Experiment Report Form

The double page inside this form is to be filled in for each experiment at the Rossendorf Beamline (ROBL). This double-page report will be reduced to a one page, A4 format, to be published in the Bi-Annual Report of the beamline. The report may also be published on the Web-pages of the HZDR. If necessary, you may ask for an appropriate delay between report submission and publication.

Should you wish to make more general comments on the experiment, enclose these on a separate sheet, and send both the Report and comments to the ROBL team.

Published papers

All users must give proper credit to ROBL staff members and the ESRF facilities used for achieving the results being published. Further, users are obliged to send to ROBL the complete reference and abstract of papers published in peer-reviewed media.

Deadlines for submission of Experimental Report

Reports shall be submitted not later than 6 month after the experiment.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the reference number of the proposal / experiment to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.
- bear in mind that the double-page report will be reduced to 71% of its original size, A4 format. A type-face such as ”Times” or ”Arial” , 14 points, with a 1.5 line spacing between lines for the text produces a report which can be read easily.

Note that requests for further beam time must always be accompanied by a report on previous measurements.

Postal address: HZDR, P.O.Box 510119, D-01314 Dresden; Germany
Phone: +49 (351) 260 3122; Fax: (0351) 260 3438.
ROBL-CRG at the ESRF, B.P. 220, F-38043 Grenoble Cedex, France
Telephone: +33 (476) 88 24 62; Fax: +33 (476) 88 2505

HZDR HELMHOLTZ ZENTRUM DRESDEN ROSSENDORF ROBL-CRG	**Experiment title:** Interaction of technetium(III,IV and IV) with neptunium in acidic media	**Experiment number**: **20-01-760**
Beamline: BM 20	**Date of experiment**: from: 03/10/2015 to: 06/10/2015	**Date of report**: 21/02/2017
Shifts: 12	**Local contact(s)**: Andre Rossberg	*Received at ROBL:*
Names and affiliations of applicants (* indicates experimentalists): Maciej CHOTKOWSKI, Damian POŁOMSKI Faculty of Chemistry, University of Warsaw, 02-093 Warsaw, Poland		

Report:

The major objectives of this project were to determine the structure of Tc in the presence of neptunium in acidic media in HNO_3/H_2SO_4 solutions.

The structures of Tc and Np complexes generated during a reaction between Tc species at +VII or +IV oxidation states and Np^{3+} or NpO_2^{2+} ions were studied by means of EXAFS at ROBL line. 15 samples containing a mixture of Tc and Np compounds in the presence or absence of nitric acid were prepared at HZDR in Dresden.

The Tc K-edge EXAFS spectra were recorded for all solutions using a fluorescence detector. The energy scales for XANES scans for Tc and Np were calibrated with Mo (Mo K-edge at 20000 eV) and Y (Y K-edge at 17038 eV) metals foils, respectively. The spectra of Tc compounds in the samples containing initially Tc(IV) and Tc(III,IV) species with addition of NpO_2^{2+} and HNO_3 show an inflection

point of pre-edge absorption peak at 21044 eV, a feature characteristic for pertechnetates. Tc was surrounded by 4 oxygen atoms (N = 3.9) at a distance of 1.74 Å (σ^2= 0.0010 Å^2). Obtained results confirmed TcO_4^- structure as a product of oxidation of reduced Tc species. In the presence of HNO_3 neptunium is transformed to species with valence states of +4 and +6. An analysis of its oxidation states showed that the concentration ratio of Np(VI)/Np(IV) species generated during Tc(VII)-Np(III) interaction in the presence of HNO_3 increases from 0.08 for 0.7M HNO_3 to 0.18 for 3M HNO_3.

Due to the various redox reactions with participation of Tc and Np species the aqueous solutions contain mixtures of both elements with various valences. The simulation based on obtained XAS results showed that reduced Tc(IV) forms exist as polynuclear, -O-Tc-O-Tc-, and mononuclear complexes of Tc. The ratio between both Tc(IV) structures strongly depends on the ratio of TcO_4^- to the reducing agent, Np^{3+}.

The obtained results have contributed to development of advanced MonteCarlo analyses of the XAS signals obtaining for a mixture containing 3 components of the same element at various oxidation states and structures.