ROBL-CRG	Experiment title: First XANES and EXAFS Measurements of Technetium Model Compounds at the Rossendorf Beamline ROBL	**Experiment number**: 20_01_02
Beamline: BM 20	**Date of experiment**: from: 20/11/98, 27/1/99 to: 29/11/98, 03/2/99	**Date of report**: 24/8/99
Shifts: 27+21	**Local contact(s)**: C. Hennig, T. Reich, A. Roßberg	*Received at ROBL:* 26.8.99

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Report:

Experimental

The structure of novel Tc complexes has been studied successfully in the framework of a collaboration between the Institute of Radiochemistry and the Institute of Bioinorganic and Radiopharmaceutical Chemistry over the last few years /1,2/. In order to evaluate the possibilities of the new Rossendorf Beamline (ROBL) for Tc EXAFS studies, we prepared four samples for a first experiment with ^{99}Tc at ROBL. The samples were 127 mMol/L $NaTcO_4$(aq), 1.3 mMol/L $NaTcO_4$(aq), $KTcO_4$(s), and $TcO_2 \cdot nH_2O$(s). Except for the 1.3 mMol/L Tc solution, the amount of Tc in the samples yielded an edge jump of ~1 across the Tc K absorption edge at 21 keV. These samples were measured in transmission mode using the Si(111) double-crystal monochromator in fixed-exit mode with an additional feedback system to minimize beam intensity fluctuations. The Tc K-edge EXAFS spectrum of the dilute solution was recorded using a four pixel Ge fluorescence detector. The energy scale of the XANES scans was calibrated with a Mo metal foil (Mo K edge at 20004.3 eV). For the EXAFS analysis, the first inflection point of the pre-edge absorption peak for the $NaTcO_4$(aq) sample was defined as 21044 eV /3/.

Results and Discussion

Fig. 1 displays the raw Tc K-edge k^3-weighted EXAFS spectrum of $NaTcO_4$(aq). The spectrum of the 127 mMol/L Tc solution was recorded in a single sweep up to k=21 Å^{-1}. During this sweep the counting time per data point was gradually increased from 2 to 20 sec. To our knowledge, this is the first Tc EXAFS spectrum of a liquid sample where it was possible to observe the fine structure of the x-ray absorption spectrum over an energy range of 1700 eV. In addition, this spectrum is an impressive demonstration of the superb quality and stability of all beamline components. It follows from the best theoretical fit to the data (Fig. 1) that Tc is surrounded by 4 oxygen atoms (N=4.1±0.1) at a distance of 1.72±0.01 Å (σ^2=0.0013±0.0004 Å^2). The EXAFS spectrum of the 100 times more dilute $NaTcO_4$(aq) sample is also shown in Fig. 1 and represents an average of four sweeps measured in fluorescence mode. The intensity of the Tc Kα fluorescence line was 1.2x10^5 counts/sec. The total count rate processed by the

fluorescence detector was $6.4x10^5$ counts/sec. Under these conditions, it was possible to analyze the Tc K-edge k^3-weighted EXAFS spectrum of the 1.3 mMol/L Tc solution up to k=15 $Å^{-1}$. The structural parameters obtained are the same as for the TcO_4^- ion in the concentrated solution, i.e., N=3.9±0.2, R=1.72±0.01 Å, and σ^2=0.0016±0.0003 $Å^2$. Our structural parameters agree with a previous Tc K-edge EXAFS measurement of a 0.2 Mol/L NH_4TcO_4(aq) sample /3/.
Fig. 2 displays the Tc K-edge XANES spectra of $KTcO_4$(s), and TcO_2•nH_2O(s). The energy of the main absorption edge defined by the first-derivative method increases from 21061.6 eV to 21065.8 eV as the Tc valence increases from IV to VII. This energy shift of 4.2 eV is in qualitative agreement with previous measurements /3/. The shape of the Tc K-edge XANES spectra reflects the symmetry of the oxygen atoms surrounding Tc. The most distinct feature of the TcO_4^- ion, which has T_d symmetry, is the pre-edge peak at 21050.8 eV. The XANES features can been used as a probe to determine the Tc speciation as it has been shown, for example, in cement waste forms /3/.
In summary, the Tc K-edge x-ray absorption measurements on Tc model compounds showed that high-quality data can be obtained for liquids and solids at the new Rossendorf Beamline. We conclude that ROBL provides excellent experimental conditions to study the structure of solid and liquid Tc complexes with a large variety of organic and inorganic ligands covering a Tc concentration range of at least two orders of magnitude.

References:
/1/ Johannsen, B., et al.; Appl. Radiat. Isot. **48**, 1045 (1997)
/2/ Jankowsky, R., et al.; J. Inorg. Biochem. **70**, 99 (1998)
/3/ Allen, P.G., et al. Radiochim. Acta **76**, 77 (1997) and references therein

Fig. 1: Raw k^3-weighted Tc K-edge EXAFS spectra (left) and corresponding Fourier transforms (right) of experimental data (solid line) and theoretical fits (dots) for 127 mMol/L (top) and 1.3 mMol/L (bottom) $NaTcO_4$(aq).

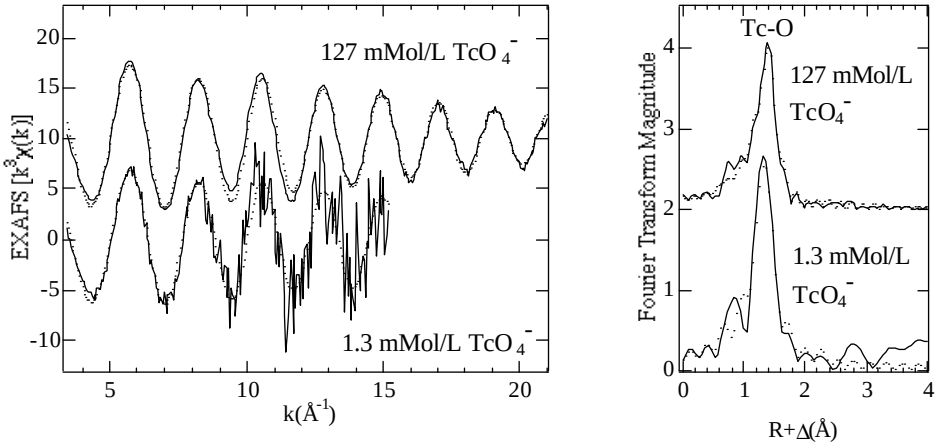

Fig. 2: Raw Tc K-edge XANES spectra of TcO_2•nH_2O(s) (top) and $KTcO_4$(s) (bottom).