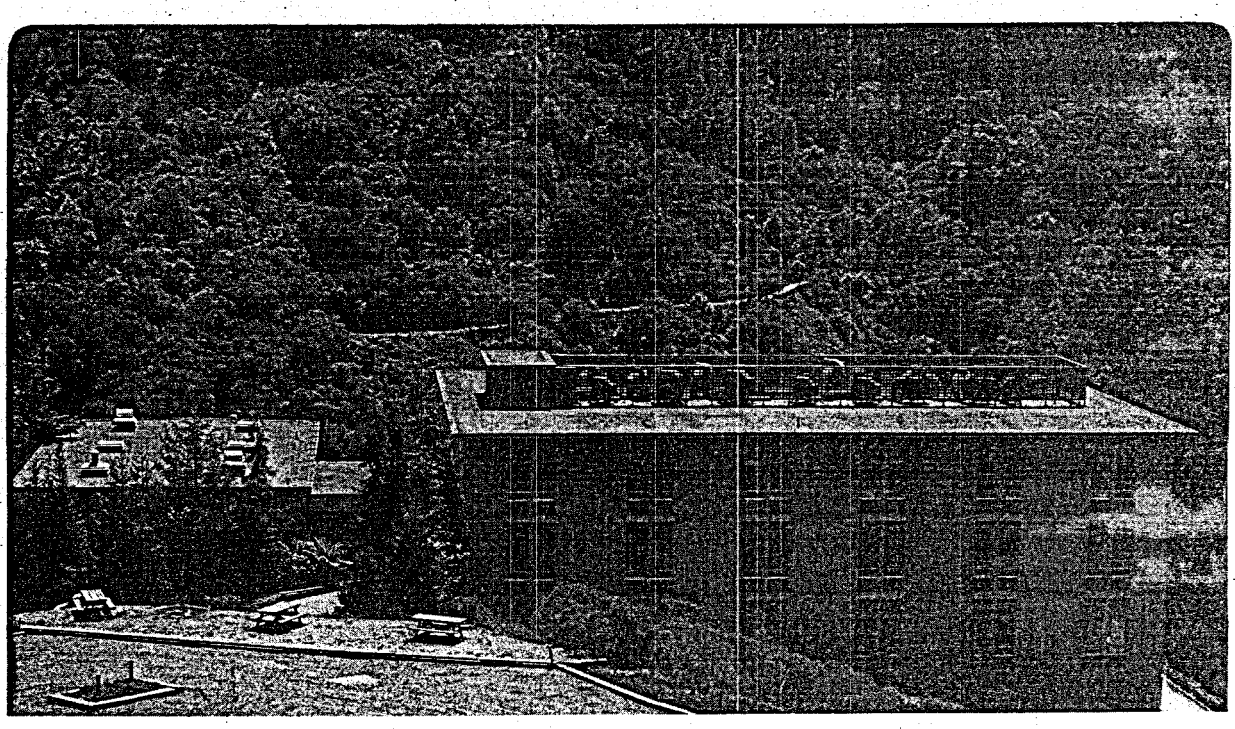
Materials & Chemical Sciences Division

ASSESSMENT OF SPECIATION TECHNIQUES INCLUDING THE APPLICATION OF PHOTOACOUSTIC SPECTROSCOPY

J. Bucher, H. Gehmecker, and N. Edelstein

August 1985

DO NOT MICROFILM COVER



Prepared for the U.S. Department of Energy under Contract DE-AC03-76SF00098

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of 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. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LBL/SRP--23344

DE87 013960

Assessment of Speciation Techniques Including the Application of Photoacoustic Spectroscopy

J. Bucher, H. Gehmecker, and N. Edelstein

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

August 1985

This document is
PUBLICLY RELEASABLE
B Steele
Authorizing Official
Date: 3/22/06

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of 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. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

This work was supported by the U.S. Salt Repository Project Office (SRPO) under Contract No. E51184025 and in part by the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

Introduction

Speciation studies describe a liquid, solid, or gas-phase composition in greater detail than in terms of gross concentrations. For example, a liquid-phase composition may specify the oxidation states of the ions. More extensive studies would report the species general solution interactions in terms of specific solvation, hydrolysis, complexation, redox, etc. reactions. Oxidation states determinations are frequently included in solubility studies analysis. Further solution species characterization is most often found in studies that deal with the behavior of a single element under carefully controlled idealized experimental conditions. These experimental results are useful for data bases utilized by modelers in their calculated predications for a nuclear waste repository safety assessment.

Note that speciation studies are secondary to solubility studies. If little or no actinide or fission products are released from a containment cannister or from the spent fuel or glass matrix, then there is little need for liquid-phase speciation studies. Under real conditions there will be instances where the solubility of a radionuclide is low enough ($< 10^{-8}$ to 10^{-9} M) so that from a barrier engineering viewpoint no further information is required about the particular radionuclide solution-phase speciation. Yet, even in this case, if additional information about the species oxidation states distribution can be relatively easily obtained for selected examples, this may prove useful. Characterization of the redox reactions under ultra-trace element concentrations will aid in establishing confidence in the idea of satisfactory radionuclide containment due to pure

secondary-phase formation or mixed compound insolubility alone. Although the redox information will not place any additional demands upon the barrier enginering requirements, it will clearly confirm that the unmodified near-field components (e.g., iron cannister material, the overpack, etc.) are controlling the Eh and/or pH conditions appropriately. It is expected that speciation study results will indicate the solution-phase existence of tervalent or trivalent ions. Representative examples are uranium, U^{4+} and its hydrolysis products $U(OH)_x^{4-x^+}$, neptunium, $Np(OH)_x^{4-x^+}$ technecium, Tc^{4+} (or ? TcO^{2+}); plutonium, Pu^{3+} ($Pu(OH)_x^{3-x^+}$, with a possible intermediate trivalent solid phase, $Pu(OH)_3$), and $Am(OH)_x^{3-x^+}$, all under reducing Eh conditions. These studies will also provide experimental verification of modeling codes and the data base.

In contrast to the above ultra-trace conditions, when the solution-phase solubilities exceed 10^{-7} - 10^{-8} M (solubility studies), identification of the solution-phase redox species is no longer simply a matter of providing supplementary confirming information. Solution speciation results are now a necessity and will indicate what types of remedial conditions need to be included in the engineered near-field barrier in order to prevent radionuclide migration beyond the barrier boundary at an unacceptable concentration level. Speciation results will indicate whether an Eh or a pH adjustment, or both, are needed to establish satisfactory solubility-limiting behavior. These studies will help decide whether the general redox conditions are being controlled by radiation induced or naturally occurring redox agents (e.g., O_2, Fe^{2+}).

Techniques need to be developed so that the solid-phase is characterizable even if it is amorphous or is in a mixed phase of radionuclides-cannister-corrosion products.

The two most utilized approaches to the determination of solution-phase species involve separation or spectroscopic techniques. Separation procedures are based mainly upon ion selective interactions and are thus sensitive to oxidation states. These procedures include such familiar methods as organic ion-exchange resin chromatography, solvent extraction, and the less often encountered variations on these methods: inorganic ion-exchange chromatography and fixed-phase solvent extraction systems.

These methods are usually applied using low pressure techniques. The use of high-pressue liquid chromatographic (HPLC) techniques, a standard technique used in separating biological materials, has not been frequently employed in separating inorganic materials. HPLC can give rapid separations and thus preserve the desired redox speciation information even under difficult experimental redox conditions. This occurs by taking advantage of the fairly slow kinetic reactions of the important radionuclides (i.e., Tc, U, Np, Pu).

Chromatography Application

To illustrate the application of separation methodology to the problem of radionuclide oxidation state speciation, results from the doctoral thesis[1] of a co-worker, Dr. Horst Gehmecker are presented. His objective was to explore the separation and identification of plutonium oxidation state distributions at low concentrations as might be found in

groundwater. He used commonly available separation materials and established the experimental conditions under which useful workable schemes for oxidation state distributions could be clearly demonstrated. Experiments were primarily done at total plutonium concentrations of 10^{-7} M or less.

Fig. 1 shows the plutonium distribution coefficients (K_D) as a function of oxidation state (Pu^{3+}, Pu^{4+}, PuO_2^{2+}) and as a function of HCℓ concentration for the strong acid organic ion-exchange resin, Dowex 50W-X8. This data suggests that ion-exchange columns can be used for a satisfactory plutonium oxidation state separation by using a single HCℓ concentration between 1--7 M. The important featureein Figure 1 is the noncrossing of the individual oxidation state distribution coefficients curves until high HCℓ concentrations (> 8.5 M) are used. This means the elution order would be PuO_2^{+}, PuO_2^{2+}, Pu^{3+}, Pu^{4+}. Operation at a fixed acid concentration means that a) if a low HCℓ concentration is used, large volumes are necessary to elute the plutonium species, or b) if a higher HCℓ concentration is used, a long column is necessary, as the differences in distribution coefficients are small. A third mode of operating an ion-exchange column is shown in Fig. 2

Instead of using a fixed acid concentration, a step-wise change of acidity is made, so that each oxidation state is selectively eluted from the ion-exchange column in a relatively small solution volume. The total volume needed for separating all the plutonium species is also small. Finer adjustment of the final acidity change could be made to obtain a Pu^{3+}, Pu^{4+} separation. But, as seen later, this may not be a necessary step when a combination of other techniques are included.

Figures 3 and 4 detail the distribution coefficients for Pu in the sytem tributylphosphate (TBP)-nitric acid. TBP is representative of neutral solvent-extraction systems and diluted TBP is the main reagent used in nuclear fuel reprocessing. Figure 3 shows the extraction behavior of Pu into a pure TBP phase from various nitric acid concentrations. Figure 4 is similar except the TBP has been sorbed upon an inert stationary material (polytrifluorochloroethylene polymer, usually known as Kel-F). This fixed-phase material can be used in a column form. It is evident from both Figures 3 and 4 that the selectivity for Pu^{4+} and PuO_2^{2+} is nonexistent. However, the difference in distribution coefficients for Pu^{4+} and Pu^{3+} is good and could be particularly useful in oxidation state speciation studies of Pu under reducing conditions. Figure 5 shows the effect of using acids other than nitric with TBP. Only the TBP-perchloric acid system shows any potential for useful species separations.

A more useful solvent extraction system is shown in Figures 6 and 7. The material, di-(2-ethylhexyl) phosphoric acid (HDEHP) is a moderately strong acid. When sorbed upon an inert fixed-phase it is similar to the previously discussed Dowex 50 cation ion-exchange resin. Also included in Figure 7 is information on PuO_2^+ distribution. As before in the TBP system, no clear discrimination between Pu^{4+} and PuO_2^{2+} is possible in these HDEHP/acid system. This may not, however, be any more than an experimental inconvenience. Unless the Pu concentration is sufficiently high so that disproportionation reactions are occurring, it is unlikely Pu^{4+} and PuO_2^{2+} would coexist. The very large distribution coefficients for Pu^{3+}, Pu^{4+}, and PuO_2^{2+} in this HDEHP system at low

acidities, would allow its use for concentrating plutonium (and the other analogous actinide systems Np and U) species from large volumes of test solutions. This ability to concentrate species without losing redox information would be especially useful in increasing the detection limit sensitivity for other actinide systems such as neptunium under reducing conditions. In order to remove either Pu^{4+} or PuO_2^{2+} from this type of column it is necessary to use a reducing agent (ascorbic acid) so that Pu^{3+} is formed.

Figures 8, 9, 10, and 11 show the results for plutonium separations from both specially prepared silica gel and for silica gel that has been sulfonated. The silica gel used (Merck, LiChrospher Si 100, 10 μm particle size) has a large surface area, ~ 250 m^2/gm, and results in an ion absorptive capacity of ~ 2 meq/gm. This capacity is similar in magnitude to a typical organic based cation or anion ion-exchange resin. The other material used is formed by attaching a sulfonic acid group, $-SO_3^-$, to the silica backbone to give: $-\overset{1}{\underset{1}{Si}}-O-SO_2^-$ groups. This material acts as a strong acid cation exchanger. Unlike its organic based resin counterpart, the sulfonated silica gel has no tendency to perturb the speciation by redox reactions as the gel has no reducing properties.

Figure 8 shows the distribution coefficients for absorption of Pu^{3+}, Pu^{4+}, and PuO_2^{2+} on LiChroprep SI 60 (a 20 μm sized equivalent to LiChrospher SI 100), as a function of HCℓ concentration. At low acidities a strong selectivity for Pu^{4+} (and presumably any tervalent actinide or higher charged fission product ion) over Pu^{3+} and PuO_2^{2+} is clearly evident. Yet, at high acid concentrations, even Pu^{4+} can be

easily eluted. For effective absorption of tervalent plutonium, a 2.5-3 hr. contact time is needed during the loading phase of the solution.

Figure 9 shows the selectivity of LiChrospher SI 100 when used in an absorption column. Loading is done at 0.01 M $HC\ell O_4$; desorption of Pu^{4+} is done with 5 M $HC\ell$. Experiments were run at a 10^{-8} M plutonium level.

Figures 10 and 11 detail the behavior of plutonium on sulfonated silica material. Figure 10 shows that a complete Pu^{3+}, Pu^{4+}, PuO_2^+, and PuO_2^{2+} redox separation can be achieved when moderate stepwise acidity changes are used. The conditions necessary for Pu^{3+} and Pu^{4+} elution are considerably milder than needed in the Dowex 50 cation ion-exchange experiments.

Figure 11 shows similar data for oxidation state mixtures. The data also indicates that when phosphoric acid is used to elute the Pu^{4+} fraction, a considerably smaller volume of eluant is needed. Experiments were run at total plutonium concentrations of either ~ 10^{-9} M or 10^{-8} M. No separation differences were observed with these ultra-trace concentration levels.

Figure 12 shows several flow sheets proposed by Gehmecker. They incorporate the use of two connected columns in each example. The first column contains silica material (see Fig. 8) which is selective for tervalent ions and retains this oxidation state, while the other redox species flow straight through to a second column. As indicated, the choice of using either Dowex 50-X8 or the sulfonated silica cation ion-exchanger is equally effective. A slight preference for the system detailed in part a) comes from considering the total eluant volumnes.

Smaller solution volumes are easier and more efficiently assayed by counting techniques. Also the totally inorganic composition of the sulfonated silica ion-exchange is useful in preventing any species reduction reactions from the column material.

The results in Table 1 illustrate the effectiveness of these separation techniques for oxidation state speciation determinations. Plutonium concentration levels of the initial mixed redox solutions were $\sim 5 \times 10^{-12}$ M. Initial redox compositions are listed in column 3 and the results determined by counting techniques (errors are at the 2 σ (sigma) level) are listed in subsequent columns. The agreement between the initial starting plutonium oxidation state composition and the experimentally determined redox species percentages is extraordinary, especially if one considers the ultra-trace concentration level used. By using a combination of absorption and cation ion-exchange columns redox speciation determinations are feasible down to the very limits of radionuclide counting detection.

Data are also included in this table which show the effectiveness of the LaF_3 coprecipitation technique for carrying tri- and tervalent actinide species. This technique is presently being used to concentrate large volumes of neptunium species from solubility measurement. Starting with $10^{-9} - 10^{-10}$ M NpO_2^+ solutions in 6 m NaCℓ, the NpO_2^+ is reduced to Np^{4+} by Fe^{2+} and then the Np^{4+} coprecipitated with LaF_3. Thus a 100 mℓ sample is reduced in volume to a few mg of LaF_3 precipitate.

Other redox speciation schemes have been given in great detail in the literature.[2] They center upon the use of solvent extraction methods

and the use of TTA (thenoyltrifluoroacetone) is frequently encountered. Most, if not all, of these liquid-liquid phase solvent extraction determinations were performed under oxidizing conditions. It is felt that the use of isolated absorption and ion-exchange columns can give better redox speciation results. This is especially useful for the case where redox speciation is examined from solubility studies done under reducing conditions (? repository conditions). Eh conditions in the columns can be maintained in a close approximation to those existing in the reducing test solutions.

Spectroscopic Applications

Spectroscopic techniques provide more versatile but less sensitive methods for speciation studies than separation techniques. All the actinide radionuclides have sharp absorption bands characteristic for each actinide ion oxidation state. These electronic transitions arise from the $5f^n$ electron configurations and the strength of these transitions is seldom large. Dilute solutions of ions or complexes of these elements (U, Np, Pu and Am) are usually weakly absorbing and more sensitive instrumental techniques are needed for accurate studies.

Table 2 lists the absorption parameters for U, Np, Pu, Am, and Tc (technicium). The entry under wavelength is for the strongest absorption band for each listed radionuclide oxidation state. Molar absorptivity is a parameter that normalizes the absorption process per unit length. The absorption spectroscopy equation is expressed as:

$$A_{abs} = A_o \cdot \alpha \cdot \ell, \qquad (1)$$

where A_{abs} is the amount of light absorped, A_o is the initial light flux, α is the absorbance coefficient and ℓ is the unit length, usually expressed in units of centimeters. The absorbance coefficient, α, can be broken into two components: c, the concentration of the absorbing species and ϵ, the extinction coefficient. Thus

$$A_{abs} = A_o \cdot \epsilon \cdot c \cdot \ell. \qquad (2)$$

The final column in Table 2, sensitivity, is an estimate of the lowest concentration detectable for each oxidation state. It is assumed that a) a conventional research UV-VIS-NIR spectrometer is used, b) the minimum detectable absorption on an expanded scale is 5×10^{-4} absorbance units (signal to noise ratio is 1:1), and c) the pathlength is 1 cm. It is evident that even for the best actinide example, PuO_2^{2+}, ~ 10^{-6} M is the limiting detectable redox species concentration. For the fission product radionuclides (e.g., technicium), an order of magnitude detection sensitivity increase is expected, as the observed transitions are not formally forbidden. Another order of magnitude increase in sensitivity for all the examples (~ 10^{-7} actinide ions, ~ 10^{-8} Tc) can be obtained by using 10 cm pathlength cells, but the solution volume also increases (> 7 mℓ needed).

These estimated detection sensitivities are strictly applicable to dilute, low ionic strength solutions, conditions that are found in other than the proposed salt repository sites. In strong salt solutions (e.g., PBB1 or PBB3 prototype brines) the various redox species listed in Table 2 will interact with chloride ion, $C\ell^-$. This interaction to form chloro complexes reduces markedly the molar absorptivity values[3-5] and hence the detection sensitivity. Despite this hinderance, useful

solution redox species determinations can still be done with absorption spectroscopy techniques for several of these actinide systems. The possible systems are principally those that involve a difference in the solution and solid-phase oxidation states. Examples are: $PuO_2 \cdot xH_2O$ (solid phase), PuO_2^+ or $PuO_2C\ell_x^{(1-x)}$ (solution phase), and $NpO_2 \cdot xH_2O$ (solid phase), NpO_2^+ or $NpO_2C\ell_x^{(1-x)}$, systems likely under oxidizing conditions; and $PuO_2 \cdot H_2O$ (solid phase), Pu^{3+} or $PuC\ell_x^{3-x}$ (system likely under the strong Fe-Fe^{2+} controlled reducing conditions) and $Am(OH)_3 \cdot xH_2O$ or $AmO_2 \cdot xH_2O$ (solid phase), $AmC\ell_x^{3-x}$ (solution phase) at low pH values and under both oxidizing and reducing conditions. Absorption spectroscopy can be used to identify the solution redox species in each of the above examples because the solution-phase concentration is large ($> 10^{-5}$ M) over some portion of the pH dependent solubility determination study. Obviously, the radionuclide concentration levels needed to apply this technique are at an unacceptable level from a near-field containment viewpoint. However this type of experimental speciation information is useful to define conditions that are needed to prevent unacceptable radionuclide release conditions. For example, well established Eh and pH conditions in the near-field boundary could prevent radioactive releases above an acceptable level.

A better use of spectroscopic techniques for speciation studies is shown in Figures 14, 15, 16, and 17. These figures show absorption spectra for Np, Pu, and Am with various $C\ell^-$ concentrations and several other ligands. As noted before, it is clear that the visible region transitions are decreasing in intensity as the chloride ion concentration increases. While not clearly obvious in the first three

figures of this group, figure 17, an expanded presentation of Am-ligand systems, shows the typical small shifts that occur in these $5f^n$-$5f^n$ transitions with complexation. It is this unique spectroscopic feature that can be exploited to examine complexation speciation.

A possible need exists to reexamine the stability constant values[6] that form the data bases used presently by the modelers. Such simple systems as the various oxidation state actinide ion-chloride interactions have literature values as follows for chloro complexation: $UO_2^{++} + C\ell^- = UO_2C\ell^+$, $K_{UO_2C\ell^+} = 58$, $K_{NpO_2C\ell^+} = .5$, $K_{PuO_2C\ell^+} = .8$; $U^{4+} + C\ell^- = UC\ell^{3+}$, $K_{UC\ell^{3+}} = 400$, $K_{NpC\ell^{3+}} = 2$, $K_{PuC\ell^{3+}} = 8$; $Pu^{3+} + C\ell^- = PuC\ell^{2+}$, $K_{PuC\ell^{2+}} = 17$, $K_{AmC\ell^{2+}} = 17$. Certainly, something is inconsistent for each grouping of redox-species-chloro complexes. Systematic comparisons for MO_2^{++} ions (M = U, Np, Pu) would not support a 60 times larger constant for UO_2^{++} when compared to NpO_2^{++} and PuO_2^{++}. A similar observation can be made for the M^{4+} systems, and the finding that trivalent actinide ions form stronger chloro complexes than the tervalent ions is clearly wrong.

From the viewpoint of other potential repository sites, chloro stability constants are of little concern. The chloride ion concentrations are simply too low to matter: Yucca Mountain - 2×10^{-4} M - 10^{-3} M.[7] The situation in a salt repository site is exactly opposite. A very large chloride concentration is expected if brines are present. This can lead to an increased inventory of radionuclides in a salt repository. Consider the system $Pu^{3+} - C\ell^-$ at a pH ≤ 7 and under reducing conditions; the stability constant $K_{PuC\ell^{2+}} = 17$; $Pu^{3+} + C\ell^- =$

$PuC\ell^{2+}$; the ratio of $PuC\ell^{2+}/Pu^{3+}$ is equal to $(K_{PuC\ell^{2+}})\cdot(A_{C\ell^-})$ [PBB3 brine] or (17)(-27) = 460 = $PuC\ell^{2+}/Pu^{3+}$. Since Pu^{3+} is the principal ion in equilibrium with a solubility controlling solid phase, its concentration must be maintained in solution. Yet, Pu^{3+} is also in equilibrium with $PuC\ell^{2+}$; and the concentration of $PuC\ell^{2+}$ is approximately 2.5 orders of magnitude larger than the Pu^{3+} concentration. Thus the total solution inventory of Pu radionuclides that might be expected is greatly increased if the chloro complexation stability constant value of 17 is correct. While it is likely this value is too large, what is the correct stability constant? Even small complexation constants in the range of 1 can have a noticeable effect.

If sensitivity calculations using the modeler's codes confirm the need for redetermination of any of the stability constants for the type of complexation systems discussed above, absorption spectroscopic techniques are the most promising experimental procedure. Data for the subtle actinide ion shifts due to complexation can be collected today in a superior manner due to the advances of modern instrumentation. The data collected can also be analyzed in a much better way than 20 years ago due to the general availability and improvement of computer peak deconvolution programs and also due to a superior understanding of formulating and applying solution activity coefficients.

Spectroscopic techniques are also needed for the resolution of the problem of tervalent actinide ion (especially Pu^{4+}) complexation with carbonate ion. This problem has held the attention of many experimenters and has caused much effort to be expended in trying to confirm the earlier Russian value[8] or to redetermine it accurately. It

is likely that a thorough understanding of the effects of carbonate complexation on a salt repository radionuclide containment site will be required for the site license.

At present, the most promising experimental approach is to examine the Pu^{4+}-carbonate system at a low pH and under high CO_2 pressures so that no complications from hydrolysis are occurring. Observation of the 470 nm Pu absorption line for perturbations due to $CO_3^{=}$ complexing would be made. Preliminary experiments have indicated that the instrumental sensitivities needed exceed the capabilities of conventional UV-VIS-NIR spectrometers. This problem requires a more sensitive alternative technique to conventional absorption spectroscopy, such as optoacoustic (OA) (photoacoustic) spectroscopy. Stump et al.[9] have demonstrated the use of OA spectroscopy for speciation studies of aqueous actinide ions.

As in absorption spectroscopy, the problem in OA spectroscopy is to measure the energy absorbed (E_{abs}) when a light beam or light pulse passes through an optically thin medium of length ℓ and absorption coefficient α. The equation, $E_{abs} = E_o \alpha \ell$, is basically the same for either technique; however the means of determining E_{abs} is radically different.

In conventional absorption work E_{abs} for a species is determined as the difference between I_o (light intensity after passing through solvent) and I (light intensity after passing through solvent plus solute). For weak absorption the problem arises of determining the difference between two large values. In OA spectroscopy, however, E_{abs}, is measured directly. The quantity evaluated is the amplitude (or integrated intensity) of a pressure wave that is generated as a result

of the degradation of the electronic absorption energy into heat within a localized area defined by the light beam. Expansion by the heated area produces the pressure wave that is proportional to E_{abs} for systems that relax primarily by non-radiative processes. This OA method is of great advantage in weakly absorbing systems and offers the possiblity of increasing the detection sensitivity by one to two orders of magnitude when compared to the limits of conventional absorption spectroscopy.

References

1. Gehmecker, H. 1985. Chemische auftrennung der wertigkeitsstufen des plutoniums. Doctoral thesis, Johannes Gutenberg-University, Mainz, Federal Republic of Germany.

2. Nitsche, H. and Edelstein, N.M. 1985. Determination of the solubilities and complexation of waste radionuclides pertinent to geological disposal at the Nevada tuff site. Topical report. Solubilities and speciation of actinide ions in near-neutral solution, LBL-18900, Lawrence Berkeley Laboratory, Berkeley, CA., Jan. 1985, and references therein.

3. Marcus, Y., Givon, M., and Shiloh, M. 1965. The chemistry of the trivalent actinides in aqueous solutions and their recovery. Proc. 3rd Intern. Conf. Peaceful Uses At. Energy, Geneva, 1965, United Nations 10, 588-596.

4. Shiloh, M. and Marcus, Y. 1966. A spectrophotometric study of trivalent actinide complexes in solution. II-Neptunium and Plutonium. J. Inorg. Nucl. Chem. 28, 2725-27722

5. Marcus, Y. and Shiloh, M. 1969. A spectrophotometric study of trivalent actinide complexes in solution. IV. Americium with chloride ligands. Israel J. Chem. 7, 31-43.

6. Phillips, S., Phillips, C., and Skeen, J. 1985. Hydrolysis, formation and ionization constants at 25°C, and at high temperature-high ionic strength. LBL-14996, Lawrence Berkeley Laboratory, Feb. 1985, and reference therein.

7. Ogard, A. and Kerrisk, J. 1984. Groundwater chemistry along flow paths between a proposed repository site and the accessible

environment. UR-LA-10188, Los Alamos National Laboratory, Los Alamos, New Mexico, 47 pp.

8. Cleveland, J.M. 1970. The Chemistry of Plutonium, Gordon and Breach, New York, p. 120.

9. Stumpe, R., Kim, J., Schrepp, W., and Walther, H. 1984. Speciation of actinide ions in aqueous solution by laser-induced pulsed photoacoustic spectroscopy. Appl. Phys. B 34, 203-206.

Solution	Oxidation State	Initial Conditions	Determination of Oxidation States			
			Silica Gel	LiChrosorb	Dowex 50	LaF_3-precp.
1	Pu^{3+}	50,0	52 ± 1,5	-	-	-
	Pu^{4+}	50,0	48 ± 1,5	-	-	-
	PuO_2^+	-	-	-	-	-
	PuO_2^{2+}	-	-	-	-	-
2	Pu^{3+}	-	-	-	-	-
	Pu^{4+}	50,0	53 ± 1,5	54 ± 1,5	55 ± 1,5	53 ± 1,5
	PuO_2^+	50,0	47 ± 1,5	46 ± 1,5	45 ± 1,5	47 ± 1,5
	PuO_2^{2+}	-	-	-	-	-
3	Pu^{3+}	-	-	-	-	-
	Pu^{4+}	50,0	50 ± 1,5	52 ± 1,5	54 ± 1,5	50 ± 1,5
	PuO_2^+	-	-	-	-	-
	PuO_2^{2+}	50,0	50 ± 1,5	48 ± 1,5	46 ± 1,5	50 ± 1,5
4	Pu^{3+}	33,3	36 ± 1,0			71 ± 2,0
	Pu^{4+}	33,3	34 ± 1,0			
	PuO_2^+	33,3	28 ± 1,0			29 ± 1,0
	PuO_2^{2+}	-	1 ± 0,3			

Table 1. Analysis of Oxidation State Determination for the Plutonium System in Synthetic Groundwater.

Table 2. Absorption Parameters for U, Np, Pu, Am, and Tc

Species	Wave Length (nm)	Molar Absorptivity (ℓ/mole-cm)	Sensitivity (mole/ℓ) ($A = 5x10^{-4}$)
Am^{3+}	503	380	1.3×10^{-6}
Am^{4+}	456	30	1.5×10^{-5}
Pu^{3+}	600	38	1.3×10^{-5}
Pu^{4+}	470	55	9.0×10^{-6}
PuO_2^+	568	19	2.6×10^{-5}
PuO_2^{2+}	830	550	9.0×10^{-7}
Np^{3+}	786	44	1.1×10^{-5}
Np^{4+}	723	127	4.0×10^{-6}
NpO_2^+	980	395	1.3×10^{-6}
NpO_2^{2+}	1223	45	1.1×10^{-6}
U^{3+}	520	140	3.5×10^{-6}
U^{4+}	650	58	8.6×10^{-6}
UO_2^+	-	-	-
UO_2^{2+}	415	8	6.3×10^{-5}
Tc^{3+}	340	4,500	1.1×10^{-7}
Tc^{4+}	485	4,300	1.2×10^{-7}
TcO_4^-	246	6,220	8.0×10^{-8}

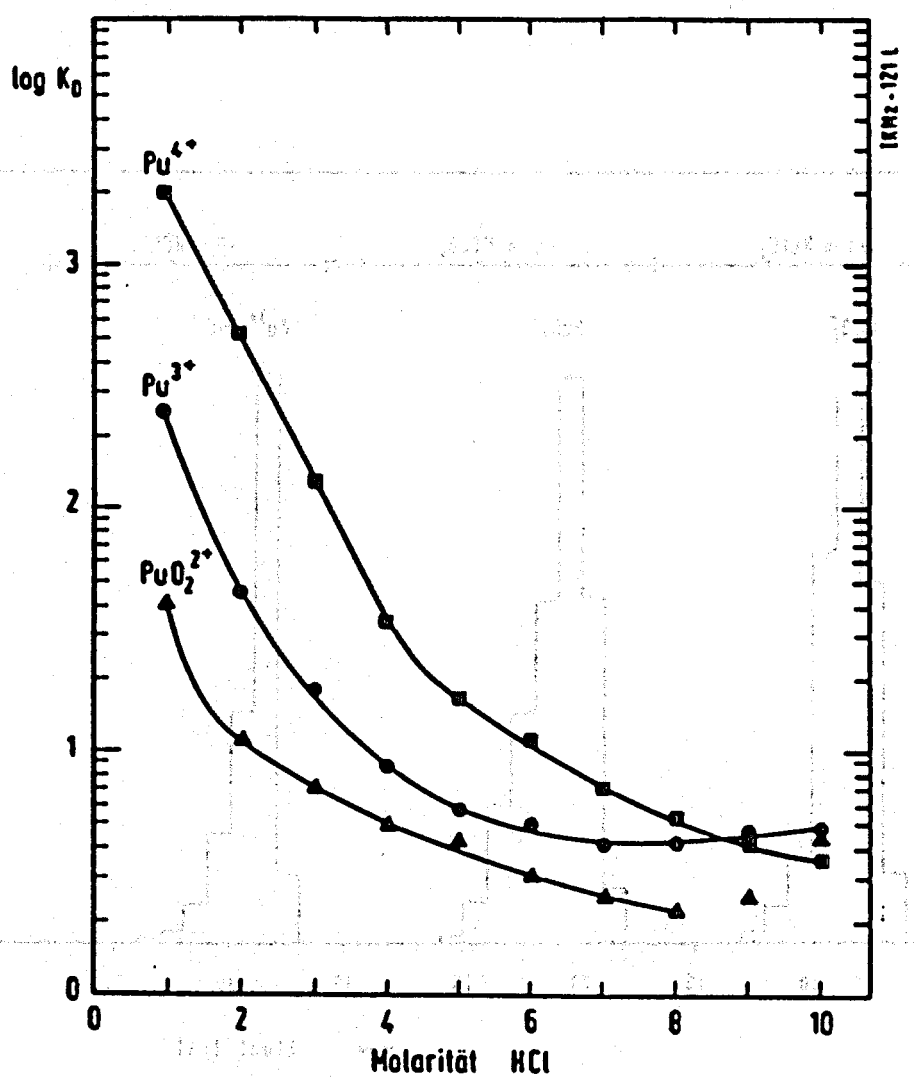


Figure 1. Distribution Coefficients for Pu^{3+}, Pu^{4+}, and PuO_2^{2+} in the System Dowex AG50-X8, Hydrochloric Acid.

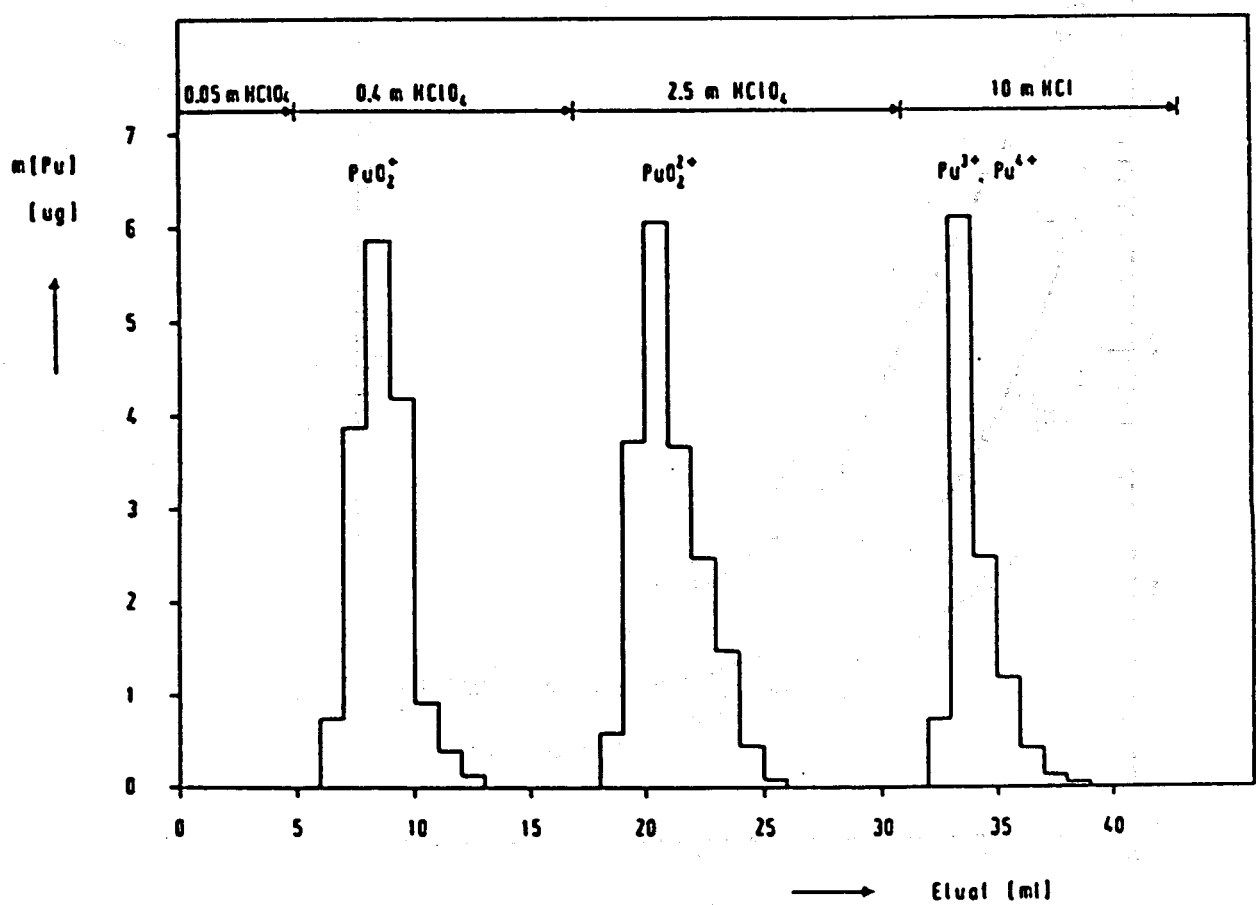


Figure 2. Eluation-Peaks for Pu^{3+}, Pu^{4+}, PuO_2^+, and PuO_2^{2+} for a (100x4)mm Dowex AG50-X8 Column, Various Acidities.

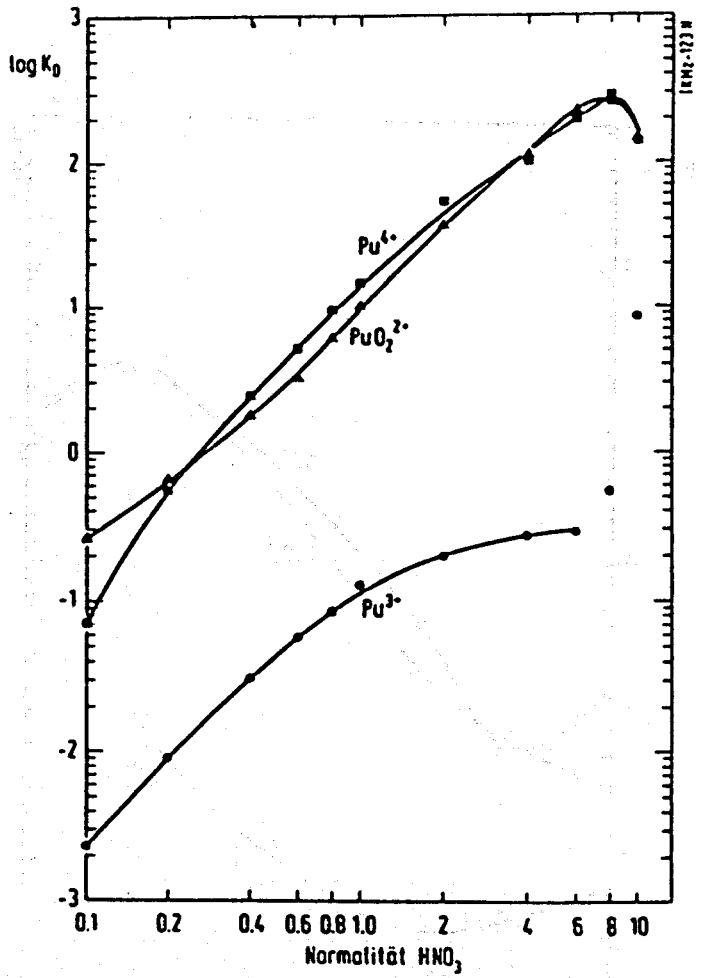


Figure 3. Distribution Coefficients for Pu^{3+}, Pu^{4+}, and PuO_2^+ in the System TBP/HNO_3. (Liquid-Liquid Phase Extraction).

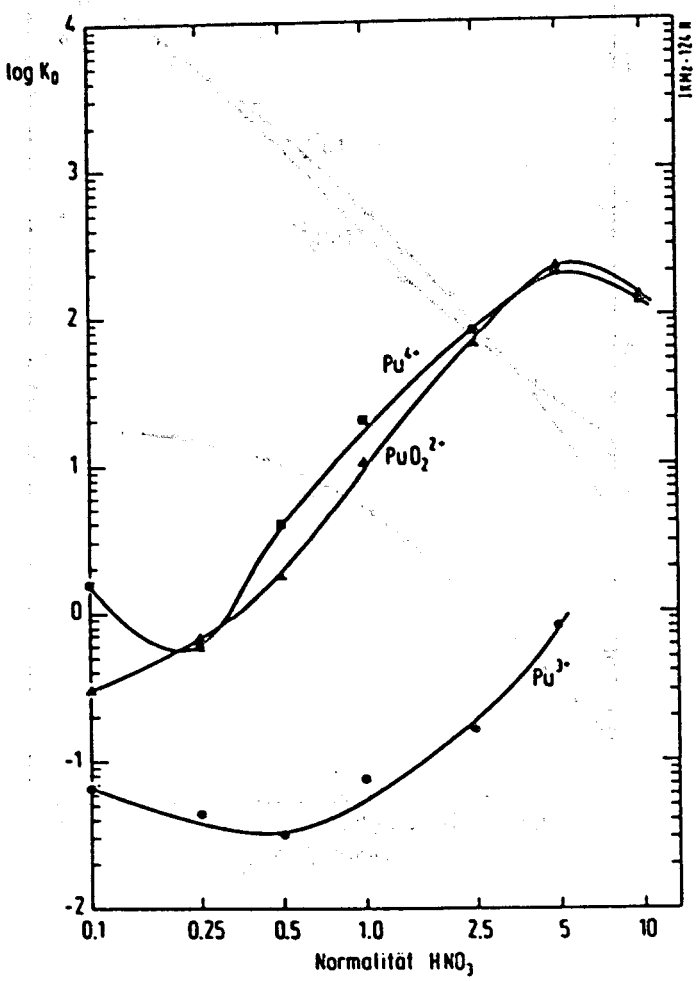


Figure 4. Distribution Coefficients for Pu^{3+}, Pu^{4+}, and PuO_2^{2+} in the System TBP/HNO_3. (TBP Sorbed on an Inert Stationary Phase).

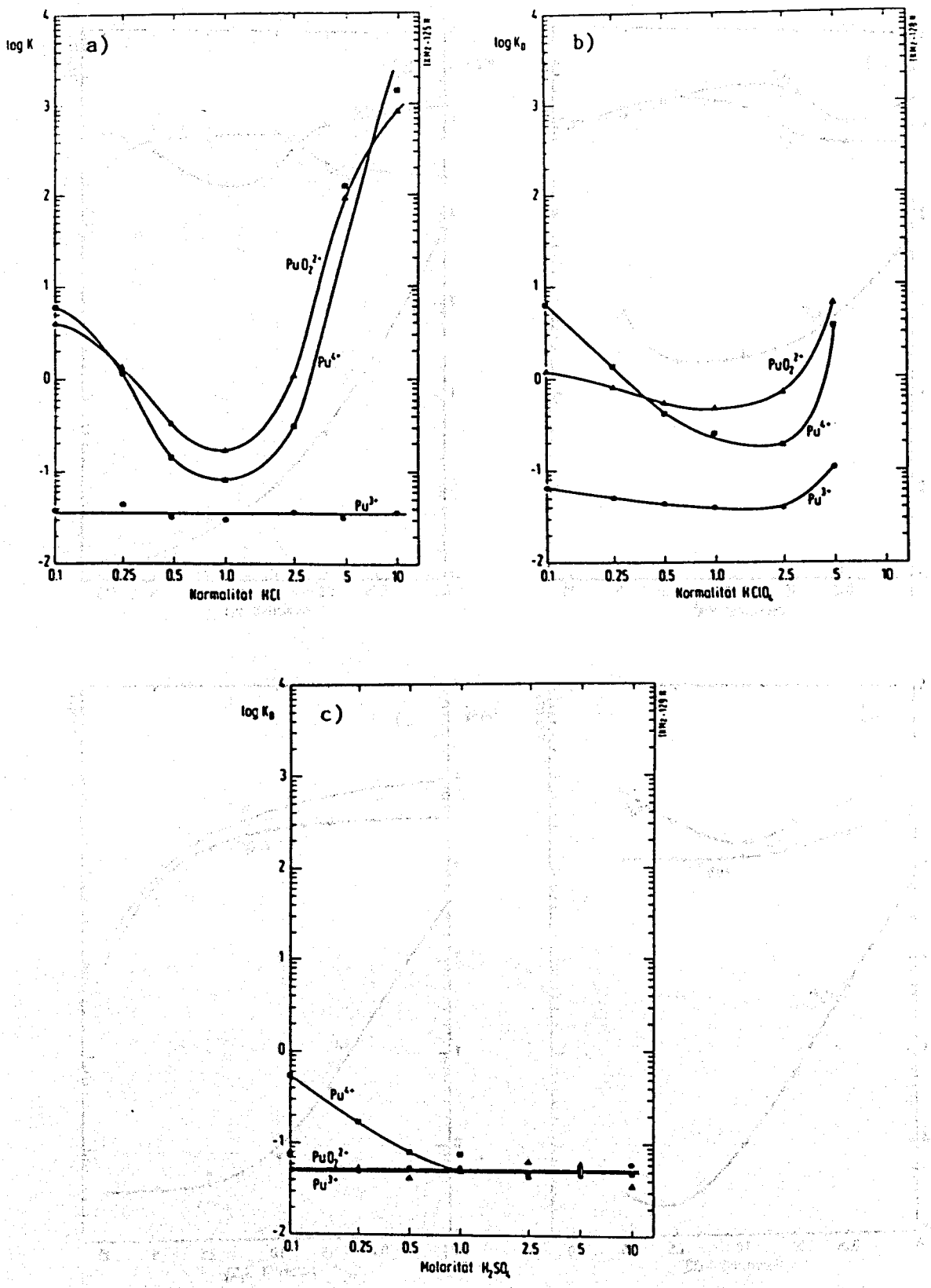


Figure 5. Distribution Coefficients for Pu^{3+}, Pu^{4+}, and PuO_2^{2+} in the System TBP/Acid. a) HCℓ, b) $HC\ell O_4$, c) H_2SO_4

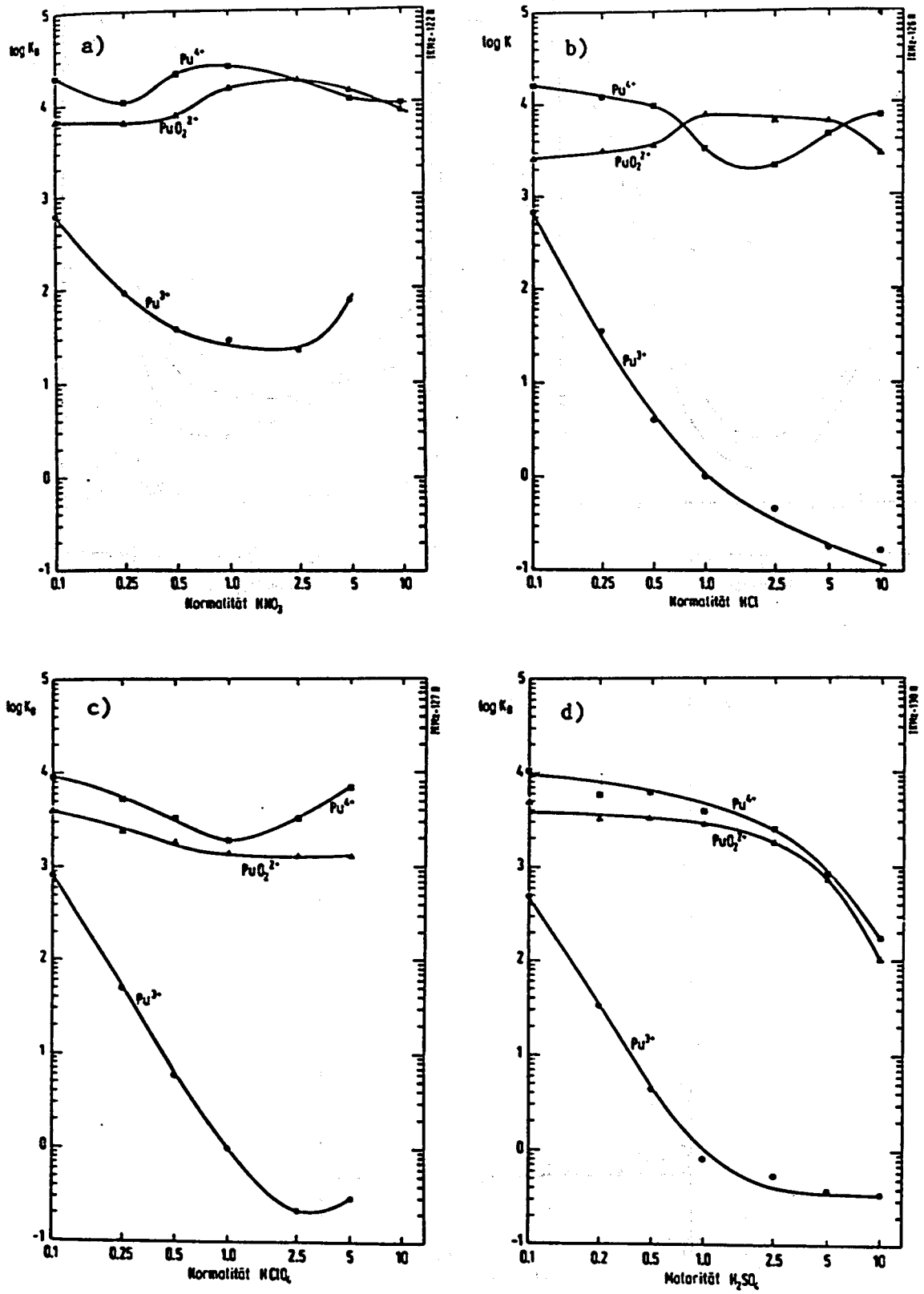


Figure 6. Distribution Coefficients for Pu^{3+}, Pu^{4+}, and PuO_2^{2+} in the System HDEHP/Mineral Acids. a) HNO_3, b) $HC\ell$, c) $HC\ell O_4$, and d) H_2SO_4

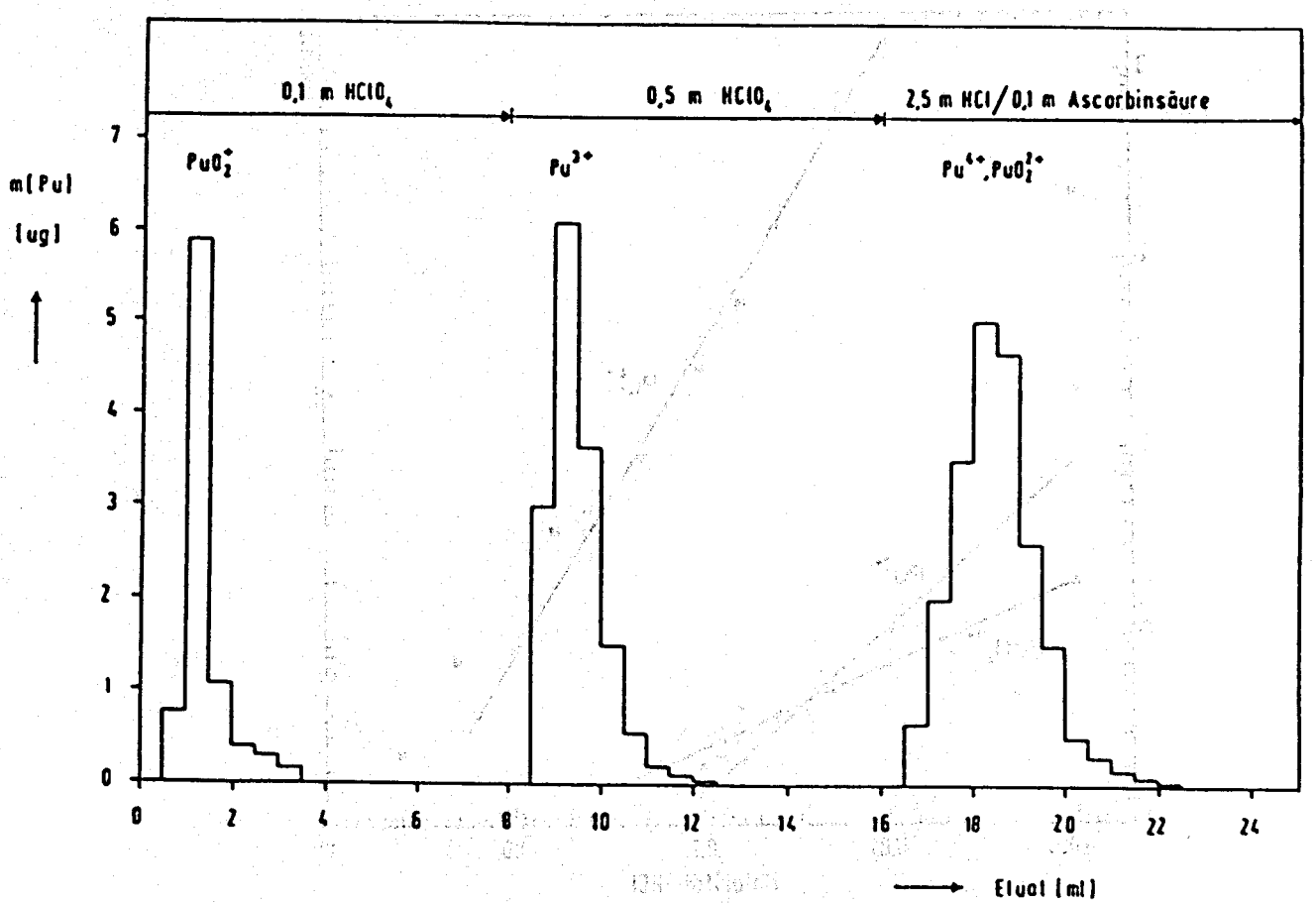


Figure 7. Elution Position of Pu^{3+}, Pu^{4+}, PuO_2^+, and PuO_2^{2+} for a HDEHP/Inert Support/Acid System.

Eluent: 0.1 M $HC\ell O_4$ (PuO_2^+), 0.5 M $HC\ell O_4$ (Pu^{3+}), 2.5 M $HC\ell$ + 0.1 M Asorbic Acid (Pu^{4+}, PuO_2^{2+})

Temperature: 22° C

Flow Rate: 0.20 mℓ/min

Column size: (100 x 4)mm

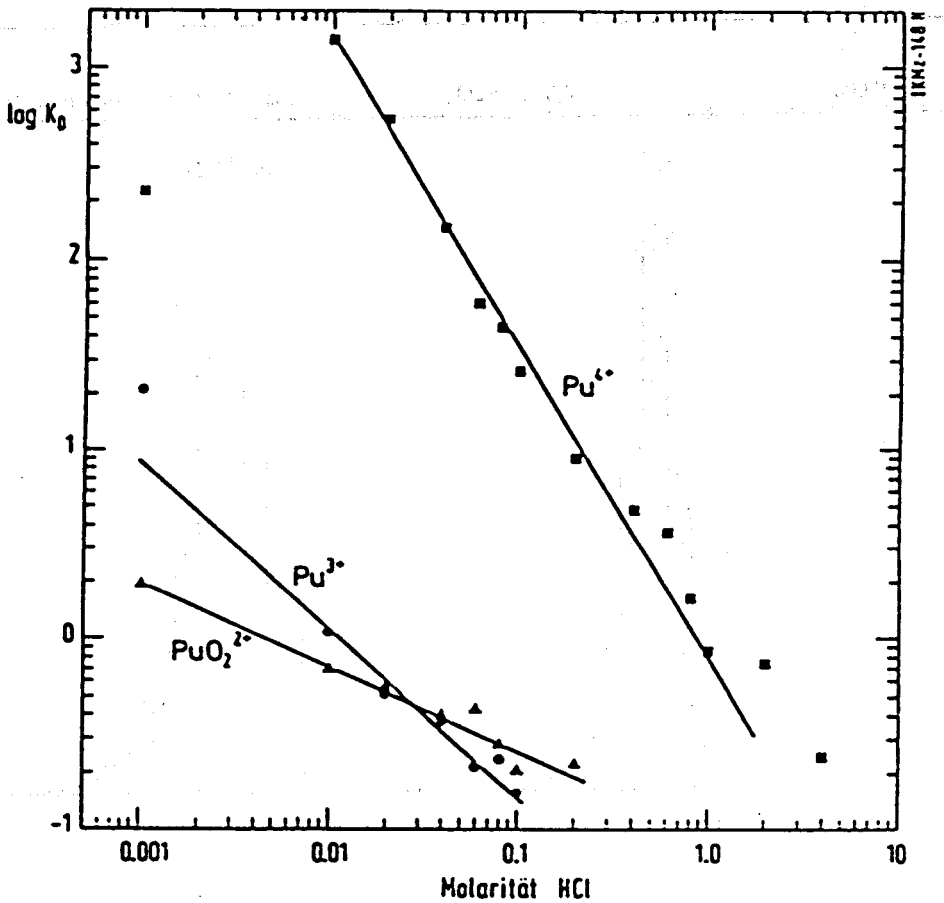


Figure 8. Distribution Coefficients for the Absorption of Pu^{3+}, Pu^{4+}, and PuO_2^{2+} on LiChroprep SI 60 as a Function of Hydrochloric Acid Concentration.

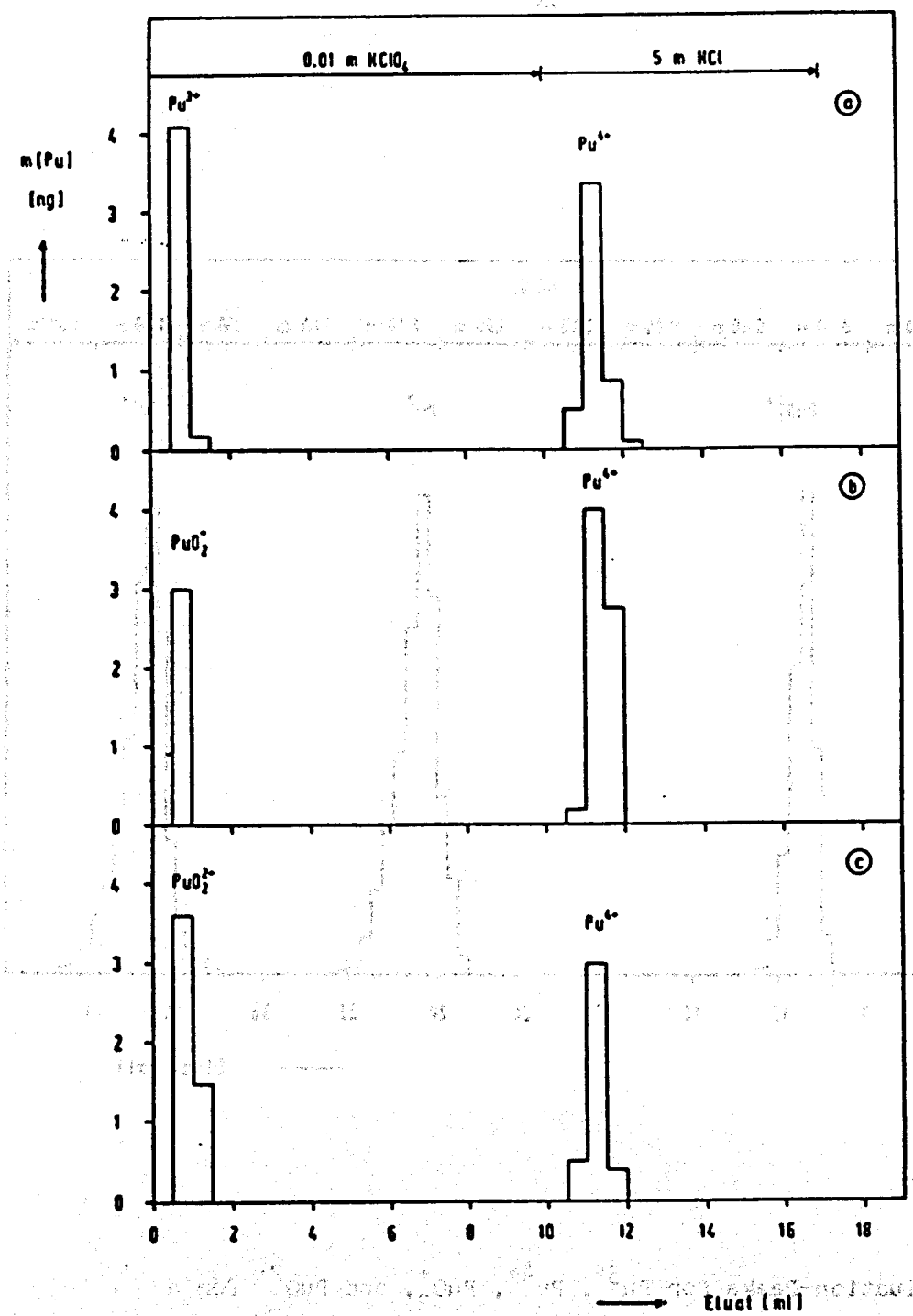


Figure 9. Separation of Various Plutonium Oxidation State Mixtures on a LiChropher SI 100 Column/Acid System

a) Pu^{3+}/Pu^{4+}; b) Pu^{4+}/PuO_2^{+}; c) Pu^{4+}/PuO_2^{2+}

Column Size: (100x4)mm

Flow Rate: 0.3 mℓ-min^{-1}-cm^{-2} (Sorption)

1.0 mℓ-min^{-1}-cm^{-2} (Desorption)

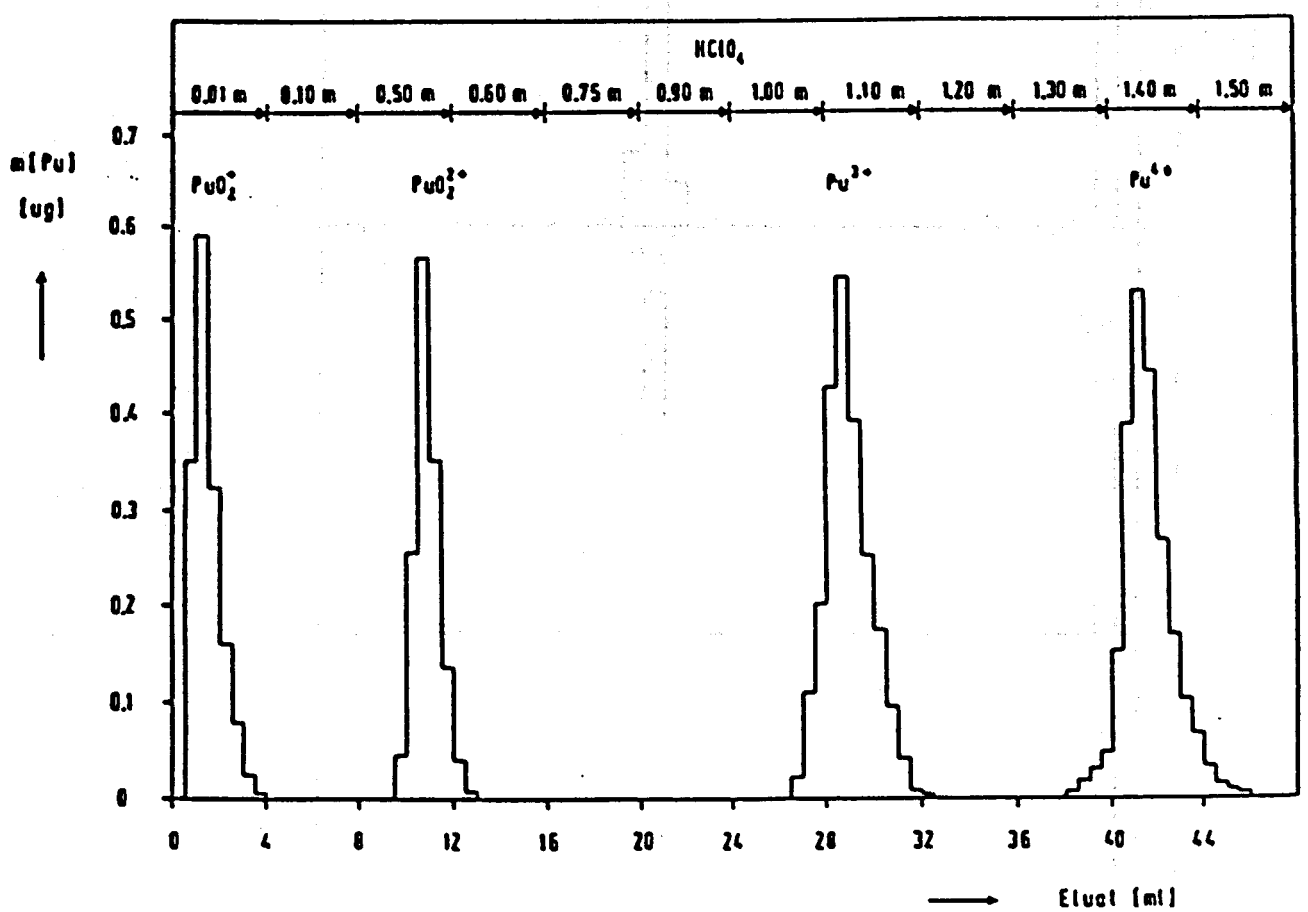


Figure 10. Eluation-Peaks for Pu^{3+}, Pu^{4+}, PuO_2^+, and PuO_2^{2+} for a (100x4)mm-cation exchange LiChrosorb/$HC\ell O_4$ system.

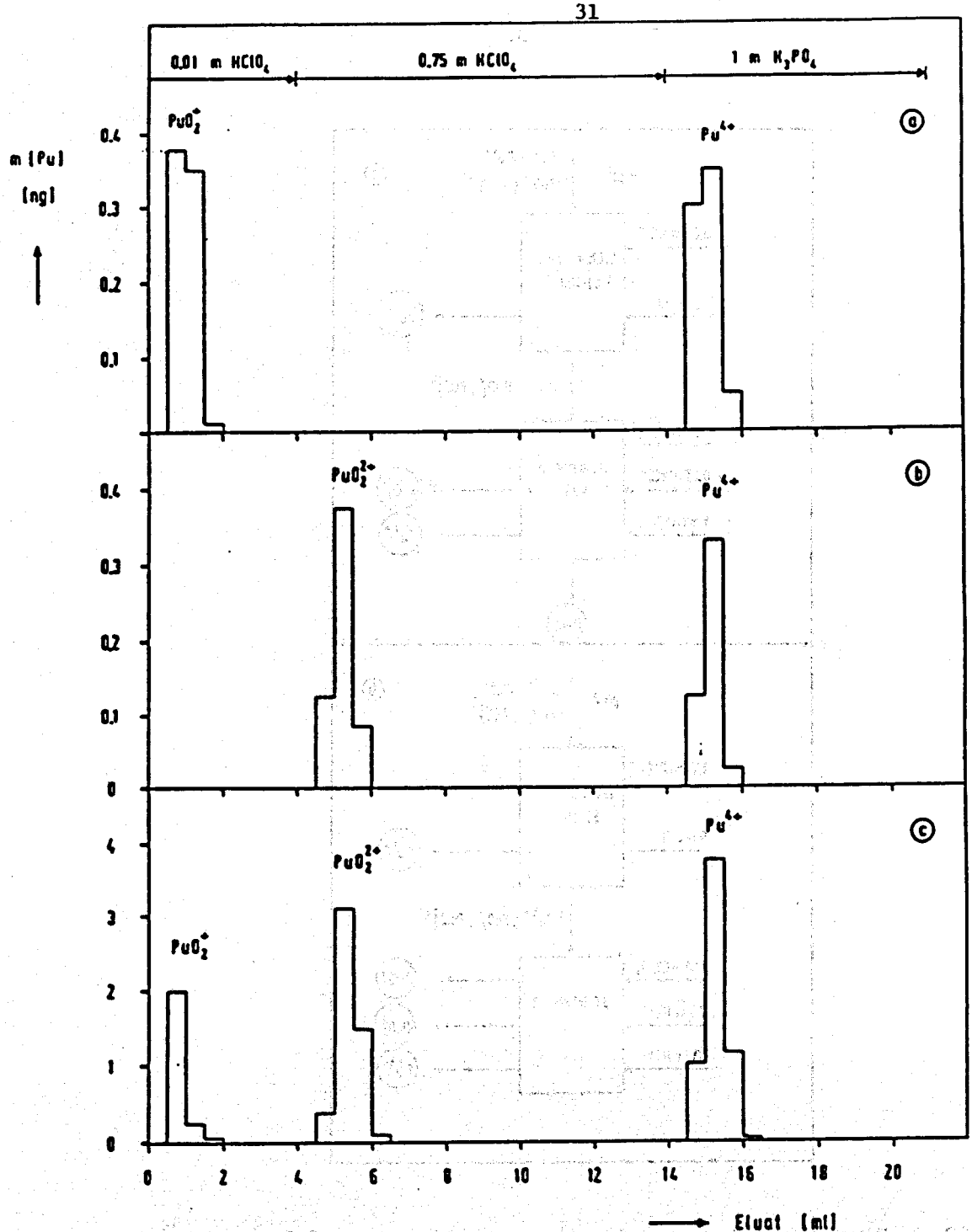


Figure 11. Separation of Various Plutonium Oxidation State Mixtures on a Sulfonated Cation-Ion Exchange Lichropher SI 100 Column/Acid Systems.

a) Pu^{4+}/PuO_2^+; b) Pu^{4+}/PuO_2^{2+}; c) $Pu^{4+}/PuO_2^+/PuO_2^{2+}$

Column Size: (100x4)mm

Flow Rate: 2.5 mℓ-min^{-1}-cm^{-2}

a,b) ~ 1.5 ng Pu; c) ~ 15 ng Pu

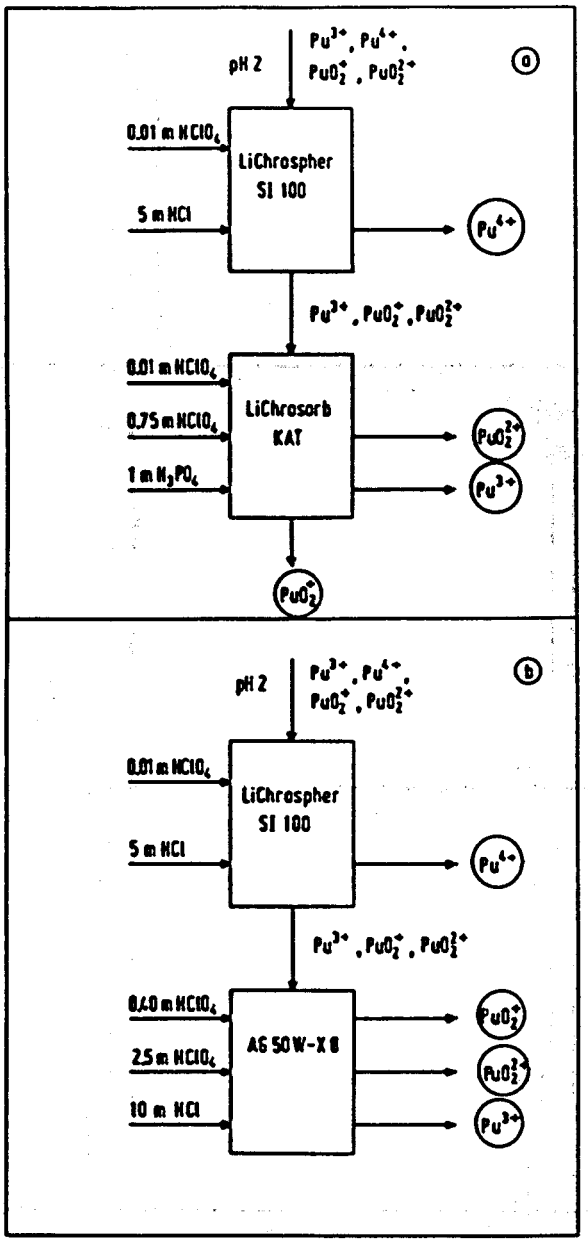


Figure 12. Flowsheet Diagrams for the Determination of Pu^{3+}, Pu^{4+}, PuO_2^+, and PuO_2^{2+} Oxidation State with Ion-Exchange Chromatography. a) Silica Gel (LiChrospher SI 100)/Acid + Sulfonated Silica Cation Ion-Exchange Material/Acid; b) Silica Gel (LiChrospher SI 100)/Acid + Dowex 50W-XB Cation Ion-Exchange Resin/Acid.

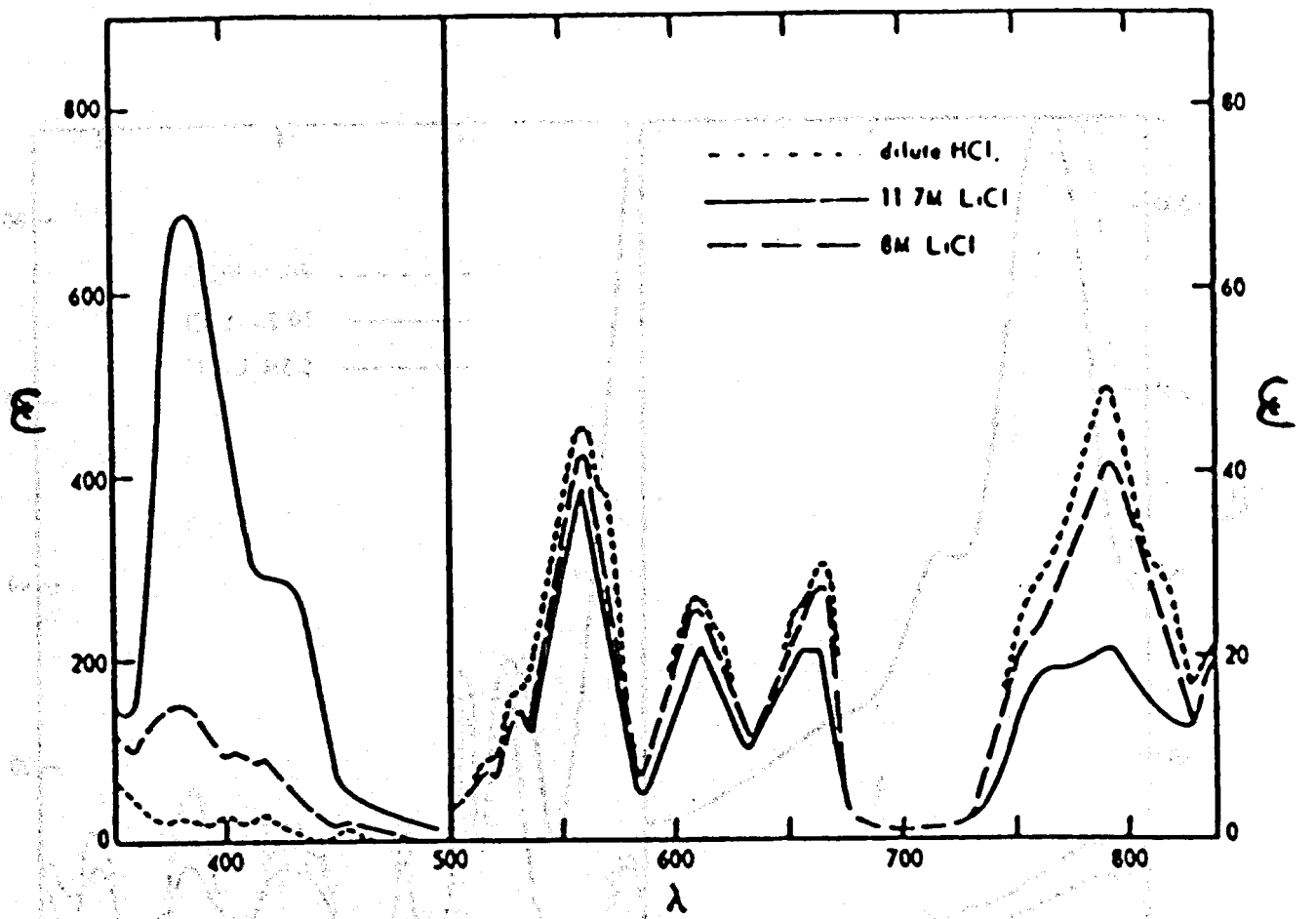


Figure 13. Absorption Spectrum of Neptunium(III) at Various Chloride Concentrations.

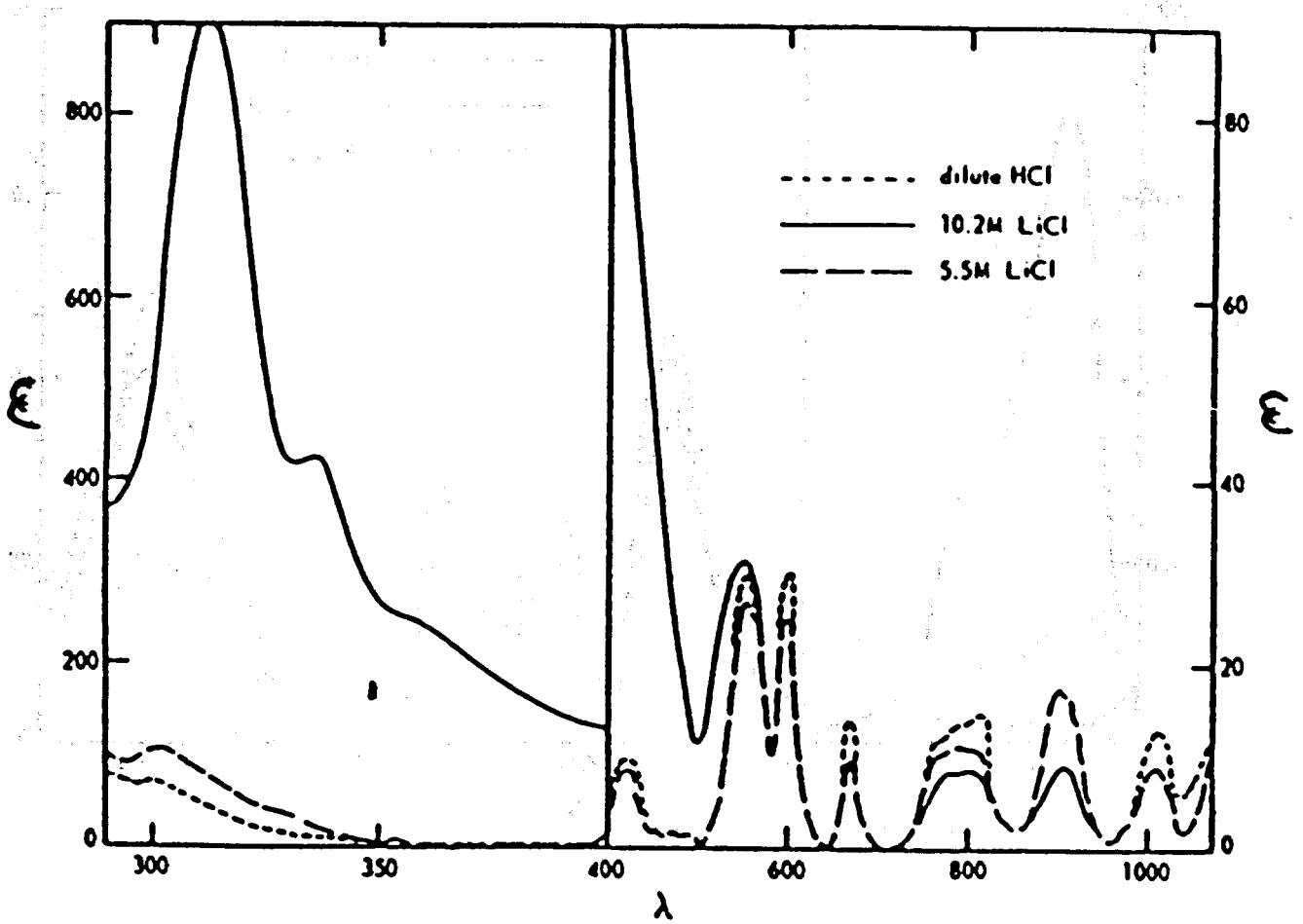


Figure 14. Absorption Spectrum of Plutonium(III) at Various Chloride Concentrations.

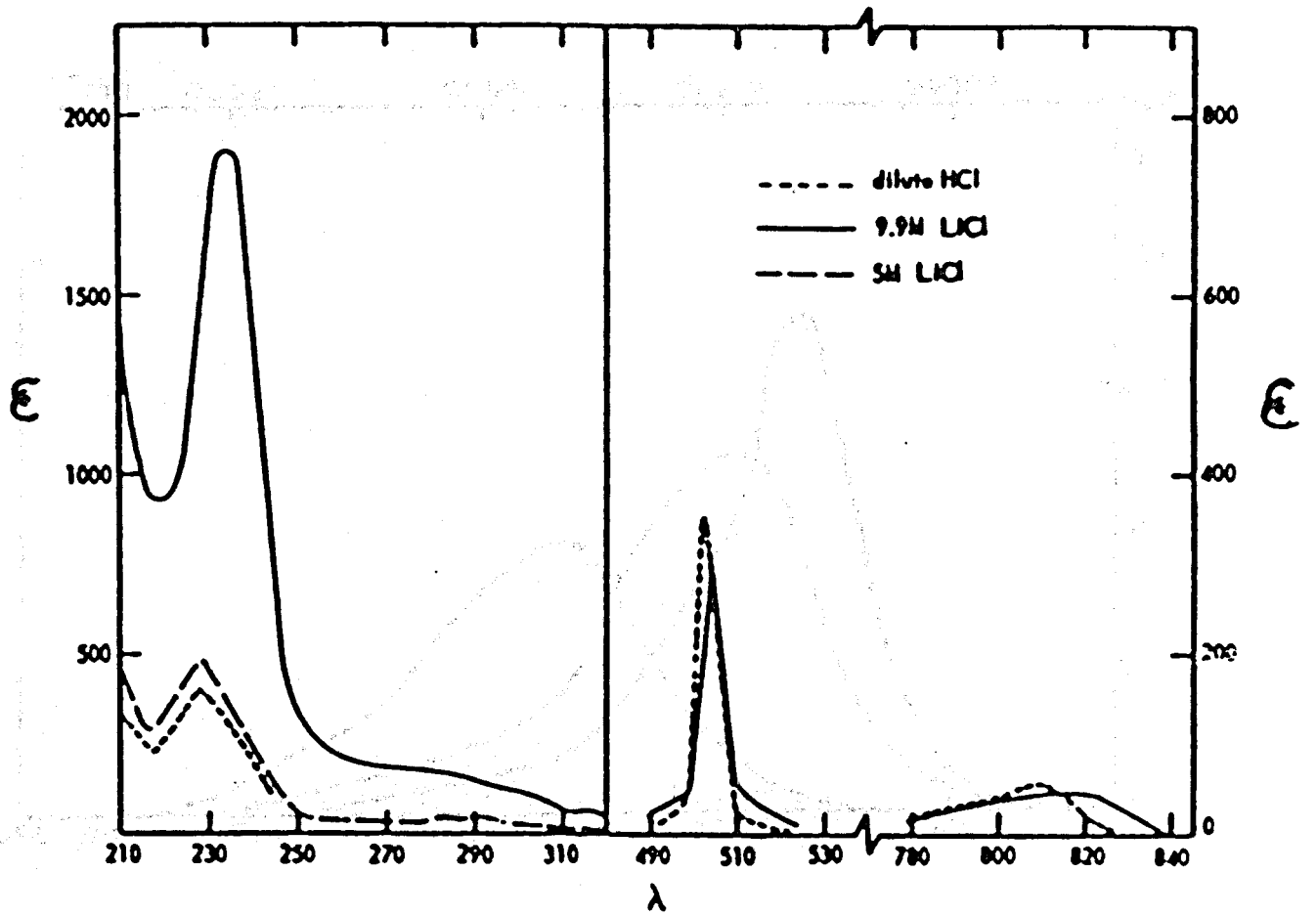


Figure 15. Absorption Spectrum of Americium(III) at Various Chloride Concentrations.

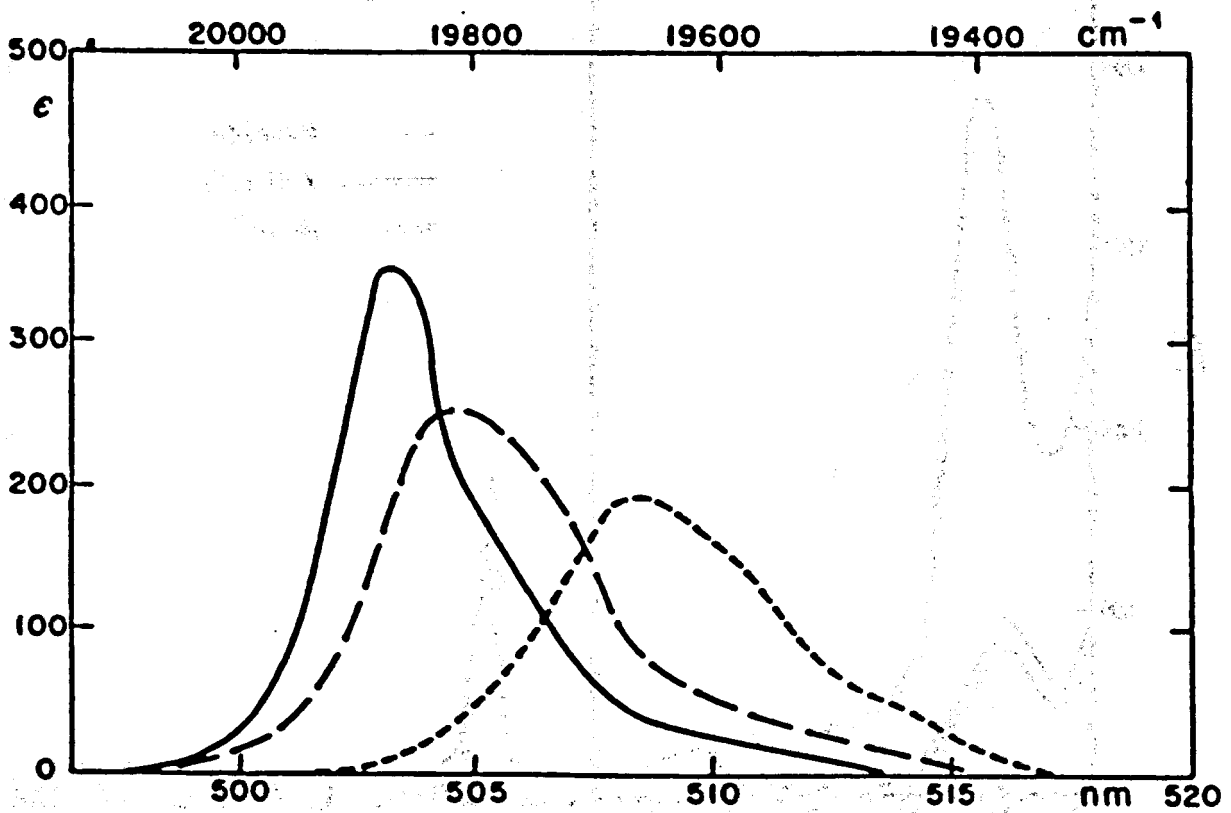


Figure 16. The 503 nm Band in the Americium(III) Spectrum:

——— 1 M $HC\ell O_4$, — — — 11.4 M Li Br,

- - - - - 6.0 M K_2CO_3 solutions. The Molar Absorbance ε in M^{-1} cm^{-1} of 0.6-2.0 mM Americium Solutions is Plotted Against the Wavelength.