

New Regularization Method for EXAFS Analysis

Tatiana Ye. Reich^{*}, Maxim E. Korshunov[§], Tatiana V. Antonova[§],
Alexander L. Ageev[§], Henry Moll[¶], and Tobias Reich^{*}

^{*}*Institute of Nuclear Chemistry, Johannes Gutenberg-Universität Mainz, 55099 Mainz, Germany*

[§]*Institute of Mathematics and Mechanics, Ural Branch of Russian Academy of Sciences, ul. S. Kovalevskaja 16,
620219 Ekaterinburg GSP-384, Russia*

[¶]*Institute of Radiochemistry, Forschungszentrum Rossendorf, P.O. Box 510119, 01314 Dresden, Germany*

Abstract. As an alternative to the analysis of EXAFS spectra by conventional shell fitting, the Tikhonov regularization method has been proposed [1]. An improved algorithm that utilizes a priori information about the sample has been developed and applied to the analysis of U L₃-edge spectra of soddyite, (UO₂)₂SiO₄·2H₂O, and of U(VI) sorbed onto kaolinite. The partial radial distribution functions $g_j(\text{UU})$, $g_2(\text{USi})$, and $g_3(\text{UO})$ of soddyite agree with crystallographic values and previous EXAFS results.

Keywords: EXAFS, Tikhonov regularization, uranium, soddyite, kaolinite

PACS: 61.10.Ht, 78.70.Dm

INTRODUCTION

To determine metrical parameters for the near-neighbor surrounding of an absorbing atom, it is common to perform least-squares fits to experimental Extended X-ray Absorption Fine Structure (EXAFS) spectra using structural models. The model that approximates the unknown structure consists of one or several coordination shells of different backscattering atoms. It is sometimes difficult to find a unique model for shell fitting if little is known about the local atomic surroundings in the sample.

The relative positions of different pairs of atoms in a sample can be described by partial radial distribution functions (RDFs) $g_j(r)$. Instead of trying to find the best structural model that fits the data, the RDFs can be determined from the EXAFS spectrum directly by solving a system of Fredholm integral equations of the first kind [2, references therein].

The algorithm described below has been developed to determine three RDFs from one EXAFS spectrum. A priori information about the sample is used to address the problem of non-uniqueness of the solutions g_j . As an example, the RDFs $g_1(\text{UU})$, $g_2(\text{USi})$, and $g_3(\text{UO})$ for soddyite, (UO₂)₂SiO₄·2H₂O, and of U(VI) sorbed onto the clay mineral kaolinite have been determined from the corresponding U L₃-edge EXAFS spectra.

THEORY

The relationship between the experimental EXAFS spectrum $\chi(k)$ and the RDFs g_j is given by the equation

$$Ag \equiv \sum_{j=1}^3 A_j g_j = \frac{4\pi\rho_0}{k} S_0^2(k) \sum_{j=1}^3 c_j \int_{a_j}^{b_j} f_j(k, r) e^{\frac{-2r}{\lambda(k)}} \times \\ \times \sin(2kr + \phi_j(k, r)) g_j(r) dr = \chi(k) \quad (1)$$

where the wave vector $k \in [c, d]$, $f_j(k, r)$ – scattering amplitude, $\phi_j(k, r)$ – scattering phase shift, $\lambda(k)$ – inelastic mean free path, S_0^2 – amplitude reduction factor, and ρ_0 – density of the sample. To determine the solutions g_j , $j = 1, 2, 3$, the system of integral equation (1) needs to be solved. This is a typical example of an ill-posed problem. For determining the solutions of (1), the following a priori information is used: Each RDF g_j consists of a small number of narrow peaks which are separated in distance by intervals Δr .

The algorithm for the determination of g_j consists of the following steps: variation Tikhonov method [1], application of separating functionals [3], and iteration method with filtration in real space [4]. Each step is described in detail in these references.

EXPERIMENTAL

As a reference compound with known crystal structure, synthetic soddyite, $(\text{UO}_2)_2\text{SiO}_4 \cdot 2\text{H}_2\text{O}$, was selected. The synthesis of the sample is described in [5]. A teflon pellet with 25 mg soddyite was prepared for U L_3 -edge EXAFS measurements in transmission mode. Two scans of the spectrum were measured at 15 K at the Rossendorf Beamline ROBL (BM20) at the ESRF.

The sample with an unknown U(VI) structure was prepared by contacting 10 μM U(VI) solution with kaolinite (4 g/L, I = 0.1 M NaClO_4) at pH 6 in air for 2 days. The wet paste obtained after centrifugation was air-dried and loaded in a Teflon sample holder. Eight scans of the U L_3 -edge EXAFS spectrum were collected at 28 K in fluorescence mode at ROBL.

The $\chi(k)$ were obtained by standard procedures [6] using EXAFSPAK [7]. The operators A_j in (1) were obtained using scattering phase and amplitude functions calculated with FEFF8.2 [8]. The crystal structure of soddyite [9] was used to define the self-consistent potential for the FEFF calculations. The multiple-scattering contribution of the linear UO_2^{2+} moiety was subtracted from the raw data prior to the analysis described below.

RESULTS

The experimental U L_3 -edge k^3 -weighted EXAFS spectrum of soddyite and the corresponding Fourier transform (FT) are shown in Fig. 1. To obtain the first solution of g_j , the variation Tikhonov method was applied:

$$\min \left\{ \left\| \sum_{j=1}^3 A_j g_j - \chi \right\|^2 + \sum_{j=1}^3 \alpha_j \|g_j\|^2 w_j^1 \right\} \quad (2)$$

α_j is a small positive parameter of the order of 10^{-7} – 10^{-5} . The calculated g_j for soddyite show significant deviations from the expected RDFs $g_1(\text{UU})$, $g_2(\text{USi})$, and $g_3(\text{UO})$ due to the non-uniqueness of the Tikhonov solution (Fig. 2). Since it is impossible to obtain a

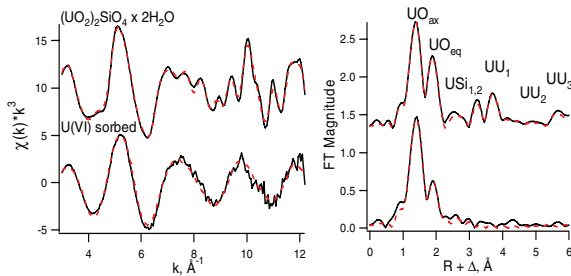


FIGURE 1. U L_3 -edge EXAFS spectra (left) and corresponding Fourier transforms (right). Solid line – experimental data, dashed line – calculated from final RDFs.

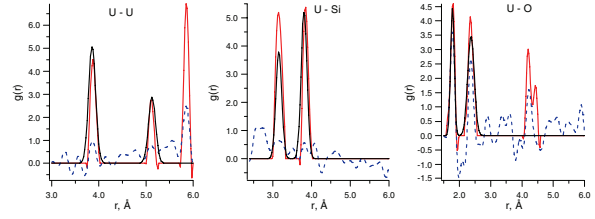


FIGURE 2. RDFs for soddyite. Black solid line – calculated based on crystal structure [9], dashed line – first Tikhonov solution, red solid line – final result.

unique solution for equation (1) from the experimental spectrum, additional a priori information is used to stabilize the Tikhonov solution (2). In particular, each peak in g_j of the first Tikhonov solution (Fig. 2) is analyzed whether it is a ‘true’ or ‘false’ peak using the method of separating functionals [3]. A negative or small parameter Δ is indicative of a ‘false’ peak (Table 1). Since the g_j of soddyite consist of two or three narrow and non-overlapping peaks (Fig. 2), segments of $g_j(r)$ where ‘false’ peaks were identified are set to zero. With this information, a new solution for g_j is determined by an iteration method with filtration in real space [4]. The final RDFs for soddyite are in close agreement with the calculated g_j using crystallographic data (Fig. 2). The coordination numbers N and interatomic distances r for soddyite are compared with those from conventional EXAFS analysis using shell-fitting [10] and single-crystal XRD [9]. Without any structural model, the first two coordination shells in $g_1(\text{UU})$, $g_2(\text{USi})$, and $g_3(\text{UO})$ could be determined. The U L_3 -edge k^3 -weighted EXAFS spectrum and FT calculated from these g_j agree with the experimental data (Fig. 1).

TABLE 1. Application of the method of separating functionals for soddyite. The peak position r is given in \AA . Negative or small positive values of Δ are indicative for ‘false’ peaks (*).

No.	U – U		U – Si		U – O	
	r	Δ	r	Δ	r	Δ
1	3.03*	-0.3	2.60	14.7	1.78	17.8
2	3.28	11.6	2.73	18.2	2.09*	-8.6
3	3.58	9.1	3.13	7.4	2.37	15.2
4	3.88	26.1	3.50	6.5	2.63*	-5.0
5	4.15	8.2	3.83	30.7	2.90*	5.3
6	4.50*	-3.1	4.08	32.2	3.38*	4.4
7	4.78*	-0.6	4.63	29.9	3.60*	4.7
8	5.10	15.6	5.00*	-8.1	3.93*	-1.5
9	5.38	14.0	5.33	20.0	4.23	18.6
10	5.55*	-10.2	5.75*	-44.1	4.88*	2.2
11	5.85	28.3			5.10*	3.1
12					5.48*	3.1
13					5.90*	5.3

When U(VI) is sorbed onto kaolinite, $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4]$, possible backscattering atoms are O, Al, Si, and U. Since Al is indistinguishable from Si by EXAFS, three RDFs $g_1(\text{UU})$, $g_2(\text{USi})$, and $g_3(\text{UO})$

were calculated from the raw U L₃-edge EXAFS spectrum (Fig. 1) using the same algorithm as for soddyite. The first Tikhonov solutions $g_2(\text{USi})$ and $g_3(\text{UO})$ are shown in Fig. 3. $g_1(\text{UU})$ is not shown since no U-U interaction was detected for U(VI). After the application of separating functionals to the first Tikhonov solution (Δ values not shown), the final solution was determined by the iteration method with filtration in real space.

As can be seen from Fig. 3, $g_3(\text{UO})$ consists of two peaks at 1.79 and 2.35 Å with N equal 1.9 (O_{ax}) and 5.1 (O_{eq}), respectively (Table 2). The RDF $g_2(\text{USi})$ displays a broad peak with a shoulder at higher r (Fig. 3). Approximately 0.7 Si/Al atoms at 3.06 Å and 0.4 atoms at 3.26 Å surround the U atom. The detection of Si/Al atoms in the near-neighbor environment of U indicates the formation of inner-sphere complexes of U(VI) with kaolinite at pH 6 and a total concentration of 10 μM U(VI). Note that no assumption was made on the distribution function for the atoms in the coordination shells, e.g., Gaussian distribution.

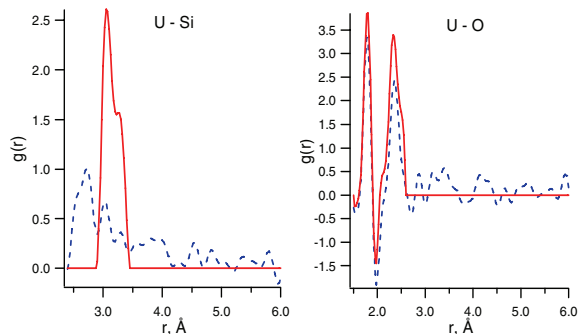


FIGURE 3. RDFs for U(VI) sorbed onto kaolinite. Dashed line – first Tikhonov solution, solid line – final result.

As can be seen from Fig. 1, the U L₃-edge EXAFS spectrum calculated according to (1) with the RDFs $g_2(\text{USi})$, and $g_3(\text{UO})$ shown in Fig. 3 agrees well with the experimental data.

TABLE 2. Inter-atomic distances r in Å and coordination numbers N for soddyite.

	U – O _{ax}		U – O _{eq}		U – Si ₁		U – Si ₂		U – U ₁		U – U ₂		U – U ₃	
	r	N	r	N	r	N	r	N	r	N	r	N	r	N
This work	1.79	2.1	2.35	4.6	3.15	1.5	3.84	1.8	3.87	1.3	5.11	1.2	5.86	4.1
EXAFS [10]	1.77	2	2.42	5	3.15	1	3.90	2	3.82	2	5.14	2	-	-
XRD [9]	1.78	2	2.38	5	3.16	1	3.81	2	3.86	2	5.15	2	5.83	4

CONCLUSIONS

To increase the reliability of EXAFS structural analysis, especially for compounds with an unknown structure, it is very useful to have several alternative approaches for data analysis. In contrast to common shell-fitting routines, the proposed algorithm does not require any structural model as input. The experimental EXAFS spectrum can be analyzed successfully if the Tikhonov regularization method is applied to intervals of the RDF where true peaks have been identified. The method of separating functionals [3] allows the determination of intervals in the RDFs where true peaks are absent.

ACKNOWLEDGMENTS

We acknowledge the European Synchrotron Radiation Facility for provision of synchrotron radiation facilities and would like to thank H. Funke, C. Hennig, A. Rossberg, and A. Scheinost for assistance in using beamline BM20. Part of this work was supported by Bundesministerium für Wirtschaft und Technologie (BMW) under contract No. 02E9653.

REFERENCES

1. Babanov, Yu. A., Vasin, V. V., Ageev, A. L., and Ershov, N. V., *Phys. Stat. Sol. (B)* **105**, 747-754 (1981).
2. Vasin, V. V., and Ageev, A. L., *Ill-Posed Problems With A Priori Information*, Utrecht: VSP, 1995, p. 255.
3. Ageev, A. L., Antonova, T. V., Reich, T. Ye., Reich, T., and Hennig, C., *Math. Modelling* **16**, 81-92 (2004) (in Russian).
4. Ageev, A. L., Korshunov, M. E., Reich, T. Ye., Reich, T., and Moll, H., *J. Inverse Ill-Posed Problems* (submitted).
5. Moll, H., Matz, W., Schuster, G., Brendler, E., Bernhard, G., and Nitsche, H., *J. Nucl. Mat.* **227**, 40-49 (1995).
6. Koningsberger, D. C., and Prins, R., *X-Ray Absorption: Principles, Applications, Techniques Of EXAFS, SEXAFS, and XANES*, New York: Wiley, 1988, pp. 673.
7. George, G. N., and Pickering, I. J., *EXAFSPAK – A Suite Of Computer Programs For Analysis of X-Ray Absorption Spectra*, Stanford (2000).
8. Ankudinov, A. L., Bouldin, C. E., Rehr, J. J., Sims, J., and Hung, H., *Phys. Rev. B* **65**, 104107 1-11 (2002).
9. Demartin, C. M., Gramaccioli, T., and Pilati, T., *Acta Cryst. C* **48**, 1-4 (1992).
10. Catalano, J. G., and Brown, G. E., Jr., *Am. Mineralog.* **89**, 1004-1021 (2004).