

Distribution Coefficients of Elements on TODGA Resin in HNO₃, HCl and HF: Application to Determination of Lu/Hf Ratio and Hf Isotopic Composition in Meteorites. A. Pourmand and N. Dauphas, The University of Chicago, Origins Lab, Department of Geophysical Sciences and Enrico Fermi Institute, 5734 South Ellis Avenue, Chicago, IL 60637 (pourmand@uchicago.edu)

Introduction: Over the last two decades Lu/Hf ratio and Hf isotopic composition have been employed to investigate the history of crust-mantle evolution and planetary chronology, particularly in conjunction with Sm-Nd systematic [1-4]. Uncertainties in the value of chondritic Lu/Hf ratio, however, have imposed complications on successful implementation of Lu-Hf systematic [1,5]. Multi-Collector Inductively Coupled Plasma Mass Spectrometry (MC-ICP-MS) has facilitated rapid, high-precision measurements of Hf isotopic composition [5]. Although, several efforts have been made in recent years to improve separation of Lu and Hf from the matrix [6-8], a simple and efficient scheme is yet to be devised. N,N,N',N' tetraoctyldiglycolamide (TODGA) has been utilized for high-level radioactive waste management of trans-uranium trivalent actinides [9-11]. It has also shown great promise for isolation of lanthanides and high-field strength elements (HSFE) [12-13] from the matrix. Nevertheless, the potential of TODGA for elemental separation and its application to geochemical analyses remain largely unexplored.

Herein we present, for the first time, an extended database of distribution coefficients for 60 elements on commercially available TODGA resin. We have also developed a robust, single-column protocol for separation of HSFE, lanthanides and actinides in meteorites and terrestrial rocks for high-precision isotope analysis.

Analytical Methodology: *Distribution coefficients* (K_d) for all elements were determined in batch experiments at 24-26°C and 8 hour equilibration in HNO₃, HNO₃ + 0.2 mol L⁻¹ HF and HCl according to the following relationship:

$$K_d = \frac{C_{\text{solid per gram dry resin}}}{C_{\text{solution per mL solution}}}$$

where C_{solid} is the amount of ions adsorbed to the resin, and C_{solution} is the amount of ions that remain in solution after resin-solution equilibration is accomplished.

Alkali flux fusion and cartridge (column) chemistry: Two sets of experiments were conducted to resolve elution curves for synthetic multi-element standard solutions and geostandards. Approximately 50 mg of rock powder from ACE, AGV2, BCR2 and BX-N was fused with Puratonic[®] lithium metaborate (LiBO₂) flux in 0.6 ml ultra-pure graphite crucibles at 1070°C

according to a modified procedure from Ulfbeck et al. (2003) [7]. The fused disks were quantitatively extracted and dissolved in 3 mol L⁻¹ HNO₃ + 0.2 mol L⁻¹ HF and loaded onto 2-mL TODGA cartridges stationed on a vacuum chamber. The effluents were collected in increments and analyzed on a Neptune MC-ICP-MS. Elemental concentrations were calculated using standard bracketing of interference-free isotopes.

Results and discussion: Distribution coefficients for 60, 58 and 12 elements in HNO₃, HCl and HNO₃ + 0.2 mol L⁻¹ HF concentrations, respectively, are presented. These results expand upon distribution coefficients published by Horwitz et al. (2005) [12] in three ways. Firstly, our study includes K_{ds} for 27 additional elements. Secondly, we extend the upper range of HCl and HNO₃ equilibration concentrations to encompass 10 and 12 mol L⁻¹, respectively. Thirdly, we also established the K_{ds} for 12 elements in HNO₃ + 0.2 mol L⁻¹ HF, which was crucial to developing our analytical procedure.

Figures 1-3 show distribution coefficients of Ti, Zr, Hf, Ta, W, Yb and Lu on TODGA on logarithmic scale as a function of HNO₃, HNO₃ + 0.2 mol L⁻¹ HF and HCl concentrations. The K_{ds} for these and other elements were instrumental in designing a simple procedure that eliminates the need for additional chromatographic and co-precipitation steps as well as evaporation of effluents at any stage of Lu-Hf analytical separation, unavoidable in other procedures [6-8]. Table 1. shows the recovery (%) of Lu and Hf from synthetic multi-element standard solutions and the geostandards. The average recovery of both elements is higher than 93 %, confirming the effectiveness of this procedure.

Interferences on Hf and Lu mass array: Our procedure ascertains complete absence of Lu and Yb, which pose isobaric interferences on Hf mass array, from the Hf fraction. Titanium, whose presence is shown to result in elevated ¹⁷⁶Hf/¹⁷⁷Hf ratios measured by ICP-MS [7], is effectively removed from the TODGA cartridge prior to elution of Hf (also see ref. [13]). Zirconium and Hf show highly similar distribution coefficients and thereby co-elute. Nevertheless, it has been shown that Zr presence does not impair efficient ionization of Hf, nor does it create mass fractionation complications or isobaric interferences on Hf masses [2, 6, 7]. The fraction that comprises Lu is collected at the final stage of the elution in low concentrations of HCl and is completely Hf-free. Ytterbium, however,

co-elutes with Lu but its isobaric interferences on Lu masses can be corrected during online measurement by monitoring non-interfering Yb isotopes [13].

High-precision measurements of Hf isotope ratios and Lu-Hf concentrations in geostandards and primitive meteorites using isotope dilution mass spectrometry will ensue in the near future.

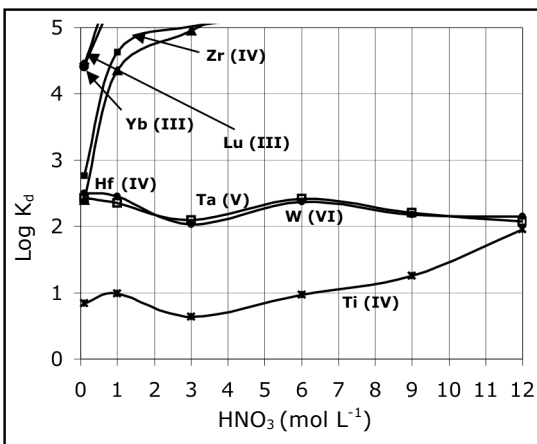


Figure 1. Distribution coefficients for Ti, Zr, Hf, Ta, W, Yb and Lu on TODGA as a function of HNO_3 concentration. Batch experiments were conducted at 24–26°C and 8 hour equilibration time. The numbers in parentheses refer to the oxidation state. Loading the sample solution at low HNO_3 concentrations, where K_d s of Lu and Hf > 5, allows complete removal of the matrix elements (including Ti) while Hf and Lu are retained.

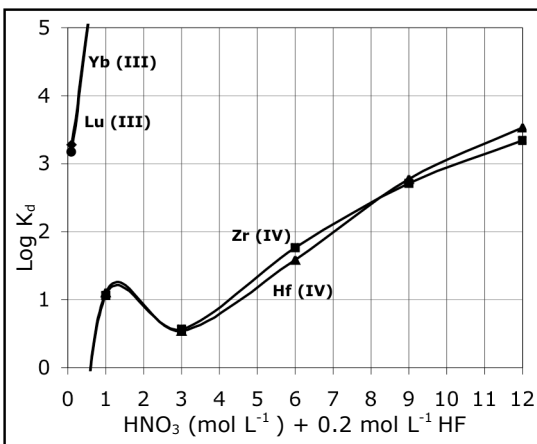


Figure 2. Distribution coefficients for Zr, Hf, Yb and Lu on TODGA as a function of $\text{HNO}_3 + 0.2 \text{ mol L}^{-1} \text{ HF}$. Hf (and Zr) is collected at low $\text{HNO}_3 + 0.2 \text{ mol L}^{-1} \text{ HF}$ concentration while Lu (and Yb) is retained. The numbers in parentheses refer to the oxidation state.

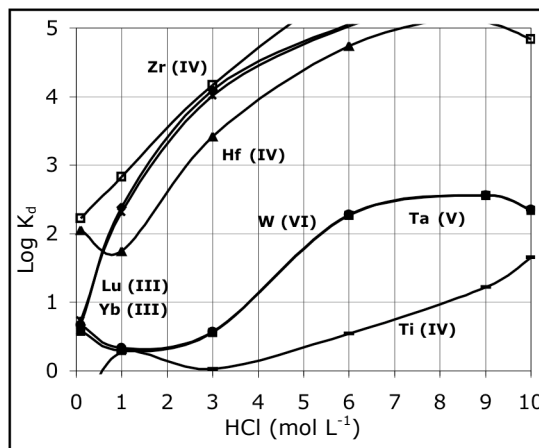


Figure 3. Distribution coefficients for Ti, Zr, Hf, Ta, W, Yb and Lu on TODGA as a function of HCl concentration. Lu (and Yb) is collected at low HCl concentration. K_d of Ta and W is below 1 in 3–4 mol L^{-1} HCl, allowing their removal prior to Hf elution. The numbers in parentheses refer to the oxidation state.

Element	Recovery (%)					Average
	ACE	AGV2	BCR2	BX-N	Standard Solution	
Lu	94	81	100	97	91	93
Hf	100	100	100	95	82	95
Hf*	100	100	90	100	91	96

Table 1. Elemental recovery (%) for Hf and Lu in geostandards and synthetic multi-element standard solution adjusted to match chondritic concentrations. Hf* refers to Hf recovery from a second cartridge chemistry to further purify Hf for high-precision isotopic analysis.

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