12/8-4-95 JS ①

UCRL-ID-119254

An Expanded Porphyrin Approach Toward Transactinium Chelation and the Development of Porphyrin-Coated Optical Fibers as Potential Actinide Sensors

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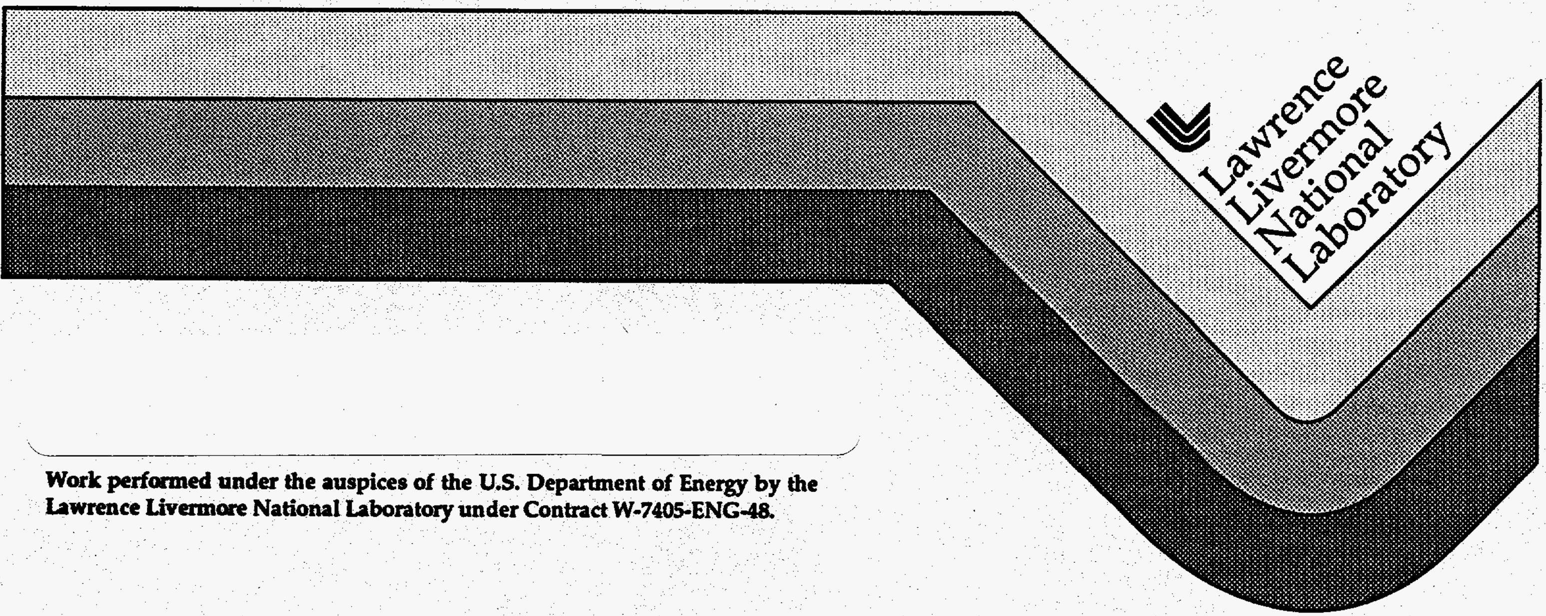
December 1994



Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-ENG-48.

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An Expanded Porphyrin Approach Toward Transactinium Chelation and the Development of Porphyrin-Coated Optical Fibers as Potential Actinide Sensors.

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Project funded by:
The Glenn T. Seaborg Institute for Transactinium Science
C & M S Directorate
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INTRODUCTION

Characterization of the contamination at DOE waste sites and facilities is necessary during environmental restoration. Characterization of toxic waste in containers and storage tanks is needed for effective waste management. Therefore, analytical and monitoring systems are needed for real-time analysis and feedback. During remediation activities, a lack of real-time analysis can lead to costly delays in operations involving people and equipment. Real-time analyses will enable uninterrupted equipment operation during restoration and avoid waiting for analytical results. In addition, groundwater monitoring may continue for many years at a very high cost if remote monitoring methods are not developed. During sampling or excavation into facilities, it is necessary to monitor the worker's environment continuously to ensure safety. On-site or in-situ chemical analysis can provide rapid screening and selection of samples while minimizing worker exposure. Short-term measurements will be required for site and waste characterization and long-term (months to years) measurements will be required for monitoring. The development of in-situ methods to measure chemical properties by specialized instrumentation capable of real-time analysis, without sacrificing sensitivity, has been identified as an area of needed development.

Absorption spectroscopy is widely used and considered to be one of the most reliable techniques available for the qualitative and quantitative determination of sample composition. With the advancements in fiber optic technology, using light for remote *in-situ* sensing of groundwater contaminants has become practical. Significant progress has been made in the area of fiber-optic chemical sensors as can be seen by the number of recent review articles.[1-5]

Porphyrin dyes are well known as highly sensitive indicators for the spectrophotometric determination of metal ions. The complexation rate at room temperature is relatively fast (time scale of minutes) and the resulting absorbance spectra of the complexes can be well distinguished and correlated to different metals. An opto-chemical sensor for the detection of heavy metals has been developed in which a porphyrin dye is electrostatically immobilized in a cation exchange membrane.[6-7] Two porphyrin dyes which have been used are meso-tetra(n-methyl-4-pyridyl) porphine (TMPyP) and meso-tetra(4-sulfonatophenyl) porphine dihydrochloride (TPPS). Due to its strong ion exchange properties, Nafion non-specifically extracts cations from the solution. A clear Plexiglas disc is a suitable substrate material for the thin (3 - 5 µm) ion-exchange membrane and allows for absorbance spectra to be obtained perpendicular to the surface. The measured absorbance has been shown to be proportional to the metal concentration and the time that the sensor resides in the solution. The sensor has shown excellent chemical and mechanical stability and can be used several times without any loss in sensitivity. Current limits of detection with this sensor are $5*10^{-8}$ M (6 ppb) Cd^{2+} and $2*10^{-7}$M (40 ppb) Hg^{2+}, other ions such as Zn^{2+} and Cu^{2+} have been quantitatively detected.

A long pathlength fiber-optic evanescent field absorption sensor has been developed and characterized[8-12] for the detection of volatile organic compounds in solution. Using this technology with the heavy metal sensor described above should provide a system that is more sensitive due to the longer pathlength. Optical fibers transmit light based on total internal reflection, which occurs when the angle of incident light is greater than the critical angle, θ_c, given by $\sin\theta_c = n_2/n_1$, where core refractive index (RI), n_1, must be greater than the cladding RI, n_2. As light propagates down the length of an optical fiber, standing waves are setup at each reflection of the core/cladding interface. A portion of the light wave, known as the evanescent field (or wave), penetrates into the cladding material to a depth given by d_p.

$$d_p = \frac{\lambda}{(2n_1\pi)\left(\sin^2\theta - \left(\frac{n_2}{n_1}\right)^2\right)^{0.5}}$$

where θ is the angle of incidence and λ is the wavelength in free space. The penetration depth of the evanescent wave is typically on the order of the wavelength, depending on the characteristics of the fiber. In the wavelength range of interest (400 - 700 nm), where the porphyrin dyes show characteristic shifts, each reflection will penetrate a depth of approximately 0.5 μm. The number of reflections in a fiber is given by $N_r = l/d * \cot\theta$. Changing the fiber sensor length, l, or the fiber diameter, d, will allow for the number of reflections to be increased, thus increasing the pathlength.

One of the limitations of the heavy metal sensor discussed above, is the limited path length of only pass through the thin membrane (3-5 μm). The effective pathlength can be increased by incorporating the evanescent wave design and increasing the number the reflections. For this study, we propose using an optical fiber coated with an ion-exchange membrane into which a porphyrin dye has been immobilized. Increasing the pathlength will increase the light/analyte interaction and therefore should lead to lower limits of detection.

PROPOSED WORK

The object of this proposed work is to develop a remote sensor for real-time measurement of actinide species and concentrations in environmental waters or process streams based on absorption spectroscopy using internal reflection spectroscopy. The work to be performed under this study was broken down into the following subtasks, with completion dates appearing in parentheses assuming a March 1, 1993 start-up.:

1) Measurement of the spectra of Nd(III), a stand-in for trivalent actinides, Pu(IV), Np(V), and U(VI) complexes with TPPS and TMPyP in aqueous solutions by standard absorption spectroscopy, determine Beer's law curves and investigate reversibility of reactions. (May 1, 1993)

2) Prepare porphyrin coated silica wafers and determine the ability of the wafers to concentrate actinides, i.e. the sensitivity and selectivity using standard absorption spectroscopy. (June 1, 1993)

3) Prepare porphyrin coatings on silica cores of optical fibers and fabricate sensor coils. (July 15, 1993)

4) Test the coated optical fiber coils to concentrate and detect actinides by internal reflection spectroscopy. (September 15, 1993)

RESULTS AND DISCUSSION

The results of the experiments performed and progress of each subtask toward producing a remote actinide sensor are presented below:

Subtask 1:

Metalloporphyrin complexes have characteristic absorption spectra from excited states of (π-π*), (d-d), (π-d)CT, and (d-π*)CT, which allow them to be distinguished from other complexes.[13] The metal ion incorporates into the inner cavity of the porphyrin molecule which has a radius of approximately 2.0 Å. Metal ions which have been previously studied in this laboratory, Cd^{2+}, Cu^{2+}, Zn^{2+}, Hg^{2+} have radii which allow them to be incorporated into the porphyrin binding cavity. Based on ionic radii, the ions which have been proposed for study with system should also fit into the porphyrin cavity (see Table I).

Instrumentation: A single beam fiber optic spectrometer, Guided Wave Model 200, was used to obtain all of the spectra. Vis/NIR optical fibers (JC4, Guided Wave Inc., El Dorado Hills, CA) offered sufficient transmission over the wavelength of interest, 400-700 nm. A 1200 line/mm holographic grating was used to disperse the light onto a silicone photodiode detector. Solution spectra were obtained in a 1 cm pathlength cuvette.

Reagents: Stock solutions of 10^{-3} M meso-tetra(n-methyl-4-pyridyl) porphine (TMPyP) were prepared from the tetratosylate salt (Porphyrin Products Inc., Logan UT) or the tetraiodo salt (Alpha Products). A 10^{-3} M stock solution of meso-tetra(4-sulfonatophenyl) porphine dihydrochloride (TPPS) (Porphyrin Products Inc., Logan UT) was also prepared. Separate stock solutions of 10^{-2} M Nd^{3+} in 1.0 M HCl and 2.5 mM $^{238}U^{6+}$ in 0.2 M $HClO_4$ were also prepared. Solution pHs were measured with a pH meter (Orion Research, Model 701A) which was calibrated against buffer solutions of pH 4.0 and 7.0 immediately before each measurement.

TABLE I

Ionic Radii (Å)[a]

Ion	CN 4	CN 6	CN 8
Nd^{3+}		0.983	1.109
Pu^{3+}		1.00	
Pu^{4+}		0.86	0.96
Pu^{5+}		0.74	
Pu^{6+}		0.71	
U^{5+}		0.76	
U^{6+}		0.73	0.86
Np^{4+}		0.87	0.98
Np^{5+}		0.75	
Np^{6+}		0.72	
Cd^{2+}	0.92	1.09	1.24
Hg^{2+}	1.10	1.16	1.28
Cu^{2+}	0.71	0.87	
Zn^{2+}	0.74	0.88	1.04

[a] taken from refs. 14 and 15.

Nd/TMPyP and Nd/TPPS study

From the stock solutions, a solution of 10^{-3} M Nd^{3+} and 10^{-5} M TMPyP was prepared and the resulting absorbance spectrum is presented in Figure 1. In aqueous solution, the location of the large Soret band of TMPyP is at approximately 430 nm and is red-shifted to 460 nm under acidic conditions. Due to the acidity of the Nd/TMPyP solution (pH = 2.9), the absorption spectrum appears to be a combination of the protonated and deprotonated porphyrin spectra (Figure 1 top). Shifts in the Soret band are not specific to the complexation of the porphyrin. Metallo-porphyrin complexation can be identified by shifts in the Q-bands which appear in the 500-700 nm range. The Q-bands also show no characteristic shift in the spectrum due to complexation with the Nd^{3+} and only appears to be a change in the protonation of the dye (Figure 1 bottom). Due to the protonation of the porphyrin dye, the Nd^{3+} is unable to overcome this complexation and no Nd/TMPyP complex is formed. As the pH was increased from 2.90 to 9.26 with a Tris buffer solution, no characteristic shift in the Q bands due to metal complexation was observed. Thus, even after TMPyP was deprotonated, metalloporphyrin complex does not form in solution.

Similar results were obtained using the porphyrin TPPS, as seen in Figure 3. Shifts in the Soret bands are observed due to protonation of the dye which are not distinguishable from the shift with Nd in solution. Protonation of TPPS also shifts the absorption band at 650 nm to 700 nm. The Nd/TPPS is also shifted approximately 700 nm, however, it does not exactly overlap with the acidified dye. This is most likely due to a different degree of protonation of the dye, although the possibility of complex formation should be investigated further.

U/TMPyP study

A solution containing (0.0298mg/ml) UO_2^{2+} and 10^{-5} M TMPyP was prepared from the stock solutions and a red precipitate formed. Under acidic conditions the dye does not usually form a precipitate, suggesting that a complex with UO_2^{2+} may be formed with the dye. The precipitate has not been analyzed. A solution containing $2.98*10^{-3}$ mg/ml UO_2^{2+} and 10^{-5} M TMPyP, was prepared from stock and no ppt. was observed. However, no characteristic shift in the absorption bands due to complexation was observed (see Figure 4). There was also no complexation observed as the pH was increased with the addition of a tris buffer solution (see Figure 5).

Subtask 2:

A standard procedure for coating a Plexiglas disc with a thin film of Nafion was used. The surface of the Plexiglas disc was twice cleaned with methanol and spun dry. A 150 μL drop of Nafion which was 5% by wt. in a mixture of lower aliphatic alcohols (Aldrich) was then placed on the surface for 15 seconds and the excess spun off. This procedures yields a Nafion layer that is approximately 3-5 μm thick. The coated disc was then allowed to soak in a 10^{-5} M solution of TMPyP for several days, after which the sensor is ready for use.

With the dye immobilized onto the ion exchange membrane the sensor was tested in Nd^{3+} solutions. The strong cation-exchange properties did not force the Nd^{3+} into complexation with dye.

Subtask 3:

The minimum length of a 400 μm core fiber required to obtained an equivalent pathlength to the 3-5 μm thickness of the Nafion membrane on the Plexiglas, is approximately 10 cm. The protective nylon jackets of the fused silica fibers were removed with hot (160 °C) propylene glycol. The polysiloxane cladding material was removed from the quartz glass core with concentrated sulfuric acid. The bare quartz fiber was then dipped into the Nafion solution and allowed to air dry. The thickness of the dip coated Nafion was not measured, but is estimated to be 6-10 μm based on other dip coating results. Once coated, the fiber was immersed in a 10^{-5} M TMPyP solution for several days. The dye was immobilized to the Nafion and not to the exposed areas of the quartz. In order to obtain a transmission spectrum of the fiber sensor, a special fiber holder assembly needs to be constructed. Several were attempted, however, none worked satisfactorily. The Nafion membrane offers little or no protection for the glass fiber which was found to be too fragile!!! for a practical sensor.

Subtask 4:

Due to the results obtained in the previous subtasks, no work was performed on this task.

SUGGESTIONS FOR FUTURE STUDIES

Complexing Agents

Lanthanide porphyrin complexes have been synthesized, however, they do not usually form readily in solution. Although changing the reaction conditions may force the metals into the porphyrin cavity, this cannot be carried out *in-situ* in the field. Recent work on the development of "expanded porphyrin" molecules indicate that complexation with lanthanides and actinides can be achieved in solution due to the enlarged binding cavity.[16,17] Currently, the "expanded porphyrin" which have been developed are not water soluble, although research is being directed in this area. The proposed work of Mody and Torres[18] may produce expanded porphyrins which would be water soluble and can be immoblilized on an ion-exchange membrane.

Complexation agents are not limited to porphyrin molecules. Other dyes have been used for the analysis of transition metals, such as, phenylazoformic acid 2-phenylhydrazide with 1,5-diphenyl-carbazide (PAPDC) [19] or Zincon tetraoctylammonium ion pair [20] and catechols. Unlike porphyrins, these molecules have an open structure which may allow them to complex more readily to the lanthanides and actinides.

Membranes

In addition to different complexing agents, future studies should investigate the possibilities of different membranes. Nafion is a strong ion-exchanger which non-specifically extracts cations out of solution which results in numerous interferences . Sol-gel glasses have received a lot of attention in the literature and have recently been demonstrated to be a suitable membrane for an optochemical sensor.[21]

Optical Fibers

Another direction which should be considered in the future of this project should be to investigate different optical fibers. As was mentioned above, bare quartz glass fibers are much too fragile to be used in a practical setting. Plastic fibers made from polymethylmethacrylate (PMMA) are commercially available, have good light transmission in the visible and are much more flexible than glass fibers. Rubber fibers made from polydimethylsiloxane (PDMS) are not commercially available but will offer greater flexibility without sacrificing light transmission. Increasing the light intensity in the evanescent wave can be achieved by putting a bend in the fiber. Thus, more flexible fibers will not only be more rugged but should also have a greater effective pathlength.

CONCLUSIONS

Developing a fiber optic sensor for the actinides is a realistic goal [22] which should be pursued. Due to the limited time of the project, only cursory studies could be performed. Trends in actinide chemistry and fiber optic sensors will allow for such a sensor to be produced in the near future. Overcoming matrix problems that are encountered in real world samples will be the next challenge to be faced in developing a remote *in-situ* actinide sensor.

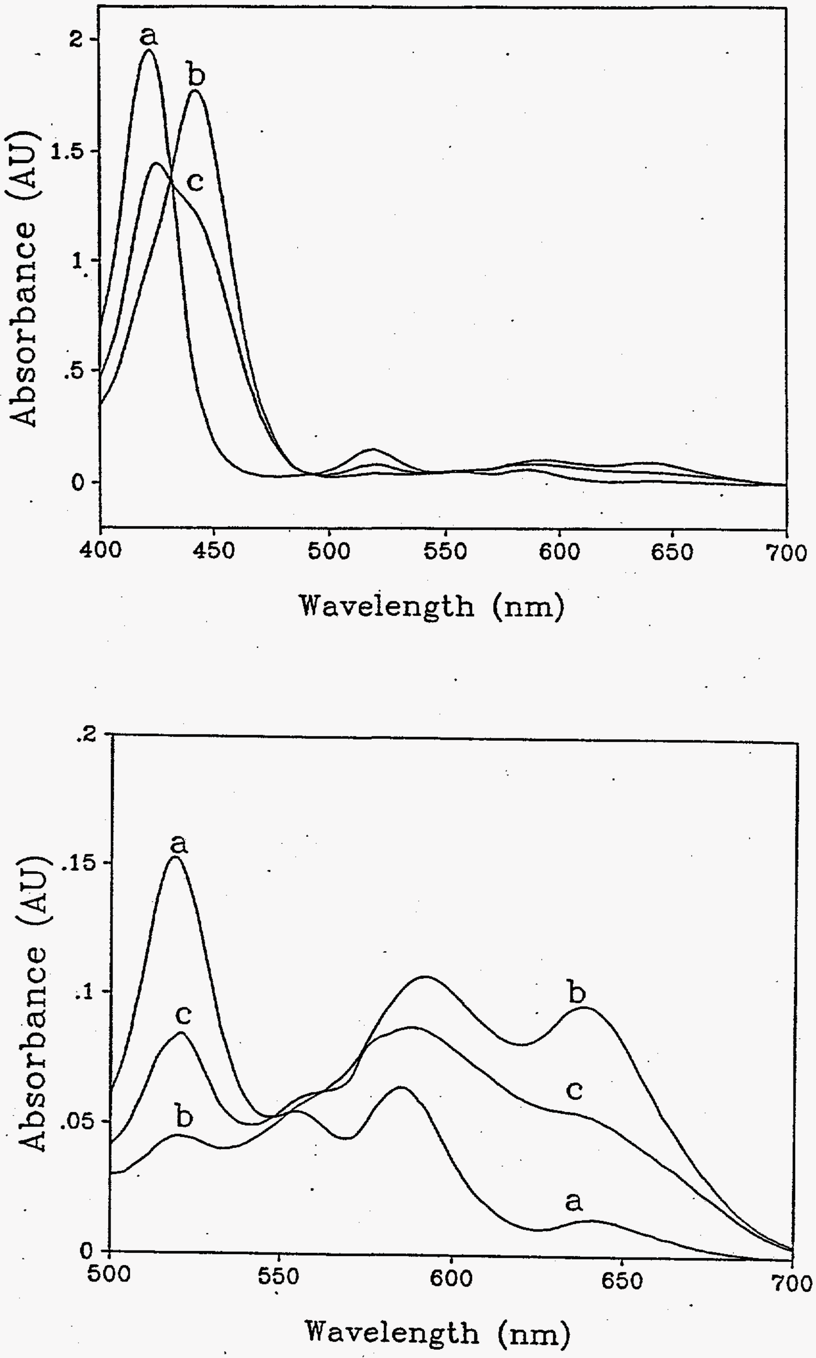

Figure 1. Spectra show the shift in the Soret bands (top) and the Q-bands (bottom, same spectra expanded for clarity). a) deprotonated 10^{-5} M TMPyP in aqueous solution, b) protonated 10^{-5} M TMPyP in acidic solution, c) 10^{-3} M Nd^{3+}, 10^{-5} M TMPyP in 0.1 M HCl.

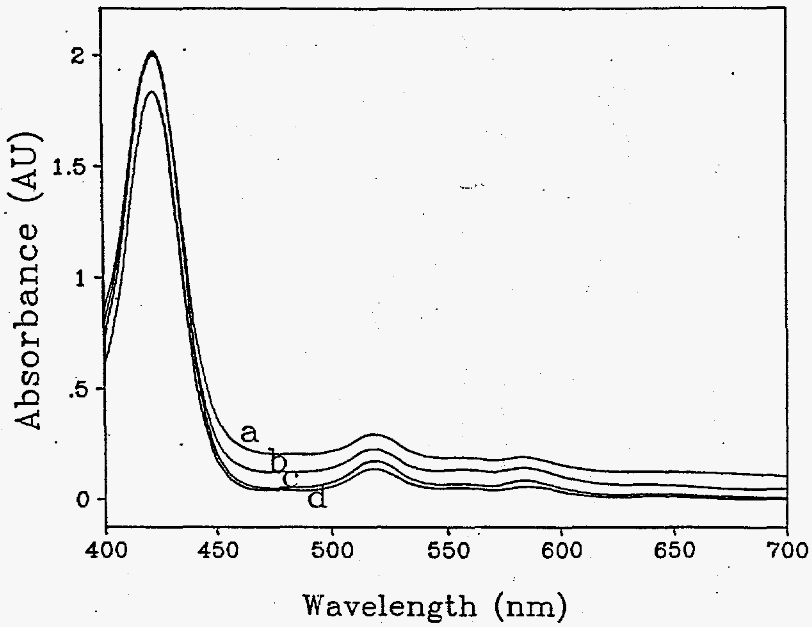

Figure 2. a) Nd/TMPyP pH = 9.13, b) Nd/TMPyP pH = 9.26, c) Nd/TMPyP pH = 9.09, d) TMPyP pH = 9.16.

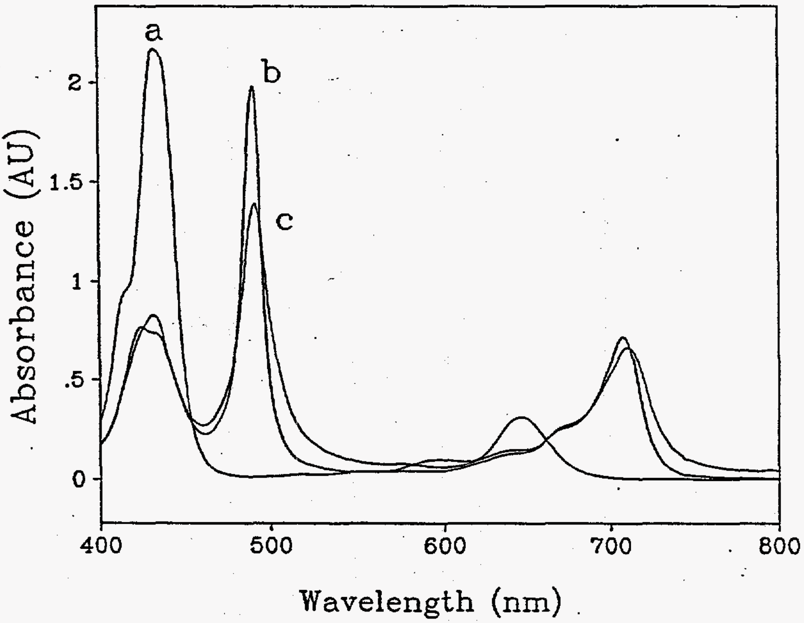

Figure 3. Nd/TPPS spectra a) deprotonated 10^{-5} M TPPS in aqueous solution, b) protonated 10^{-5} M TPPS in acidic solution, c) 10^{-3} M Nd^{3+} and 10^{-5} M TPPS in 0.1 M HCl.

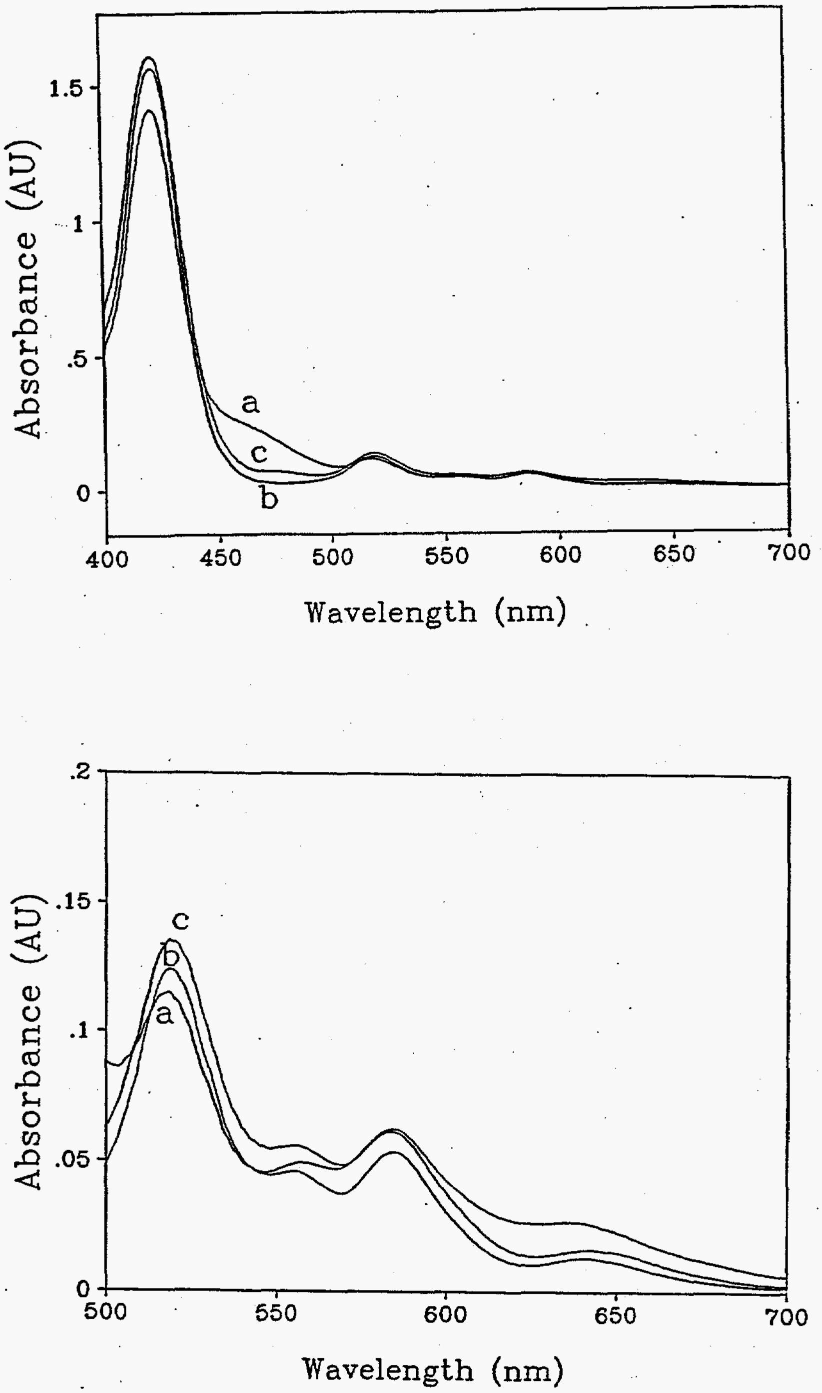

Figure 4. Spectra show the shift in the Soret bands (top) and the Q-bands (bottom, same spectra expanded for clarity) a) deprotonated 10^{-5} M TMPyP in aqueous solution, b) protonated 10^{-5} M TMPyP in acidic solution, c) 10^{-4} M UO_2^{2+} 10^{-5} M TMPyP in 0.1 M HCl.

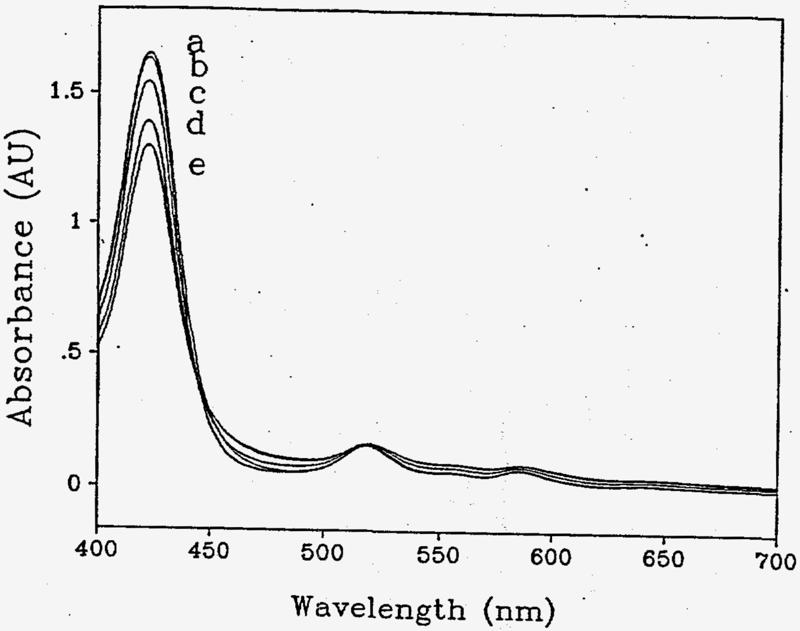

Figure 5. 10^{-4} M UO_2^{2+} and 10^{-5} M TMPyP adjusted with a tris buffer to the following pHs a) 2.75, b) 4.0, c) 6.2, d) 7.5, e) 8.05.

REFERENCES

1. R.A. Lieberman, "Recent progress in intrinsic fiber-optic chemical sensing II", *Sens. and Act. B*, **11**, 43-55, 1993.
2. R.A. Lieberman,"Recent progress in intrinsic fiber-optic chemical sensing", *Chemical, Biochemical, and Environmental Fiber Sensors II*, **1368**, 15-24, 1990.
3. M.A. Arnold,"Fiber-optic chemical sensors", *Anal. Chem.*, **64**, 1015A-1025A, 1992.
4. O.S. Wolfbeis, Fiber Optic Chemical Sensors and Biosensors, CRC Press, Boca Raton 1991.
5. W.R. Seitz,"Chemical sensors based on immobilized indicators and fiber optics", *CRC Crit. Rev. Anal. Chem.*, **19**, 135-173, 1988.
6. R. Czolk, J. Reichert, and H.-J. Ache, "An optical sensor for the detection of heavy metal ions", *Sensors and Actuators A*, **25-27**, 439 -441, 1991.
7. R. Czolk, J. Reichert, and H.-J. Ache, "Sensitive spectrophotometric determination of cadmium with tetra(p-sulfophenyl) porphyrin (TPPS)," *Sensors and Actuators B*, **7**, 540, 1992.
8. M.D. DeGrandpre and L.W. Burgess, *Anal. Chem.*, **60**, 2582-2586, 1988.
9. M.D. DeGrandpre and L.W. Burgess,"A fiber-optic FT-NIR evanescent field absorbance sensor", *Appl. Spectrosc.*, **44**, 273-279, 1990.
10. J. Bürck, J.-P. Conzen and H.-J. Ache,"A fiber-optic evanescent field absorption sensor for monitoring organic contaminants in water", *Fres. J. Anal. Chem.*, **342**, 394-400, 1992.
11. J.-P. Conzen, J. Bürck and H.-J. Ache, "Characterization of a fiber-optic evanescent wave absorbance sensor for nonpolar organic compounds", *Appl. Spectrosc.*, **47,** 753-763, 1993.
12. G.L. Klunder, J. Bürck, H.-J. Ache, R.J. Silva, R.E. Russo, "Temperature effects on an evanescent field absorption sensor", submitted to *Appl. Spectrosc.*
13. S. Cotton, Lanthanides & Actinides, Oxford University Press, New York, 1991.
14. J.E. Huheey, Inorganic Chemistry: Principles of Structure and Reactivity, 2nd Ed., Harper and Row, New York, 1978.
15. K. Kalyanasundaram, Photochemistry of Polypyridine and Porphyrin Complexes, Academic Press, London, 1992.
16. J. L. Sessler and A.K. Burrell, *Top. Curr. Chem.* **161**, 177-273, 1991.

17. J.L. Sessler, T. Murai, G. Hemmi, "A water-stable Gadolinium (III) complex derived from a new pentadentate "expanded porphyrin" ligand", *Inorg. Chem.*, **28**, 3390-3393, 1989.
18. T.D. Mody and R.A. Torres, "An Expanded Porphyrin Approach Towards Transactinium Chelation", Research Proposal submitted to The Glenn T. Seaborg Institute for Transactinium Science.
19. K.J. Ewing, T.G. Bilodeau, J. Jaganathan, G.M. Nau, I.D. Aggarwal, and G.E. Robitaille, "Detection of trace levels of mercury in aqueous systems via a fiber optic probe", *Chemical, Biochemical, and Environmental Fiber Sensors V*, September, 1993, Boston, MA, #2068-38.
20. I. Oehme, B. Prokes, I. Klimant, T. Werner, and O.S. Wolfbeis, "Optical sensor for copper(II) ion", *Chemical, Biochemical, and Environmental Fiber Sensors V*, September, 1993, Boston, MA, #2068-44.
21. S.C. Kraus, R. Czolk, J. Reichert, and H.J. Ache, "Optimization of the sol-gel process for the development of optochemical sensors", *Sens. and Act. B*, **15-16**, 199-202, 1993.
22. T.Hirschfeld, T. Deaton, F. Milanovich, and S. Klainer, "Feasibility of using fiber optics for monitoring groundwater contaminants", *Opt. Eng.*, **22**, 527-531, 1983.