



Chemometric analysis: Uranium(VI) hydrolysis by UV-Vis spectroscopy

G. Meinrath^{a,b,c,*}

^aInstitute of Geology, TU Bergakademie Freiberg, G.-Zeunerstr. 12, D-09596 Freiberg, Germany

^bInstitute of Inorganic Chemistry, TU Bergakademie Freiberg, Leipziger Str. 2, D-09596 Freiberg, Germany

^cRER Consultants, Schießstattweg 3a, D-94032 Passau, Germany

Abstract

By application of factor analysis and statistics to 25 UV-Vis absorption spectra of hydrolyzed U(VI) solutions, single component-spectra of oligomeric U(VI) hydrolysis species $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$ ($=(\text{UO}_2)_3(\text{OH})_5^+$) are obtained. These two species are able to interpret all 25 spectra quantitatively. High molar absorptions of the characteristic low-energy electronic transition of U(VI) are found: $101 \pm 2 \text{ l mol}^{-1} \text{ cm}^{-1}$ for $(\text{UO}_2)_2(\text{OH})_2^{2+}$ at 421.8 nm and $474 \pm 7 \text{ l mol}^{-1} \text{ cm}^{-1}$ for $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$ at 429.0 nm. Drastically higher integral oscillator strengths f for these oligomeric species compared to $\text{UO}_2^{2+}(\text{aq})$ are obtained: $f_{22} = 2 \times 10^{-3}$ and $f_{35} = 6 \times 10^{-3}$, while $f_{10} = 1.7 \times 10^{-4}$. Statistical analysis of target transformation analysis is made by Jackknife statistics and compared to Clifford's calculational method. © 1998 Published by Elsevier Science S.A.

Keywords: Chemometrics; Factor analysis; Hydrolysis; Spectroscopy; Speciation; Uranium(VI)

1. Introduction

In a variety of fields, understanding hydrolytic behaviour of uranium(VI) is essential, e.g. in characterizing sorption states [1], in assessing UO_2 pellet corrosion for nuclear waste disposal [2], in uranium mining area remediation [3] or assessing solution compositions in mineralogy [4]. Hydrolytic behaviour of uranium(VI) was studied continuously during the past 50 years, as shown, e.g. by a time distribution analysis in Ref. [5]. Until recently however, assessment of solution composition could only be made by calculations based on proposed formation constants. These proposed formation constants of uranium(VI) hydrolysis species however, are quite scattered and recent reviews have not agreed even on the number of hydrolysis species actually formed [6]. Thus, formation constants are given with large uncertainties, in turn resulting in wide margins for possible species composition in a given solution [7]. UV-Vis spectroscopy is applied to tackle this controversial question in a quantitative manner. To resolve the strongly overlapping spectral bands of hydrolyzed U(VI) solutions, factor analysis has been proposed previously [8]. The present contribution

completes previous work. Due to restricted space, a summary only is presented with a full account to be given elsewhere [7].

2. Results and discussion

Absorptions above 10^{-3} cm^{-1} have been reported for hydrolyzed U(VI) solutions in the range pH 2.9 to pH 4.8 and $4.2 \times 10^{-4} \text{ M U(VI)}$ to $5.3 \times 10^{-3} \text{ M U(VI)}$, readily accessible for UV-Vis spectroscopy. These conditions correspond to the concentration range studied in the overwhelming amount of currently available literature data.

In Table 1, some experimental conditions studied in selected references are given for illustration. It is evident that investigation of U(VI) hydrolytic behaviour is preferentially studied at elevated U(VI) concentrations, while few data are available for U(VI) concentrations below 10^{-4} M . Only studies at a constant ionic strength of 0.1 M have been included in Table 1 because (a) these studies are compatible with conditions discussed here and (b) the pH range accessible for experimental study is probably even more limited at higher ionic strengths due to formation of sparingly soluble uranates. There is agreement in recent

*Institute of Geology, TU Bergakademie Freiberg, G.-Zeunerstr. 12, D-09596 Freiberg, Germany.

Table 1

Experimental conditions and methods summarized from some representative studies of U(VI) hydrolysis reported in literature for $I=0.1$ M solutions at 25°C

Log[U(VI)] range	pH range	Method	Conditions	Ref.
-2 to -3.5	4–4.8	Sol.	NaClO ₄	[12]
-2.5 to -4	4–4.8	Sol.	NaClO ₄	[10]
-2.5 to -4.6	4.3–5.7	Sol.	NaClO ₄	[9]
Tracer	5.3–7.3	Extr.	NaClO ₄	A
-3	2.8–4.8	Tit.	KNO ₃	B
Tracer	4.5–7	Extr.	NaClO ₄	C
-2.7 to -3	5–8.5	Tit.	NaClO ₄	D
-3 to -3.3	3–7	Tit.	KNO ₃	E
-3	3.8–4.7	Tit.	NaClO ₄	F
-1 to -4	2.5–12.5	Tit.	NaNO ₃	G
-2.7 to -3.7	3.2–6	Tit.	KNO ₃	H
-2 to -3.3	1.9–6.1	Tit.	NaClO ₄	I

sol., solubility study; extr., solvent extraction; tit., potentiometric titration. (A) G.R. Choppin, J.N. Mathur, *Radiochim. Acta* 52/53 (1991) 25; (B) M.K. Kotvanova, A.M. Evseev, A.P. Borisova, E.A. Torchenkova, S.V. Zhakarov, *Moskow Univ. Chem. Bull. (USA)* (1984) 37; (C) M.S. Caceci, G.R. Choppin, *Radiochim. Acta*, 33 (1983) 207; (D) L. Maya, *Inorg. Chem.*, 21 (1982) 2895; (E) P.A. Overwoll, W. Lund, *Anal. Chim. Acta* 143 (1982) 153; (F) A. Vainiotalo, O. Mäkitie, *Finn. Chem. Lett.* (1981) 102; (G) N.K. Pongi, G. Double, J. Hurwic, *Bull. Soc. Chim. Fr.* (1980) I-347; (H) R.N. Sylva, M.R. Davidson, *J. Chem. Soc. Dalton Trans.* (1979) 465; (I) C. Tsymbal, Report CEA-R-3476 (1969), CEA/Saclay (1969).

literature that $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$, the solubility limiting solid of U(VI) under ambient conditions and $\text{pH} < 7$, readily transforms to a sodium containing uranate at $\text{pH} > 7$ even at low ionic strength of $I=0.1$ M NaClO_4 [9–12]. Formation of uranates with other cations, e.g. Ca^{2+} , Mg^{2+} or Ni^{2+} is reported [4,13]. Thus, in studies at higher concentrations of background electrolytes, the solubility of U(VI) will be further reduced, requiring detailed analysis of these new phases and their specific interaction with the system to be studied.

Hence, a series of investigations from different laboratories have been devoted to a precise assessment of $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$ solubility limits [9–12] in the past half decade. Previous knowledge has been found sparingly and questionable [11]. Results are summarized in Ref. [12].

In Fig. 1, the location of 25 solutions in the U(VI)–pH diagram are shown together with solubility limits of $\text{UO}_3 \cdot 2\text{H}_2\text{O}(\text{s})$ under given conditions. From these solutions, UV-Vis spectra are collected in the range 340–520 nm. Signal-to-noise ratios have been improved by averaging multiple scans. By reference to Table 1, it becomes evident that these 25 solutions cover the U(VI)–pH region investigated in previous studies and therefore allow for direct comparison. Analysis of these spectra has been made by factor analysis (FA) [14]. Factor analysis is a versatile method to uncover structures and correlations in data and is able to analyze large amounts of data simultaneously. FA therefore is widely applied from psychology [15] to digital image processing [16]. Only a brief outline of FA

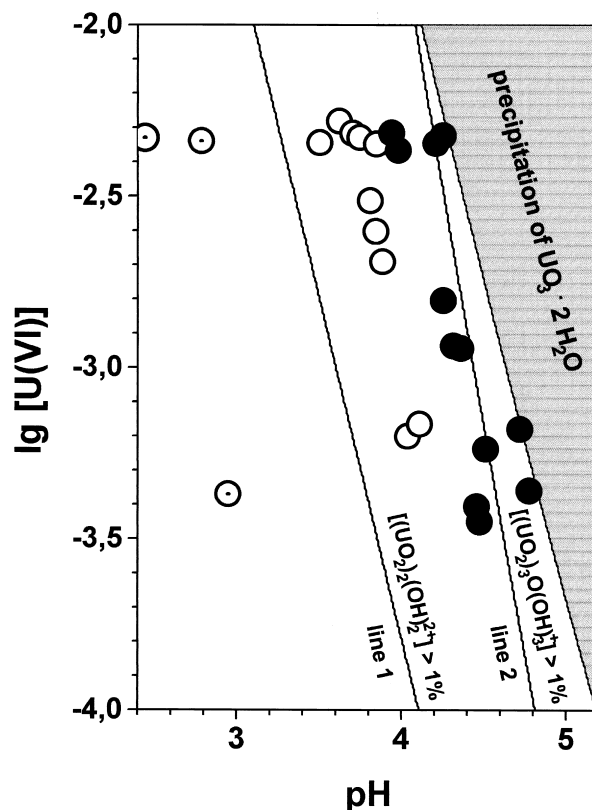


Fig. 1. Uranium(VI) concentrations and pH of 25 samples. The samples identified to contain $\text{UO}_2^{2+}(\text{aq})$ only are given by dot-centered open circles; solutions composed of both $\text{UO}_2^{2+}(\text{aq})$ and $(\text{UO}_2)_2(\text{OH})_2^{2+}$ are symbolized by open circles, while three-component solutions are given by dark circles. The borderline, where relative species concentration of $(\text{UO}_2)_2(\text{OH})_2^{2+}$ is above 1% is given by line 1, while line 2 indicates presence of $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$ at 1%.

procedure will be given to allow for discussion of results. Tutorials can be found, e.g. in Refs. [14,17].

In the first step of FA, the number n of factors contributing significantly to the overall variance in the data is determined by abstract factor analysis (AFA). In AFA, experimental data are summarized in a matrix \mathbf{A}_{rc} of r rows of absorbances a_r , measured at r different wavelengths λ_r , in c different solutions are decomposed into the eigenvalues and eigenvectors of \mathbf{A}_{rc} , e.g. by singular value decomposition (SVD):

$$\mathbf{A}_{rc} = \mathbf{U}\mathbf{S}\mathbf{V}^T \quad (1)$$

where \mathbf{U} is a unitary matrix of column eigenvectors, \mathbf{S} a diagonal matrix of the square roots of eigenvalues λ , and \mathbf{V} a unitary matrix of row eigenvectors.

From statistical analysis of the eigenvalues λ and the corresponding eigenvectors, the number n of significantly contributing factors was found to be $n=3$ [7,8]. This result was invariant for matrices composed of different numbers of experimental spectra, e.g. 16 [7], 23 [8], 25 and 26 [8] spectra. Thus, further analysis was made by the reduced

data matrix $\mathbf{A}_{rc}^{\#} = \mathbf{E}_{rn}^{\#} \mathbf{C}_{nc}^{\#}$, where $\mathbf{E}_{rn}^{\#} = \mathbf{U}_{rn} \mathbf{S}_{nn}$ and $\mathbf{C}_{nc}^{\#} = \mathbf{V}_{nc}$. The subscript n indicates that only the eigenvectors associated with the $n=3$ largest eigenvalues are included into the respective matrix. Hence, AFA reduces the amount of data to be handled as well as the noise in the data matrix $\mathbf{A}^{\#}$.

Matrix $\mathbf{E}_{rn}^{\#}$ encloses information on single-component spectra of the species responsible for experimental variance, however in an abstract mathematical form and void of physical meaning. By matrix multiplication with a suitable transformation matrix \mathbf{T} by target transformation factor analysis (TFA) according to Eq. (2)

$$\mathbf{A}^{\#} = \mathbf{E} \mathbf{C} = \mathbf{E}_{rn}^{\#} \mathbf{T}_{nn} \mathbf{T}_{nn}^{-1} \mathbf{C}_{nc}^{\#}, \quad (2)$$

abstract eigenvectors are transformed into physically meaningful matrices \mathbf{E} and \mathbf{C} . \mathbf{E} holds the single component spectra of the respective species, while \mathbf{C} holds the individual species concentrations of the n species in each of the c solutions. Until here, no chemical model applies. A chemical model is eventually introduced to interpret the individual species concentrations in matrix \mathbf{C} . With the knowledge of pH of each of the $c=25$ solutions, conditional formation constants of the relevant species can be obtained, whose scatter provides additional information on the consistency of the complete study.

Essential advantages of the chemometric approach are (a) no prior model is needed and (b) all data are treated simultaneously. Especially the latter advantage immediately uncovers inconsistencies in the data analysis that might go unnoticed by a case-to-case spectral deconvolution.

Strategies to obtain the transformation matrix \mathbf{T} are discussed elsewhere [7,8]. Resulting single component spectra of the species $\text{UO}_2^{2+}(\text{aq})$, $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$ ($=(\text{UO}_2)_3(\text{OH})_5^+$) are given in Fig. 2. The dashed lines give 99% confidence limit evaluated by jackknifing [18]. Evaluating uncertainties by the Jackknife approach is an alternative approach compared to the previously adopted Clifford method [7,8]. While Clifford's approach assesses confidence limits from differences between the original data matrix \mathbf{A} and the factor-reduced data matrix $\mathbf{A}^{\#}$, jackknifing uses the variance within the reduced data matrix $\mathbf{A}_n^{\#}$. As has been shown by Efron and Gong [19], the Jackknife is essentially a resampling procedure, lacking the need for a Monte Carlo procedure while offering a simpler calculation of the statistical parameters. On the other hand, jackknifed variances are larger than, e.g. bootstrap variances. Compared to the Clifford approach [7], jackknifed 99% confidence limits in Fig. 2 are larger for about a factor of 2.

Resulting conditional formation constants $\log K'_{22}$ and $\log K'_{35}$ for each solution are given in Table 2. In calculating the data of Table 2, uncertainties in both the concentrations in matrix \mathbf{C} as well as in pH are included. Methodology for assessment of uncertainties in pH measurement is outlined in the Appendix section of Ref. [7].

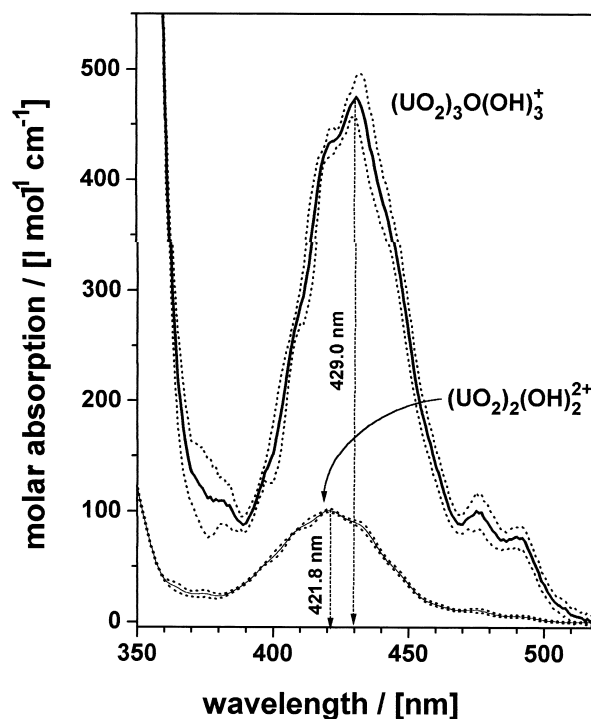


Fig. 2. Single-component UV-Vis absorption spectra of $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$. Dashed lines represent jackknifed 99% confidence limits.

Application of the single component spectra in Fig. 2 to deconvolution of a three-component spectrum at $\text{pH } 4.361 \pm 0.015$ is given in Fig. 3. The dashed lines give 95% confidence limits for each species contribution as well as the added over-all 95% confidence limit. It is evident that these single component spectra are readily able to deconvolute the experimental observation. Furthermore, precise statistical assessment is possible, thus avoiding over-interpretation and bias due to mean-value calculation only.

Table 2

Conditional formation constants $\log K'_{22}$ and $\log K'_{35}$ from the 25 spectra together with jackknifed 95% confidence limits (uncertainty in pH determination is included into each confidence limit)

pH	Log K'_{22}	Log K'_{35}
3.939 ± 0.029	-6.131 ± 0.083	-17.284 ± 0.192
3.980 ± 0.027	-6.000 ± 0.096	-17.281 ± 0.185
4.209 ± 0.038	-6.175 ± 0.147	-17.065 ± 0.312
4.252 ± 0.025	-6.216 ± 0.090	-17.414 ± 0.198
4.254 ± 0.016	-6.282 ± 0.053	-17.084 ± 0.156
4.316 ± 0.021	-6.278 ± 0.095	-17.143 ± 0.206
4.361 ± 0.015	-6.268 ± 0.069	-17.196 ± 0.180
4.378 ± 0.016	-6.266 ± 0.061	-17.081 ± 0.155
4.456 ± 0.016	-6.315 ± 0.059	-16.875 ± 0.186
4.474 ± 0.020	-6.325 ± 0.059	-16.810 ± 0.178
4.512 ± 0.017	-6.252 ± 0.098	-17.320 ± 0.239
4.718 ± 0.019	-6.333 ± 0.173	-17.308 ± 0.375
4.776 ± 0.014	—	-17.310 ± 0.083
weighted average	-6.237 ± 0.103	-17.203 ± 0.157

Only three-component spectra are considered.

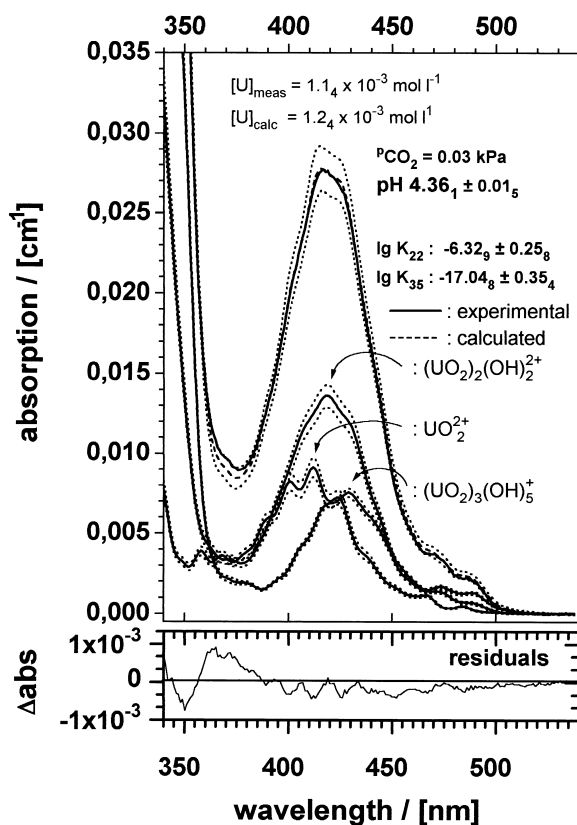


Fig. 3. Application example of the single-component UV-Vis spectra to a three-component spectrum at pH 4.361 ± 0.015 . Dashed lines give 95% confidence limits.

Deconvolution of further spectra are shown elsewhere [7,8,20].

3. Conclusions

Only three factors, identified as UO_2^{2+} , $(\text{UO}_2)_2(\text{OH})_2^{2+}$, $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$, are necessary to interpret hydrolyzed U(VI) solutions in a U(VI)–pH range, where current knowledge proposes a series of further species, e.g. $(\text{UO}_2)_3\text{OH}^+$ and $(\text{UO}_2)_3(\text{OH})_4^+$. Comparison of Table 1 with Fig. 1 strongly suggests that these species have entered discussion on basis of studies in supersaturated solutions. It has further to be noted that a structure of these additional hydrolysis species has apparently never been discussed. For species verified here by UV-Vis spectroscopy, detailed structural analyses are available [21,22].

Formation constant $\log K'_{22}$ has been reported rather consistently, ranging between $-5.68 \leq \log K'_{22} \leq -6.45$. In contrast, formation of $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$ has been reported with a scatter of more than two orders of magnitude $-15.64 \leq \log K'_{35} \leq -17.7$ in 0.1 M solutions, despite comparable experimental conditions. In Fig. 1, line 1 indicates the region where $(\text{UO}_2)_2(\text{OH})_2^{2+}$ has 1% species concentration, while line 2 indicates $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$ with calculated relative species concentration of 1%. Fig. 1

shows that $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$ is formed only in minute relative amounts in a pH region close to the saturation limit and therefore can not be detected precisely by concentration-dependent methods. UV-Vis spectroscopy is in a more comfortable situation because of high molar absorptions found for these species: $\epsilon_{421.8} = 101 \pm 2 \text{ l mol}^{-1} \text{ cm}^{-1}$ for $(\text{UO}_2)_2(\text{OH})_2^{2+}$ and $\epsilon_{429.0} = 474 \pm 7 \text{ l mol}^{-1} \text{ cm}^{-1}$ for $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$ to be contrasted with $\epsilon_{413.8} = 9.7 \pm 0.2 \text{ l mol}^{-1} \text{ cm}^{-1}$ found for UO_2^{2+} . The lowest $(\text{UO}_2)_3\text{O}(\text{OH})_3^+$ concentration speciated in this study was $(1 \pm 0.25) \times 10^{-6} \text{ mol l}^{-1}$.

Calculating integral oscillator strengths f from the spectra Fig. 2 in the range $19000\text{--}26000 \text{ cm}^{-1}$, $f_{22} = 2 \times 10^{-3}$ and $f_{35} = 6 \times 10^{-3}$ are obtained, much larger than $f_{10} = 1.7 \times 10^{-4}$ found for $\text{UO}_2^{2+}(\text{aq})$ [23]. Nevertheless, the fluorescence life times of these species are longer ($\tau_{22} = 2.9 \mu\text{s}$ and $\tau_{35} = 7 \mu\text{s}$ [24]) than for $\text{UO}_2^{2+}(\text{aq})$ ($\tau_{10} = 1 \mu\text{s}$) [25], despite the fact that oscillator strength and fluorescence lifetime are inversely related by theory [23]. This finding indicates an interesting relationship between excitation, emission, oligomerization and quench in uranyl(VI) compounds and offers an interesting field of further research. The correlation between absorption and emission spectra of U(VI) hydrolysis and carbonato species will be discussed in a forthcoming contribution [26].

Acknowledgements

This work was supported by Deutsche Forschungsgemeinschaft DFG.

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