# Supplementary Material

Quantifying Neptunium Oxidation States in Nitric Acid through Spectroelectrochemistry and Chemometrics

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**This Supporting Information contains the following:**

Pages: 6

Figures: 8

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Multivariate curve resolution–alternating least squares (**MCR-ALS) details**

Nonrandom estimates can help shorten the iterative optimization process and avoid convergence at local optima. Initial estimates of **C**-type or **ST**-type matrices are often chosen by which profile is less overlapped. Constraints are often classified as equality or inequality constraints. Several of the most common constraints include non-negativity, unimodality, and closure. Non-negativity is an example of an inequality constraint and applied when the measured values of concentration and response profiles (i.e., spectra) are assumed to be non-negative. The unimodality constraint allows the presence of only one maximum per profile, and the closure constraint is applied when the principle of mass balance is fulfilled. The closure constraint forces the sum concentration of each component to be equal to a constant value across all samples included in the model and is an example of an equality constraint.

**Chart, histogram

Description automatically generated**

**Figure S1.** Applied potential as a function of time.

**Diagram

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**Figure S2.** Kennard–Stone (KS)-selected near-infrared (NIR) calibration spectra.

Chart, line chart

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**Figure S3.** Explained **Y**-variance plot for the KS-NIR-partial least squares regression (PLSR) model.

Chart, scatter chart

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**Figure S4.** 3D scores plot from PLS-2 model generated from KS-selected NIR spectra.

**Figure S5.** Synthetic NIR spectra generated from the mixture design.

Chart, scatter chart

Description automatically generated

**Figure S6.** 3D scores plot from the mixture PLS-2 (M-PLS-2) model.

Chart

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**Figure S7.** MCR-ALS results from trimmed NIR spectra (a) component concentrations and (b) component spectra.

Diagram

Description automatically generated

**Figure S8.** Hotelling’s (Hot) T2 statistic with the (red line) critical limit for samples collected during the rapid Np(III) to Np(VI) scan (Factor-1).

**Table S1.** Mixture design selected samples

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Run** | **Np(VI)** | **Np(V)** | **Np(IV)** | **Np(III)** | **Space type** | **Build type** |
| 1 | 0.625 | 0.125 | 0.125 | 0.125 | Axial | Lack of fit |
| 2 | 0.5 | 0 | 0.5 | 0 | CentEdge | Model |
| 3 | 0.5 | 0 | 0 | 0.5 | CentEdge | Model |
| 4 | 0 | 0 | 0.5 | 0.5 | CentEdge | Model |
| 5 | 0.125 | 0.125 | 0.625 | 0.125 | Axial | Lack of fit |
| 6 | 0 | 1 | 0 | 0 | Vertex | Model |
| 7 | 0 | 0.5 | 0 | 0.5 | CentEdge | Model |
| 8 | 0.25 | 0.25 | 0.25 | 0.25 | Center | Lack of fit |
| 9 | 1 | 0 | 0 | 0 | Vertex | Model |
| 10 | 0 | 0 | 1 | 0 | Vertex | Model |
| 11 | 0 | 0.5 | 0.5 | 0 | CentEdge | Model |
| 12 | 0 | 0 | 0 | 1 | Vertex | Model |
| 13 | 0.125 | 0.125 | 0.125 | 0.625 | Axial | Lack of fit |
| 14 | 0.125 | 0.625 | 0.125 | 0.125 | Axial | Lack of fit |
| 15 | 0.5 | 0.5 | 0 | 0 | CentEdge | Model |

\*Abbreviation CentEdge (center edge). Space type points describe the location within a given factor space and Build type points describe how a model describes the point(s) mathematically.