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A novel time-resolved laser fluorescence spectroscopy system for research on complexation of uranium(IV)

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ABSTRACT

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To date only a small number of studies have investigated the chemical speciation of complexes and the fluorescence properties of metal ions whose emitted fluorescence lifetime is in the range of only few nanoseconds. This is due to a lack of advanced methods which allow the conduction of these measurements. In the current study we set up a new time-resolved laser fluorescence spectroscopy system with which the fluorescence properties of metal ions with very short fluorescence lifetimes such as uranium(IV) and its compounds can be investigated. By studying the fluorescence properties of uranium(IV) in per-chloric acid, we showed uranium(IV) to have a detection limit of 5×10^{-7} M and a fluorescence decay time of 2.74 ± 0.36 ns. We further investigated the fluorescence properties of uranium(IV) with fluoride.

Our data revealed the formation of a 1:1 complex of uranium(IV) and fluoride. The corresponding complex formation constant of uranium(IV) fluoride UF³⁺ was found to be log β^0 = 9.43 ± 1.94. Our results demonstrate that our novel time-resolved laser fluorescence spectroscopy system can successfully conduct speciation measurements of metal ions and their compounds with very short-lived fluorescence lifetimes. Using this laser system, it is possible to analytically investigate such elements and compounds in environmentally relevant concentration ranges.

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1. Introduction

In order to predict the behaviour of hazardous metals such as uranium in the environment, it is important to understand their physical properties and the chemistry of these elements and their compounds. Aqueous uranium species can be found in submillimolar to micromolar concentrations in the environment [1,2]. Under anoxic and reducing redox conditions, uranium(IV) in particular should be considered in such concentration ranges, also as previous studies have shown that the solubility of uranium(IV), depending on the pH, is in this range [3,4]. Hence, research on the speciation of uranium(IV) requires highly sensitive analytical methods.

Various spectroscopic techniques have been used to study the chemical structure of trace actinides such as uranium(IV) and to determine complex formation constants. However, there are several advantages of the time-resolved laser-induced fluorescence spectroscopy (TRLFS) over other spectroscopic analytical methods. First, the high sensitivity of TRLFS allows the investigation of actinide complexation in environmentally relevant concentrations in the submicromolar range. Using TRLFS, Geipel et al. [5 and references

therein] described the detection limits of various actinide ions for speciation analyses. Depending on the metal ion, these were at least one order of magnitude lower compared with conventional UV-vis spectroscopy or laser-induced photoacoustic spectroscopy (LIPAS) [6]. Second, TRLFS is a fast analytical technique, making the measurement of samples less time-consuming compared with LIPAS. Furthermore, time-resolved fluorescence spectroscopy has been shown to be a very powerful analytical method to study complex matrices in the environment. Excitation wavelength of the laser beam and the resulting fluorescence spectrum are element-specific. This makes TRLFS a very selective and sensitive method for studying fluorescent metals and their complexation reactions, i.e. their speciation, by using spectral and temporal features [7] without being invasive and destroying the original sample. The interpretation of the spectra produced by TRLFS provides structural information by clarifying the chemical speciation.

A number of studies have used TRLFS to investigate actinides and in particular the speciation of uranium(VI). While aqueous uranium(IV) has been studied using other (spectroscopic) techniques [6,8,9], to date no study has used TRLFS. This may be due to the fact that uranium(IV) was considered lack luminescence with the exception of uranium(IV) phosphate in solution [10 and reference therein]. A first description of the fluorescence properties of uranium(IV) in aqueous solution was published only few years ago. A detailed description of the excitation of uranium(IV) in perchlorate

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medium, its transition energies and fluorescence spectra was provided by Kirishima et al. [10]. Other studies have focused on how the luminescence of uranium(IV) originates [11–13], however, these studies gave mixed results. The laser system used by Kirishima et al. [10], however, did not allow the investigation of all aspects of the fluorescence of uranium(IV). The excitation laser beam used in their study had a minimum pulse width of 20 ns, which was longer than the uranium(IV) luminescence lifetime and therefore overlaid the U(IV) fluorescence. Furthermore, although they predicted a measurable uranium(IV) concentration of 1×10^{-6} M, the technical possibilities at the time only allowed the detection of uranium(IV) of a concentration of 1×10^{-4} M. In order to be of practical relevance, however, TRLFS should be able to detect uranium(IV) in environmentally relevant concentration ranges.

Only recently we have been able to set up a laser system that provides the technical prerequisite to extend research on very short-lived fluorescence emitting metals like uranium(IV) and its compounds. We focused on the fluorescence properties of uranium(IV) in an acidic medium. We aimed to determine the minimum detectable uranium(IV) concentration as well as the fluorescence lifetime of uranium(IV) as an important distinctive feature in the characterization and speciation process.

We first applied our novel fluorescence spectroscopy system to study uranium(IV) fluoride. Uranium(IV) fluorides – single compounds and even mixtures of different uranium(IV) fluorides with U(VI) fluorides) [14] – have been investigated intensively. The great amount of data available on uranium(IV) fluorides together with the easy handling make U(IV) fluorides an ideal compound for experiments on the complexation of uranium(IV). By determining the complex formation constant of the uranium(IV) fluoride complex we confirmed the accurate functioning of the laser system.

2. Experimental

2.1. Instrumentation

The novel laser system consists of a Nd:YAG laser combined with a MOPO-SL (Spectra-Physics Laser, Inc., Mountain View, CA) as excitation source, a spectrograph (Acton Research SpectraPro 300i, Acton, MA) and an intensified CCD camera (PicoStar HR, LaVision, Inc., Göttingen, Germany). The laser system operates at wavelengths between 220 and 1800 nm. A schematic representation of the complete fluorescence spectroscopy system is shown in Fig. 1.

A flash lamp-pumped Nd:YAG laser {1} generates laser pulses of 1064 nm wavelength. The output energy averages 1300 mJ per pulse, the pulse width is $\sim 10 \text{ ns}$ with a pulse-to-pulse stability of $\pm 2\%$. By directing the laser through several non-linear optical devices, the 2nd and the 3rd harmonics are generated and laser pulses leave the Nd:YAG with a pulse width of 8 ns at a wavelength of 355 nm. The outgoing laser beam pumps an optical parametric oscillator system {2}. Approximately 80% of the laser beam is channelled directly into the power oscillator (PO). The remaining 20% are directed into the master oscillator (MO) where the required wavelength is created by double-pumping a BBO crystal. By using a grating spectrograph, only the desired wavelength with a fullwidth at half maximum (FWHM) of approximately 0.2 cm^{-1} leaves the laser cavity of the master oscillator. The master oscillator line seeds the power oscillator, and the PO amplifies the pulse, which then passes through the optional frequency doubler and is directed into a glove box onto the sample filled in a quartz cuvette {3}.

For our experiments, we set the excitation wavelength to 245 nm. The corresponding pulse width shows an average of 2 ns producing a pulse energy of 3-4 mJ at a repetition rate of 20 Hz. The laser beam diameter is approximately 3.5 mm with a divergence of less than 1 mrad. The pulse-to-pulse stability of the outgoing laser beam at that wavelength is more than 8%. The room temperature was kept constant at 21 ± 1 °C to ensure stable working conditions during the operation of the laser system.

The sample holder with the quartz cuvette {3} was placed in the glove box under inert atmosphere (N₂) with an oxygen concentration of less than 10 ppm. The temperature in the glove box was 21.5 ± 1 °C. The laser beam was directed into a quartz cuvette with 1 cm pathlength. A delay generator (Stanford Research Systems, Inc., Sunnyvale, CA) {8} corrects the time difference between the electrical trigger for the generation of the laser pulse and the optical pathway of the laser pulse through the laser system. This difference was 545 ns.



Fig. 1. Setup of the laser system with fluorescence detection.

Fluorescence radiation emitted from the sample in the cuvette was focused on an entrance slit of an optical fibre connected to a spectrograph {4} set at 500 nm with a grating of 300 grooves/mm. Detection of the fluorescence was performed by an intensified CCD camera {5} with an optical gate width of down to 80 ps. For the recording of the fluorescence spectra, the camera was internally cooled down to $-11 \,^{\circ}$ C using the Peltier effect. A delay generator (LaVision, Inc., Göttingen, Germany) {7} enables time delays of up to 20 ns with a minimum stepsize of 25 ps after application of the laser pulse. An amplifier (Kentech Instruments Ltd., Wallingford, UK) {6} is connected to the camera. All parameters of the spectrograph and the camera as well as the recording and storage of the data were computer-controlled using the software DaVis 6.1.1 (LaVision, Inc., Göttingen, Germany) {9}. All spectra were analysed using Origin 6.1 and 7.5 (OriginLab Corporation, Northampton, MA, USA). Spectra were recorded between 265 and 465 nm.

2.2. Reagents

Unless stated otherwise, all chemicals were of analytical reagent grade. Uranium nitrate hexahydrate $UO_2(NO_3)_2 \cdot 6H_2O$ was used as starting material for the preparation of uranium(IV) stock solution in perchloric acid medium ($w_{HCIO_4} = 70 - 72\%$, Merck). It was obtained from Chemapol/LaChema whereas sodium fluoride NaF for the fluoride stock solution was obtained from Nünchritz. Deionized water was used throughout the experiments. Preparation and measurements of solutions and samples were done in a glove box under nitrogen atmosphere with an oxygen concentration of less than 10 ppm.

Uranium(IV) was prepared by electrolytic reduction of a 0.01 M uranium(VI) in 0.1 M perchloric acid stock solution in a twocompartment cell using platinum electrodes as anode and cathode. The intensity of the current and the voltage is adjusted as necessary until uranium(VI) was fully reduced to uranium(IV). The amount of uranium(VI) in all samples was determined to be less than 5%, which was controlled using a TRLFS system as described by Moll et al. [15]. For the determination of the detection limit and the fluorescence decay time of uranium(IV), dilution series of decreasing U⁴⁺ concentrations in 0.1 M and 1 M perchloric acid medium were prepared and samples were analysed. All recorded data were evaluated using Origin. In order to study the complexation of uranium(IV) with fluoride, a uranium stock solution was electrolyzed as described before. Again, several sample series with constant uranium(IV) concentrations were prepared. The concentration of fluoride added to the samples varied between tenfold stoichiometric deficiency and eightfold stoichiometric excess with respect to the uranium(IV) concentration. All samples were prepared in 0.1 M perchloric acid medium.

3. Results and discussion

3.1. Determination of the detection limit of uranium(IV)

To determine the detection limit of uranium(IV), its concentration in the samples was decreased stepwise from 1×10^{-3} M to 1×10^{-8} M. The recorded spectra were deconvoluted (Fig. 2) using Gaussian functions for peaks with fitting parameters such as peak wavelength, peak height and full-width at half maximum. The number of peaks relevant for the identification of uranium(IV) and their approximate positions was preset. All other parameters were not restricted. With a correlation coefficient of $R^2 = 0.982$, the following peaks were identified: 290, 318, 320, 336, 339, 344, 350, 394 and 410 nm. These data are in accordance with previous studies [10,16] and therefore, prove the presence of U⁴⁺.



Fig. 2. Deconvolution of 1×10^{-2} M U(IV) in 0.1 M HClO₄.

All spectra were then analysed in terms of the ability to deconvolute specific peaks or not. It was shown that a uranium(IV) concentration of 5×10^{-7} M was detectable. Overlaying all the spectra from the highest to the lowest uranium(IV) concentration, as shown in (Fig. 3), resulted in a clear decrease in the fluorescence intensity. However, not all uranium(IV)-specific peaks could be deconvoluted to the minimal detectable uranium(IV) concentration due to different fluorescence intensities of the single peaks. The minor peaks at 290, 318, 339, 344 and 350 nm are observable down to 1×10^{-4} M, depending on the peak. The more prominent peaks at 320, 336, 394 and 410 nm can be deconvoluted down to a uranium(IV) concentration of 5×10^{-7} M. As a result, laser-induced fluorescence spectroscopy provides a powerful tool for examining aqueous uranium(IV) at very low, environmentally rel-



Fig. 3. Fluorescence spectra of uranium(IV) at different concentrations in perchloric acid.

Table 1

Overview of the fluorescence lifetimes of U(IV) at different concentrations and pH values.

c(U ⁴⁺)[M]	pН	Fluorescence lifetime [ns]	pН	Fluorescence lifetime [ns]
1×10^{-3}	1	2.74 ± 0.13	_	_
1×10^{-4}	1	2.88 ± 0.43	0	3.05 ± 0.49
1×10^{-5}	1	2.49 ± 0.31	-	-
1×10^{-6}	1	2.60 ± 0.11	0	2.55 ± 0.22
$5 imes 10^{-7}$	-	-	0	2.61 ± 0.27

evant concentrations. The amount of uranium(IV) measurable by our fluorescence spectroscopy system is almost two orders of magnitude below the detection limit of the LIPAS [6], and one and a half orders of magnitude lower compared to UV–vis spectroscopy. Furthermore, our data have confirmed the minimum detectable uranium(IV) concentration predicted by Kirishima et al. [10] and to even lower it by half an order of magnitude down to 5×10^{-7} M.

3.2. Determination of the uranium(IV) fluorescence lifetime

A dilution series with uranium(IV) concentrations between 1×10^{-3} and 5×10^{-7} M was prepared from the uranium(IV) stock solution. Time-resolved fluorescence spectra of these samples were recorded in the decay time range of 0-20 ns. The increment was varied between 25 and 1000 ps. All spectra were analysed using Origin software. We were able to detect a monoexponential decay of the fluorescence, which means that there was one uranium(IV) species present in the samples under the applied conditions. Table 1 gives an overview of the averaged fluorescence lifetimes of different uranium(IV) solutions. The fluorescence lifetime of aqueous uranium(IV) in perchloric acid medium in a pH range between 0 and 1 was determined to be $t = 2.74 \pm 0.36$ ns (Fig. 4). As the fluorescence lifetime and the average laser pulse width differ in less than 1 ns, the decay of the fluorescence was tracked over several lifetimes. This procedure allows to measure the uranium(IV) fluorescence lifetime that is just a little longer than the applied laser pulse.

3.3. Investigation of concentrational quenching effects

Perfilev et al. [11] observed luminescence quenching due to concentrational effects only at uranium concentrations greater than 1×10^{-3} M, and described $\log I_{\text{lum}}$ to be linearly dependent on $\log([U(\text{IV})])$ for [U(IV)] between 4×10^{-6} and 1×10^{-3} M. However, this phenomenon cannot be excluded from the beginning when investigating fluorescence properties of uranium(IV) in



Fig. 4. Fluorescence lifetime of uranium(IV) in perchloric acid.



Fig. 5. Dependency of $\log(I_{lum})$ on $\log([U(IV)])$ to determine concentrational quenching effects.

concentrations around 1×10^{-3} M. Therefore, the dependency of the fluorescence intensity on the uranium(IV) concentration was investigated. The results are shown in Fig. 5. The data of fluorescence measurements clearly indicate a linear correlation between log I_{lum} and log([U(IV)]). Additionally, the fluorescence liftetimes determined at varying uranium(IV) concentrations are all in the acceptable error range. The sample containing 1×10^{-3} M uranium(IV) does not display a significantly shortened fluorescence decay time. As a result, no quenching due to concentrational effects was observable.

3.4. Complexation and fluorescence properties of uranium(IV) fluoride

A number of studies have investigated uranium(IV) fluoride solutions and uranium(IV) systems, providing useful insights into the behaviour of uranium(IV) in (perchloric acid) solution, as well as in the chemical species of solved uranium(IV). Some studies have also focused on uranium(IV) fluoride complexation reactions with varying U(IV): F ratios [9,17–21]. The amount of data obtained by these studies together with the easy handling makes uranium(IV) fluoride an ideal system for describing the complexation between the reactants.

Uranium(IV) fluoride samples were prepared and measured. Table 2 provides an example of a sample series. Fluorescence spectra of the complexation between uranium(IV) and fluoride are given in Fig. 6. Starting sample was pure U(IV) in 0.1 M HClO₄, which served as a reference point. Fluoride was added stepwise while the uranium(IV) concentration was kept constant. Measurements commenced with a tenfold stoichiometric deficiency. The first spectrum did not show a change in comparison with the pure U(IV) spectrum. Neither a decrease in the fluorescence intensity nor a shift of peak nor a general change in the spectrum shape was observed.

A slow increase of the fluoride concentration up one-forth of the uranium(IV) concentration resulted in a stepwise decrease of the fluorescence intensity compared with the original U(IV) spectrum. This was shown clearly by the two prominent sharp peaks at 320 and 410 nm. The minor peaks at 318, 339 and 344 nm could not be deconvoluted due to the low fluorescence intensity. At a fluoride concentration half the uranium(IV) concentration, almost no fluorescence was measurable. Further addition of fluoride resulted in a slow change of the spectrum. A new broad peak at 320 nm replaced the original U(IV) peak. In addition, a broad peak appeared in the wavelength range between about 350 and 450 nm. This peak only showed one broad band with no detailed structure. The newly formed spectrum had fully developed when

Table 2

Overview of a sample series for TRLFS measurements of the complexation of uranium(IV) with fluoride at $pH \sim 1$.

Sample no.	c(U ⁴⁺) [M]	$c(F^{-})[M]$
0	1×10^{-3}	0
1	1×10^{-3}	1×10^{-4}
2	1×10^{-3}	$2 imes 10^{-4}$
3	1×10^{-3}	$3 imes 10^{-4}$
4	1×10^{-3}	$\textbf{3.4}\times10^{-4}$
5	1×10^{-3}	$4 imes 10^{-4}$
6	1×10^{-3}	4.4×10^{-4}
7	1×10^{-3}	$5 imes 10^{-4}$
8	1×10^{-3}	$6 imes 10^{-4}$
9	1×10^{-3}	6.4×10^{-4}
10	1×10^{-3}	$\textbf{6.8}\times10^{-4}$
11	1×10^{-3}	$7.2 imes 10^{-4}$
12	1×10^{-3}	$7.6 imes 10^{-4}$
13	1×10^{-3}	$8 imes 10^{-4}$
14	1×10^{-3}	$\textbf{8.8}\times10^{-4}$
15	1×10^{-3}	$1 imes 10^{-3}$
16	1×10^{-3}	$2 imes 10^{-3}$
17	1×10^{-3}	$5 imes 10^{-3}$
18	1×10^{-3}	$8 imes 10^{-3}$
19	0	$1 imes 10^{-3}$

a stoichiometrical uranium(IV): fluoride ratio was reached. A further increase of the fluoride concentration resulted in an increase in the fluorescence intensity until the fluoride concentration was twice the uranium(IV) concentration. Further enhancement of the fluoride–uranium(IV) ratio did not lead to a significant change in the fluorescence intensity. Small changes in intensity may have been the result of instrumental measurement error.

Both the broad peak at 320 nm as well as the band between 350 and 450 nm were evaluated separately with regard to their respective fluorescence decay time. They do not differ significantly from the fluorescence lifetime of U⁴⁺ as well as from each other. For the peak at 320 nm, the decay time average was 2.60 ± 0.76 ns. The fluorescence lifetime of the broad band between 350 and 450 nm was 2.80 ns ± 1.08 ns. The overall fluorescence decay time of the whole spectrum was determined to be 2.83 ± 0.19 ns. These findings indicate that there was one species present in the solution. Broadening



Fig. 6. Fluorescence spectra of the uranium(IV) fluoride complex formation.



Fig. 7. Slope analysis of the complex formation of uranium(IV) with fluoride to determine the complex stoichiometry.

of the peaks could have been an indicator for the parallel existence of two or more species that superimpose each other. The results of the fluorescence lifetimes contradict this assumption. Hence, an explanation for the broadening of the peak and the band cannot be given so far.

Then, all spectra were deconvoluted. To determine the elemental composition of the uranium(IV) fluoride complex(es), the $\log([complex]/[U(IV)]_{free})$ against $\log([F^-]_{free})$ of the samples 2–14 was plotted. The graph is shown in Fig. 7. The slope represents the U(IV): *F* ratio. The complex formation constant can be derived from the intersection of the linear fit with the *y*-axis. Further calculations allow the determination of the complex formation constant at infinite dilution. The analysis used in the following paragraph has been described in previous publications [22,23].

The plot displays a slope of 1.05 ± 0.20 . Thus, the U(IV): *F* ratio is 1:1, i.e. the following reaction (1) has taken place:

$$U^{4+} + F^- \to UF^{3+} \tag{1}$$

The corresponding complex formation constant obtained from the intersection was shown to be $\log K(\text{UF}^{3+}) = 10.33 \pm 1.94$ at a temperature of 21.5 ± 1 °C and at an ionic strength of I = 0.1 M. To extrapolate the complex formation constant to infinite dilution, the Davis equation (2) was applied [23]:

$$\beta(I) = \beta^0 \cdot \Pi_{\nu_i}^{\nu_i} \tag{2}$$

After transforming and logarithmizing equation (2), the complex formation constant at infinite dilution, β^0 , can be calculated as follows:

$$\log \beta^{0} = \log \beta(I) - (\log \gamma_{1:1} - \log \gamma_{U^{4+}} - \log \gamma_{F^{-}})$$
(3)

The activity coefficients γ of UF³⁺, U⁴⁺ and F⁻ were calculated using Eq. (4):

$$\log \gamma_i = -z_i^2 \cdot A \frac{\sqrt{I} - B \cdot I}{1 + \sqrt{I}} \tag{4}$$

z: ion charge, *A*: constant 0.5091, *B*: constant 0.2, and *I*: ionic strength.

The calculated activity coefficients were: $\log \gamma_{1:1} = -1.009$, $\log \gamma_{U^{4+}} = -1.794$ and $\log \gamma_{F^-} = -0.112$. From the complex formation constant determined and the activity coefficients calculated, the complex formation constant at infinite dilution was found to be $\log \beta^0 = 9.43 \pm 1.94$. This value is in good agreement with previous studies reporting a value for UF³⁺ of $\log \beta^0 = 9.42 \pm 0.51$ [21]. The large error shows the complexity of working with an element emit-



Fig. 8. Dependency of the emitted fluorescence of uranium(IV) fluoride on the applied excitation wavelength.

ting fluorescence that is as short-lived as the one of uranium(IV). Furthermore, stability of the laser performance over time adds to the challenge of investigating short-lived fluorescence. Despite these difficulties, we were able to show the accurate performance of our novel laser system.

3.5. Investigation of the dependency complex formation–excitation wavelength

There are different explanations for the changes observed in the fluorescence intensity and in the shape of the spectrum. They can be due to changes in the concentration of free uranium(IV) and the corresponding formation of uranium(IV) fluoride complexes. However, an alternative explanation would be that a different amount of energy was required to excite the uranium(IV) fluoride complex, which would lead to a shift in the excitation wavelength. To clarify this issue, we further assessed the dependency of the complex formation and excitation wavelength. As described by Kirishima et al. [10], U⁴⁺ has one of the greatest absorptions at a wavenumber of 40820 cm⁻¹, which corresponds to a wavelength of 245 nm. Therefore, excitation of free uranium(IV) at a wavelength of 245 nm leads to the emission of fluorescence. However, it may be possible that there is a shift in energy for the excitation of bound uranium(IV) or the whole uranium(IV) complex, respectively. Thus, one sample consisting of $1\times 10^{-3}\,M$ U(IV) and $8\times 10^{-3}\,M$ F^- was chosen. The excitation wavelength applied to the sample was varied between 235 nm and 255 nm in a stepwise manner with 1 nm steps. Five selected spectra are shown in Fig. 8. An overview of all spectra can be found online as supplementary material.

Comparing the spectra recorded at different excitation wavelengths with those obtained from the uranium(IV) fluoride complexation showed that the change in the intensity and in the shape of the complexation spectra were caused by a decrease in the concentration of free uranium(IV) and the correlating formation of UF³⁺. The changes were not, however, caused by a shift in the excitation wavelength for newly formed complex. The emitted fluorescence of the sample gets to a maximum at the excitation wavelength of 244 nm, which correlates with the known excitation wavelength of 245 nm for uranium(IV).

Moreover, the appearance of a new peak at 272 nm starting at an excitation wavelength of 246 nm can be observed. This peak reached a maximum at an excitation wavelength of 248 nm and decreased to a minimum at the next excitation wavelength step. Then, its luminescence intensity increased again until it reached its maximum at the final excitation wavelength of 255 nm. In addition, the peak moved slowly from 272 to 280 nm. The reasons for this phenomenon are currently unclear, however it is unlikely to be caused by the presence of uranium(V). Although the excitation wavelength of 255 nm indicates uranium(V), the deconvoluted fluorescence spectrum does not display a peak as given by Steudtner et al. [24] who described one peak for uranium(V) with a maximum at 440 nm in the range of 250–600 nm.

4. Conclusions

Research investigating the chemical properties of hazardous metals such as the actinides is essential in order to predict their physical behaviour in the environment and their interaction with the geo- and biosphere. Time-resolved laser fluorescence spectroscopy is a powerful and highly sensitive analytical tool with which metals such as uranium can be studied in environmentally relevant concentration ranges. We set up a novel laser fluorescence spectroscopy system that provides very short laser pulses of about 2 ns. This allows us to directly study complex formations of aqueous metals such as uranium(IV) or americium(III) whose fluorescence was spatially dispersed by a grating spectrograph and measured in a time-resolved manner by an intensified CCD camera.

Uranium(IV) was chosen as a representative example of an actinide with a very short fluorescence lifetime. The detection limit of uranium(IV) was 5×10^{-7} M. Furthermore, the fluorescence decay time of uranium(IV) under certain conditions was measured. Its fluorescence lifetime of 2.74 ± 0.36 ns has not been reported before.

The uranium(IV) fluoride system was shown to be ideal for studying complexation between a metal ion and a reactant by measuring the fluorescence properties. Our data revealed the formation of a 1:1 uranium(IV) fluoride complex. The corresponding complex formation constant of UF³⁺ measured was shown to be log β^0 = 9.43 ± 1.94, which is in accordance with previous studies [21]. Thus, our results have demonstrated that our novel laser fluorescence spectroscopy system can successfully applied to study the speciation and determine complex formation constants of compounds, which emit very short-lived fluorescence of only few nanoseconds.

5 Computer programs

TRLFS spectra were recorded using DaVis 6.1.1 (LaVision, Inc., Göttingen, Germany) software. All spectra were analysed using Origin 6.1 and 7.5 (OriginLab Corporation, Northampton, MA, USA).

6 Supplementary material

Fluorescence spectra of a uranium(IV) fluoride sample, to which excitation wavelengths between 235 and 255 nm in a stepwise manner in 1 nm steps were applied, are available online at http://www.sciencedirect.com

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2009.04.013.

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