

## TRLFS Studies on Luminescence Enhancement of U(VI) Using Oxidants for Quencher Species in Samples

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### 1. Introduction

The pulse laser-based method detects photo-luminescent emission of U(VI) so that it is highly sensitive for non-isotopical determination of total uranium concentration. Thus, this method has been used for detection of trace quantity of uranium in the environmental, geological, and bioassay samples. One of widely-used pulse laser-based methods is kinetic phosphorescence analysis (KPA), of which instrument is commercially available. The intensity and lifetime of characteristic phosphorescence at 515-520 nm of hexavalent uranium are measured with an excitation wavelength of 425 nm. Particularly in KPA the use of phosphate-based luminescence enhancing agent (LEA) leading to the formation of uranyl-phosphate complexes extends the luminescence (LM) lifetime of uranium (> ~200  $\mu$ s) and subsequently the overall luminescence intensity.

In KPA, however, an extensive sample pretreatment procedure is required to reduce the luminescence quenching effects of ions and molecules present in samples [1,2]. During such procedures the uranium species in low oxidation states are also oxidized to hexavalent uranium so that the measurement of the total uranium concentration can be achieved. In general, a series of high temperature dry and wet ashing procedures is implemented prior to the addition of LEA to decompose the interfering substances.

The aim of this study is to examine the characteristics of the interfering species exhibiting significant quenching effects and to develop a way of minimizing the time required for the sample pretreatment step particularly for certain oxidizable quencher species. In fact, in a previous study we reported that significant LM quenching effects are observed from those possessing chemical reduction capability such as Fe(II) and cysteine [3]. Under such sample conditions it is shown that the conventional KPA is not applicable due to the short lifetime (< ~ 1  $\mu$ s), therefore a time-resolved laser-induced fluorescence spectroscopy (TRLFS) capable of monitoring shorter LM signal should be applied. In this study we examined oxidation reactions of selected strong quenchers including Fe(II), thiols, ascorbate and iodide with various oxidizing agent such as hydrogen peroxide, persulfate, monopersulfate and others. It is found that most of oxidizing agents tested are effective for oxidation of Fe(II) and U(IV) and some for thiols, thus enhancing the LM intensity of U(VI) after oxidation reactions. More importantly, for a few oxidants the oxidation reaction time required for full oxidation of millimolar levels of oxidizable quenchers

is shorter than a few hours at room temperature. This implies that such simple room-temperature oxidation method may replace the time-consuming ashing procedure for samples containing oxidizable quenchers. The characteristics of oxidation reactions between the selected oxidants and quenchers were examined in detail including reaction kinetics and temperature effects.

### 2. Experimental

The stock solution of uranium(VI) perchlorate was prepared as described elsewhere [4]. Cysteine, ascorbic acid, ferrous sulfate, hydrogen peroxide, ammonium persulfate (APS), potassium monopersulfate (MPS), potassium dioxide and nitric acid were used as received from Sigma-Aldrich for preparation of quencher and oxidant solutions. All solutions were handled in an Ar-filled glove box. Finally, each sample solution was 1:1.5 (v/v) mixed with a homemade-LEA (50 mM  $\text{Na}_4\text{P}_2\text{O}_7$ , 0.4 M  $\text{H}_3\text{PO}_4$ , pH 2.0) and transferred into a 1-cm quartz cuvette cell (Starna Scientific, Essex, UK). The final pH of the solution mixture was slightly elevated, but less than 2.1.

To collect LM spectra of U(VI) a gated ICCD-based TRLFS system was used as described elsewhere [4], with a gate delay time of 4  $\mu$ s and a width of 500  $\mu$ s. The LM intensity was calculated by area-integration of each spectrum. The LM lifetime was measured separately by analyzing the LM decay waveform recorded at 518 nm using an oscilloscope connected to a monochromator-PMT system.

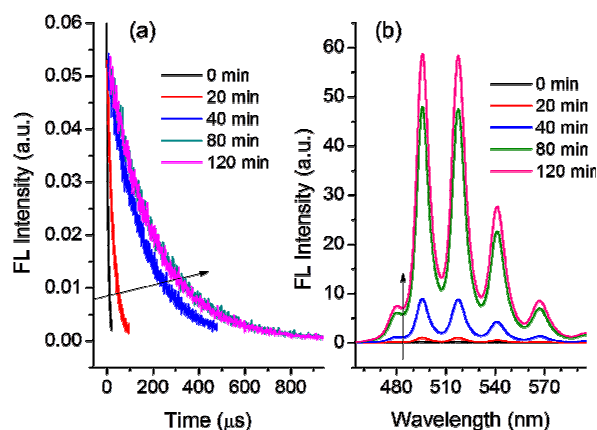


Figure 1. The effect of oxidation reaction between monopersulfate (MPS) and ascorbic acid, a LM quencher, on the LM lifetime (a) and spectral intensity (b) of hexavalent uranium. At zero minute the sample was mixed with MPS. ( $[\text{U}_{\text{total}}] = 30 \mu\text{M}$ ;  $[\text{MPS}] = 20 \text{ mM}$  at room temperature)

### 3. Results and Discussion

#### 3.1. Recovery of U(VI) LM Lifetime and Intensity by Oxidizing Reagent

In the presence of ascorbate, a strong quencher, the LM lifetime as well as the overall spectral intensity were drastically reduced as shown in Fig.1 (before the oxidant was added). Such quenching effects are dependent on the ascorbic acid concentration and thought to result from the collisional deactivation of excited state U(VI) population. Further speculation on the quenching process will be presented in detail.

However, after the addition of an oxidizing agent (monopersulfate, MPS) both LM lifetime and intensity of U(VI) were gradually recovered as shown in Fig. 1 (a) and (b). The recovery reached at a plateau value in each case in 2 h, which was about 75% as compared to the LM intensity measured from a blank sample not containing ascorbic acid and the oxidant. This strongly suggests that ascorbic acid is oxidized by MPS and transformed into a chemical form that is much less effective on U(VI) LM quenching.

#### 3.2. Fe(II) and Cysteine Oxidation and LM Intensity Recovery by Various Oxidants

In a previous study Fe(II) ions and cysteine were tested as major strong LM quenchers in a sulfate-reducing bacteria culture media. In Fig. 2 a test sample solution mimicking the culture media was prepared containing both Fe(II) and cysteine at 1 mM each. Then, various oxidants were tested by adding them in excess (> 10 mM). The LM intensity change over time was monitored via TRLFS by comparing the LM intensity with one measured from a blank sample not containing the quenchers and the oxidant, MPS.

As shown in Fig. 2 the LM intensity of uranium was recovered up to approximately 80% in 2 h for MPS. Other oxidants were found less effective than MPS. Interestingly, the use of the conventional acidic oxidants, i.e., HNO<sub>3</sub> only or HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> mixture resulted in a negligible luminescence change in 2 h. Thus, we conclude that MPS is capable of oxidizing both Fe(II) and thiols at room temperature so as to be a good candidate oxidant for the LM enhancement of U(VI). Particularly for thiols we speculate that the sulfurhydryl (-SH) group oxidizes beyond the formation of disulfides, i.e., to form sulfinic or sulfonic acid moieties. In contrast, some oxidants including APS and H<sub>2</sub>O<sub>2</sub> were found only effective for oxidizing Fe(II) to Fe(III) under the same reaction condition.

### 4. Conclusion

In this study, some strong LM quenchers affecting U(VI) LM intensity were identified using the TRLFS technique. We found that such strong quenching effects

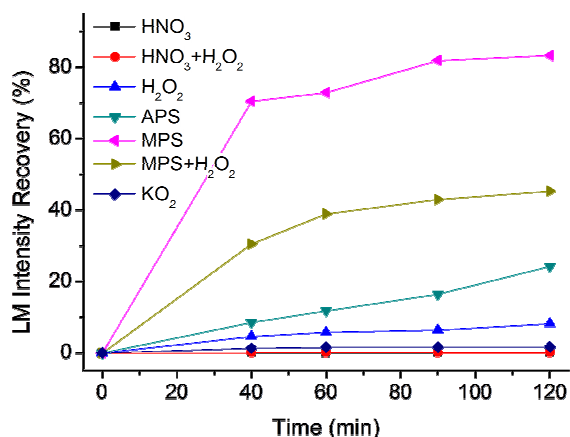


Figure 2. LM intensity change over time upon the addition of the selected oxidants at room temperature. Oxidant concentrations as follows from top to bottom oxidant in the graph legend; [HNO<sub>3</sub>] = 1 M; [HNO<sub>3</sub>]/[H<sub>2</sub>O<sub>2</sub>] = 1 M/48 mM; [H<sub>2</sub>O<sub>2</sub>] = 23 mM; [APS] = 20 mM; [MPS] = 20 mM; [MPS]/[H<sub>2</sub>O<sub>2</sub>] = 20 mM/2 mM; [KO<sub>2</sub>] = 15 mM. ([U<sub>total</sub>] = 30 μM; [Fe(II)] and [cysteine], 1 mM each).

can be attenuated for the quenchers capable of being oxidized by oxidizing agents, such as H<sub>2</sub>O<sub>2</sub>, MPS and APS. By using the proposed oxidation procedure the LM lifetime and intensity were recovered up to ~ 80% in 2 h at room temperature. Therefore, such simple oxidation step may replace the conventional sample ashing procedure for certain samples possessing oxidizable quenchers. The reaction characteristics of oxidants and temperature effects will be discussed in more detail.

#### Acknowledgements

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