

Combining Tc K-/L₃-edge X-ray absorption spectroscopy and ab initio calculations of Tc redox speciation in complex aqueous systems: A success story

K. Dardenne, N. DiBlasi, S. Duckworth, R. Polly, X. Gaona, T. Pruessmann, J. Rothe, M. Altmaier, H. Geckeis

¹ Institute for Nuclear Waste Disposal (INE), Karlsruhe Institute of Technology, P.O. Box 3640, D-76021 Karlsruhe, Germany

⁹⁹Tc is a low energy beta emitter with a high fission yield from both ²³⁵U (~6.1%) and ²³⁹Pu (~5.9%). Its long half-life ($t_{1/2} = 2.121 \times 10^5$ a) and large inventory in spent nuclear fuel makes it a radionuclide of particular interest in the context of safety assessment of repositories for radioactive waste. Many small organic molecules capable of strong aqueous complexation interactions, such as gluconate (GLU), citrate, and ethylenediaminetetraacetic acid (EDTA), may be present in nuclear waste disposal scenarios which can potentially increase the solubility and mobility of Tc. For these reasons, it is essential to understand the impact of complexing organic ligands on the speciation and oxidation state of Tc under relevant boundary conditions.

A new setup for “tender” X-ray spectroscopy (spectral range ~2–5 keV) in transmission or total fluorescence yield detection mode based on a He flow cell has been developed at the INE-Beamline for radionuclide science (KIT Light Source, KIT, Germany). This setup allows handling of radioactive specimens with total activities up to one million times the exemption limit. For the first time, Tc L₃-edge X-ray absorption near edge structure (XANES) measurements (~2.677 keV) of Tc species in liquid (aqueous) media are reported [1], clearly outperforming conventional K-edge spectroscopy as a tool to differentiate Tc oxidation states and coordination environments.

In the gluconate system, the combination of wet-chemistry experiments (measurements of pH, E_h, and [Tc]) and advanced spectroscopic techniques (K- and L₃-edge X-ray absorption fine structure spectroscopy) confirms the formation of a very stable Tc(V)–gluconate complex under anoxic conditions, whereas Tc(IV)-GLU complexes dominate the aqueous speciation of Tc under reducing conditions [1].

In this contribution, we report on a series of Tc oversaturation solubility studies under reducing, anoxic conditions coupled with spectroscopic measurements and theoretical calculations. The same methodology as applied for the Tc-GLU system is used to investigate two additional organic ligands (L) with relevance for repository conditions: L = EDTA and citrate. Tc is added to the aqueous solutions as NaTc(VII)O₄ and reacted at constant pH = 9, ionic strength (0.7 M NaCl-NaOH-Na_xL), and ligand concentration (100 mM), employing SnCl₂ as a redox buffer. Long-term equilibrated solutions are analyzed by pH and E_h measurements, liquid scintillation counting to determine aqueous Tc concentration, UV-Vis-NIR spectroscopy as well as Tc K- and L₃-edge XANES for selected samples.

The coupling of L₃-edge XANES spectroscopy measurements and relativistic multiconfigurational ab initio methods opens new perspectives in the definition of chemical and thermodynamic models for Tc species of relevance in the context of nuclear waste disposal, environmental remediation or pharmaceutical applications.

Acknowledgements: This work is partly funded by the German Federal Ministry for Economic Affairs and Climate Action (BMWK) within the framework of the VESPAII project (02E11607C). We thank the Institute for Beam Physics and Technology (IBPT) for the operation of the storage ring, the Karlsruhe Research Accelerator (KARA).

[1] Dardenne, K. et al. (2021) Inorg. Chem. 60, 12285-12298.