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Detection of uranyl ion via fluorescence quenching and photochemical oxidation of calcein

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Abstract

This paper reports the detection of uranyl ion via fluorescence quenching of a dye molecule followed by the selective photocatalysis of the dye molecule by excited state uranyl. We have found that selectivity can be obtained when calcein, a highly fluorescent fluorescein-type dye, is quenched by complex formation with uranyl in solution at low concentrations. Following the quenching by uranyl, the entire sample is excited at a wavelength that is strongly absorbed by uranyl at 425 nm. This produces the excited state uranyl ion that has a large oxidation potential and photocatalytically decarboxylates the dye, breaking the dye/metal bond. The photocatalysis product is highly fluorescent and produces an increase in the fluorescence signal. The detection limit for uranyl via quenching is 60 nM and via photocatalysis is 40 nM. Interfering metal ions such as iron and chromate have little effect on the amount of fluorescence regenerated since their absorbance bands, modes of quenching, and photochemistry are different from uranyl.

Keywords: Photooxidation; Uranyl; Hydrogen abstraction; Calcein

1. Introduction

There has been a renewed interest in low-cost rapid techniques for measuring actinides and other heavy metal contaminants in environmental water [1–9]. One uranium species of interest is the uranyl ion, UO_2^{2+} because it can be found in soils and in low-pH water runoff in and around nuclear waste sites and processing facilities.

One of the most sensitive and selective methods for the remote and in situ detection of uranium in aqueous solutions is time-resolved laser induced fluorescence (TRLIF) [1–3,5,7,9–11]. TRLIF is able to determine uranium concentration and speciation under a variety of harsh conditions with low detection limits (10^{-13} M). Laser sources are required, increasing overall cost and extensive signal deconvolution is required, increasing the response time. For simplicity and cost effectiveness, optical sensors are also being developed to provide simple, rapid and cost effective initial detection of uranyl ion. An optical uranyl sensor described by Lerchi et al. [12] is based on a plasticized poly(vinyl chloride) membrane with a colorimetric uranyl-selective ionophore. This sensor is reversible with a reported detection limit of ∼500 nM at pH 3.6. A similar optical uranyl sensor uses arsenazo III as the colorimetric U(VI) probe [13]. This sensor is an integrating device with a detection limit of 1.9 μM for a 2 min exposure to a uranyl solution.

Uranyl photochemistry is widely studied in the literature for a multitude of applications [14–23]. The use of uranyl photochemistry as a quantitative method in solution has been previously reported. Nemodruk and Bezrogova [16] reported a photochemical technique based on the reduction of U(VI) to U(IV) by ethanol, followed by vanadometric titration of the U(IV). The authors report a detection limit of 74 μM. In a similar method, Riggs [17] demonstrated improved sensitivity for measuring uranyl through reduction to U(IV) via an aliphatic alcohol, followed by a colorimetric detection. Typically colorimetric methods of this type show strong interference from iron(III), Cr(III) and Cu(II).

We are exploring fluorescent indicator methods for uranyl detection that can subsequently be applied to simple, easy to use optical sensors. In this work, it was discovered that UO_2^{2+} can be detected at low concentrations by fluorescence quenching of a fluorescein analog dye, calcein. Calcein (*N*,*N*-bis(carboxymethyl)aminomethylfluorescein) (Fig. 1, inset) is used primarily in the EDTA titration of

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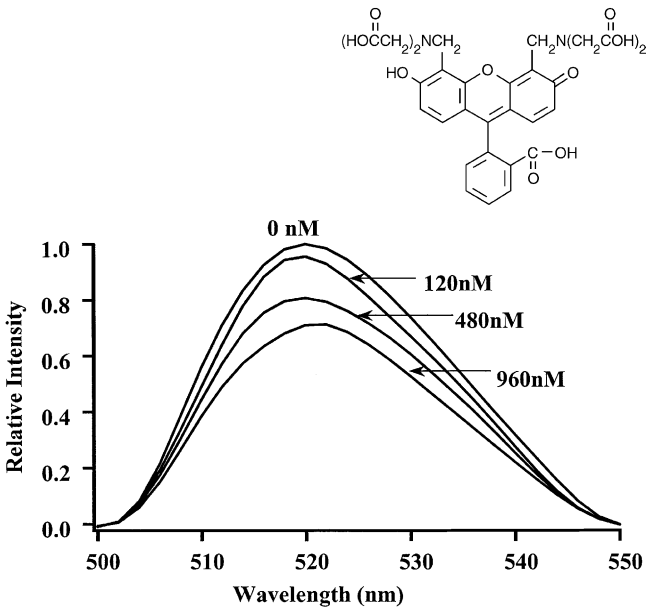

Fig. 1. Emission spectra of 800 nM calcein after addition of 0, 120, 480 and 960 nM UO_2^{2+}. Excitation is at 492 nm, pH 4.0 in barbituric acid buffer. Inset: structure of calcein.

Ca^{2+} in the presence of magnesium at high pH [24]. It has also been used for the detection of a variety of metal ions including Zn(II), Al(III), Cu(II), Ni(II) via quenching at pH 7.4, Ba(II), Ca(II) Mg(II), Sr(II) and Cd(II) via the formation of a fluorescent product at high pH [25–27] and in a variety of clinical applications for Ca^{2+} detection [28]. Calcein has also been incorporated into a fiber-optic Ca^{2+} sensor by covalent attachment to cellulose via a reaction with cyanuric chloride [29].

Although calcein provides excellent sensitivity for the detection of uranyl in solution via fluorescence quenching, iron(III) and chromate are major interferences because the two metals also quench calcein fluorescence very efficiently. However, we have observed interesting photochemistry in the quenched calcein/uranyl complex. Calcein, a highly fluorescent dye, is efficiently quenched by uranyl and subsequently undergoes a photochemical reaction with excited state uranyl to generate a highly fluorescent product. Furthermore, with the proper selection of excitation wavelength, this photochemical reaction is *selective* for uranyl over iron and chromate. In preliminary experiments, we show that this photochemical response can be used to selectively measure uranyl in aqueous solution when iron or chromate ions are present.

2. Experimental

2.1. Apparatus and materials

All fluorescence measurements were obtained using a lab-built fluorometer. The resolution of the monochromators was typically 2.5 nm (1.25 mm slits) and 2.25 nm (1.25 mm slits) for the excitation and emission monochromators, respectively. Fluorescence lifetimes were measured using a 337 nm pulsed nitrogen laser system (Laser Science, Cambridge, MA, Model VSL-337) operating at 20 Hz with a 2 ns full-width half-maximum (FWHM) pulse width and 100 μJ/pulse. The 520 nm emission was collected using a digital oscilloscope (LeCroy Model 9350L) to monitor the PMT (Hammamatsu R2949 PMT) photocurrent. The instrument response function (typically FWHM of less than 4 ns) was deconvoluted from the fluorescence decay profile using Andre's fast Fourier deconvolution method [30] and the resulting data were fitted to single exponential decays. Absorption spectra were measured using a Perkin Elmer model Lambda 14 scanning UV–Vis spectrophotometer.

Analytical grade chemicals were used as received. Deionized, distilled water was used for all samples. Uranium oxynitrate hexahydrate was obtained from Alfa (Ward Hill, MA). Barbituric acid and indicator-grade calcein were purchased from Aldrich (Milwaukee, WI). Iron(III) nitrate, sodium dichromate and trace-metal grade nitric acid were obtained from Fisher Scientific (Fair Lawn, NJ). Potassium hydroxide was purchased from EM Science (Gibbstown, NJ).

2.2. Safety

While naturally occurring, uranium is a gamma and alpha emitter and should be handled appropriately. Gloves, protective clothing and mask should be worn. Fume hoods should be used and the area monitored for radiation. Waste should be placed in appropriately labeled waste containers.

3. Sample preparation and measurements

Water >18 MΩ resistivity was used in all solutions. All glassware was cleaned by boiling for 1 h in 4 M trace-metal grade nitric acid followed by triple rinsing with water. An 80 μM stock solution of calcein was prepared. The pH of the stock solution was 4.3 and was stable for 3 days when stored in the dark. Fresh 4 μM calcein solutions were made daily by diluting the stock. A 1 mM uranyl stock solution was prepared by dissolving 50.2 mg of $UO_2(NO_3)_2{\cdot}6H_2O$ in 100 ml of water. This stock solution was stable for months when stored in the dark. The pH of the uranyl stock solution was 2.8. At this pH the formation of $(UO_2)OH_n$ species is limited to less than 0.2% of the total UO_2^{2+} concentration [6,31]. Exact UO_2^{2+} concentrations were determined by spectrophotometric titration using potassium ferrocyanide [19]. The standardized UO_2^{2+} stock solution was used to prepare dilutions as needed. Solutions of other metal ions were prepared by diluting stock solutions of the corresponding metal nitrates in distilled water. A pH 4 buffer solution was prepared by dissolving 0.60 g of barbituric acid in 1 l of water and adjusting to pH 4 using 0.15 g KOH (4.7 mM barbituric acid, 2.7 mM KOH). Samples for the quenching

measurements were made by adding 5 ml of calcein dye stock solution, 10 ml of barbituric acid buffer and an appropriate amount of uranyl or other metal solution to 25 ml volumetric flasks and diluting to the mark with distilled water. For all uranyl solutions used in quenching experiments, the concentrations were 800 nM calcein, 1.9 mM barbituric acid and 1.1 mM KOH. For lifetime measurements buffered dye samples were prepared using the same dye concentrations as in the quenching experiments, but with excess metal ion concentration.

All calcein fluorescence spectra were measured on 2 ml samples using 492 nm excitation, slightly off the peak of the calcein excitation maximum to minimize photodegradation of the dye. The optimum excitation wavelength for the UO_2^{2+}-catalyzed photooxidation of calcein was determined in a separate experiment by measuring relative fluorescence recovery as a function of excitation wavelength. The solutions were made by adding 0.37 μM uranyl to 800 nM calcein. A similar experiment was performed to determine the excitation wavelength dependence of calcein photodegradation resulting from the addition of chromate to the calcein solution (Fig. 5). The solutions were made by adding 4.6 μM dichromate to 800 nM calcein. No effect was observed for lower concentrations of chromate. An excitation wavelength of 425 nm, corresponding to a maximum in the excitation and absorbance spectra of complexed uranyl ion and little response from chromate quenched calcein, was used for photooxidation experiments.

After a sample was quenched with uranyl and the fluorescence measured, the excitation wavelength was changed to 425 nm for photooxidation experiments. The excitation monochromator slits were opened to 5 mm to maximize the light intensity. The intensity of the 425 nm light used for photolysis was approximately 800 μW at the sample. In all photolysis experiments, samples were irradiated for 20 min with stirring. Temperature was monitored to ensure that the sample was not heating. Progress of photolysis was monitored by measuring the fluorescence intensity of the solution every 5 min by briefly setting the excitation wavelength back to 492 nm and reducing the slits. For deoxygenated samples, nitrogen gas was bubbled through the sample for 1 h prior to photolysis. For all figures, relative fluorescence recovery was taken as change in calcein fluorescence intensity relative to the fluorescence intensity just prior to photolysis (i.e., quenched) minus the change in fluorescence intensity of an identically exposed blank calcein solution (i.e., containing no uranyl).

4. Results and discussion

4.1. Chemistry of uranyl in solution

Free U^{6+} does not exist in aqueous solutions [32]. Its speciation is highly dependent upon the existence of coordinating molecules in the surrounding medium and pH [31,32]. The uranyl ion is known for its ability to form stable complexes with a variety of ligands including H_2O, Cl^-, NO_3^-, acetic acid, lactic acid and oxalic acid [20,33–35]. The absorbance spectrum of uranyl in solution has been highly investigated. In perchloric acid, it consists of 24 resolvable bands between 180 and 500 nm which shifts upon complexation with ligands [20].

The photocatalytic nature of uranium was first reported in 1805 [21] and has been the subject of numerous studies [22,23,36–39]. The uranyl excited state oxidation potential is very high at approximately 2.6 V [36,37,39]. The mechanisms of uranyl photooxidation have been the subject of many reviews [22,23,39]. Two main mechanisms have been proposed: the kinetic encounter and the complex formation theory [22,38,39]. Both processes proceed through short-lived U(V) species. According to the complex formation theory, ground state uranyl is first complexed with a ligand (LH) containing electron-withdrawing groups (OH, carbonyls, etc.). When the uranyl is subsequently excited, it abstracts a hydrogen $LH \rightarrow L^{\bullet}$ from its nearest neighbor carbon as it is reduced to U(V). In the case of carboxylic acids (see calcein, Fig. 1), the main action of the U(VI) on the ligand is the decarboxylation at the alpha carbon with subsequent production of CO_2. This mechanism leads to greater photooxidative selectivity because uranyl is bound directly to the sites upon which it acts as shown by Eqs. (1) and (2). U(V) is autooxidized in the presence of oxygen to regenerate U(VI) (Eq. (3)):

$$U(VI) + LH \Leftrightarrow U(VI)LH \quad (1)$$

$$U(VI)LH + h\nu \Leftrightarrow U(V) + L^{\bullet} \quad (2)$$

$$U(V) + \tfrac{1}{2}O_2 \rightarrow U(VI)\,[\text{as } UO_2^{2+}] \quad (3)$$

4.2. Quenching data

The inset of Fig. 1 shows the structure of calcein. UO_2^{2+} and other metal ions bind to the carboxylate groups. Fig. 1 also shows the fluorescence emission spectrum of calcein in pH 4 solution and UO_2^{2+}-quenched spectra obtained after addition of UO_2^{2+}. We found pH 4 to be the optimum for efficient uranyl quenching. The fluorescence lifetime of calcein with and without uranium present is 5.5 ± 0.1 and 5.2 ± 0.1 ns, respectively, indicative of static quenching and a stable complex.

A Stern–Volmer plot of the normalized inverse fluorescence intensity versus uranyl concentration is shown in Fig. 2a for five concentrations of UO_2^{2+} ranging from 0 to 960 nM. Each point is the average of five measurements. The Stern–Volmer quenching constant K_{sv} is obtained from the slope of the linear curve and is related to the concentration of species in solution by

$$K_{sv} = \frac{[FQ]}{[F][Q]} \quad (4)$$

For uranyl, K_{sv} at pH 4 is equal to 6.3×10^5, which indicates that at a concentration of 960 nM quencher (uranyl)

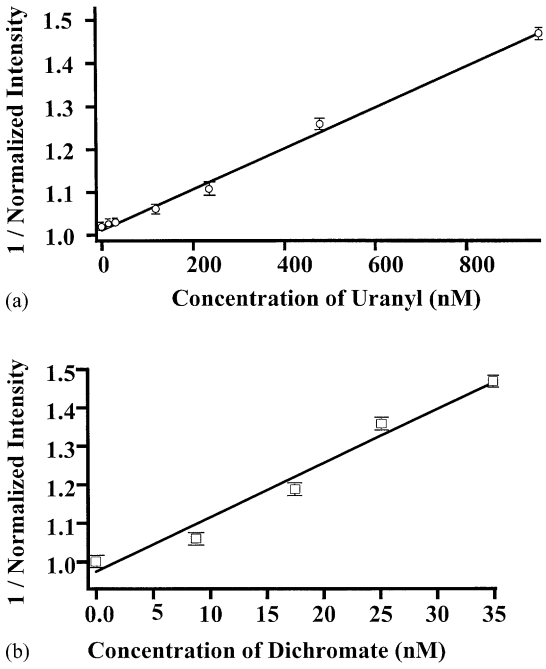

Fig. 2. (a) Stern–Volmer plot showing quenching of calcein by uranyl ($K_{sv} = 4.71 \times 10^5$ l/mol); (b) Stern–Volmer plot of quenching of calcein by dichromate ($K_{sv} = 1.44 \times 10^7$ l/mol). Each measurement is an average of five replicates. The error bars show ±1 standard deviation.

and 800 nM fluorophore (calcein) the maximum amount of complex formed is 480 nM or 60%. This assumes a 1:1 complex; however, the value could be lower since we were not able to find a reference to indicate that calcein and UO_2^{2+} form a 1:1 complex. The detection limit for UO_2^{2+} based on calcein quenching alone was determined to be 60 ± 6 nM. Fig. 2b shows a Stern–Volmer plot for calcein with dichromate. This plot shows that chromate is a much better quencher of calcein than UO_2^{2+} and is thus a major interference in the detection of UO_2^{2+} by calcein quenching. The Stern–Volmer quenching constant for dichromate is 1.4×10^7 for a 25-fold lower dichromate concentration. This indicates an association of calcein and dichromate at 11:1, which can only occur in a dynamic quenching model.

4.3. Photochemical measurements

The data resulting from the wavelength optimization experiments is shown in Fig. 3a and b. In Fig. 3a, the percentage fluorescence increase varies with wavelength and corresponds to the UO_2^{2+} excitation spectrum (lower curve of Fig. 3a), with the highest rate of UO_2^{2+}-catalyzed calcein photooxidation occurring for 440 nm excitation. When uranyl is excited at the proper wavelength, it abstracts a hydrogen from the carboxylic acid functional group, destroys the chelating site and results in a molecule that can no longer be quenched by uranyl ion yet still contains the main chromophore component, thus the fluorescence increases.

Unlike UO_2^{2+}, the photoresponse of the calcein solution with 4.6 μM dichromate was negative everywhere except around 425 nm where it was closer to zero (upper curve of Fig. 3b). A negative photoresponse indicates a further loss of calcein fluorescence intensity following photoexcitation at the indicated wavelength. Although a significant negative response occurs where chromate absorbs (lower curve of Fig. 3b) the dichromate response did not closely mirror the absorbance spectrum as it did for uranyl.

Since dichromate is an anion, stable complexes with the negatively charged carboxylic acid functional groups in calcein in solution are unlikely. Thus, the dichromate must be associated with the more positively charged chromophore region of the dye. Any photochemical reaction by dichromate on the dye molecule leads to disruption of chromophore conjugation and resultant product with little fluorescence. The fluorescence lifetime of calcein in the presence of excess chromate was decreased from that of free calcein, but could not be accurately determined as the signal was not resolvable from the instrument response. However, this decrease is indicative of dynamic, rather than static, quenching.

The selection of the optimum photochemical wavelength is the most crucial step in obtaining selectivity in this experiment. This is because of wavelength-dependent competing effects, including direct photodegradation of the calcein dye, interfering metal ions with known photochemical properties as well as nonphotoactive absorbers that could dissipate the light energy as heat, rendering it useless for photooxidation. Although 440 nm gives optimal response for UO_2^{2+} alone, in the presence of chromate and iron(III) one needs to examine the most selective wavelengthm, i.e., what wavelength gives a high uranium fluorescence increase but a negligible effect from other interfering ions in solution. In this report, we chose 425 nm to eliminate the interference from dichromate. Selectivity is therefore only limited by the ability to isolate a uranyl excitation band from absorption bands of known interferences.

Fig. 4a shows the photooxidative calcein fluorescence recovery time response for 40, 160 and 630 nM UO_2^{2+} exposed at 425 nm. The dye concentration was 800 nM assuring a slight excess of dye for all concentrations of UO_2^{2+} used. Significant relative fluorescence recovery was observed after 5 min for all concentrations of UO_2^{2+}. The magnitude of the response was observed to be concentration-dependent. This concentration dependence is shown quantitatively in Fig. 4b. Here, the relative fluorescence recovery after 20 min of photolysis at 425 nm is plotted versus UO_2^{2+} concentration. Based on this curve a detection limit of 40 ± 7 nM was obtained.

Many factors affect the efficiency of UO_2^{2+} photooxidation, primarily the amount of dissolved oxygen in the sample and light intensity. Since oxygen is required (Eq. (3)) for the sensitized photoxidation to recycle uranyl from U(V) to U(VI), removal of oxygen from the system decreases the photooxidation rate and the slope of the relative fluorescence

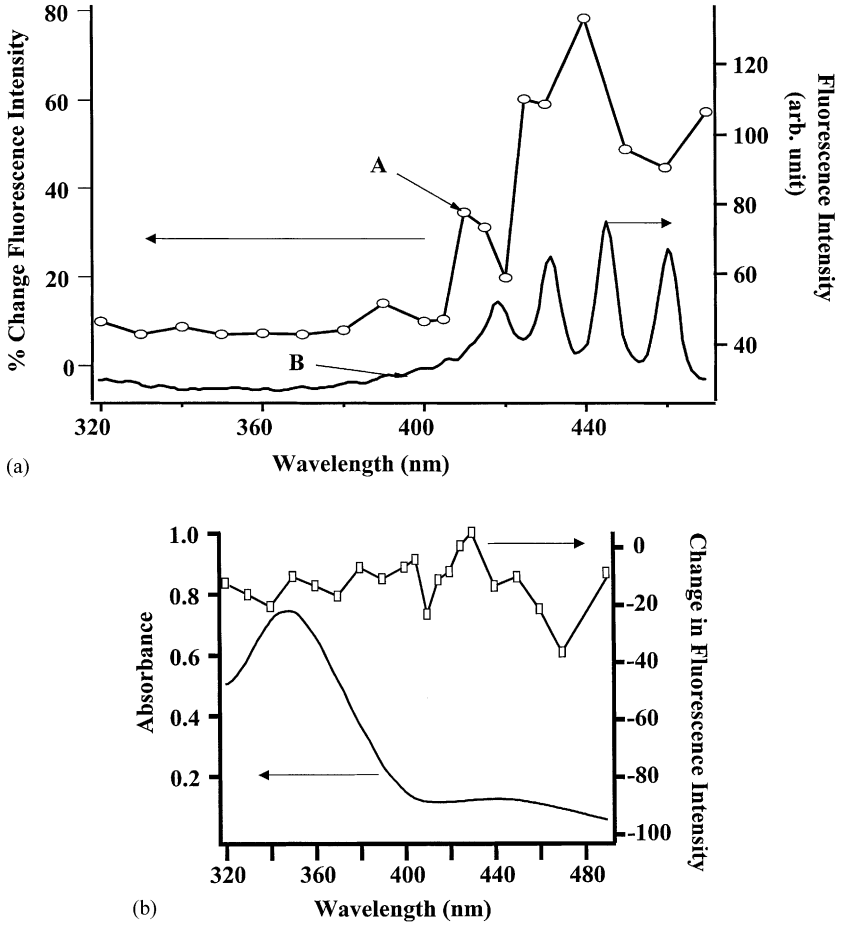

Fig. 3. (a) Excitation spectrum of uranyl (lower curve). Excitation wavelength-dependence of the photochemical response of calcein to uranyl following photolysis for 30 min using ~800 μW at 425 nm (upper curve). The solutions used for these measurements were made by adding 370 nM uranyl to 800 nM calcein. For simplicity, error bars are not shown, but are typically 3–4% of signal. (b) Absorbance spectrum of chromate (lower curve). Excitation wavelength-dependence of the photochemical response of calcein to chromate following photolysis for 30 min (upper curve). The solutions used for these measurements were made by adding 460 nM dichromate to 800 nM calcein. For simplicity, error bars are not shown, but are typically 3–4% of signal.

response curve. This was observed experimentally using deoxygenated samples.

As described above, the photochemical method was found to be highly selective for uranyl in the presence of two primary interferences, chromate and iron(III). This is illustrated in Fig. 5 and the data are tabulated in Table 1. This figure shows the time response of relative fluorescence recovery for 315 nM UO_2^{2+} in the presence of 1400 nM iron(III) and 280 nM dichromate. At these concentrations neither metal had an effect on the UO_2^{2+} photoresponse after 20 min of photolysis. Concentrations up to 5 mM chromate did not have an effect, but concentrations above 50 μm iron decreased the recovery. In the case of UO_2^{2+}, the calcein chromophore is left intact after photolysis since the primary action is cleavage of the alpha-carbon on the carboxylate group [22,23,39]. Although this photoproduct has not yet

Table 1
Table of relative responses (increase in fluorescence intensity from the quenched state) of calcein photooxidation after 20 min exposure to ~800 μW of light at 425 nm[a]

Uranyl ion concentration (nM)	Chromate concentration				Iron concentration		
	0 nM	140 nM	280 nM	555 nM	0 nM	700 nM	1400 nM
160	20.2 ± 3.7	18.6 ± 2.2	20.1 ± 1.8	18.3 ± 1.0			
315	26.2 ± 5.6	23.2 ± 1.4	24.0 ± 3.7	25.9 ± 3.9	26.2 ± 5.6	24.9 ± 6.2	19.1 ± 2.2
630	30.8 ± 7.4	34.2 ± 2.1	29.2 ± 6.0	27.2 ± 7.2	30.8 ± 7.4	32.2 ± 3.6	28.2 ± 5.3

[a] Responses for 160, 315 and 630 nM uranyl alone, and for uranyl at these same concentrations with 140, 280 and 555 nM dichromate, and for 315 and 630 nM uranyl with 700 and 1400 nM iron(III). The average of triplicate measurements are shown with the standard deviations of each.

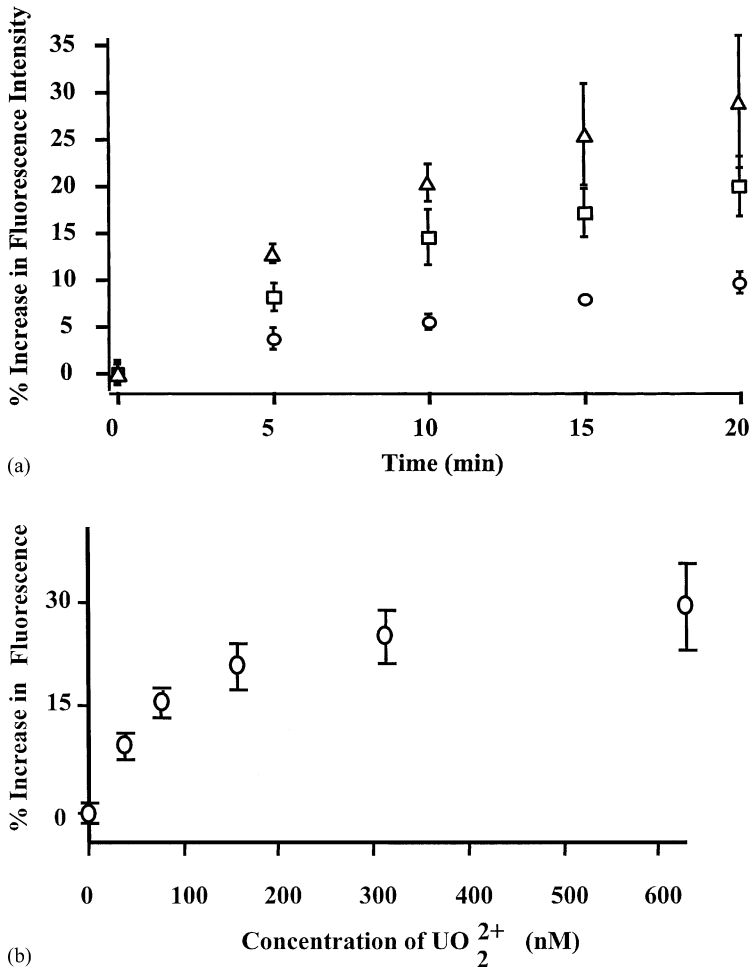

Fig. 4. (a) Time dependence of relative fluorescence recovery for 800 nM calcein quenched with uranyl upon exposure to approximately 800 μW of light at 425 nm. Uranyl concentrations shown are 40 nM (circles), 160 nM (squares), 630 nM (triangles). (b) Uranyl concentration-dependence of relative fluorescence recovery for 800 nM calcein following 20 min of photolysis using approximately 800 μW of light at 425 nm.

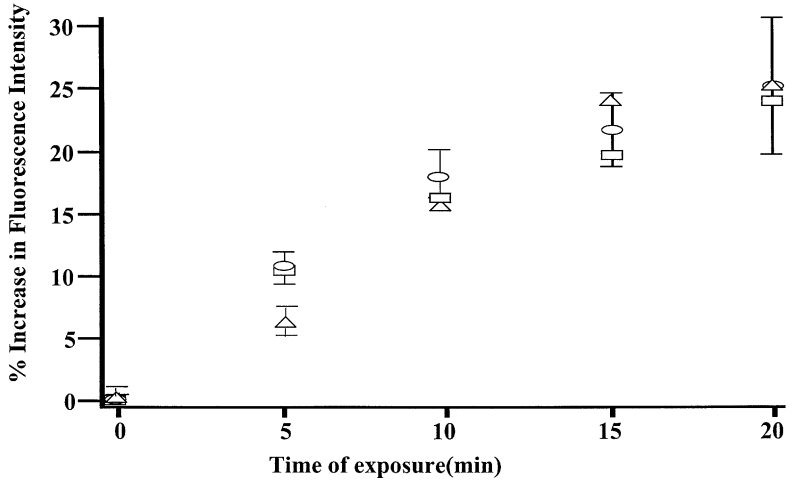

Fig. 5. Relative fluorescence recovery of 800 nM calcein quenched by 315 nM uranyl (circles), 315 nM uranyl with 280 nM chromate (squares) and 315 nM uranyl with 1400 nM iron (triangles). All data points are the average of three measurements. Error bars show ±1 standard deviation.

been identified its movement on a TLC plate is quite different from calcein.

Certain anions can also have an effect on uranyl photooxidation and should be considered in the experiment design [22]. The effect of chloride, carbonate and nitrate ions, at concentrations of 2 mM, on the relative calcein fluorescence recovery of samples containing 315 nM uranyl has been investigated. Nitrate had no effect on relative fluorescence recovery at this concentration. The chloride-containing sample showed lower rates of fluorescence recovery initially but after about 15 min this rate was the same as for a chloride-free uranyl solution. For uranyl responses measured after 20 min of photooxidation chloride had no effect. The response of the uranyl solution with carbonate present showed only half of the calcein fluorescence recovery after 20 min that was observed for a carbonate-free sample.

5. Conclusions

The use of photochemistry in combination with fluorescence quenching of an indicator dye, calcein, can provide improved selectivity for the determination of UO_2^{2+} in the presence of chromate and iron, compared to calcein quenching alone. Additionally, the photochemical effect can be used without loss of sensitivity. Detection limits of about 60 nM were measured for quenching experiments and 40 nM for photooxidation experiments. Chromate and iron(III) do not significantly interfere with this technique.

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