

Understanding Extractions of Used Nuclear Fuel: the Effects of Radiolysis and ⁹⁹Tc Speciation

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Introduction

- The build-up of tributyl phosphate (TBP) degradation compounds has been proven to reduce separation of U from fission products in used nuclear fuel (UNF), but specific causes of this are poorly understood.
- To address this gap in fundamental knowledge, TBP degradation species and the radiolysis-induced redox chemistry of Tc must be studied with respect to their impact on separations under UNF reprocessing conditions.
- This work requires optimized liquid-liquid extraction for Tc and other major fission products (Ce, Zr, U) in the HNO₃/TBP/dodecane system, in the presence of TBP degradation compounds like dibutyl phosphoric acid.
- Characterization by IR, multinuclear NMR, and XAS will provide P and Tc speciation and coordination environment, from which extraction dependence on Tc redox chemistry or TBP degradation products may be inferred.

Method

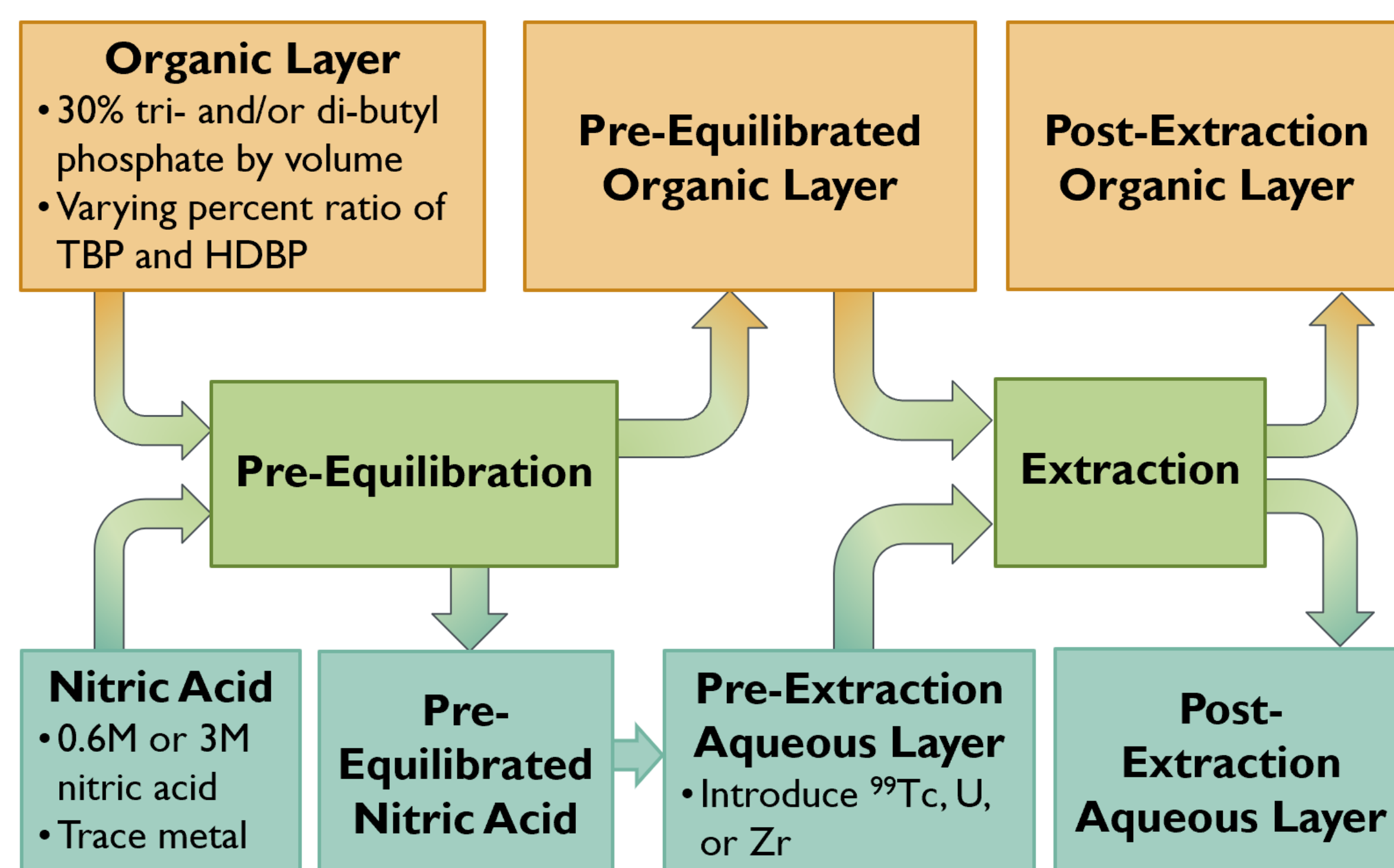


Figure 1: Simplified diagram of solvent preparation and extraction procedure

- Liquid-liquid extraction is a reliable technique for determining the partitioning of solutes in a biphasic system. All organic layers are 70% dodecane (v/v), and 30% a combination of tri- and/or dibutyl phosphate
- Optimal ⁹⁹Tc extraction from aqueous phase occurs at 0.6 M HNO₃ [1]
- Partitioning of a solute (e.g., ⁹⁹Tc) into the organic phase, followed by separation of the phases and radioactivity measurement on a detector, provides distribution ratios, $D = [\text{solute}]_{\text{org}}/[\text{solute}]_{\text{aqu}}$
- Resulting separations are subject to characterization techniques such as XAS and NMR (⁹⁹Tc is quadrupolar and very sensitive to NMR, where distortion from cubic environments results in chemical shift and a broadened signal).

Results

Table 1: Sample distribution ratios of ⁹⁹Tc in biphasic systems of 0.6M HNO₃ and TBP/HDBP/dodecane as determined by liquid scintillation^(a)

TBP / HDBP / Dodecane	Tc Only	Tc + 40mM U	Tc + 10mM Zr	Tc + 20mM Zr
30/0/70	0.420 (0.085)	1.525 (0.452)	0.381 (0.465)	0.611 (0.117)
21/9/70	0.325 (0.051)	0.429 (0.144)	0.414 (0.070)	
15/15/70	0.225 (0.070)	0.689 (0.771)	0.173 (.117)	0.103 (0.141)

(a) The liquid scintillation counter required a 1000x dilution of activity in the extracted layers, of which 100 μL was added to 4.5 mL of scintillation cocktail. High error samples will be rerun in low-quenching cocktail.

Table 2: Karl-Fischer Titrations of biphasic systems for water content determination of organic phase pre- and post-extraction

	Organic [H ₂ O], ppm		
TBP/DBP/Dodecane	30/0/70	21/9/70	15/15/70
Pre-Extraction	10.5 (0.1)	15.1 (0.3)	15.6 (0.3)
20mM Tc only	16.4 (0.3)	12.0 (0.1)	16.3 (0.1)
20mM Tc + 40mM U	6.4 (1.1)	8.5 (0.2)	7.8 (0.1)
20mM Tc + 10mM Zr	11.6 (0.3)	14.7 (0.1)	15.2 (0.1)
20mM Tc + 20mM Zr	12.3 (0.1)	16.2 (0.3)	16.3 (0.1)

- The slightly increased polarity of dibutyl phosphoric acid over tributyl phosphate results in more extraction of water into organic phase. Water and nitric acid extraction data will provide insight for metal extraction mechanisms.
- Multinuclear NMR (³¹P, ⁹⁹Tc) will be performed on separated phases, to corroborate XAFS data on Tc speciation in extraction systems.

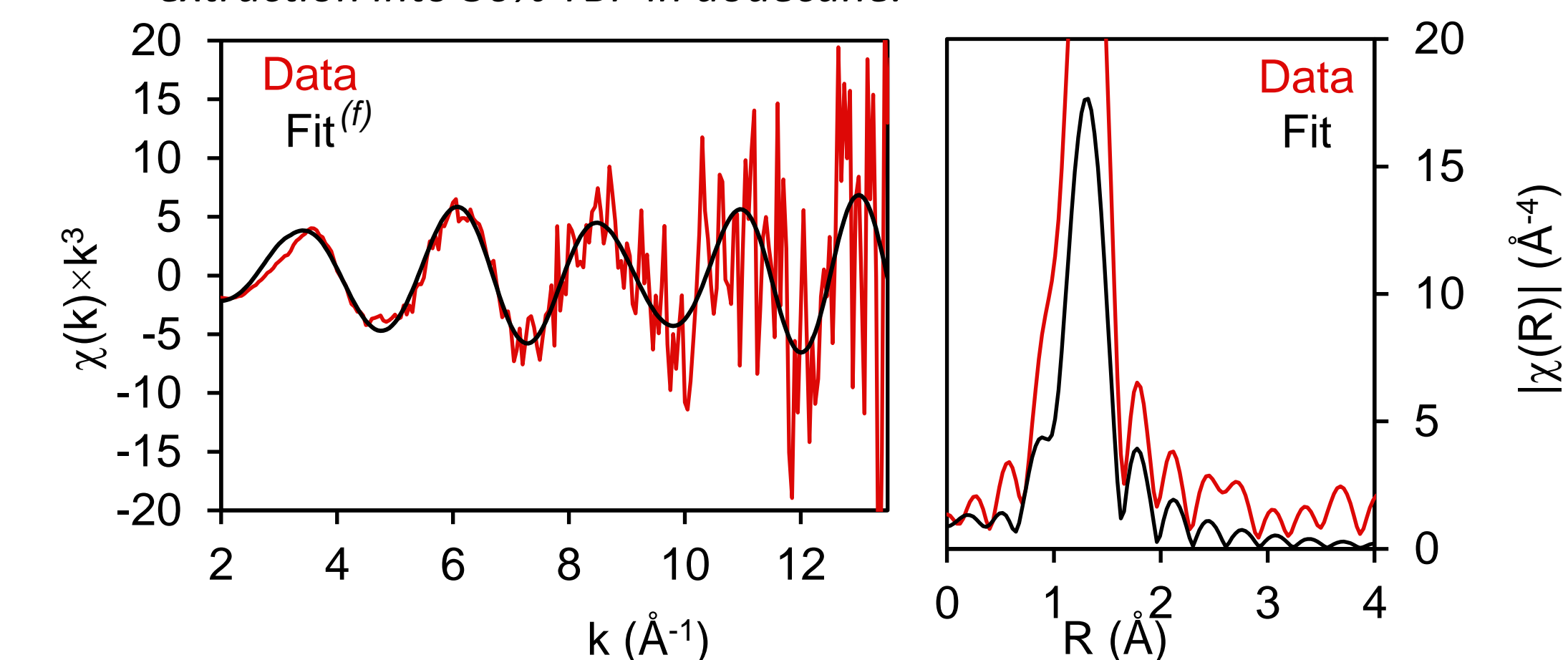
Table 3: Extended X-ray absorption fine structure (EXAFS) fitting parameters for ⁹⁹Tc extracted into 30% TBP in dodecane.^(b)

Neighbor	# of Neighbors	Distance (Å)	σ ² (Å ²)	p(F) ^c	Model
O	4	1.72(1)	0.002(8)	0.11	4 O at 1.74 Å
O	2	2.18(2)	0.002(3)	0.0452	4 O at 1.74 Å
O	2	1.96(1)	0.001(9)	0.0452	4 O at 1.74 Å

(b) S₀²=0.9 (fixed); ΔE=8.9eV; fit range 3<k<13; 1<R<3; 14.3 data; 6 parameters; r=0.049. ⁹⁹Tc occurs here in its (VII) state as TcO₄⁻

(c) Probability that the fit improvement by adding the scattering shell is due to random error

Figure 2: Sample extended X-ray absorption fine structure^(d) of ⁹⁹Tc extraction into 30% TBP in dodecane.^(e)



(d) EXAFS data obtained at BNL on 6-BM beamline. k is photo-electron wavenumber, χ(R) is oscillations as a function of distance from central atom.

(e) Tc concentration determined to be 6 mM in organic phase by D-value.

(f) Theoretical scattering curves calculated with Feff6 [1], F-test applied to fit for each shell contribution [2]

- Extended X-ray absorption fine structure (EXAFS) can provide local structural information for the atom in question. The above fit is derived from the crystal structure of KTcO₄, where Tc is the atom of interest.

Summary & Discussion

- Liquid-liquid extractions (LLE) have provided ⁹⁹Tc distribution ratios in used nuclear fuel (UNF) simulant.
- ⁹⁹Tc is coextracted with U, and Zr
- These extractions are being characterized by Karl-Fischer and acid-base titrations, as well as IR, multinuclear NMR, and EXAFS to assess impact of Tc and TBP degradation products on U recovery from UNF
- Preliminary data show TcO₄⁻ as dominant Tc species before (by IR) and after (by EXAFS) irradiation (⁶⁰Co gamma irradiation at BNL), and HDBP as dominating reduction in ⁹⁹Tc D-values.
- Deepening the understanding of Tc speciation in these conditions may also influence the recovery valuable early actinides from used nuclear fuel.

References

- George, K., et al. "A review of technetium and zirconium extraction into tributyl phosphate in the PUREX process", 2022, *Hydrometallurgy*, 211.105892
- Mustre de Leon, J., et al. "Ab initio Curved-Wave X-ray-Absorption Fine Structure.", 1991, *Phys. Rev. B* 44: 4146-4156.
- Downward, L., et al., "A Variation of the F-test for Determining Statistical Relevance of Particular Parameters in EXAFS Fits.", 2007, *AIP Conf. Proc.* 882:129

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