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Uranium and Lanthanide Speciation by Thermal Lensing Spectrophotometry*

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Groundwater systems act as an efficient vector for the transport of many metal ions. The transport is influenced by the solubility of sparingly soluble solid phases, by the sorption on mineral surfaces and on colloidal material, but also by the speciation of the soluble metal complexes. Accurate predictions regarding any of these processes require information on the physicochemical factors controlling solution equilibria relations.

Complex computer models are often used to estimate the impact of toxic metals on the environment, e.g., leaching of heavy metals from waste dumps or radionuclides from nuclear waste repositories. There are, however, very few experimental methods that can be used for a direct determination of the speciation at the very low concentrations usually encountered in nature. The purpose of this study is to evaluate the suitability of Thermal Lensing Spectrophotometry (TLS) for the identification of dissolved chemical species [1]. Examples of the application are given for the conversion of neodymium and hexavalent uranium free ions to complete complexation in carbonate solutions.

Experimental

The details of the experimental set-up for TLS studies have been described previously [2, 3]. A dye laser (8 cuvettes configuration) consisting of an oscillator cavity and an amplifier was pumped by an excimer laser operated at the XeCl emission of 308 nm with a power of 130 mJ/pulse. The dyes used to cover the wavelength range of interest are mentioned in the text with their trade names. A He–Ne laser (632 nm) was used as a probe beam. The intensity at the beam centre was measured after an optical path of about 3 m.

The carbonate concentration in the U(VI) solutions was varied by adding $NaHCO_3$ and by bubbling nitrogen at constant partial pressure of CO_2. The ionic strength of the solutions was buffered at 0.5 M with $NaClO_4$. The CO_3^{2-} concentrations were calculated from the known dissociation constants of carbonic acid and the pH measurements.

Results and Discussion

When a medium is irradiated with a laser tuned to an absorption band, a temperature rise occurs with a usually negative change in the refractive index [4, 5]. The diverging lens formed in the solvent affects the propagation path of the laser beam leading to a change of the spot size measured in the far field. The relative change of intensity of the laser radiation at the beam centre is monitored throughout a pinhole with a photodiode and is recorded as the Thermal Lensing Signal according to

$$\frac{I_{(0)} - I_{(\infty)}}{I_{(\infty)}} = -\frac{2.3P(\mathrm{d}n/\mathrm{d}T)}{\lambda k}A \qquad (1)$$

where $I_{(0)}$ and $I_{(\infty)}$ are the beam intensities in the absence and in the presence, respectively, of the thermal lens; n is the refractive index; T the temperature (K); P the laser power (W); λ the wavelength (cm); k the thermal conductivity (W cm^{-1} K^{-1}); and A the sample absorbance.

This equation has a general validity in spectrophotometry. However, the development of the thermal lens benefits from the larger light flux of laser excitation. Different optical arrangements can be used to detect the thermal lens effect. The earliest studies used a single laser beam. In the double beam configuration, a probe laser beam colinear with the excitation beam senses the thermal lens and its intensity variation is measured after blocking the heating beam. The excitation can be obtained both with continuous wave (cw) and pulsed dye lasers.

The lens formation is a time-dependent process reaching an equilibrium value when the rate of laser heating equals the rate of heat loss due to the thermal conductivity of the solvent. Figure 1 shows the wave form of the TLS signal of a 4×10^{-6} M U(VI) solution, as observed by the photodiode and obtained by pulsed laser excitation. The relaxation time of the lens (in the order of 50 ms) is sufficiently fast to re-establish the initial conditions between two successive energy depositions by the laser triggered at a repetition rate of 10Hz. Moreover, the short pulse

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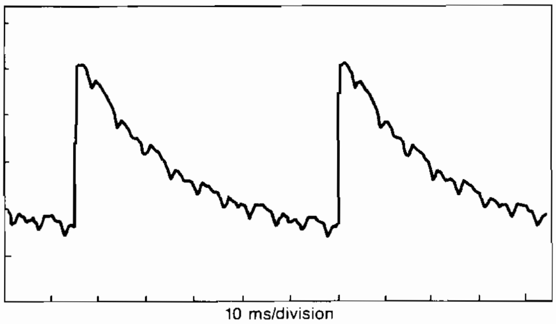

Fig. 1. Temporal dependence of the TLS signal detected by the photodiode. $[U(VI)] = 4 \times 10^{-6}$ M in 0.1 M $NaHCO_3$; $\lambda = 448$ nm. Ripple due to the power supply is also shown.

duration (about 10 ns) rules out interferences on the lens due to heat dissipation by convection.

The solubility of $UO_2CO_{3(s)}$ is U-shaped and the lowest solubility of about 10^{-5} M is found in the carbonate concentration range where the uncharged complex $UO_2CO_{3(aq)}$ predominates. The solubility increases at higher carbonate concentrations due to the formation of anionic complexes $UO_2(CO_3)_2{}^{2-}$ and $UO_2(CO_3)_3{}^{4-}$ [6–9]. By using a sufficiently low total concentration of U(VI) one can avoid both the formation of the trimer $(UO_2)_3(CO_3)_6{}^{6-}$ and the formation of solid UO_2CO_3. We used these conditions and recorded the TLS absorption spectra of $UO_2(CO_3)_2{}^{2-}$ and $UO_2CO_{3(aq)}$ which cannot be obtained by conventional spectrophotometric methods.

As previously reported [3], a detection limit (Signal/Noise = 3) of 5×10^{-8} M was measured for U(VI) at 448 nm in 0.1 M $NaHCO_3$ (molar absorption coefficient 25). To be conservative and accepting a value of $S/N = 30$, the determination limit of 5×10^{-7} M corresponds to an absorbance value of 10^{-5} cm^{-1}. This allows investigation of the U(VI) equilibria relations below the solubility limit of 10^{-5} M. Moreover, as shown in Fig. 2, in the $U(VI)/CO_2/H_2O$ system the different carbonato complexes are sufficiently well separated to permit the acquisition of their individual spectra by TLS. These measurements require accurate corrections of the signal detected by the photodiode for the wavelength dependence of the dye laser energy. Figure 3 shows the recorder tracings of the laser energy (Coumarin 450 dye) as measured by the pyroelectric detector, and the uncorrected spectrum of the species $UO_2(CO_3)_3{}^{4-}$ in the region 435–475 nm at a total uranium concentration of 4×10^{-6} M. The same spectrum is given in Fig. 4 after the correction procedure.

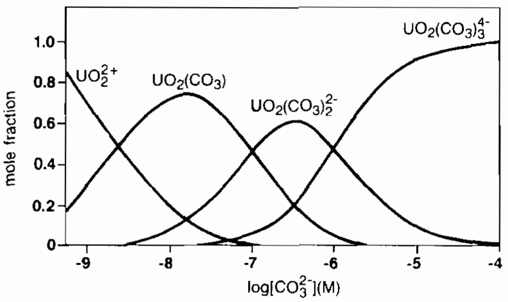

Fig. 2. Distribution of U(VI) species in the system H_2O/CO_2 under conditions where the hydrolysis is negligible. The thermodynamic data of Grenthe *et al.* [6] were used to construct the diagram.

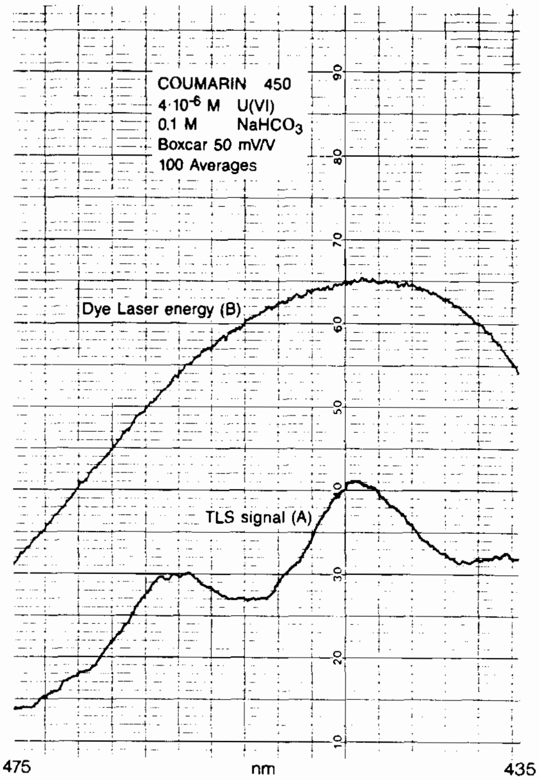

Fig. 3. Recorder tracings of the raw thermal lens signal and the laser energy.

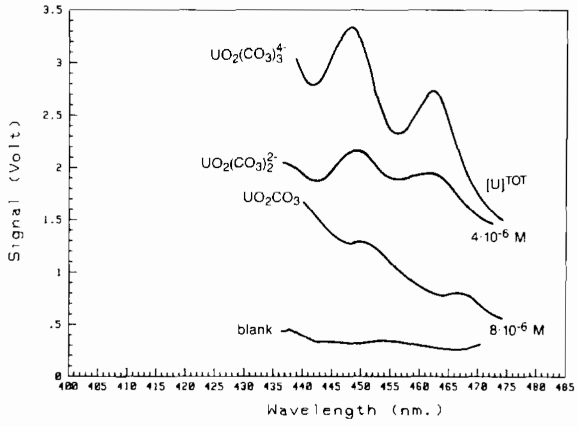

Fig. 4. Thermal lensing spectra of U(VI) solutions in 0.5 M $NaClO_4$ at $CO_3{}^{2-}$ concentrations corresponding to the peaks of the speciation diagram (Fig. 2). Conditions: Coumarin 450 dye; dye energy 3.3 mJ/pulse; data acquisition 100 averages.

Also reported are the spectra of the U(VI) solutions at the carbonate concentrations corresponding to the peaks of the speciation diagram shown in Fig. 2. Although deconvolution should be performed to eliminate the small contributions of the other species, they describe to a first approximation the spectra of the individual species $UO_2(CO_3)_2^{2-}$ and $UO_2CO_{3(aq)}$. A combination of several other dyes (Stilbene 420 and Stilbene 1) was used to extend the wavelength scan down to 400 nm. Nevertheless, the corresponding TLS tracings could not be matched at a crosspoint. This is a limitation of the technique because of changes with wavelength of the thermal lens parameters and because of the different output characteristics of the dyes. However, the scaling of the different portions of a spectrum can be done when a standard solution containing a mixture of stable absorbing species with known spectral features is used. This has been done for the TLS spectrum of the uncomplexed uranyl ion in 0.5 M $NaClO_4$ at pH 2 (Fig. 5). Four different dyes were used to cover the wavelength interval from 380 to 450 nm.

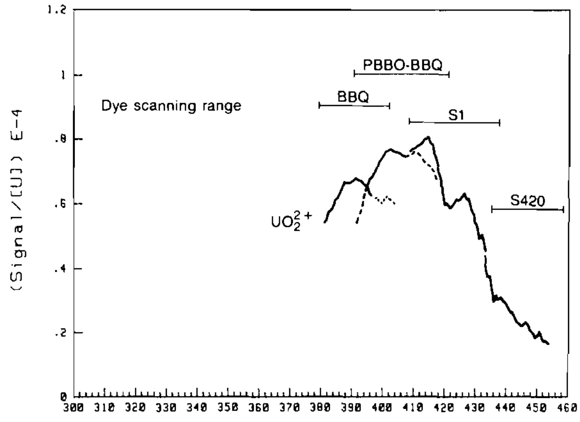

Fig. 5. Multi-dye thermal lensing spectrum of the uncomplexed uranyl ion in 0.5 M $NaClO_4$ at pH 2. The scanning range of the dyes used is indicated.

The decrease in the TLS signal in the U(VI) carbonate solutions is accompanied by a bathochromic effect on the absorption maxima. The molar absorption coefficients calculated from the spectra include an enhancement factor E dependent upon the experimental set-up. They are, therefore, apparent coefficients, unless the enhancement factor is measured. This value may be obtained in an indirect way using an internal standard with known molar absorption coefficients ϵ. Ferri *et al.* [8] determined the ϵ values for $UO_2(CO_3)_3^{4-}$ at 445 nm and 459 nm, obtaining 23.6 and 16.9 $cm^{-1} M^{-1}$, respectively. Using these values, the E factor calculated from the upper spectrum in Fig. 4 was found to be $(3.15 \pm 0.15) \times 10^4$. By substitution, the ϵ coefficients of the various carbonato complexes were measured at the wavelength of the maximum absorption. They are reported in Table I.

TABLE I. Molar Absorption Coefficients of the U(VI) Mononuclear Carbonato Complexes Measured from TLS Spectra

Species	λ^a (nm)	ϵ ($cm^{-1} M^{-1}$)
$UO_2(CO_3)_3^{4-}$	448	23.8
	462	19.4
$UO_2(CO_3)_2^{2-}$	449	14.6
	463	13.0
$UO_2CO_{3(aq)}$	450	3.8
	467	2.1

[a] Wavelengths of the absorption maxima.

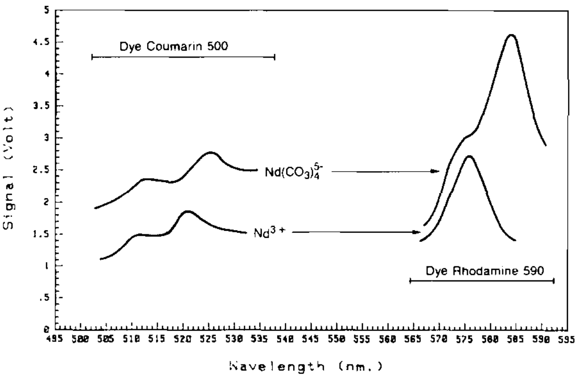

Fig. 6. Thermal lensing spectra of 2×10^{-5} M neodymium solutions in the presence (1 M K_2CO_3) and in the absence (0.1 M $HClO_4$) of carbonate ions with blank subtraction. Absolute signal levels are not directly comparable.

TABLE II. Calculated TLS Determination Limits ($S/N = 30$) for Several Oxidation States of Actinides^a

Element	λ (nm)	ϵ ($cm^{-1} M^{-1}$)	Determination limit (M)
Am(III) in 1 M $HClO_4$	503	350	3×10^{-8}
	810	30	3×10^{-7}
U(IV) in 1 M $HClO_4$	500	30	3×10^{-7}
	650	60	2×10^{-7}
Pu(IV) in 1 M $HClO_4$	473	56	1×10^{-7}
	654	36	3×10^{-7}
Pu(IV) in 1 M $NaHCO_3$	425	90	1×10^{-7}
Pu(V) in 0.2 M HNO_3	519	6	2×10^{-6}
	569	20	5×10^{-7}
Pu(V) in 1 M Na_2CO_3	480	30	3×10^{-7}
	500	25	4×10^{-7}

[a] A practical detectable absorbance of 10^{-5} cm^{-1}, as found in the present work, was used in the calculations.

Variation of TLS spectral features due to complexation was also observed for Nd(III). Figure 6 shows the bathochromic displacement and the increase in intensity of some bands during the conversion of the aquo ion Nd^{3+} to $Nd(CO_3)_4^{5-}$ [10]. The two TLS spectra were obtained at 2×10^{-5} M total neodymium in a 1-cm cell. Similar changes were previously reported at higher neodymium concentrations (7×10^{-4} M) using a differential double beam thermal lensing set-up which compensates for the solvent absorption [11].

Conclusions

The following remarks can be made on the advantages and disadvantages of TLS for chemical speciation studies.

(i) No alterations in solution equilibria occur during the experimental observation of the system.

(ii) Determination limits ($S/N = 30$) corresponding to absorbance values ranging from 10^{-5} to 10^{-4} cm^{-1} are realistic. Table II shows the calculated limits for some oxidation states of actinides. They are several orders of magnitude lower than those obtained by conventional spectrophotometry.

(iii) Concentration limits are influenced by the fluctuations in the stability of the probe laser and the spatial variations of the pulsed dye laser. The excitation beam quality can be improved by using a cw laser which has, however, a lower spectral coverage.

(iv) No increase in sensitivity occurs on increasing the cell pathlength, since the thermal lens develops only at the waist of the laser beam.

(v) Changes in the laser divergence with wavelength (*i.e.*, spot sizes and waist locations) and the different output characteristics of the dye laser hinder the relative scaling of multi-dye spectra. An internal standard is needed. This allows the determination of enhancement factors and the calculation of molar absorption coefficients.

(vi) So far, the energy efficiency of the dyes decreases drastically above 800 nm. This limits the wavelength range that can be investigated.

(vii) Due to the sensitivity of the technique, the scattering arising from the presence of suspended particles in the solution might cause problems. This can, however, be used to detect colloids.

(vii) The energy absorbed by the soluble species might not be completely transformed into thermal energy, contributing then to the formation of the lens, but it could partly be dissipated as radiant energy (fluorescence). Thus, it is not *a priori* expected that TLS absorption bands show the same relative intensities as those of the absorption spectrum, even though the bands occur at the same λ values.

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