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Aqueous Solutions of U(VI) as Studied by Time-Resolved Emission Spectroscopy (TRES) : A Round-Robin Test

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Results are presented of an interlaboratory round-robin study of the application of time-Resolved Emission Spectroscopy (TRES) to the speciation of uranium(VI) in aqueous media. This involved 13 independent laboratories, using various instrumental adevices and data

analysis methods. In some cases, experimental data from a laboratory were analysed using different softwares. Samples were prepared based on appropriate speciation diagrams and in general were found to be chemically stable for at least six months. Four different types of aqueous uranyl solutions were studied: (i) acidic medium where $UO_2^{2+}{}_{aq}$ is the single emitting species, (ii) uranyl in the presence of fluoride ions, (iii) uranyl in the presence of sulfate ions, and (iv) uranyl in aqueous solutions under various pH conditions, promoting hydrolysed species. Results between the laboratories are compared in terms of number of decay components, luminescence lifetimes and spectral band positions. The potentials and limitations of TRES in uranyl analysis and speciation in aqueous solutions are discussed.

Index Headings: **Uranium(VI); Intercomparison; Speciation**

1. INTRODUCTION

Time-Resolved Emission Spectroscopy (TRES) is being increasingly used for the study of various aspects of the (photo)chemistry of actinides in solution. Among the luminescent actinides, uranium, as the U(VI) oxidation state, can be considered as a model element and has been the subject of numerous studies for questions relevant to photophysics, nuclear fuel cycle or to environmental problems.

The fundamentals of the photophysics of the uranyl ion have been extensively studied, both in solution and in the solid state.[1-6] Particular emphasis has focussed on the nature of the excited states involved, and on the non-radiative deactivation mechanisms and other kinetic aspects of excited uranyl ion decay. Although these studies have shown that electronic excitation is localised within the UO_2^{2+} group, and the lowest absorption and emission maxima are only slightly affected by coordinated ligands, vibrational fine structure is observed in both absorption and luminescence spectra, and this depends both on the nature and symmetry of the species,[7] such that different spectral signatures are observed for each emitting uranyl species. In addition, and of particular relevance to TRES studies, these different emitters have markedly different lifetimes (τ), such that they can be characterised by observation within different time windows. Chemical U(VI) studies with TRES include the determination of equilibrium and reaction rate constants[8-10] and analytical aspects such as the

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detection of trace amounts of radioactive luminescent species.[11-13] From the above comments, it is clear that uranyl luminescence in solution is of interest to a large community of scientists for both fundamental and applied reasons.

Examination of the data that have been published on the spectroscopic characteristics of U(VI) in solution reveals large differences between the reported data in terms of the lifetime of the excited state, τ, and emission spectra, even for samples which should be chemically identical. The most striking discrepancies appear for the system U(VI)/H_2O at various pH values, where, for the same species, lifetimes ranging from $\tau = (8.3 \pm 0.3)$ µs[14] to $\tau = (80 \pm 5)$ µs[12] have been reported, while differences in the position of the maximum of the emission peaks of more than 3 nm can be found in the literature.[12,15]

Considering the great importance of U(VI) chemistry in relation to both its behaviour in natural systems and its relevance to studies by TRES, such discrepancies need to be elucidated in order to improve our understanding of the phenomena involved, and to obtain reliable values of both spectral maxima and lifetimes of the various species involved. To this end, the French *Groupement de Recherches* PRACTIS has sponsored the organization of a round-robin test aiming at defining the potential, together with the limitations, of TRES as a tool for the study of U(VI) behaviour in aqueous solution. Such an approach seems the best way to address the increasing demand for accurate quality assurance and control on levels of uranium under environmental conditions.

2. METHODOLOGY OF THE ROUND-ROBIN TEST

2. 1. Speciation calculations. Theoretical speciation in solution was used as a basic tool to predict the presence of the various species and to adjust the chemical compositions. The theoretical predictions were performed by means of the JCHESS software developed by *Ecole des Mines de Paris,*[16] using the OECD/NEA thermodynamic database,[17] although some interrogations remain on some of the formation constants, especially for the various carbonato species.[18]

For the calculations, the values of pCO_2 ($3x10^{-4}$), together with the dissociation constants of H_2SO_4 and HF were taken into account. The uranium concentration was chosen equal to or below $5x10^{-6}$ M, in order to avoid precipitation of uranium as schoepite around pH 5 and to ensure that most of the participants would be able to detect the luminescence whatever their experimental setups.

Solution A only contains $UO_2^{2+}{}_{aq}$ as a luminescent species. To avoid hydrolysis and carbonate complexation, an aqueous solution of perchloric acid (1 M) was chosen because of its very weak complexing ability.[19]

Solution B was designed to contain one species in common with solution A together with another uranyl complex formed by addition of sodium fluoride. Around pH 2, $UO_2^{2+}{}_{aq}$ and UO_2F^+ are dominating the speciation, while UO_2F_{2aq} concentration is roughly two orders of magnitude below.

Solution C contains $UO_2^{2+}{}_{aq}$ and other species formed by addition of sodium sulfate. Around pH 1.5, two dominant species ($UO_2^{2+}{}_{aq}$ and UO_2SO_{4aq}) and one minor species (~ 1 %) ($UO_2(SO_4)_2^{2-}$) are present.

Solutions D, E, F and G were aimed at testing the importance of different hydrolysed U(VI) species. The variation of $UO_2^{2+}{}_{aq}$, UO_2OH^+, $UO_2(OH)_{2aq}$ and of minor species such as $(UO_2)_2(OH)_2^{2+}$, $(UO_2)_3(OH)_5^+$, UO_2CO_3 and $(UO_2)_2CO_3(OH)_3^-$ are represented in Figure 1, while Table I summarizes the theoretical results of all the speciation calculations.

2. 2. Sample preparation and chemical analysis. A stock solution ([U(VI)] = 10^{-2} M, [$HClO_4$] = 1 M) was obtained by dissolving UO_3 (Cogema/Pierrelatte) in an aqueous solution of $HClO_4$ (perchloric acid, 70%, Prolabo, Normapur and ultrapure water, Millipore, MILLIQ+). Aqueous stock solutions of NaF (10^{-2} M, Prolabo, Normapur) and Na_2SO_4 (10^{-1} M, Prolabo, Ultrapur) were also prepared. Successive dilutions of the stock solutions were performed to reach the required final compositions. Sodium hydroxide pellets (Merck) were dissolved in ultrapure water to adjust pH (solution E). pH measurements (pH-meter and electrode: DMA 7113, Metrohm) were performed in a thermoregulated cell (T = 298 K, controlled with a temperature probe PT100) after calibration with three buffer solutions (pH = 1, 4 and 7) under similar conditions.

The quartz cuvettes were filled with the freshly prepared solutions and were sealed by laser heating of the glass. A code number, which is engraved at the top, is composed of a letter, ranging from A to E, corresponding to the sample type and of a number, corresponding to the rank of preparation of the cuvette. For a given type of sample (A to E), 16 cuvettes were prepared, from which 13 were sent to the different participants and 3 were kept for chemical analysis. The remaining stock solutions were kept in hermetically closed glass flasks (with no possible contact with air, at T = 293 K). The exact compositions of the samples are given in Table I.

The samples were prepared in May 2001 and shiped in class A containers in order to prevent any radioactive damage. Most of the measurements were performed between June and August, although some were done in October and November. All results were received by November, 30th, 2001. By the end of November, (six months after start of experiments), chemical tests were performed in order to check the stability of the solutions over this period. The chemical analysis involved the remaining solutions which had been used, together with the three remaining cuvettes of each sample type. Ionic chromatography was used to determine the F^- and SO_4^{2-} concentrations, ICP-QMS was used for uranium (together with ICP-SF-MS for low concentration values) and potentiometry for ClO_4^-. The chemical composition and pH values were very stable for samples A, B, C, D and F (variation within the experimental uncertainty). In contrast, sample E, and to a lesser extent sample G, presented shifts in the pH values and decreases in the total uranium concentration as illustrated in Table I. These changes are almost certainly attributable to the high pH values of the solutions, which favour uranium adsorption on the walls of the containers.

2. 3. Data to be extracted from the samples. The following questions were asked for each sample :

i. type of decay (mono or multi-exponential) and number of components,
ii. values of the corresponding lifetimes,
iii. peak positions for the global emission spectrum,
iv. in case of multi-exponential decays, peak positions associated to each lifetime,
v. in case of multi-exponential decays, relative intensities of each component, with indication of the spectral range used for such a determination,
vi. value of the relative global fluorescence efficiency, taking sample « A » as a reference (100% fluorescence efficiency), with an indication of the spectral range used for such a determination.

The participants were asked to perform all the measurements at T = 298 K. An estimation of the uncertainty in the lifetime measurement was requested, based only on repeated measurements of the same sample. Finally, general information on the experimental setup, data analysis methods and computer programs were requested.

The sample compositions were kept secret, so that it was impossible to use chemometric treatment or other statistical methods to compare samples. Furthermore, no blank sample was provided. This has an important implication in relation to the intensity values observed (questions v. and vi.). In this sense, the round-robin test is much more difficult than any

standard situation, for which the chemical composition is known. Therefore, the aim of this test is not to derive any equilibrium or reaction rate constant for the processes occurring, but rather it is to assess the potential of TRES for such determination in the case of aqueous solutions of uranyl ion.

2. 4. General overview of the round-robin test. Two laboratories were not able to provide any data because of technical problems. As is usual, details of these groups have been nevertheless included in the figures. Two laboratories performed the experiments at temperatures different from T = 298 K (293 and 296 K). However, this does not seem to have any noticeable impact onto the results, as compared to the other laboratories.

One participant performed two runs with slightly different setups (moving and changes in the lenses used to collect light) while the lifetime data were processed using two different programs. Therefore, these two sets of measurements have been considered as corresponding to two different « laboratories », and are indicated with two distinct code numbers.

A large variety of data formulation was provided by the participants. The lifetimes results came in various forms including no value (although at least one emission peak was indicated), estimated values (for example $\tau > 10$ µs), limits (for example 1 µs $< \tau <$ 10 µs), and precise values (with and without uncertainties). In two cases, lifetimes and/or associated intensities were given for various wavelengths for each sample. In agreement with the participants, only the averages have been considered.

Some spectral components were described as « structureless » or « indiscernible from others » or were not characterized at all, although a lifetime was given. In one case, the emission spectra were characterized by peak values and individual FWHM (Full Width at Half Maximum) of the peaks. Although this data is very interesting, this information was not requested from the participants because it was considered, on the basis of previously published papers, that too few laboratories could give such details, making such information of rather limited value for the round-robin test. As a consequence, the FWHM data have not been included in the discussion of the results.

To the best of our knowledge, this is the first round-robin test organised in this field. In order to evaluate the reliability of the test itself, a global criterium has been defined to estimate the compliance of a given data set with the list of questions of the round-robin test : A data set is considered to fully match the demand of the round-robin test if, for each sample, (i) each component is defined by a precise lifetime value or limits (see above), (ii) for each

component at least one emission peak is given or any equivalent indications, such as « structureless », (iii) in the case of a multicomponent spectrum (as stated by the participant), values for all the associated intensities are provided, regardless of the range of wavelengths used to get this value. Laboratories 1, 3, 9, 12 and 13 correspond to this criterium. This certainly means that the round-robin test was difficult, as already stressed. It is important to note that this is by no means a measure of the reliability of the laboratories of concern or of their detection abilities.

2.5. Data analysis and presentation of the results. A code number has been randomly attributed to each laboratory, ranging from 1 to 14. For anonymity reasons, these numbers are used only in the discussion of the spectroscopic results (section 4). In the sections dealing with setups and data processing (sections 3 and 5), no code number is given.

The number of laboratories which provided a result is different, depending upon the data of interest, with a maximum of 12 independent items. This renders sophisticated statistical data treatment probably inappropriate, at least in some cases. Although well-established procedures of characterization of interlaboratory tests exist,[20] comprising the removal of « outlier » values, it was decided to limit statistical treatment and data censoring to a minimum.

For a given data set, the figures provided by the participants were considered with all their digits, in order to calculate the mean value, M. The error, σ, was then calculated according to :

$$\sigma = \frac{1}{N}\sum_{N}\left|(Exp - M)\right|$$

where N is the number of experimental results and Exp is the data provided by lab. #x. According to the derived σ value (usually limited to one digit), the significant number of digits of M was then set, and the results are presented as (M ± σ) [units]. In a few cases, very high and/or very low values were removed, and a comparison is made between the primary and « corrected » averages. The uncertainties provided by the participants are, in most cases, largely underestimated as compared to the calculated σ value. This is partly due to the fact that these two quantities are not of the same nature, as the participants were asked to derive an uncertainty on the basis of repeated measurements of the same sample, while the σ value is obtained for different aliquots of a same stock solution and different apparatus. Considerable dispersion was observed among the relative intensities associated with the different lifetimes,

so that these data cannot be discussed further. Such a dispersion is partly due to the different excitation wavelengths used but may also be a consequence of the absence of blank sample and emission correction (for some of the laboratories) or indeed differences in the data analysis.

Considering that none of the participants observed more than 3 lifetimes in any of the samples, the lifetime values were arbitrarily classified in three categories at most : « short » (τ_1), « medium » (τ_2), and « long » (τ_3), even though this may not correspond to the chemistry prevailing in the sample. As expected from the various chemical compositions of the samples, the values to be included in a given category do not necessarily coincide from one sample to the next. This subjective approach aims at facilitating the first global data analysis by evidencing trends in the results. In a few cases, a lifetime value was difficult to ascribe to a precise category and the attribution has been made on the basis of the other data provided for the sample of interest, as discussed in the text (see also below in this section).

The number of detected peaks was not constant either for a given laboratory for different samples or for a given sample for various laboratories. For cases where at least two lifetimes were indicated, when only the emission peaks of the global spectra were given the emission peaks were not considered in the data treatment. Unless stated elsewhere, as discussed in the text, the peak values of a given sample can be grouped into 6 categories at most, referred to as P1 to P6. The criterium chosen to insert a given peak value in a precise category was that it makes as small a contribution as possible to the global standard deviation. However, this classification may become subjective and specific cases will be discussed in the text.

In principle, a given lifetime should be associated with a particular group of emission peaks in order to fully characterize an emitting species. However, this bi-modal description could not always be achieved because the information provided by the participants was not complete in all cases. Associated lifetime and peaks, when provided, have been treated as a whole so that if the lifetime corresponds to the « medium » lifetime category, the emission peaks provided by the participant were also considered to be associated to this medium emission spectrum and *vice-versa*. On the other hand, although some lifetime values have been considered as « outliers » and are not considered in the average, the associated emission peaks have not been automatically discarded from the mean.

In the text, the general expression « the participants » or its equivalents refer only to those laboratories which provided data for the category under discussion. For each sample, the chemical composition and its consequences in terms of speciation are briefly recalled.

Particular cases are then discussed before the general trends are examined and discussed. Whenever possible, comparisons are made with previously published values and conclusions are derived.

3. SETUPS AND METHODS

Table II displays the various experimental setups used, as indicated by the participants (one laboratory provided no information and no data). The participant who received two code numbers (see section 2.5) is included only once in this Table, as changes were mainly related to data processing. In this table, the equipements have been grouped according to similarities so that no connection can be made with the laboratory code number.

3. 1. Excitation. The excitation wavelength chosen by seven laboratories is 266 nm (pulsed quadrupled Nd :YAG laser). The other excitation characteristics are rather similar from one laboratory to the other, in particular the average energy entering the sample.

3. 2. Light collection and detection. None of the participants used Time Correlated Single Photon Counting (TCSPC) or Circularly Polarized Luminescence (CPL) devices. The detection systems were either composed of a monochromator (but in one case, where cut-off filters were used) connected to a photomultiplier tube and then to a fast oscilloscope (PM detection) or of a diode array detector (or CCD camera) and subsequent electronic detection device (diode detection). Five laboratories are equipped with the PM detection alone, four laboratories with the diode detection alone, one laboratory uses the mixed system (diode and PM detection) and one laboratory is using a continuous excitation mode (no time-resolution). In addition to these basic setups, three laboratories are equipped with a fluorimeter. Two laboratories collect light through optical fibers.

The diode detection systems are mainly provided by the same manufacturing company so that four of these systems are very similar. In the case of the PM detection, similar characteristics are also obtained. However, in one case the PM chosen may be slightly less sensitive than the others. In fact, three laboratories are equipped with PM having very similar characteristics, from which two also possess the same type of monochromator and oscilloscope. Only 3 laboratories make emission corrections by use of standards or any other method, while 5 laboratories do not correct their emission spectra (4 did not answer this question).

3. 3. Data processing. In contrast to what is observed with data acquisition, the softwares and data analysis methods are very different.

For decay analysis, a first group of 8 laboratories uses commercial packages (EXCEL, IBH, IGOR PRO4, Kaleidagraph, Origin, Sigma Plot), a second group of 3 laboratories has written « home made » programs and one laboratory uses either a commercial package (Origin) or home made programs.

For emission spectra analysis the same variety is observed, with commercial packages for 5 participants (Dylor, Grams-32, IGOR PRO4, Origin) and home made programs (2 participants). The other participants either did not indicate their choice or did not provide emission data.

Concerning the mathematical basis on which the data (decay or emission) are fitted, most of the participants did not give detailed descriptions. For lifetime analysis, either linear or non-linear methods are used; Marquardt and simplex algorithms are cited and two participants indicated tests based on residuals. For emission data, the information obtained is even scarcer: the spectra are fitted with gaussian or lorentzian/gaussian functions in two cases. The emission data acquired with one of the diode detection systems are fitted starting by the longest lived component parameters. For one of the PM detection systems, each decay is fitted independently (lifetime and relative intensities), from which the emission spectra of each component are reconstructed. These two methods are directly linked to the type of detection system used. One laboratory uses target factor analysis both for decay or emission spectra. Nothing is indicated by the other participants.

3. 4. Conclusion on setups. Considering the similarities in equipement (see Table II), it is difficult to explain why the measurement capacities of the different institutions were so dissimilar, some being near their detection limits, while others were still largely above, as could be inferred from the spectra provided. In the list of participants which could provide all the information requested, one can find two different excitation wavelengths, mixed detection system (PM and diode), diode detection system alone, PM detection system alone, light collection with and without optical fibers, commercial data treatment packages and home made programs. Therefore, none of the specific technical options examined in the above sections appears to be a definite hindrance to sensitive measurements.

4. EXPERIMENTAL RESULTS

4. 1. Sample A. Chemically speaking, sample A contains only $UO_2^{2+}{}_{aq}$ as a luminescent species. Sample A was the only one for which practical problems occured. The lab. #9 sample was broken prior to measurements and a crack in the cuvette was observed in case of lab. #11, once the measurements were performed. Lab. #12 indicated that the measured lifetime showed a pronounced decrease within the first two hours of measurements before the lifetime remains constant. No leak was observed in the cuvette. This unexpected phenomenon could not be explained. Therefore, the lifetime values for sample A of labs. #9, 11 and 12 were not considered. All other participants observed a single lifetime. The results will be therefore discussed considering a single lifetime category and its associated emission peaks, ascribed to the single fluorescent species derived from the speciation, $UO_2^{2+}{}_{aq}$.

Whatever the excitation wavelength used, sample A is, by far, the most luminescent for all the participants. The mean lifetime is equal to $\tau = (7.9 \pm 0.7)$ µs. This value is in very good or good agreement with values published for chemical composition and temperature conditions very close to that of sample A : $\tau = (7.9 \pm 0.3)$ µs for $[HClO_4] = 1.02$ M and T = 23°C[21] or $\tau = (8.1 \pm 0.6)$ µs for $[HClO_4] = 1$ M, T = (24 ± 2)°C[22] or $\tau = 7.5$ µs for $[HClO_4] = 1$ M, room temperature.[23]

The emission peak values corresponding to $UO_2^{2+}{}_{aq}$ are reported in Table III and results are presented in Fig. 2. The calculated σ values appear to be higher for the first and last peaks than for the other peaks, which is mainly due to the limited number of laboratories which provided data (see Fig. 2). Note that the σ values below 1 nm are smaller than the effective wavelength step used by some of the participants. The peak emission values obtained through the round-robin test appear to be in good agreement with previously published values for $UO_2^{2+}{}_{aq}$ for various chemical compositions, as can be seen in Table III.

The band at 470 nm (which is not observed by all the groups, see Table III) seems to have a different origin from the other peaks. The structure in the emission spectrum is normally associated with the O=U=O symmetric stretch vibration, which has an energy of about 880 cm^{-1}.[24] If the peaks in Table III are converted into wavenumbers and then the differences between successive peaks (Δν) are calculated, all the peaks P2 to P6 have about the same separation (872 ± 14 cm^{-1}), but the separation between the 470 nm (P1) and the 487.9 nm peak (P2) is considerably smaller (781 cm^{-1}). This may be associated with some "hot" band, and is likely to be more strongly affected by variations in temperature than the other peaks. The 470 nm peak is probably best left out of any comparative studies.

Asa whole, the round-robin test provides a very good spectroscopic characterization of $UO_2^{2+}{}_{aq}$ in a 1 M $HClO_4$ aqueous solution, through lifetime and emission peaks. As the chemical composition of sample A is rather easy to prepare and considering its overall good stability over six months, this may be a first step towards the conception of a lifetime and emission standard for the radiochemical community using TRES.

4. 2. Sample B. The speciation calculations indicate that sample B contains the same chemical species as sample A, $UO_2^{2+}{}_{aq}$ (67%, ≈ 8.4 10^{-7} M), together with UO_2F^+ (≈ 33%, ≈ 4.1 10^{-7} M), the other complexes being below 1% (below 10^{-8} M).

Whatever the excitation wavelength used, sample B is significantly less luminescent than sample A, with a global relative intensity (question vi.) equal to 13 % at most. Nevertheless, lifetime values were provided by 10 laboratories. From these, two laboratories observed a mono-exponential decay behaviour, seven laboratories a bi-exponential behaviour and a single laboratory a tri-exponential behaviour.

First, the three lifetime categories defined above (see section 2.5) were used to sort the data: $\tau_1 = (0.6 \pm 0.3)\mu s$, $\tau_2 = (3.9 \pm 0.7)\mu s$ and $\tau_3 = (27 \pm 11)\mu s$. Although the single lifetime value of 1 µs provided by lab. #7 appears closer to the « short » lifetime category than to the « medium » lifetime category, it has been considered as a « medium » lifetime, due to the associated emission peaks. If this value is not considered, one gets: $\tau_2 = (4.3 \pm 0.2)\mu s$. Table IV presents the emission peaks of the three lifetime categories detected in sample B, together with the values derived for $UO_2^{2+}{}_{aq}$ (sample A), for the sake of comparison.

Wheter sample B comprises a single lifetime or at least two distinct lifetimes has a very important physical implication. Should the luminescence decays contain a single lifetime, although two different ground-state chemical species are present in the solution, this means that the photochemical processes occur on a much shorter time-scale than the decays to the ground states so that significant mixing of excited states occurs.[25] Conversly, if the decays are multi-exponential, this implies that the photochemical processes are very slow as compared to the individual decays. In our opinion, the distinction between mono/multi-exponential decay is more meaningfull than distinction between single/bi/tri-exponential decay, because the first case underlines a precise photochemical process while the second case also includes problems of detection and resolution of short lifetimes.

The question of the mono- or multi-exponential behaviour of U(VI)/F^- aqueous solutions has been long debated in the literature: One publication[26] presented only

monoexponential decays, from which the conclusion that photochemical processes were very efficient was derived. In another paper devoted to this system, a bi-exponential decay was observed for $UO_2^{2+}{}_{aq}$ and the first complex, while the second excited complex formation was thought to be very fast as compared to the decays, leading to a monoexponential behavior for high F^- concentrations.[27] Finally, another publication states that the free $UO_2^{2+}{}_{aq}$ and the two first successive fluoride complexes lead to multiexponential behavior of the decays.[28] All these experimental studies were performed for different ionic strengths and overall chemical compositions of the samples, that are also different from the chemical conditions prevailing in sample B. As a consequence, no consensus can be infered from the literature. On another hand, the data collected in this round-robin test can be safely considered to be extracted from identical samples. However, no information can be deduced from the round-robin data about the mono- or multi-exponential nature to be obtained in other publications dealing with U(VI)/F^- aqueous solutions, due to large differences in ionic strength.[26-28]

One of the two laboratories observing a single decay is the one which performed the experiment twice with slightly different setups but identical cuvette (see section 2.4). In the second run, a bi-exponential decay is observed, and no explanation could be given of this difference, which sheds some doubts on both data sets. In neither set of data are emission peaks provided, so that these two data sets are very limited. The other laboratory providing a single decay gives τ = 1 µs, a value which appears somewhat as an outlier (see above). Therefore, these two data sets appear somehow doubtful, so that the round-robin test gives reasonable evidences that the sample B decays are multi-exponential in nature, although no definite consensus could be obtained on this question. In the following, the round-robin data will be only discussed on the assumption that they actually correspond to a multi-exponential behavior of sample B decay. To be consistent, in this discussion, the two data sets with a single lifetime value are *not included*. In Table IV, this has no impact onto M and a very limited effect on σ (increase of 10% in σ for P2 and P5).

Assuming a multi-exponential behavior, the three lifetime categories observed are to be ascribed to $UO_2^{2+}{}_{aq}$ and the first two fluoro complexes. Examination of Table IV allows one to conclude that the emission peaks of the short lived species of sample B are very similar to those of $UO_2^{2+}{}_{aq}$ as characterized in sample A. By contrast, the other two lifetime categories (medium and long lifetimes) are characterised by emission peaks that cannot be reasonably ascribed to $UO_2^{2+}{}_{aq}$. One can note a red shift of all the peaks from the short to the medium (roughly 5-6 nm) and then to the long lived component (roughly 4 nm). No comparison is possible with the emission wavelengths published for a U(VI)/HF/water

mixture, because of the large differences in the chemical compositions ([HF] = 0.67 M[29]).The published lifetime values (1.75 μs or 2.4 μs for $UO_2^{2+}{}_{aq}$ and 50μs for the first complex,[28] or 75 or 150 μs for the first two fluoride complexes[27]) or those indicated in another paper (τ = 300 μs, average value ascribed to the 1 :3 and 1 :4 complexes)[29] do not correspond to the lifetime values given in Table IV. Furthermore, in sample B, the τ_1 value ascribed to $UO_2^{2+}{}_{aq}$ is very different from that obtained for sample A. These large discrepancies in the $UO_2^{2+}{}_{aq}$ lifetime values are thus ascribed to changes in the medium composition. The effect of the medium on the $UO_2^{2+}{}_{aq}$ lifetime is a well-known phenomenon, which has received detailed attention in the case of perchlorate-based supporting electrolytes.[30] It would thus appear reasonable to suppose that a similar effect occurs for uranyl complexes. To our knowledge, this question has never been studied. However, a quantitative description of such an effect is clearly out of the scope of the round-robin test.

From the comparison of the data for samples A and B, it can be concluded that the species $UO_2^{2+}{}_{aq}$ can be characterized by a set of emission peaks, that are not liable to significant changes as a function of the chemical surrounding (in aqueous solution). This conclusion could also be drawn from the data collected in Table III. In contrast, the $UO_2^{2+}{}_{aq}$ lifetime is very sensitive to the chemical composition of the medium (in a wide sense) and cannot therefore be used for general characterization. Any lifetime value should be accompanied by the exact description of the chemical composition of the solution in which this has been measured for the ease of comparison.

On a more general aspect, the round-robin results provide evidence for the critical importance of a reliable determination of the decay behavior (multi- or mono-exponential decays) to correctly assess the importance and role of the photochemical processes in the system under study. Specifically, changes from mono- to multi-exponential behavior upon changes in the softwares should be resolved.

4. 3. Sample C. This sample contains two dominant species, $UO_2^{2+}{}_{aq}$ (≈50%, $2x10^{-6}$ M) and the 1 :1 sulfato complex (≈50%, $2x10^{-6}$ M), while the other complexes are below $5x10^{-8}$ M.

This sample is more luminescent than sample B, as can be concluded from the relative global fluorescent yields (question vi.), which range from 32 to 72% (excitation wavelength at 266 nm). This fact can only partially be attributed to the increase, as compared to sample B, in the amount of free $UO_2^{2+}{}_{aq}$. From the eleven laboratories providing lifetime values, four

detected a single component (labs. #2, #5, #7 and #14), four detect two components and three observe a tri-exponential decay. Only one laboratory indicates that the various components observed cannot be spectrally resolved (no spectral shift). Therefore, the emission peaks provided in this case are considered only once.

Few papers have appeared in the litterature on the U(VI)/SO_4^{2-} system as studied by TRES. In one paper,[27] the authors conclude that nothing can be firmly assessed on the mono- versus multi-exponential aspect. The other two papers,[14,15] both issued from the same institute, clearly state that a multiexponential behavior is observed. In these studies, a large range of pH and uranyl or sulfate ion concentrations was investigated but, as with sample B, comparison is almost impossible with the round-robin test, because of differences in total ionic strength and other characteristics. In one paper,[14,15] the attribution is as follow : $UO_2^{2+}{}_{aq}$: $\tau < 3$ µs ; UO_2SO_{4aq} : $\tau = (11.5 \pm 0.3)$ µs ; $UO_2(SO_4)_2^{2-}{}_{aq}$: $\tau = (8.3 \pm 0.3)$µs. No values for the emission peaks is provided. In the second study,[14,15] a more complete description is given : UO_2SO_{4aq} : $\tau = (4.3 \pm 1)$ µs emission peaks located at 493 – 514 – 538 and 565 nm ; $UO_2(SO_4)_2^{2-}$: $\tau = (11 \pm 2)$ µs, same positions of the emission peaks. No comments on the lifetime changes for UO_2SO_{4aq} were made.

Again, the question of a mono- or a multi-exponential behavior of sample C is crucial but the round-robin data do not allow to conclude on this point. Similarly to the sample B case, the round-robin data have been first sort according to three categories. A close examination of the three categories of emission peaks reveals that none of the three emission spectra derived is in good agreement with that of $UO_2^{2+}{}_{aq}$ as determined from sample A (data not shown). As a conclusion, one can say that $UO_2^{2+}{}_{aq}$ is *not* recognized by the participants as a luminescing species in this system. This fact cannot be related to a poorly fluorescent sample, as sample B, which is less luminescent, delivers more coherent data. This negative information can be interpreted in two different ways, depending on the assumption made concerning the decay behavior.

Assuming a multi-exponential decay, two possibilities can be evoked to explain such difficulties: i) the effective emission peaks of the various complexes might differ only slightly from those of $UO_2^{2+}{}_{aq}$. This renders the analysis difficult, whatever the amount of light collected, so that $UO_2^{2+}{}_{aq}$, although detected (most probably with the lowest lifetime) cannot be characterized through its emission peaks. In this respect, note that the average successive spectral shifts observed by the participants are below 3 nm, a value to be compared to the red shifts of 4 to 6 nm observed in sample B. Thus, one can set a limit of (roughly) 5 nm to the

red shifts of the various uranyl species below which the spectral analysis appears tedious. Considering that the difference between P2 and P3 for $UO_2^{2+}{}_{aq}$ is equal to 22 nm (see Table III), this means that no more than four different species (including $UO_2^{2+}{}_{aq}$) can be reasonably observed by TRES. ii) the relative quantum yields of the various species are not in favour of the $UO_2^{2+}{}_{aq}$ detection so that none of the three categories should be ascribed to $UO_2^{2+}{}_{aq}$. However, this hypothesis has to be discarded. Considering the speciation, if $UO_2^{2+}{}_{aq}$ is not detected, then one of the three components has to be an hydrolysed form of U(VI), which is at least four orders of magnitude less abundant than $UO_2^{2+}{}_{aq}$. Therefore, it would be difficult to explain why $UO_2^{2+}{}_{aq}$ is unambiguously detected in sample D (see below, section 4.4) while the speciation in that case is even more favourable to the detection of the U(VI) hydrolysed forms (see Fig. 1).

On the other hand, if the assumption of a mono-exponential decay is made, the fact that $UO_2^{2+}{}_{aq}$ is not detected through its emission peaks in sample B is perfectly normal. Considering only those participants who detected a single lifetime, the emission peaks are coherent but are clearly different from those observed in sample A. This would correspond to a large mixing of the various excited species, so that both the single lifetime and the emission spectrum correspond to an intricated mixture of the various excited species. The average lifetime is equal to $\tau = (1.9 \pm 0.4)\mu s$. To be coherent with the assumption of a large photochemical mixing, as illustrated in the emission spectrum, the "intrinsic" $UO_2^{2+}{}_{aq}$ lifetime should be way below this value. Actually, the spectroscopic characteristics observed by labs. #2, 5, 7 and 14 are very close to those observed by the other participants for the first category (same emission peaks and lifetime within σ values). Another explanation to the single lifetime behavior could thus be that these laboratories could not detect the additional components, most probably because of a too small relative intensity. However, this hypothesis cannot be firmly assessed and the question of rapid photochemical processes is still unresolved in this system. Nevertheless, as a previous publication on this system derived an equilibrium reaction rate constant in very good agreement with the NEA recommendations,[14] it can be inferred that these difficulties can be overcome by accumulation of data and comparison to well-defined samples, which was not possible in this blind test.

4.4. Samples D, E, F and G. These four samples correspond to various pH values of the system U(VI)/H_2O (see section 2.1). As a consequence, they will be analysed in the same section, although discussion about samples G and E will be limited due to the chemical changes observed in the test cuvettes.

In sample D (pH = 2), labs. #1 and 7 are the only participants observing a single decay. In sample F (pH = 3.5), only lab.#7 still observes a single decay (see Figs. 3, 4). In fact, only lab. #7 indicates a mono-exponential behavior for the whole series, while the other participants observe a multi-exponential behavior in *at least* one of the samples. A cross-check analysis of the lab. #7 data for sample E (randomly chosen in the series) has been performed (see section 5) which strongly supports the assumption that the decay is in fact bi-exponential. Thus, the data will be discussed on the basis of a multi-exponential behavior. This is in agreement with numerous previous publications dealing with the hydrolysed U(VI) species[22,24,31-34] but is in disagreement with a single publication which clearly states that monoexponential decays are found, whatever the chemical conditions examined.[35] In this publication, reference is made to a previous publication on the U(VI)/H_2O system (in part from the same authors) where a multi-exponential decay is observed, but no comment is made on such a fundamental discrepancy.

Although the speciation is not in favour of the detection of any other species than $UO_2^{2+}{}_{aq}$ in sample D (see Table 1), six participants detect at least two species. This fact highlights the dramatic effect of the quantum yield onto the detection limit of species that would be neglected on the basis of speciation calculations alone. This illustrates the great interest and value of TRES for speciation but, turning the argument around, this imposes the restriction that great care must be taken in the use of speciation diagrams to ascribe species.

There is a reasonable agreement between the emission peaks associated to the short lifetime of sample D and those of $UO_2^{2+}{}_{aq}$ and again τ_1 is very different from the value in sample A. This has to be expected, as sample D is the most favourable sample for the detection of free uranyl ion. The agreement is not so good for sample F but remains acceptable, considering the increasing amount of the other species. Lifetime values for τ_2 and τ_3 and emission spectra derived from this round-robin test are difficult to compare with the literature for two main reasons: (i) the chemical compositions are different, (ii) the quantum yields are unknown, which hampers any attribution in the present work. From such a comparison (data not shown), the only conclusion that can be drawn with some confidence is that the τ_3 emission spectrum does not correspond to the 1 :2 complex as determined from the literature. Conversely, one set of published data for the emission spectrum of the 1 :2 complex appears rather close to that of $UO_2^{2+}{}_{aq}$, as derived from the round-robin test.

As already stressed, the choice of three categories is arbitrary and may not correspond to the chemical reality. Indeed, there are indications that some of the data might well be the

result of data processing limitations while analysing too much components. For example, considering the speciation, it is very surprising that lab. #13, which already detects three components at pH 2 still detects three components only at pH ≈ 4.52. Lab. #1 observes a redshift for all the emission peaks associated to τ_1 from sample F to E (e.g. for P3, from ca. 510.4 nm in sample F to 519.6 nm in sample E) and labs. #1 and 12 observe an additional peak in the τ_1 emission spectra of sample E which cannot be inserted into the UO_2^{2+} spectra, while the other peaks do correspond to UO_2^{2+}. All these results are difficult to explain under the assumption of only three different luminescent species for the four samples.

Although the limitations of such a test are clear, in terms of number of solutions examined, it has to be stressed that the presence of additional peaks as noted by a few laboratories in this round-robin test is not unimportant for the chemical analysis of this system. In the case where the $\log_{10} K$ values would be assumed for the various equilibria, as is commonly done in the literature,[12,14,15,22,23,31,32] this would restrict the species attributions to those being present in the pH range for which the peaks are observed. In the case where the $\log_{10} K$ values would be sought from the TRES measurements, as has been done for various systems,[8,14,33,36] this would set some limits to the equilibrium reaction constants involving these species.

As a matter of fact, it appears that the system containing hydrolysed uranyl species in aqueous solution is rather tedious to study and requires numerous solutions to be fully characterized. Most probably, references should be made to well defined solutions containing few species in order to correctly describe them. Without this precaution, as was the case in the round-robin test *per se*, any species attribution and K determinations appear very difficult as soon as three components are observed in the decay spectra.

5. DATA PROCESSING

As a complement to this round-robin test, few trials have been performed to assess the potential role of data processing onto the results discussed above. It is clearly out of the scope of this paper to make a comprehensive study of this question. Only a few specific points, relevant to this round-robin test, have been examined by exchanging files between participants. For a given exchange, always based on double volunteering, files, transmitted by the organiser, were cleared from all indication of to whom they belong and to which sample they correspond. The participant in charge of analysing the files was asked to use his own data

processing method. Comments from each side, when available, were transmitted through the organiser.

Although the question of data processing is very important, the discrepancies observed and discussed in section 4 cannot be entirely ascribed to differences between the data processing systems. For example, two participants use the same commercial package Kaleidagraph for decay analysis. It is very improbable that such a commercial package will deliver different results for the same file, when processed by different users. However, for sample A, the two laboratories provided lifetime data that differ from slightly more than their indicated error bars and, for sample B, one detected a short and a medium lifetime, while the other one detected a medium and a long lifetime.

In a first step, it has been observed that programs suited for data issued from PM detection systems are not able to handle data issued from diode detection systems and vice-versa. In a second step, data obtained from sample A were exchanged between some of the participants for a cross-checked lifetime analysis. Although not perfect, the agreement between commercial packages and home made programs of all kinds is rather good. However, this is a minimum requirement, as sample A appears to be a simple case, corresponding to a monoexponential decay, with enough light to ensure good statistics.

Other limited tests have been performed with other samples and the agreement between various fitting procedures is not so good as in the case of sample A. In particular, lab. #7 considers its sample E decay as monoexponential (τ = 30 μs), while the cross-checked analysis by another participant gives a bi-exponential behavior (τ_1 = 1.4 μs, τ_2 = 25.2 μs). Figure 5 displays (in a logarithmic scale) the data of concern. The curvature at low time values would pledge for a multi-exponential beahvior.

6. CONCLUSION

Although this first round-robin test devoted to U(VI) speciation in aqueous solution was a success in terms of number of participants and results that were obtained, it is of course not perfect and the improvements needed will hopefully be remembered in the future, if other tests of this kind are performed. In particular, the absence of blank and twin samples should certainly be considered as a defect of the organisation of the test. Nevertheless, the information obtained is very instructive.

The spectroscopic signature of a given U(VI) species can be made through its emission spectrum, not through its lifetime value. A complete description of the medium

(chemical composition and total ionic strength value) is necessary to allow comparison if lifetime values are provided: evidence has been obtained on the effect of the medium on the lifetime for free U(VI) and most probably, uranyl complexes, in this study. However, although the argument of an effect of the medium onto the lifetimes has been used in this work to overcome the discrepancies observed between the round-robin test results and published data, it should be used with caution. In particular, the argument that « impurities » always behave as fluorescence quenchers so that long lifetime values should always be favoured as compared to shorter, « less correct » values, should be used sparingly (see for instance discussion in[12]).

Although no precise setup option appears crucial for the spectroscopic studies of simple solutions, as all the participants mainly agree for samples A and B, it is probable that the study of more complex systems, such as samples C to E, requires the use of standard solutions for emission spectra and lifetimes. This would require additional work from national bureau of standards. In this sense, this work is a first step towards the conception of such standards and it seems that sample A can be already used as an internal standard. However, even with calibrated apparatus, it seems unrealistic to get a refined analysis of very complex systems as the limit of detection appears to be three components in the decay spectra and four components in the emission spectra. This is an important point, as the round-robin test has also evidenced the great sensitivity of TRES to minor species (in terms of speciation) due to with very high quantum yield, as compared to $UO_2^{2+}{}_{aq}$. In this respect, it is possible that some improvements of the programs and methods, such as global analysis in the case of PM detection systems[37,38] or chemometrics (diode detection systems)[39] may be of some help. The rather large discrepancies observed, especially regarding the number of components, points at the necessity for the community to improve the data fitting procedures.

Since the presentation of the round-robin test results during a one-day workshop which gathered almost all the laboratories involved, eight of the participating laboratories indicated their will to improve either their systems or computer programs (or both). In one case (lab. # 8), the improvements have been performed before the end of this paper draft, so that lifetime values are now available and appear to be perfectly in line with the values obtained in the round-robin test (samples A, and B). Another laboratory is now calibrating the emission spectra using standards. These facts are taken as a very positive indication for the future of TRES as a tool for U(VI) speciation.

Finally, it should be stressed that the conclusions that have been drawn from this round-robin test on TRES potentials and limitations for U(VI) speciation may not be directly

applicable to other luminescent probes, such as Am, Cm or Eu, although the methodology of the test itself can be re-used. As discussed in the text, the TRES performances are highly correlated with the spectroscopic characteristics of U(VI), such as spectral distances between the bands. For the other luminescent probes cited above, these characteristics differ considerably from that of U(VI).

Acknowledgment

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Table and figure captions

TABLE I. Composition of the seven samples, results of the chemical analysis (pH and uranium concentration, see text) and calculated speciations.

TABLE II. Description of devices. (a): excitation wavelength (nm)/pulse duration (ns)/repetition rate (Hz)/average power (mJ or mW)
(b): monochromator (trade and reference type); photomultiplier (trade and reference type); oscilloscope (trade and reference type).
n. i. : no information. DAD: Diode Array Detector.

TABLE III. Values of the wavelengths of the emission peaks of $UO_2^{2+}{}_{aq}$ as determined in sample A (first line) and positions of the emission peaks ascribed to $UO_2^{2+}{}_{aq}$ as reported in the literature.
(b): no data

FIG. 1. Speciation diagram for [U] = 10^{-6} M, [$HClO_4$] = 10^{-2} M, $pCO_2 = 3x10^{-4}$.

FIG. 2. Sample A: values of the wavelengths of the six categories of emission peaks associated to the single lifetime.

FIG. 3. Sample D: (◊) values of the « short » lifetime, τ_1 (µs) ; (●): values of the « medium » lifetime, τ_2 (µs) ; (□): values of the « long » lifetime, τ_3 (µs). Solid lines: average of all values of a given category. Error bars provided by the participants. No error bar for a given data point means no error provided or error smaller than the data point.

FIG. 4. Sample F: (◊): values of the « short » lifetime, τ_1 (µs) ; (●): values of the « medium » lifetime, τ_2 (µs) ; (□): values of the « long » lifetime, τ_3 (µs). Solid lines: average of all values of a given category. Error bars provided by the participants. No error bar for a given data point means no error provided or error smaller than the data point.

FIG. 5. Logarithmic display of sample E decay (see text).

Sample	initial composition (M)	initial pH and ionic strength (M)	Final pH (in cuvettes) and U(VI) concentration (max/min) (10^{-6}M)	Calculated speciation
A	$HClO_4$: 1 UO_2^{2+} : $5x10^{-6}$	0 1.0	not measured 4.88 (4.63/5.12)	100% $UO_2^{2+}{}_{aq}$
B	$HClO_4$: $1.25x10^{-2}$ UO_2^{2+}: $1.25x10^{-6}$ NaF: 10^{-4}	1.96 $1.25x10^{-2}$	1.95 1.2 (1.14/1.26)	67% $UO_2^{2+}{}_{aq}$ 33% UO_2F^+ ~0.7% UO_2F_{2aq}
C	$HClO_4$:$4x10^{-2}$ UO_2^{2+}: $4x10^{-6}$ Na_2SO_4:10^{-2}	1.43 $5.5x10^{-2}$	1.40 3.82 (3.63/4.00)	50%$UO_2^{2+}{}_{aq}$ 50%UO_2SO_{4aq} ~1% $UO_2(SO_4)_2^{2+}$
D	$HClO_4$: 10^{-2} UO_2^{2+}: 10^{-6}	2.07 10^{-2}	2.04 0.957 (0.908/1.00)	~100%$UO_2^{2+}{}_{aq}$ < 0.1% UO_2OH^+
E	$HClO_4$: adjusted UO_2^{2+}: 10^{-6}	4.52 (adjusted) $<10^{-4}$	5.81 0.345 (0.328/0.361)	75% UO_2^{2+} 20% UO_2OH^+ 5% $UO_2(OH)_{2aq}$ 0.2% $(UO_2)_2(OH)_2^{2+}$ 0.1%UO_2CO_3
F	$HClO_4$: $3.1x10^{-4}$ UO_2^{2+}: 10^{-6}	3.56 $3x10^{-4}$	3.61 1.07 (1.02/1.13)	98% UO_2^{2+} 2% UO_2OH^+ <0.1% $UO_2(OH)_{2aq}$
G	$HClO_4$: 10^{-4} UO_2^{2+}: 10^{-6}	4.07 10^{-4}	4.31 0.819 (0.777/0.861)	95% UO_2^{2+} 5% UO_2OH^+ 0.5% $UO_2(OH)_{2aq}$

TABLE I. Composition of the seven samples, results of the chemical analysis (pH and uranium concentration, see text) and calculated speciations.

	excitation		detection	
lab	laser type	laser characteristics (a)	PM detection (b)	diode detection (c)
a	Nd:YAG	266 nm/15 ns/5 Hz/1 mJ	n. i. Hamamatsu R3896 H.P. 54510A	n. i. Princeton DAD
b	Nd:YAG	266 nm/n. i/15 Hz/1 mJ	Jobin-Yvon, H10-Vis Hamamatsu, 928S Tektronik, TDS 3012	
c	Nd:YAG	266 nm/6-8 ns/10 Hz/0.1-3 mJ	Jobin-Yvon Triax 320 Hamamatsu R928 Tektronix TDS 340	
d	Nd:YAG	266 nm/6-8 ns/10 Hz/6 mJ	Jobin-Yvon HV20-Vis Philips XP2020 Textronik TDS3052	
e	Nd:YAG	266 nm/9 ns/10 Hz/4 mJ	Scientific measurement 82-410 Hamamatsu R928 Lecroy 9410	
f	Nd:YAG	355 nm/3-5 ns/10 Hz/8 mJ	cut-off filters (420-550 nm) Hamamatsu R2949 Lecroy 9310	
g	Nd:YAG	266 nm/n. i./15 Hz/2 mJ		Acton Research

				Princeton CCD
h	Nd:YAG + OPO	337 nm/8 ns/10 Hz/2 mJ		Princeton Acton 300i Princeton CDD
i	Excimer XeCl	343 nm/n. i./20 Hz/3-7 mJ		Acton Research Pro 275 Princeton DAD
j	Nd:YAG	266 nm/n. i./20 Hz/15 mJ		Acton Research EGG- 1455
k	Ti:saphire (continuous)	283 nm/n. i./n. i./10 mW	steady state spectrometer Edinburgh Instr. FL 920	
l	Nd:YAG	355 nm/n. i./10 Hz/90 mJ		

TABLE II. Description of devices. (a): excitation wavelength (nm)/pulse duration (ns)/repetition rate (Hz)/average power (mJ or mW) (b): monochromator (trade and reference type); photomultiplier (trade and reference type); oscilloscope (trade and reference type). n. i. : no information. DAD: Diode Array Detector.

	P1	P2	P3	P4	P5	P6	Reference
Mean (nm)	470	487.9	509.8	533.6	559.8	588	this work
σ (nm)	± 2	± 0.8	± 0.6	± 0.6	± 0.6	± 2	
	470	488	509	533	559	588	[12]
	(b)	488.3	509.8	533.5	(b)	(b)	[14]
	(b)	487	510	533	560	(b)	[31]
	(b)	488	509	534	558	(b)	[21]
	473	488	510	534	560	587	[22]
	(b)	490	511	535	560	589	[40]

TABLE III. Values of the wavelengths of the emission peaks of $UO_2^{2+}{}_{aq}$ as determined in sample A (first line) and positions of the emission peaks ascribed to $UO_2^{2+}{}_{aq}$ as reported in the literature.

(b) : no data

	P1 (nm)	P2 (nm)	P3 (nm)	P4 (nm)	P5 (nm)	P6 (nm)
τ_1	473	489	510	534	560	589
(0.6 ± 0.3)µs	± 2	± 3	± 3	± 3	± 2	± 3
τ_2	481	494	515.5	540	566	596.9
(4.3 ± 0.2)µs	± 3	± 1	± 0.8	± 2	± 1	± 0.6
τ_3	478.1(*)	498	519.3	543.5	568.6 (*)	(b)
(27 ± 11)µs		± 2	± 0.7	± 0.6		
UO_2^{2+} (a)	470	487.9	509.8	533.6	559.8	588
(7.9 ± 0.7)µs	± 2	± 0.8	± 0.6	± 0.6	± 0.6	± 2

TABLE IV. Values of the wavelengths of the emission peaks corresponding to the three lifetimes (short, medium, long) detected in sample B.

(a): Emission peaks as reported from Table III.

(*): Value provided by a single participant (σ = 0, by definition).

(b): No data.

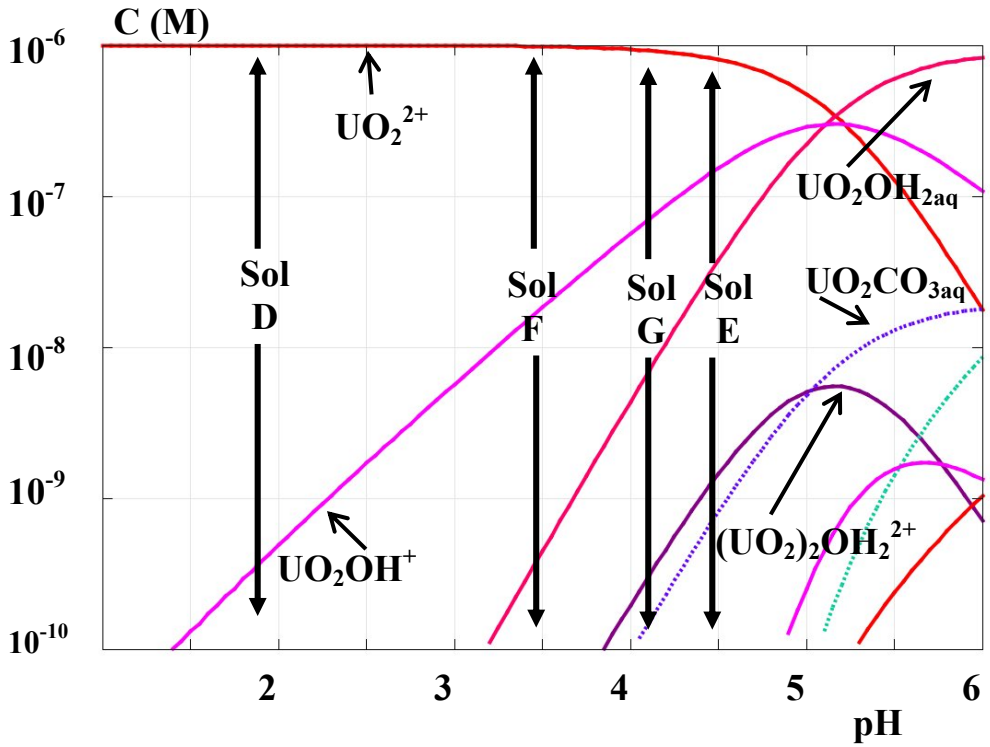

FIG. 1. Speciation diagram for [U] = 10^{-6} M, [$HClO_4$] = 10^{-2} M, pCO_2 = $3x10^{-4}$.

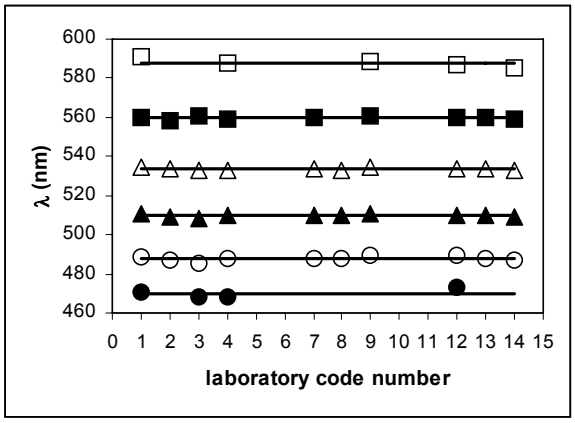

FIG. 2. Sample A : values of the wavelengths of the six categories of emission peaks associated to the single lifetime.

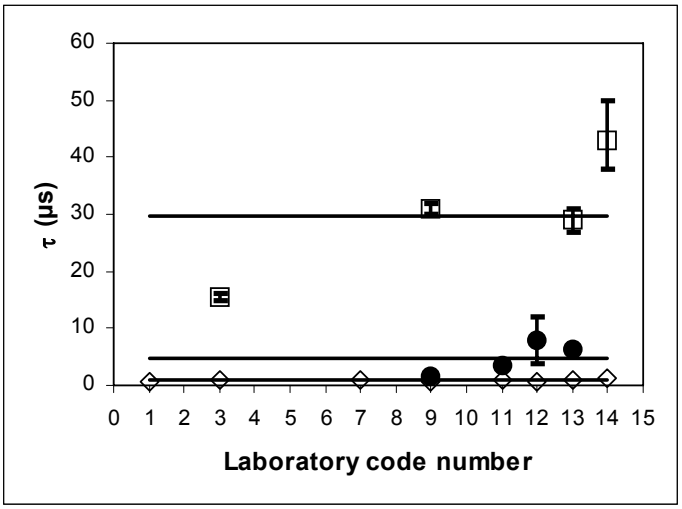

FIG. 3. Sample D: (◊): values of the « short » lifetime, τ_1 (µs) ; (●): values of the « medium » lifetime, τ_2 (µs) ; (□): values of the « long » lifetime, τ_3 (µs). Solid lines : average of all values of a given category. Error bars provided by the participants. No error bar for a given data point means no error provided or error smaller than the data point.

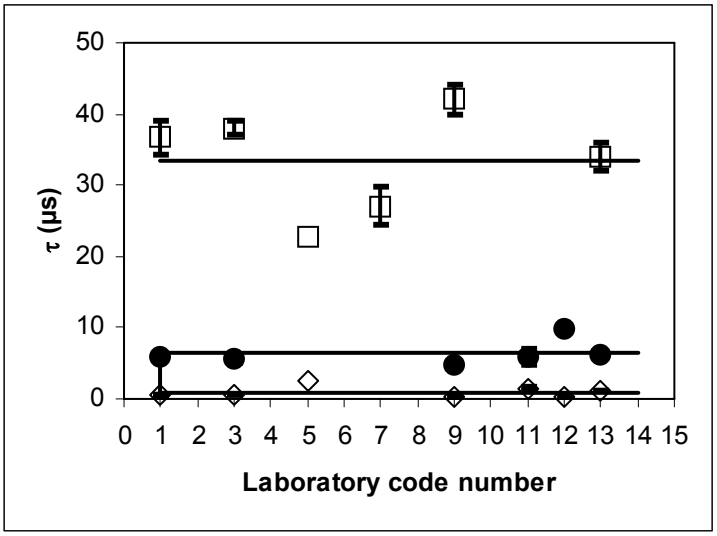

FIG. 4. Sample F: (◊): values of the « short » lifetime, τ_1 (µs) ; (●): values of the « medium » lifetime, τ_2 (µs) ; (□): values of the « long » lifetime, τ_3 (µs). Solid lines: average of all values of a given category. Error bars provided by the participants. No error bar for a given data point means no error provided or error smaller than the data point.

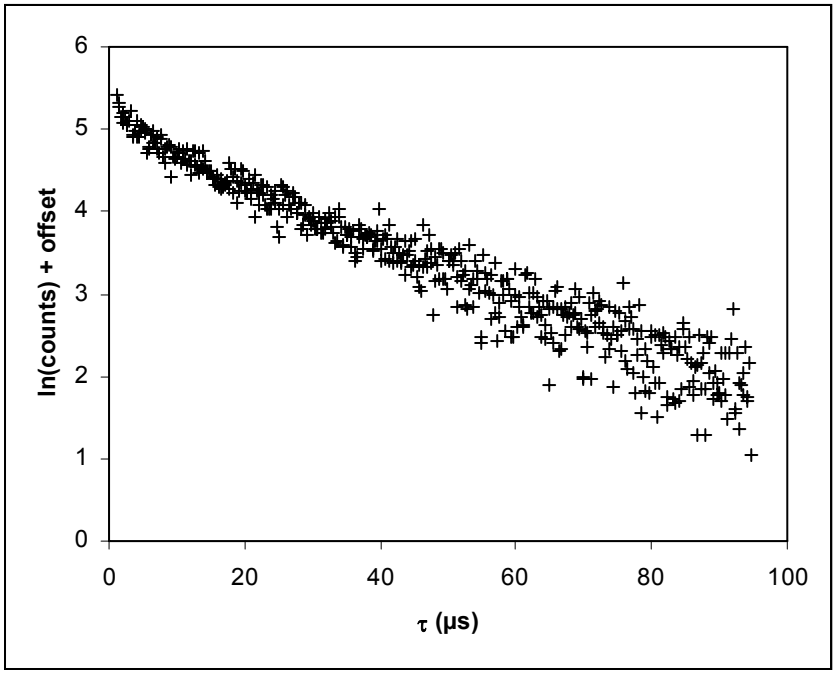

FIG. 5 : Logarithmic display of sample E decay (see text).

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