

Applying Two-Dimensional Correlation Spectroscopy and Principal Component Analysis to Understand How Temperature Affects the Neptunium(V) Absorption Spectrum

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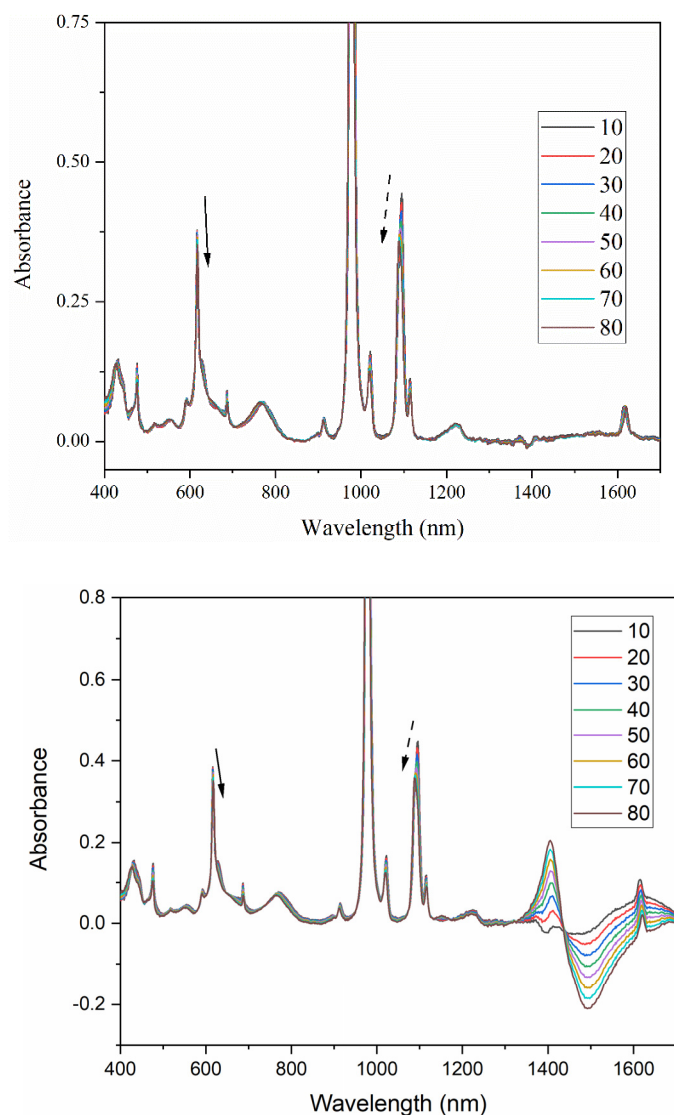


Figure S1. Absorption spectra of 0.17 M Np(V) in 1 M HNO₃ as a function of temperature (10–80 °C) (top) with background subtraction and (bottom) without subtracting the background. Np(VI) is present at $\leq 1\%$. The notional direction of wavelength and intensity for peaks at 616 and 1094 nm are shown by the solid and dashed arrows, respectively. Features including the small positive peak that grows with temperature near 1156 nm, the broad negative band from 1180–1310 nm, and broad positive/negative peaks from 1350–1700 nm are related to the NIR water bands.

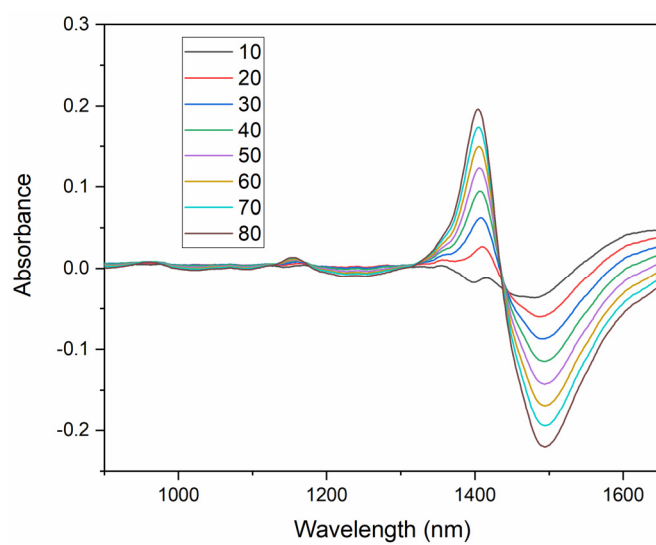


Figure S2. NIR absorption spectra of 1 M nitric acid ($T = 10\text{--}80\text{ }^{\circ}\text{C}$). The spectrometer was referenced to deionized water at $20\text{ }^{\circ}\text{C}$.

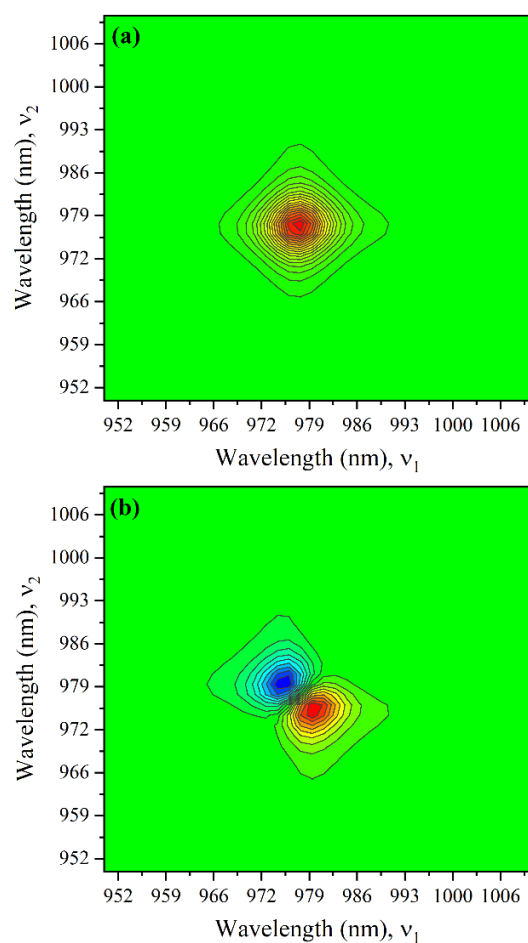


Figure S3. Synchronous (top) and asynchronous 2D-COS spectra for Np(V) from 950–1005 nm with varying temperatures (10–80 °C) and zero reference. Red regions represent positive correlations, blue represents negative correlations, and green is null. Sample contained 0.017 M Np in 1 M HNO₃.

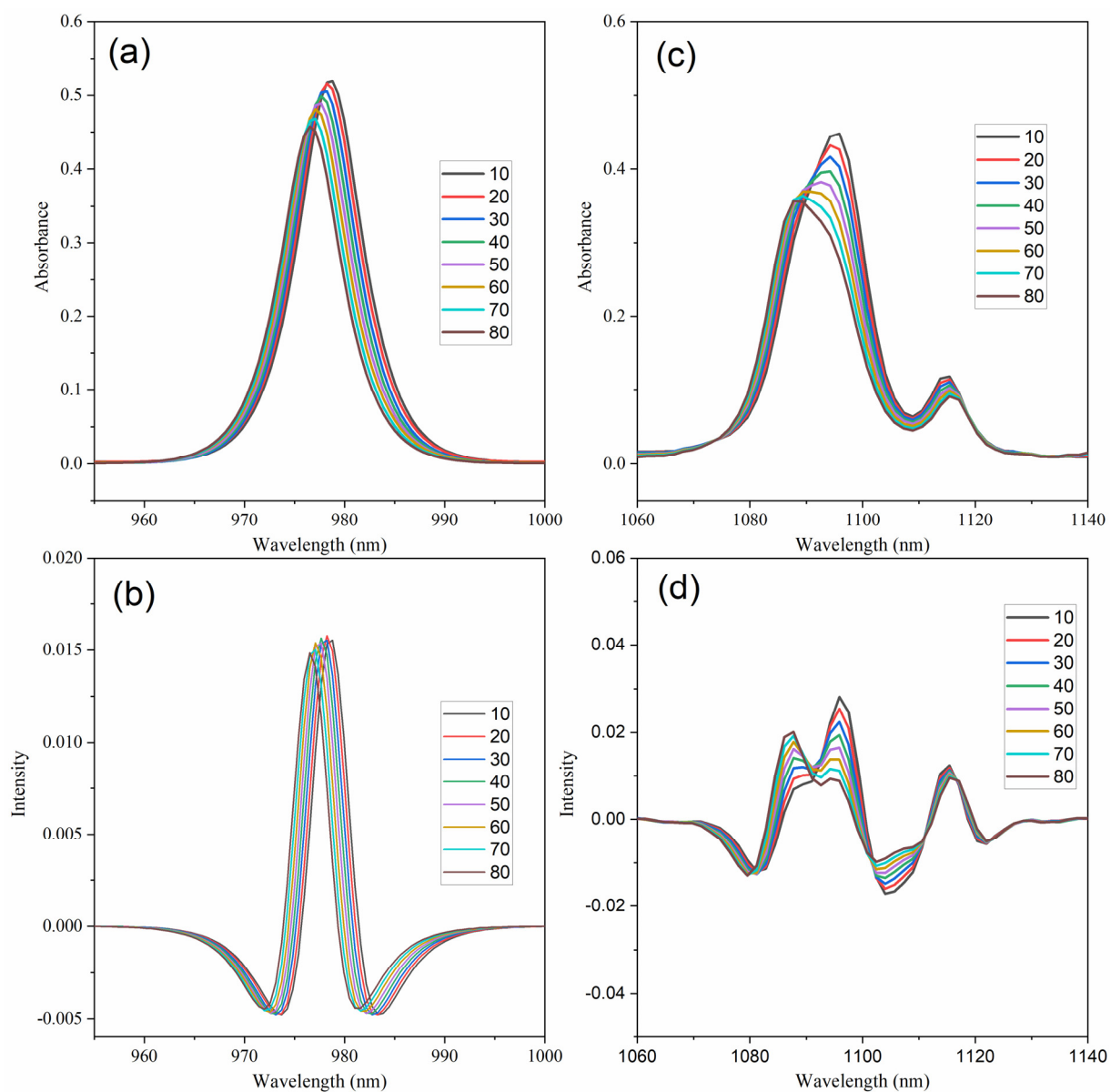


Figure S4. Absorption spectra of 0.017 M Np(V) (a, b) and a 0.17 M Np(V) solution (c, d) in 1 M nitric acid with varying temperatures of 10–80 °C. Second derivative spectra were calculated using a third-order polynomial and seven smoothing points.

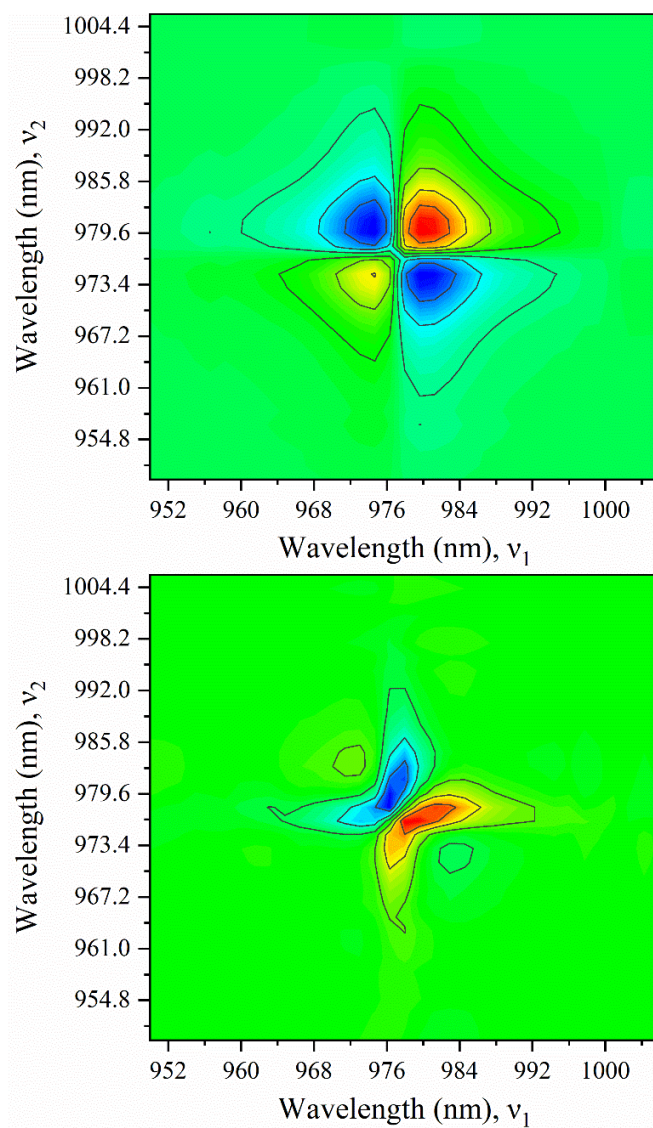


Figure S5. (top) Synchronous and (bottom) asynchronous 2D correlation spectrum of the 980 nm peak with average reference. Sample contained 0.017 M Np in 1 M HNO₃.

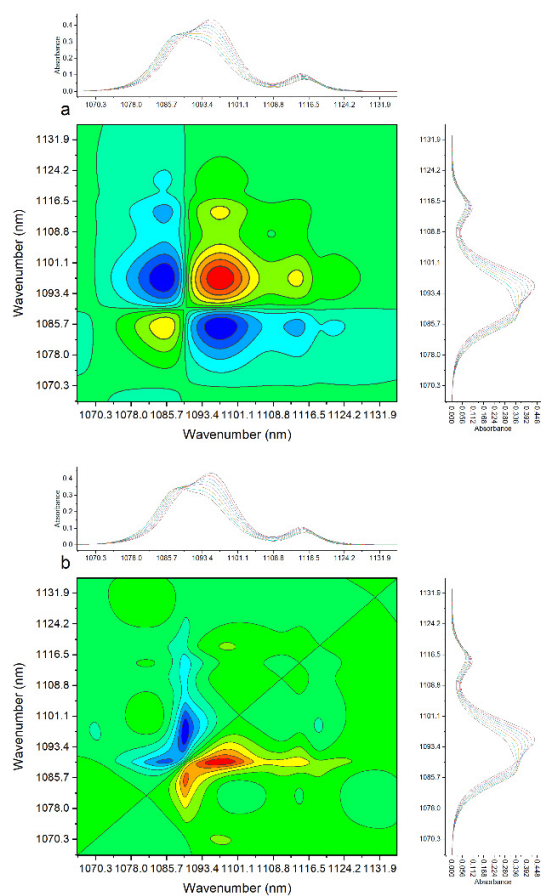


Figure S6. (a) Synchronous and (b) asynchronous 2D correlation spectrum of peaks at 1094 and 1115 nm with average reference. Sample contained 0.17 M Np in 1 M HNO₃.

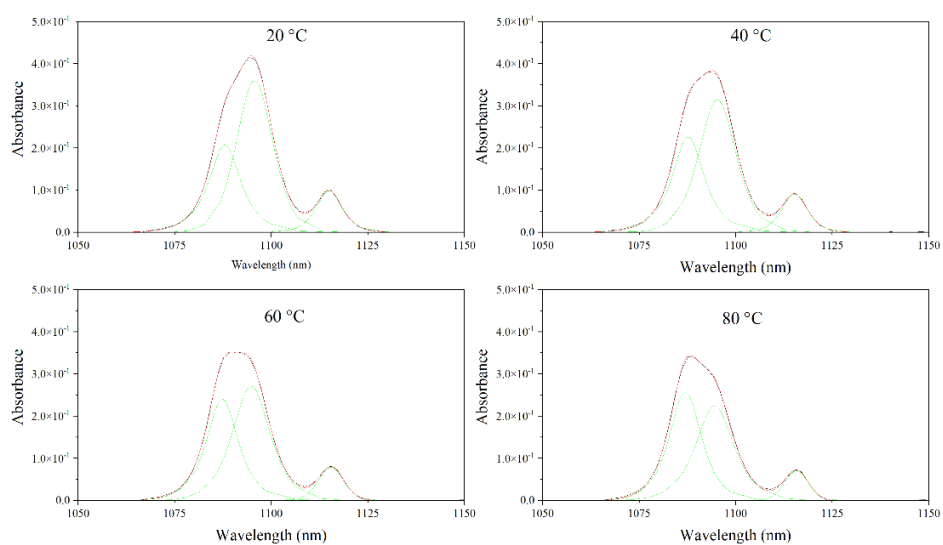


Figure S7. Peak fits of the region from 1050–1150 nm. The relative heights of the 1087 and 1096 nm components change significantly with temperature. Sample contained 0.17 M Np in 1 M HNO₃.

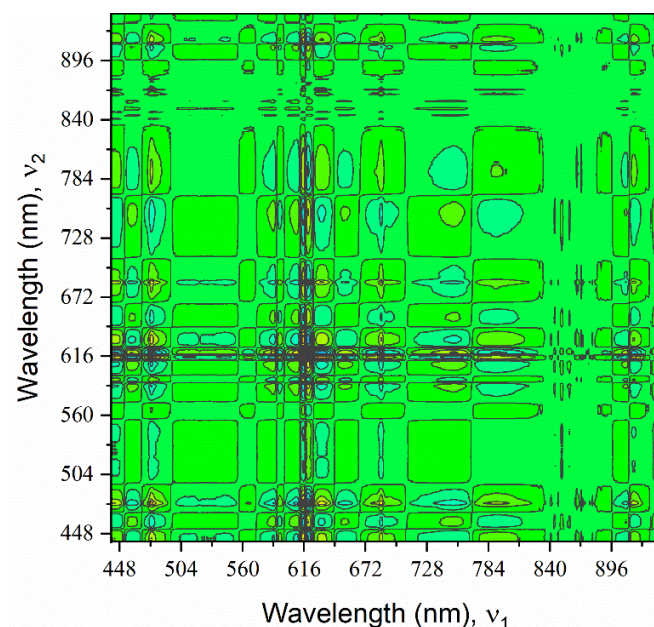


Figure S8. Synchronous 2D-COS spectrum from 440–930 nm. Sample contained 0.17 M Np in 1 M HNO₃.

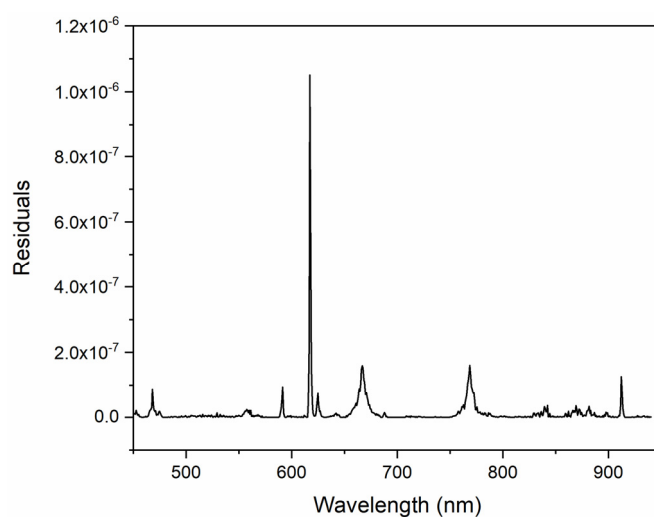


Figure S9. MCR residuals plot with two components.

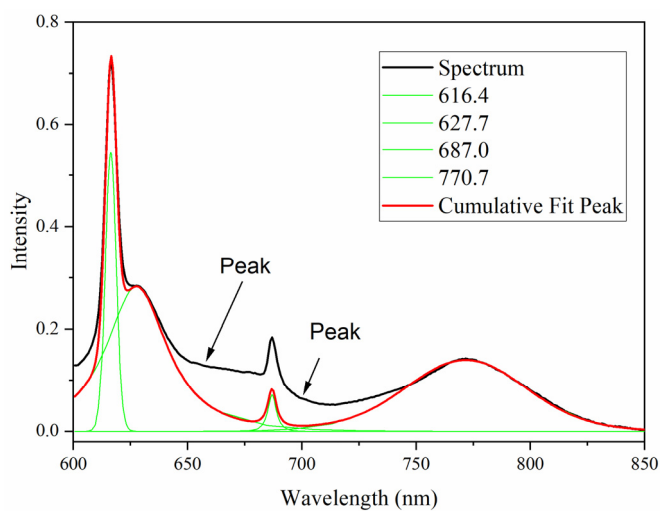


Figure S10. Example peak fit from 600–850 nm notionally showing regions where additional peaks could be located. Sample contained 0.34 M Np in 1 M HNO₃.

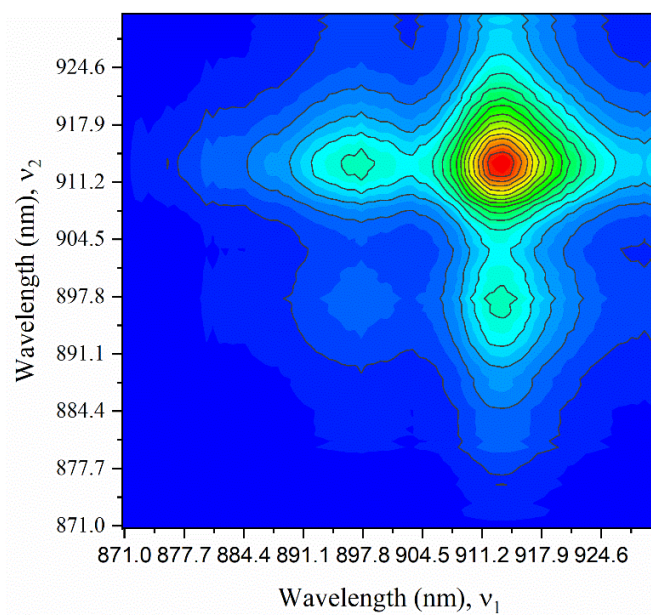


Figure S11. Two-dimensional synchronous spectrum from 870–925 nm with a zero-order reference. Sample contained 0.17 M Np in 1 M HNO₃.

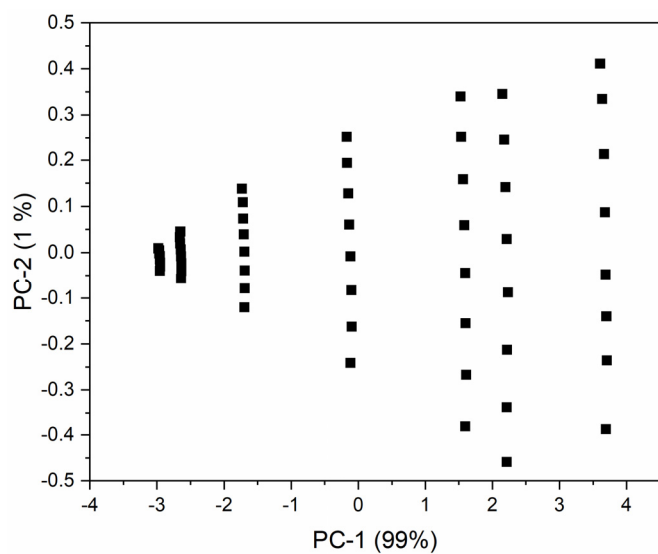


Figure S12. Two-dimensional scores plot of PC1-PC2 for seven Np(V) concentration levels (0.034–0.89 M) with varying temperatures (10–80 °C) from 450–950 nm.

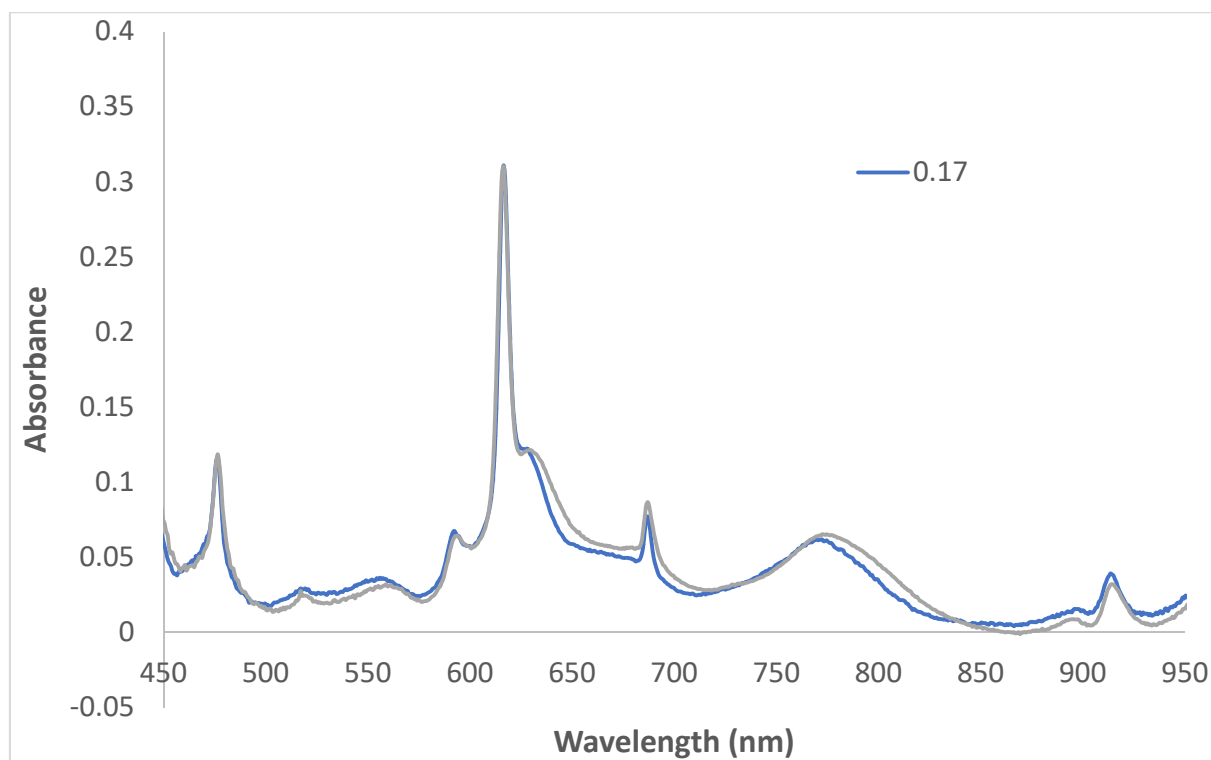


Figure S13. Comparison of absorption spectra of 0.17 M Np and 0.89 M Np solutions using a 1 and 0.2 mm optical path length, respectively. Spectra were normalized to the 616 nm peak.

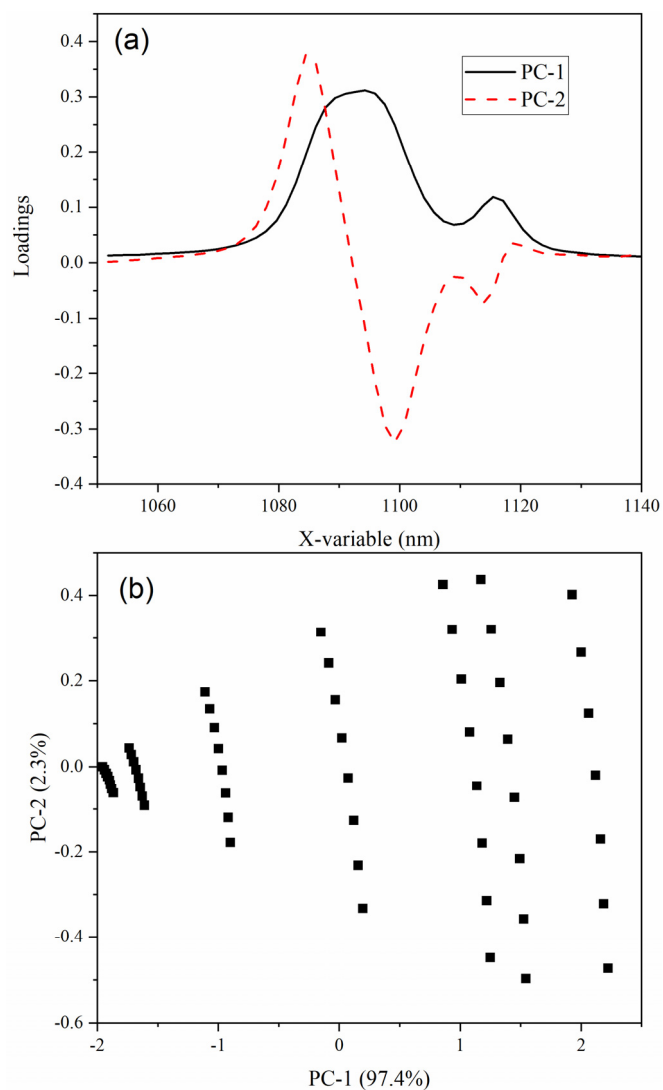


Figure S14. (a) Loadings and (b) 2D scores plot of PC1-PC2 for seven Np(V) concentration levels (0.034–0.89 M (left – right) with varying temperatures (10–80 °C) from 1050–1140 nm.

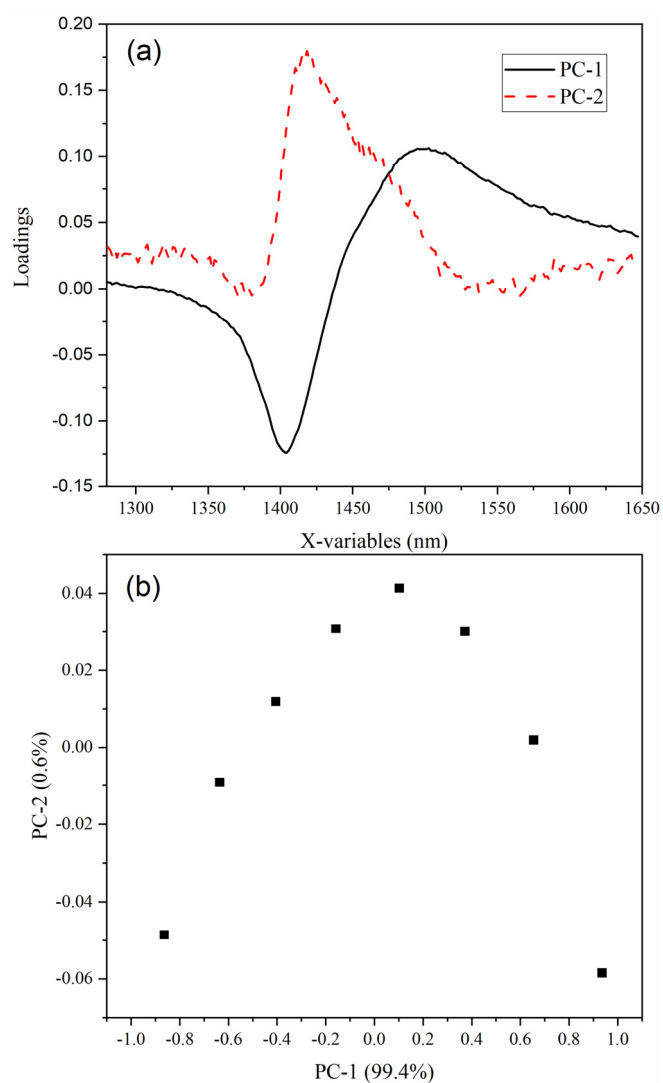


Figure S15. (a) Loadings and (b) 2D scores plot for PC1-PC2 with 1 M HNO₃ and varying temperatures (10–80 °C) from 1280–1650 nm.

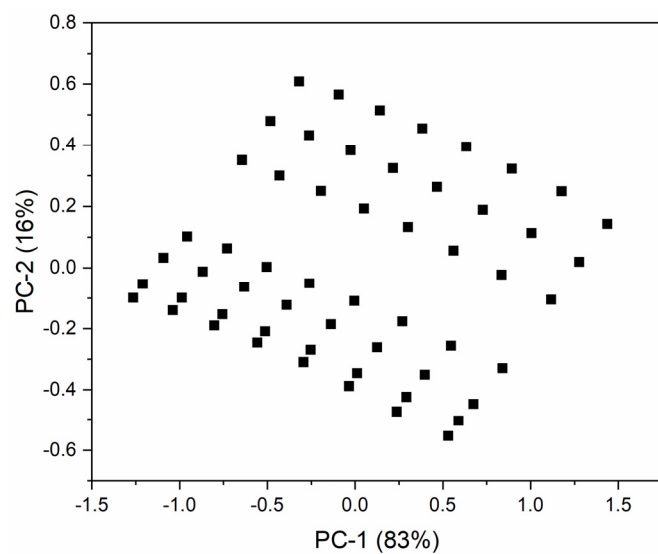


Figure S16. Two-dimensional scores plot of PC1-PC2 for seven Np(V) concentration levels (0.89–0.034 M [left to right]) with varying temperatures (10–80 °C) from 1300–1650 nm.