

# A DROPLET-BASED MICROFLUIDIC SOLVENT MICROEXTRACTION SYSTEM FOR THE DETERMINATION OF LANTHANIDE AND ACTINIDE LIQUID-LIQUID EXTRACTION KINETICS

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## ABSTRACT

In this presentation we will describe recent work [1] on a method to obtain liquid-liquid extraction mass transfer coefficients using droplet-based microfluidics. We demonstrated its utility by measuring, for the first time, the mass transfer coefficients of the full series of stable Lanthanides and Yttrium under TALSPEAK conditions, a liquid-liquid extraction system relevant to nuclear waste recycling. The microfluidic system combined the properties of a Lewis cell (constant interfacial area) and a highly stirred tank (rapid mixing capabilities), with the additional benefits of miniaturization, allowing safe experimentation on the radioactive species of interest.

## INTRODUCTION

This presentation describes a recently developed microfluidic method [1] to determine liquid-liquid extraction rate constants of stable lanthanide ions under TALSPEAK conditions. Separation of the minor actinides (Am, Cm) from the lanthanides at an industrial scale remains a significant technical challenge for closing the nuclear fuel cycle and the recycling of nuclear waste. TALSPEAK, developed in the 1960's, is a liquid-liquid extraction method that has been tested on the pilot scale and is considered the most robust process for An/Ln separation [2]. However, no satisfactory methods exist to quantify kinetic rate constants of radioactive, slow rare earth liquid-liquid extraction processes with known interfacial area. Additionally, the lack of mass transfer coefficients for the extraction precludes the industrial-scale scaling up of TALSPEAK. TALSPEAK is characterized by an organic phase containing bis-2-ethylhexylphosphoric acid (HDEHP) in n-dodecane and an aqueous phase containing diethylenetriamine-N,N,N',N'',N'''-pentaacetic acid (DTPA) and lactic acid.

The system described combines recent advances in fabrication of droplet-based microfluidic device using excimer laser technology with previously described microfluidic liquid-liquid extraction techniques [3] to enable complete phase separation in linear distances (~150  $\mu\text{m}$ ) that are useful for obtaining kinetic data without blurred results.

## RESULTS AND DISCUSSION

The microfluidic device consists of a single piece of 100  $\mu\text{m}$  ID, excimer laser micromachined FEP tubing (Fig. 1), two syringe pumps, and several valves to enable refilling (not shown in figure). The FEP tubing is micromachined to contain a droplet generator, a channel for the extraction to occur, and a phase separator. One syringe pump is used to control the flow rates. Flow rate determines residence time in the system, and varying flow rates allows multiple time points to be probed.

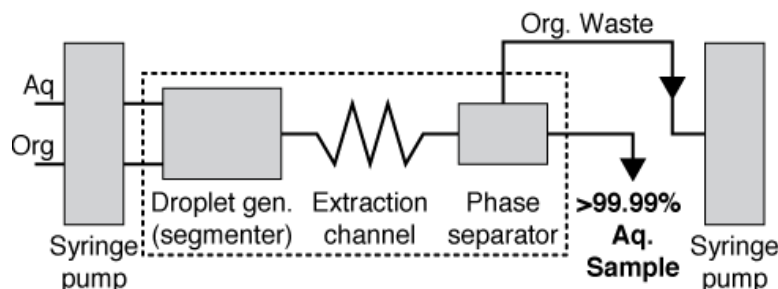


Figure 1: Device Schematic: The device consists of a single piece of excimer laser micromachined FEP tubing (area within dotted line), placed within a tee, two syringe pumps, and several valves to enable refilling (not shown). The FEP tubing is micromachined to contain a droplet generator, a channel for the extraction to occur, and a phase separator.

The organic to aqueous ratio can be controlled by varying syringe sizes, or by using an additional inlet syringe pump. The second syringe pump is used to set the percentage of aqueous outflow from the system, and is tuned until greater than 99.99% separation is achieved in less than 150  $\mu\text{m}$  of device length (Fig. 2). Aqueous outflow is collected in aliquots for offline analysis using ICP-MS.

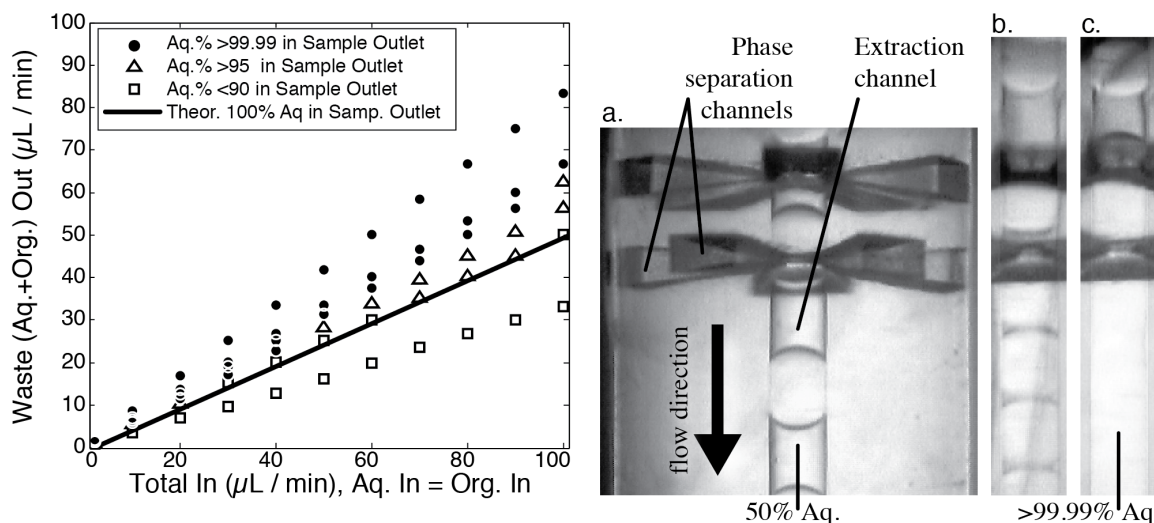


Figure 2: Device Operating Regime: (left) A graph showing the percentage of aqueous in the sample stream as a function of inlet (aqueous + organic) and waste outlet flow rates. Experimental data was obtained with droplets of an aqueous solution of 14 lanthanides (each at 0.1 mM) in a carrier fluid of 1 M HDEHP in dodecane (1:1 volumetric ratio). The device utilized 2 rows of 5 radially-arranged phase separation channels, with  $1\mu\text{m} \times 10\mu\text{m}$  dimensions at the tip. (right) Photos of the device during use at three different inlet/outlet ratios, resulting in a) zero flow through the phase separation channels, i.e. 50% aqueous in the sample outflow; b)  $<90\%$  aqueous in the sample outflow; and c)  $>99.99\%$  aqueous in the sample outflow.

Lanthanide mass transfer coefficients under TALSPEAK conditions were obtained using the system (Fig. 3). The aqueous sample streams were analyzed at each time point using ICP-MS to quantify all cations simultaneously, and interfacial mass transport rate constants were determined for each cation (Figure 3).

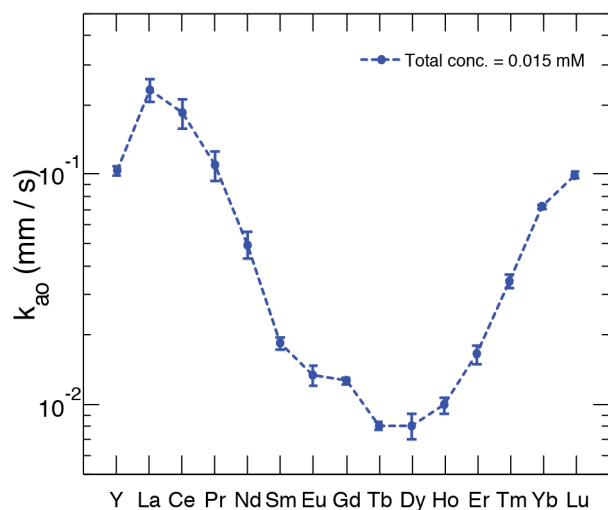


Figure 3: Typical mass transfer coefficients obtained using the device. To illustrate the utility of the device, it was used to measure the mass transfer kinetics of Yttrium and the full series of stable Lanthanides under TALSPEAK conditions. The organic phase was 0.1 M HDEHP in *n*-dodecane. The aqueous phase was 0.05 M DTPA and lactic acid. The initial concentration of each cation was 0.015 mM. The collected aqueous sample stream was analyzed at each time point using ICP-MS to quantify all cations simultaneously.

#### ACKNOWLEDGEMENTS

This work was supported by the U.S. Department of Energy, Office of Nuclear Energy, Fuel Cycle Research and Development Project under Contract DE-AC02-06CH11357. Argonne National Laboratory is operated for the U.S. Department of Energy by UChicago Argonne, LLC. We thank Heidi Park for contributions to writing and editing this manuscript. The submitted manuscript has been created by UChicago Argonne, LLC, Operator of Argonne National Laboratory ("Argonne"). Argonne, a U.S. Department of Energy Office of Science laboratory, is operated under Contract

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