



	Experiment title: EXAFS/XANES studies on the speciation of Tc(IV) in the presence of complexing organics and fulvic acids	Experiment number: CH 1671
Beamline: BM20	Date of experiment: from: 27/02/04 to: 02/03/04	Date of report: 31/08/04
Shifts: 12	Local contact(s): Dr. Harald FUNKE	<i>Received at ESRF:</i>
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Introduction

The redox-sensitive fission product technetium-99 (Tc) is of great interest in nuclear waste disposal studies because of its potential for contaminating the geosphere due to its very long half-life (2.13×10^5 year) and high mobility under oxidising conditions, where technetium forms pertechnetate (TcO_4^-) [1]. Under suitable reducing conditions, e.g. in the presence of an iron(II) containing solid phase which can act as an electron donor, the solubility can be limited by the reduction of pertechnetate followed by the formation of a surface precipitate [2]. However, upon association with mobile humic substances (HS), the solubility of reduced Tc species may be drastically enhanced [3].

A first XANES measuring campaign (performed at ESRF, March 2001, CH-1050) demonstrated for the first time that pertechnetate was reduced to Tc(IV) and Tc(IV)-HS species were formed in Gorleben sand/Gorleben groundwater (rich in humic acids) reducing systems. These results were published in *Radiochimica Acta* [4].

A second EXAFS/XANES campaign (performed at ESRF, July 2002, SI-790) was then performed on samples in which TcO_4^- was reduced by various solid phases (pyrite, magnetite, Gorleben sand, Boom Clay), both in absence and presence of humic acids (HA). These experiments were set up in order to elucidate the chemical environment of Tc in these systems on atomic scale. The data from these experiments showed very interesting and surprising results, because all spectra could be fitted with a hydrated amorphous Tc(IV) oxide phase, independent of the reducing surface used and of the eventual presence of HA. These results could only mean that Tc(IV) oxide colloids were formed and precipitated upon reduction of TcO_4^- , and that these colloids could also interact with the organic colloidal material from Gorleben and Boom Clay HA. This latter observation was confirmed by batch sorption experiments with Tc and Boom Clay suspensions from which an interaction constant could be derived describing the interaction of a neutral Tc(IV) species and dissolved HA [5]. The results from the above described EXAFS/XANES data were incorporated in an article published in *Environmental Science & Technology* [6].

The aim of a third EXAFS/XANES campaign was to investigate the universality of the observed interaction between Tc(IV) colloids and HA for other organic molecules. Therefore batch systems were set up at KU Leuven in which TcO_4^- was chemically reduced to Tc(IV) in presence of 9 reference organic compounds varying in size from small to large (citric acid, hydroxybenzoic acid, pyrogallol, glutamate, isosaccharinic acid, aurintricarboxylic acid, calconcarboxylic acid, Laurentian fulvic acid, Fluka humic acid) and of Boom Clay HA. These samples still yielded the same colloidal Tc(IV) spectra in presence of large humic acid molecules (Fluka HA and Boom Clay HA) as observed before, however different spectra were now obtained in

the presence of small dissolved organic molecules. At that time no performant modeling capabilities were accessible, due to which only single scattering analysis of the data was possible. Based on only SS analysis it was not possible to elucidate an exact structure for the complexes formed.

In order to further elucidate the behaviour of Tc(IV) in the presence of organic matter (colloid association and/or complexation), a new, fourth, EXAFS/XANES campaign was set up in which the experience of the third campaign was used to specifically investigate Tc(IV) complexation in function of the pH with complexing agents resulting in strong complexes.

Experimental setup

TcO₄⁻ was chemically reduced to Tc(IV) and contacted with sufficient amounts of 1) small reference organic molecules (salicylic acid, protocatechuic acid, pyrogallol, gallic acid as natural decay products of lignin or polyphenol [11] and representative for the main complexing functional group geometries on FA and HA) and 2) fulvic acids. The systems were buffered in order to obtain a series covering both acidic and basic pH (2-10) so as to obtain a range of competition between H⁺ and Tc(IV) for the complexing sites. TcO₄⁻ reduction and subsequent association with the organic molecules was monitored as a function of time by Gel Permeation Chromatography, UV-VIS to determine the speciation of Tc(IV)/organic complexes. All samples were then preconcentrated and transferred into heat-sealed poly-ethylene microtubes as a slurry. A total of 20 samples were prepared to be measured at the ESRF.

Results

Although the research on the results of this fourth campaign and its precessor is not yet finished completely, some main conclusions could already be drawn:

1) The technique used for the preparation of the samples produced relatively pure samples with technetium concentrations high enough for XAS-measurements in fluorescence mode and in some cases also transmission mode. The complete XAS campaign resulted in spectra for 10 samples. Due to the installation of a new monochromator crystal in the beamline optics (BM20), the raw spectra contain more glitches as compared to the previous campaigns. Although data extraction was more difficult, good EXAFS spectra were obtained.

2) As described in literature [7, 8] and observed in the results of the previous session, Tc(IV) species formed chelates with most smaller organic molecules by means of a ligand exchange between the hydrolysed Tc(IV) molecules and functional groups present on the organics. For all samples the presence of an organic Tc-complex could be identified by SS analysis of the spectra (exafspak/feff8.28)[9].

3) The structure extracted from the spectra of a pertechnetate standard solution was nearly identical to the optimized structure obtained from DFT¹-calculations (ub3lyp/lanl2dz) (Table 2 ; Fig 1) which was in accordance with the results of Gancheff *et al.* [10] and [11].

Table 1: Parameters for the TcO₄⁻ structure obtained from EXAFS analysis and DFT.

	DFT (ub3lyp/lanl2dz)		EXAFS ⁺⁺	
	d(Tc-O) (Å)	N	R (Å)	σ ²
SS: Tc-O	1.75561	4.01961	1.72546	0.00164
MS: Tc-O-O		12.0588	3.19108	0.00577

⁺⁺ E₀=2.91059, Scale=0.94658, Expected resolution=0.116355 Å. All parameters were floated during the fit, except for the coordination number N_{MS} = 3 * N_{SS} and E₀ which was forced to be identical for all paths.

4) In the pH range from 4 to 9 the protocatechuic and pyrogallol-complexes were identified as similar monomeric di-phenol complexes, in contrast with the dimeric structure of the citric acid Tc(IV) complex measured in the third campaign. Both phenolic complexes were modeled by DFT-calculations (ub3lyp/lanl2dz) to obtain a more detailed structure of the complexes. The interatomic distances obtained from the model and from the EXAFS spectra coincided within 0.1Å, the expected error on both techniques. Based on FEFF-calculations (feff 8.2) on the modeled structures a MS path, between 2 carbon atoms of the rigid aromatic

¹ Density Functional Theory

structure could be identified in the spectra. Other less rigid MS paths from the FEFF- calculations could not be identified up until now.

Table 2: Atomic coordinates for the structure Fig 1.

#	Elem	X	Y	Z
1	Tc	0.000000	0.000000	0.000000
2	O	1.013600	1.013600	1.013600
3	O	-1.013600	-1.013600	1.013600
4	O	1.013600	-1.013600	-1.013600
5	O	-1.013600	1.013600	-1.013600

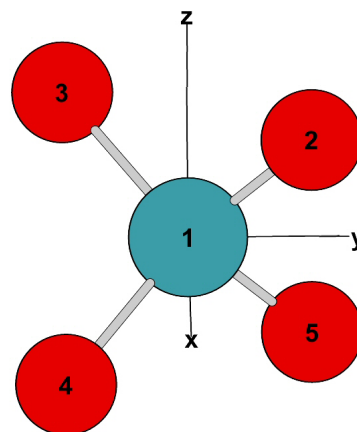


Fig 1: DFT (ub3lyp/lanl2dz) optimized structure of TcO_4^-

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