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.

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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: 15/07/2015 to: 18/07/2015	**Date of report**: 21/02/2017
Shifts: 12	**Local contact(s)**: Andre Rossberg	*Received at ROBL:*

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Report:

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

The structures of Tc and Np complexes generated during a reaction between Tc species at selected oxidation states and Np(III and VI) ions were studied by means of EXAFS at ROBL line. 6 samples containing a mixture of Tc and Np compounds and reference samples containing initially Tc(IV) or TcO_4^- 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+} show an inflection point of pre-edge absorption pe ak at 21044 eV, a feature characteristic for pertechnetates. Data fitting was applied in further analysis of the results. 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. The results of the experiments show that in strongly acidic media the pertechnetates are reduced by Np(III) to technetium(IV) species while Np(III) ions are transformed not only to Np(IV) but also to Np(VI) as is shown in Table 1.

Table 1. Fraction analyses of final Tc and Np species.

Initial oxidation states and concentrations of Tc and Np	Percentage of final oxidation states of Tc and Np			
	Tc(VII)	Tc(IV)	Np(VI)	Np(IV)
1 mM Tc(III/IV) + 11 mM Np(VI)	100	0	75	25
1 mM Tc(VII) + 6mM Np(III)+ 5 mM Np(IV)	0	100	8	92
2 mM Tc(VII) + 6mM Np(III)+ 5 mM Np(IV)	11	89	7	93
3 mM Tc(VII) + 6mM Np(III)+ 5 mM Np(IV)	36	63	7	93

Neptunyl(VI) ions are generated probably by a disproportionation of Np(V) ions, the latter species are unstable products of Tc(VII)-Np(III) interaction. An analysis of the samples containing various concentrations of technetium and fixed concentration of neptunium in acidic media confirms a multistep pathway of Tc(red)-Np(ox) interaction. These observations point out to a significant role of Tc(V) and Np(V) in redox chemistry of both elements.