



## Sorption of uranyl ions on titanium oxide studied by ATR-IR spectroscopy

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### ABSTRACT

ATR-IR spectroscopy was used to study the sorption of uranyl ions ( $10^{-4}$  M) onto titanium oxide (mixture of rutile and anatase). A circulation setup, filled with a solution in D<sub>2</sub>O, allowed recording of the evolution of the antisymmetric O=U=O stretching of uranyl species onto titanium oxide particles deposited on the ATR crystal. The band centered at  $915\text{ cm}^{-1}$  has been decomposed in two Gaussian peaks at  $920$  and  $905\text{ cm}^{-1}$ . From these values, and the observation that the ratio of the areas of the two peaks vs pH was constant, we have proposed that uranyl sorption on titanium oxide in the pH range 4–7 leads to the formation of one surface complex where uranium atoms have two different chemical environments. A trimer surface complex linked by two uranium atoms to the titanium oxide surface would be consistent with this interpretation.

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### 1. Introduction

The long-term safety of radioactive waste depositories is based on the sorption of radionuclides on engineered and natural barriers placed around the depositories. To predict the safety of such depositories at very long term, it is necessary to extrapolate sorption data measured at the laboratory scale to real systems and to very long times. Models used for this purpose must represent as accurately as possible the real sorption processes, otherwise the long-term prediction would be hazardous. Fitting of macroscopic sorption data, i.e., sorbed amount vs pH or vs concentration in solution, is not sufficient for that purpose, since it often leads to several possible sets of surface complexes and sorption constants [1,2]. To increase the reliability of modeling, information about surface charge and structure of surface complexes is needed.

The structure of surface complexes can be deduced from several spectroscopic methods, mainly X-ray absorption and infrared and fluorescence spectroscopies. Due to its ability to probe chemical bonds, infrared spectroscopy is a technique of choice for analyzing surface complexes. However, water strongly absorbs IR, and methods based on internal reflection spectroscopy have been developed to analyze wet samples. The use of the evanescent wave forming in water in contact with a medium with a higher refractive index in which an IR radiation is propagating limits the absorbance of water and probes a thin sample layer. This technique, called attenuated total reflection (ATR), can be performed directly onto metallic oxides suspensions, but Hug [3] developed a procedure of coating the

ATR element by a layer of colloidal mineral particles. For reviews addressing the current state of knowledge in the use of ATR-IR to determine surface complexes between inorganic ions and oxyhydroxide surfaces, the reader is referred to Lefèvre [4].

Uranium (VI) is a common actinide found in natural media and in radioactive waste. Moreover, it is often taken as a model for other actinides found in radioactive waste. Titanium oxides are good models for oxides, due to their stability, their low solubility in a wide pH range allowing study of the sorption of uranyl ions in the domain where they are highly soluble, and their well-known structure. Surface properties of titanium oxides have been extensively studied due to their photocatalytic properties [5]. Several studies about the sorption mechanism of uranyl ions onto titanium oxides have been published, in the absence of complexing ions [6–8], or in the presence of anions (carbonate, chloride, etc.) [8–11] in relation to sorption in seawater. These latter studies were connected to the objective of extracting uranium from seawater (where uranium concentration is about  $3.3\text{ mg/L}$  [12]). Most of these studies have only brought macroscopic information, such as the distribution coefficient ( $K_D$ ) or the effect of solution composition (pH, ionic strength, carbonate, etc.) on the sorbed quantity. More recently, Vandenborre and colleagues [13–15] have studied uranyl sorption on rutile and anatase using several spectroscopic methods (time-resolved laser fluorescence spectroscopy and second-harmonic generation) and have concluded on two different surface complexes depending on pH. Data from complementary spectroscopies would be interesting to confirm this result.

In this paper, we present results of ATR-IR spectroscopy of uranyl complexes sorbed on titanium oxide (mixture of anatase and rutile). Until now, ATR-IR has been mainly used for character-

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**Table 1**  
Characteristics of titanium oxide

Reference	Alfa Aesar No. 40458
Crystal structure	Mixture of rutile and anatase
Purity	99.9%
Specific surface area	223 m <sup>2</sup> /g
Isoelectric point	5.2

izing surface complexes of “light” oxoanions  $MO_n^{m-}$  ( $CO_3^{2-}$ ,  $SO_4^{2-}$ ,  $PO_3^{2-}$ , etc.) through the absorption of IR by M–O stretching [4]. For heavier oxoions, like  $UO_2^{2+}$ , the analysis is possible by recording the double bond (U=O) stretching [16], but the low frequency (around 900  $cm^{-1}$ ) leads to a decrease of the signal/noise ratio due to absorption of water. To avoid this interference, heavy water was used [17], and for the first time to our knowledge, in a circulation system allowing recording of the effect of the change of pH on the same sample. In addition to IR spectroscopy, we have performed batch measurements of the sorption of uranyl, zetametric measurements to determine the evolution of the surface charge and turbidimetric measurements to detect eventual precipitation in solution.

## 2. Materials and methods

### 2.1. Titanium oxide

Titanium oxide is a commercial powder (Alfa) and consists of a mixture of anatase (about 80%) and rutile (Table 1). Surface areas and porosities were determined by nitrogen adsorption and desorption on a Coulter SA 3100 instrument, after degassing 30 min at 120 °C, using the Brunauer–Emmett–Teller (BET) model for surface area and the Barrett–Joiner–Halenda (BJH) model for the estimation of the porosity. The pore distribution is as follows: 14% whose diameter is less than 6 nm, 38% between 6 and 20 nm, 34% between 20 and 80 nm, 14% whose diameter is higher than 80 nm. Transmission electron microscopy has shown agglomerates of ca. 100 nm of small particles (5–20 nm). The measured specific area of 223 m<sup>2</sup>g<sup>-1</sup> is consistent with spherical particles of ca. 6.5 nm in diameter.

### 2.2. ATR-IR spectroscopy

Measurements were performed in a homemade liquid cell containing 6 mL of solution and connected to a 100-mL polyethylene vessel through a peristaltic pump. The geometry of the ZnSe crystal (50 × 10 × 2 mm) and its double-sided coating led to 25 reflections. A thin layer of TiO<sub>2</sub> particles was deposited on both sides of the crystal by a procedure detailed elsewhere [16]. The total mass added on each face was about 0.5 mg. NaNO<sub>3</sub> 0.1 M was chosen as a background electrolyte since it has low complexing properties toward uranyl ions and no absorption in the mid-IR range (except around 1370  $cm^{-1}$  where NO<sub>3</sub> stretching takes place). The experimental procedure was similar to that of Peak et al. [18], allowing adjusting and measuring of the pH and addition of the uranyl stock solution. Nitrogen is continuously flowed over the solution to avoid contamination by CO<sub>2</sub>. The particle film was in contact with the aqueous solution which was circulating at 1 mLmin<sup>-1</sup>. Spectra were recorded at a resolution of 4  $cm^{-1}$  with 128 coadded scans, with a dry air-purged Nicolet spectrometer using OMNIC software for the data processing. A linear baseline was observed between 865 and 1000  $cm^{-1}$  with a slight drift during the experiment duration. The coated crystal was first washed by flowing the electrolyte solution (0.1 M NaNO<sub>3</sub>), and then the background spectra were recorded. The spectra of sorbed uranyl/nitrate ions were recorded every 5 min by flowing a 10<sup>-4</sup> M uranyl solution with increasing pH. This concentration was found to be the lowest value leading

to a sufficient signal/noise ratio. When the increase in the spectrum intensity with time is less than 5%, corresponding to about 15–20 min, the equilibrium state was assumed to be reached and the pH was raised by addition of NaOH. The solutions have been prepared in D<sub>2</sub>O 99.8% to avoid interference between absorption of H<sub>2</sub>O and uranyl bands [16]. Values of pH measured with an electrode standardized in H<sub>2</sub>O solutions are given. pD values can be determined by use of the equation  $pD = pH + 0.40$  [19].

### 2.3. Turbidimetry

Turbidity measurements of uranyl solutions were performed with a Hach 2100N turbidimeter, to control eventual precipitation of hydrolyzed species.

### 2.4. Sorption

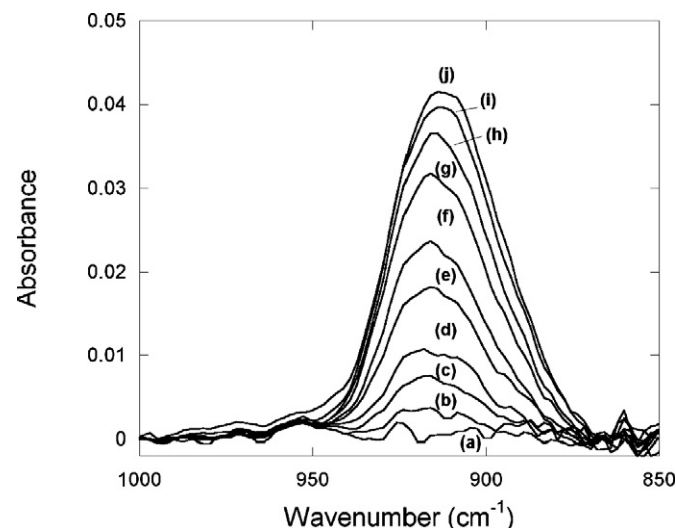
The sorption was studied with kinetic conditions close to ATR experiments. A suspension of TiO<sub>2</sub> with 64 mg/L solid concentration in 10<sup>-4</sup> M UO<sub>2</sub>(NO<sub>3</sub>)<sub>2</sub> was prepared in a 100 mL reactor. The initial pH was adjusted at 1 with HNO<sub>3</sub>, the suspension was stirred for 20 min, and then 3 mL was withdrawn and filtered with a 0.025- $\mu$ m membrane (Millipore). Then, the pH value was increased by addition of NaOH, and after 20 min, a new sample was withdrawn. The uranyl sorbed quantity was deduced from the concentration in solution determined by ICP-OES.

### 2.5. Electrophoretic measurements

The zeta potential measurements were carried out using a Malvern Zetasizer Nano zetameter. After optimization, a concentration of TiO<sub>2</sub> of 250 mg/L was chosen. Each measurement was performed 3 times. pH was adjusted with HNO<sub>3</sub> and NaOH and ionic strength was fixed at 0.1 M with NaNO<sub>3</sub>.

## 3. Results

IR spectra of uranyl sorbed on titanium oxide as a function of the pH values of the flowing solution are shown in Fig. 1. A band centered around 915  $cm^{-1}$ , whose intensity increases with pH, is observed. This band can be assigned to the antisymmetric stretching  $\nu_3$  of the uranyl ion sorbed onto TiO<sub>2</sub>, since the intensity increases with pH in the same manner as the sorbed quantity (see



**Fig. 1.** ATR-IR spectra of uranyl sorbed on TiO<sub>2</sub> ([U] = 10<sup>-4</sup> M, NaNO<sub>3</sub> = 0.1 M in D<sub>2</sub>O) for several pH meter readings: respectively 2.3, 2.9, 3.3, 3.6, 4.1, 4.4, 5.0, 5.4, 6.2, and 7.0 from (a) to (j).

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