	<b>Experiment title:</b> EXAFS/XANES studies on the speciation of Tc(IV) in mixtures of low and high molecular weight organics	<b>Experiment number:</b> CH 1931
	<b>Beamline:</b> BM20	<b>Date of experiment:</b> from: 13/07/05 to: 16/07/05
<b>Shifts:</b> 12	<b>Local contact(s):</b> Dr. Christophe HENNIG	
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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 ( $2.13 \times 10^5$  year) and high mobility under oxidising conditions, where technetium forms pertechnetate ( $\text{TcO}_4^-$ ) [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].

Previous EXAFS/XANES campaigns (CH-1050, SI-790, CH-1454, CH-1671) performed at ESRF have demonstrated that pertechnetate is reduced to Tc(IV) in reducing natural systems containing humic matter [4, 5]. A large fraction of this Tc(IV) was observed to be in a colloidal form and associated with the organic matter through a “hydrophobic” interaction mechanism. The results from the last campaigns however also proved (unpublished) that in the presence of small organic molecules, different spectra were obtained for Tc(IV), i.e. Tc(IV) was not in the colloidal form. Some spectra could already be fully modelled, e.g. with pyrogallol as natural organic matter precursor. It was found that Tc(IV) can make chelating complexes with pyrogallol at neutral to high pH by means of a ligand exchange between the hydrolysed Tc(IV) molecules and –OH functional groups present on the organics. EXAFS modelling was thereby supported by Density Functional Theory calculations (ub3lyp/lanl2dz [6]).

#### Experimental setup

The main objective of experiment CH-1931 was two-fold :

1) to obtain spectra for Tc(IV) reference compounds whose atomic model is known from literature in order to verify the pursued analysis methodology.

Experimentally  $\text{TcO}_4^-$  was chemically reduced to Tc(IV) and different “Tc(IV) reference compounds”:  $\text{TcCl}_6^{2-}$  [10], Tc(IV)-acetyl acetate [7]) were prepared.

2) to study the contribution of both above described mechanisms in the association of Tc(IV) with mixed systems of small organic molecules and humic substances.

Experimentally, mixed systems of Tc(IV) complexes with small organic molecules and colloidal Tc(IV) interacting with large humic substance molecules were prepared. Chemically reduced Tc(IV) was therefore contacted with 1) pyrogallol (containing phenol ligands), 2) citric acid (containing carboxyl ligands) and 3) humic substances (colloidal interaction) at a fixed pH and with mixtures of two of these compounds.

All samples were preconcentrated and transferred into heat-sealed poly-ethylene microtubes as a slurry.

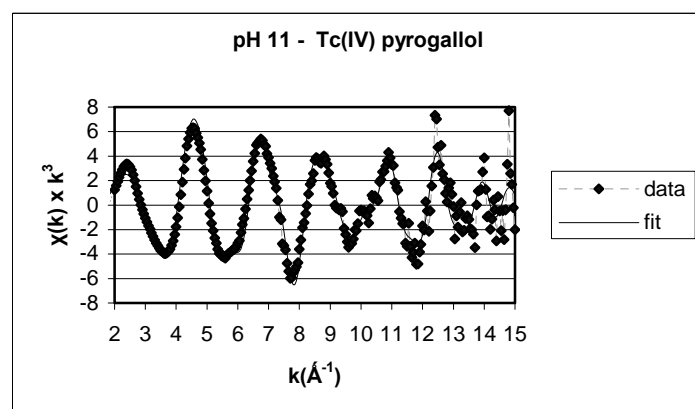
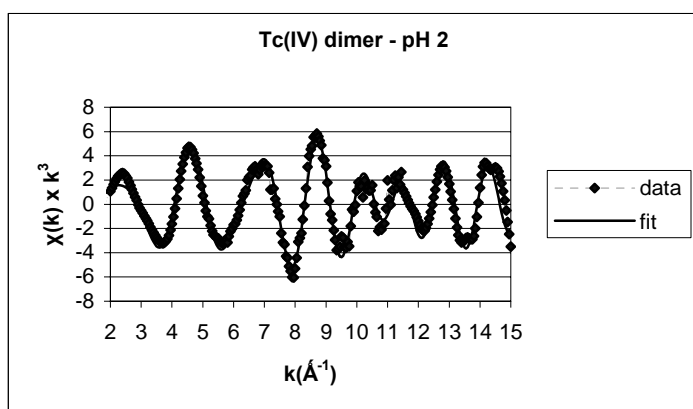
## Results

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 17 samples. The installation of a new monochromator crystal in the beamline optics (BM20) solved a problem with glitches in the raw spectra as compared to the 4th campaign.

2) XANES analysis of the reference spectra and the pure samples revealed that the relation between the edge shift and the formal oxidation state is not straightforward and highly depends on the ligands and structure of the species under investigation. This observation corresponds to previous literature data [8].

Compound	formal oxidation state	K edge shift (eV)
$\text{TcO}_4^-$	VII	0
$\text{Tc}(\text{acac})_3$	III	-8.34
$\text{TcCl}_6^{2-}$	IV	-9.16

3) In the pH range from 2 to 11, using pure pyrogallol as complexing agent a competition mechanism was observed between Tc(IV) dimer/polymer formation (dominant pH 2; see fig.) and the formation of monomeric and dimeric pyrogallol complexes (dominant pH 5 – 11). Next to the formation of monomeric and dimeric complexes, a pH dependant change in complex structure was also observed, yielding 5-coordinated complexes at the lower pH range (pH 5) and 6-coordinated complexes at high pH (pH 11; see fig).



## References

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