

Micro Scale Monitoring and Analysis of Phase Transfer Kinetics During Solvent Extraction

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Microfluidic devices (MFDs) allow for the study of solvent extraction (SX) in ideal, controlled environments. Minimizing fluid volumes by utilizing these devices provides the benefits of higher throughput, low sample volumes and low waste production, which contribute to a reduction in exposure for radioactive applications and harsh environments. While advancements have been made in MFDs, effective on-chip detection methods are lacking. By using MicroRaman detection, details of SX can be better understood on-line, without the need for off-line techniques to analyze samples. Furthermore, MicroRaman technology can allow for detection and determination of short-lived intermediate species in SX, allowing for a more comprehensive understanding of transient species and mass transfer.

I. INTRODUCTION

The use of Raman spectroscopy is an effective methodology to study solutions on a macro- or micro-scale.^{1,2,3,4,5,6} The transition to a MicroRaman probe has shown to be an effective on-chip detection method to monitor local interfaces and provide real-time data collection of solutions within the MFD.^{5,6} Feasibility studies have illustrated that the probe focal point, 69 μm , fits well within the confinements of a MFD channel that has a width of 300 μm .

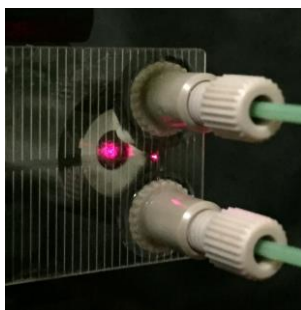


Fig. 1 A T-junction microfluidic device with the MicroRaman probe positioned at the start of the channel.

A MicroRaman probe in conjunction with a MFD allows the capability to pair the system with multivariate analysis in-situ. Chemometric analysis, (specifically partial least squares (PLS) in this application), facilitates the modeling of complex systems, such as those in harsh

environments. A T-channel MFD with two inlet ports meeting at a T-junction, followed by a perpendicular, longer micro-channel with a single outlet, allows two separate phases to flow through the MFD channel (Fig 1). The flow of each phase is controlled by a programmable syringe pump so that when the two phases meet at the T-junction of the device, alternate organic and aqueous phase droplets in a 1:1 ratio are produced and enter the perpendicular channel. These alternating droplets flow down this channel, which is 38 mm in length, and the droplet interaction at the interface is monitored in-situ by Raman spectroscopy.

This methodology is novel as the MicroRaman probe is focused on the microchannel within the MFD, which is positioned on a translational stage. This system allows for real-time monitoring of the kinetics by Raman spectroscopy along the axial length of the channel. There is sufficient length to allow equilibrium to be achieved between the two phases in the MFD. Post-analysis sampling was performed to validate equilibrium conditions. Using this type of on-line analysis allows for the determination of kinetics and transient species in a variety of harsh environments, minimizing sample consumption and worker exposure in the process.

II. RESULTS

The MicroRaman probe (Spectra Solutions Inc. Raman fiber optic spectrometer, continuous wave 670 nm diode-pumped solid state laser, and high-throughput volume phase holographic grating) collected spectra measurements from 200 cm^{-1} to 3800 cm^{-1} , with a resolution of 6 cm^{-1} . Flow rates on the syringe pumps were optimized to generate a 1:1 droplet volume of alternating phases as they entered the outlet channel. The MFD was positioned on a translational stage with XYZ positioning, allowing the MicroRaman probe to be focused at different distances from the T-junction along the micro-channel (Fig. 2). The MicroRaman probe set up is also paired with a charge-coupled device video camera to provide live video images of the micro-channel at the same focal point of the MicroRaman probe. The onboard video allowed easy flow rate adjustments and visual confirmation of droplet sizes and interfacial curvature.

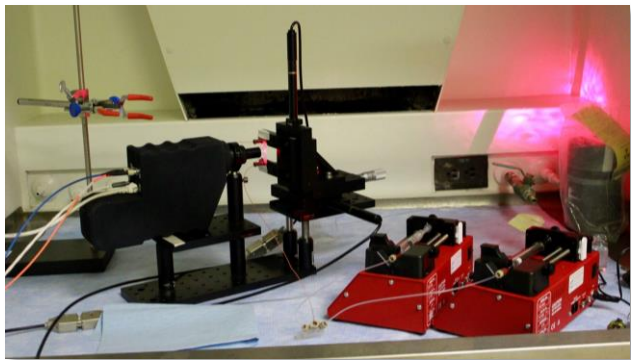


Fig. 2 The MicroRaman probe set up with the organic and aqueous syringe pumps.

By moving the MFD translational stage, while maintaining focus of the MicroRaman laser excitation beam in the micro-channel, Raman spectra were collected at different distances from the T-junction along the length of the outlet channel to determine real-time kinetics. Further, the concentrations of HNO_3 present in the organic and aqueous phases at the specified distances along the micro-channel could be determined from chemometric modeling. Each point collected along the outlet channel has a corresponding measured distance in mm from the T-junction, which is the origin point of extraction. The droplet velocity through the channel is known, thus each measured distance point can be converted to a time point. Together, these points generate a profile of the HNO_3 concentration versus time in each respective phase, which have been used to predict forward and reverse rates of interfacial mass transfer coefficients.⁷

Initial proof of concept studies have involved basic extraction systems modeled from the Plutonium Uranium Reduction EXtraction (PUREX) process. The extraction of HNO_3 by tributyl phosphate (TBP) in *n*-dodecane was measured by the MicroRaman in the microfluidic channel (spectra shown in Fig 3) and the results were compared to those obtained in a classic Lewis-Cell extraction system. The extraction of HNO_3 in the described system occurs according to Equation 1.



The $\text{HNO}_3 \cdot \text{TBP}$ adduct formed in the extraction process at or close to the interfacial region between the organic and the aqueous phase. Rates of extraction were measured by determining the concentration of HNO_3 in each respective phase as a function of time.

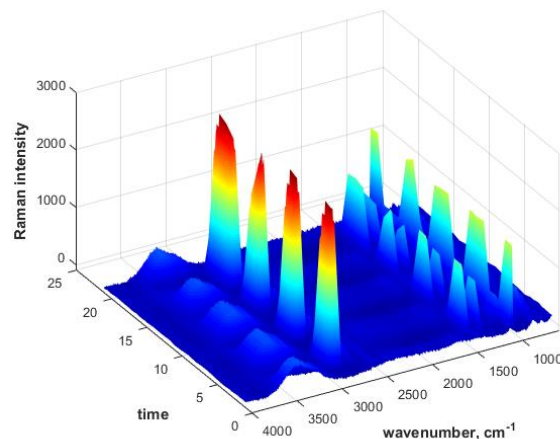


Fig. 3 A representative Raman spectra illustrating the alternating organic and aqueous phase droplets flowing past the MicroRaman probe as a function of time. Spectra were collected at in the micro-channel.

From these feasibility studies, the research has expanded the applicability of the chemometrics analysis with MicroRaman capability by incorporating the effects of impurities on solvent extraction. Of specific interest is the effect of crud formation in SX that reduces extraction efficiency. In systems that contain TBP along with radioactive components, degradation products such as dibutyl phosphate (DBP) and monobutyl phosphate (MBP) are produced due to the radiolysis and hydrolysis of TBP. Both DBP and MBP can combine with metal species in the extraction (most readily U, Pu, and Zr), forming crud at the interface between the organic:aqueous phases and reducing the extraction efficiency (Fig. 4).

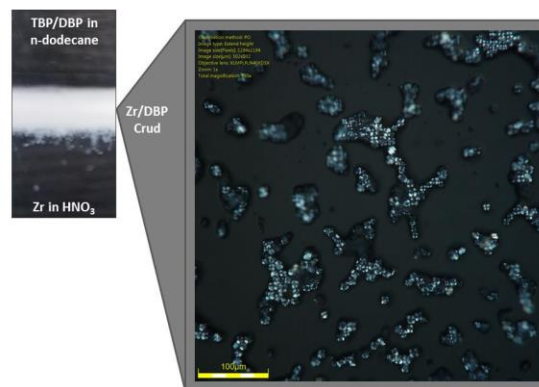


Fig. 4 A microscope image of Zr/DBP crud formed at the interface of HNO_3 and TBP in *n*-dodecane.

To examine the effect of these degradation products on the biphasic SX of HNO_3 by TBP, the current research is using MFDs to perform SX. The extraction time scales with the square of the diffusional distance so by decreasing the length scale of the extraction, the rate of mass transfer increases until the kinetically controlled

regime is achieved. At this point, the SX is controlled by its respective kinetics. The results of these studies are ongoing.

III. CONCLUSIONS

This research shows the advancement of on-line spectroscopic monitoring in the study of used nuclear fuel reprocessing. Initial testing illustrated the effectivity and efficiency of using a MicroRaman probe to analyze an extraction occurring within a MFD of HNO₃ by TBP in n-dodecane. This work is being expanded by incorporating metal species, variable concentrations of analytes, and organic impurities in the SX experiments. The MFD channel is also providing a unique environment to study transient species to better understand the complexities in SX between phases.

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