Simultaneous Determination of U (VI) and Nitric Acid on a Microfluidic Chip

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Abstract

Simultaneous quantitative analysis of actinides and nitric acid in nuclear fuel reprocessing is critical; however, conventional absorption spectroscopy faces a fundamental limitation: it relies on a single fixed optical path length, which forces a compromise between sensitivity and dynamic range for multi-analyte detection. This limitation is particularly problematic for the analysis of radioactive materials in glovebox environments. This paper presents a monolithic microfluidic chip fabricated from polymethyl methacrylate (PMMA) that integrates multiple different optical path lengths (2, 5, and 10 mm) on a single platform to overcome this limitation. The chip features self-aligning channels that enable seamless fiber-optic coupling with UV-Vis and near-infrared spectrometers, thereby supporting simultaneous measurements. By employing Partial Least Squares Regression (PLSR) to deconvolve the interfering spectra of U(VI) and nitric acid, we demonstrate that simultaneous determination of these species can be achieved under their respective optimal conditions. The chip platform significantly reduces sample and reagent consumption and streamlines the operational procedure to a single pipetting step, providing decisive advantages for safe, high-throughput analysis within radioactive gloveboxes and representing a new paradigm for spectroscopic measurements in the nuclear fuel cycle.

Full Text

Preamble

Simultaneous Determination of U(VI) and Nitric Acid on a Microfluidic Chip

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Abstract

The simultaneous quantification of actinides and nitric acid in nuclear fuel reprocessing is critical, yet conventional absorption spectroscopy faces a fundamental limitation: its reliance on a single, fixed optical path length, which forces a compromise between sensitivity and dynamic range for multiple analytes. This constraint is particularly problematic for the analysis of radioactive materials in glovebox environments. Herein, we present a monolithic microfluidic chip fabricated from poly-methyl methacrylate (PMMA) that integrates multiple, distinct optical path lengths (2, 5, and 10 mm) on a single platform to overcome this limitation. The chip features self-aligning channels for seamless optical fiber coupling to UV-Vis and NIR spectrometers, enabling simultaneous measurements. By employing partial least squares regression (PLSR) to deconvolute mutually interfering spectra of U(VI) and nitric acid, we demonstrate the concurrent determination of these species under their individual optimal conditions. The chip-based platform drastically reduces sample and reagent consumption and simplifies the workflow to a single pipetting step, offering decisive advantages for safe, high-throughput analysis within radioactive gloveboxes and representing a new paradigm for spectral measurement in the nuclear fuel cycle.

Keywords: Microfluidic chip, uranium, nitric acid, PLSR

Introduction

Absorption spectrometry remains a cornerstone analytical technique for the quantification of actinides, particularly uranium and plutonium, within nuclear fuel reprocessing streams. Although our previous studies have established various on-line and off-line methods for the simultaneous determination of uranium, plutonium, and nitric acid in complex matrices [1, 2], a fundamental constraint persists: these conventional approaches rely on a singular, fixed optical path length for all analytes. This inherent limitation compromises the analytical sensitivity and dynamic range for certain species, as their optimal absorbance values cannot be attained concurrently. Introducing multiple path lengths to accommodate different analytes leads to instrumental complexity, elevated reagent consumption, and cumbersome operational protocols—significant disadvantages for the analysis of radioactive samples within gloveboxes. Another drawback of conventional measurement methods is the difficulty of manipulating tiny quartz cuvettes with bulky gloves inside a glovebox, making them prone to slipping and shattering, which consequently compromises operational efficiency.

Microfluidic technology offers a compelling paradigm to address these challenges by enabling the flexible integration and miniaturization of operational units on a monolithic platform. Compared to conventional benchtop systems, microflu-

idic chips are orders of magnitude smaller, require only microliters of sample and reagents, and offer rapid analysis with excellent mass-transfer efficiency [3, 4]. In the context of spent-fuel reprocessing, these attributes translate into decisive advantages: the drastic reduction in sample volume and the potential for full automation minimize radiation exposure to both personnel and equipment, thereby extending equipment service life. Furthermore, deployment within gloveboxes curtails the generation of radioactive waste and significantly reduces the instrument footprint. The ability to integrate multiple analytical processes onto a single chip further simplifies workflows and enhances overall efficiency.

The integration of absorption spectroscopy with microfluidic chips can effectively mitigate many limitations of conventional methods. On-chip measurements dramatically reduce sample consumption. Crucially, distinct optical path lengths can be monolithically fabricated into a single chip, enabling simultaneous, multi-component analysis under their respective optimal conditions without the need for complex external optical realignment. The incorporation of optical fiber technology further facilitates the seamless coupling of spectroscopic instrumentation with these microfluidic devices.

The broader research community has actively explored the utility of microfluidics within the nuclear fuel cycle, generating a wealth of knowledge for online process monitoring. Investigators have successfully coupled microfluidic devices with a suite of spectroscopic techniques, including Raman, UV-Vis, X-ray fluorescence (XRF), and mass spectrometry, to achieve quantitative analysis of various radionuclides, consistently reporting high analytical fidelity and robust performance metrics [5-11].

In this study, we present a multi-channel microfluidic chip integrated with UV-Vis and NIR spectrometers via optical fiber coupling. Chemometric models were developed to enable the simultaneous determination of U(VI) and nitric acid utilizing distinct, on-chip optical path lengths. This approach overcomes a key limitation of conventional methods, where U(VI) and nitrate must be quantified simultaneously at a compromise path length (e.g., 2 mm) due to the excessively high absorbance of aqueous samples in the near-infrared region.

Experimental Section

Chip Design and Fabrication

Poly-methyl methacrylate (PMMA) was selected as the substrate material due to its excellent optical transmittance (>92%, 287–2600 nm) in the UV-Vis-NIR range [12], chemical resistance to nitric acid, and γ-irradiation tolerance up to 50 kGy [13]. The multi-channel microfluidic chip was assembled from two PMMA substrates. Micro-channels and optical features were fabricated by high-precision micro-milling using carbide end-mills, followed by thermal compression bonding for permanent sealing (Fig. 1).

The micro-channels had a uniform cross-section of 400 µm × 400 µm and incorporated three distinct optical paths with path lengths of 2 mm, 5 mm, and 10 mm. Each optical path featured a pair of self-aligning fiber channels. To interface with the spectroscopy instruments, two pigtailed silica fibers (core diameter: 200 µm) were inserted from the light source and spectrometer into opposite ends of these self-aligning channels. The apertures of the alignment channels were precisely dimensioned to match the fiber connectors, ensuring repeatable and straightforward positioning.

Fig. 1 [Figure 1: see original paper] Schematic of the exploded view of the multi-channel chip

Micro-lenses were deliberately omitted from the channel terminations. The reason is that micro-milling cannot produce the optically smooth surfaces required for functional lenses; rough-surfaced lenses would introduce stray light and scattering peaks that obscure critical analytical features. To compensate for the optical losses inherent in this lens-free configuration, the PMMA windows separating the self-alignment channels from the main micro-channel were thinned to 1 mm during the fabrication process. Furthermore, air mirrors serving as total internal reflection elements were micro-milled along both sides of each optical path (Fig. 2). These mirrors served a dual function: laterally confining the probe beam within its intended path while preventing optical crosstalk from adjacent channels [14].

Fig. 2 [Figure 2: see original paper] Top photograph of the air mirrors along both sides of the optical path

Reagents and Solutions

Nitric acid (HNO_3, analytical grade) and nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, analytical grade) were purchased from Macleans Reagent (Shanghai) Limited Company. The uranium standard solution was obtained from the Department of Radiochemistry, China Institute of Atomic Energy. All aqueous solutions were prepared using deionized water (resistivity ≥ 18 M$\Omega \cdot$ cm).

Instrumentation and Setup

A balanced deuterium–halogen light source (AvaLight-D(H)-S-BAL) was used together with two spectrometers: an AvaSpec-HSC1024x58TEC-EVO for the UV-Vis region and an AvaSpec-NIR512-2.5-HSC-EVO for the near-infrared region.

The simultaneous determination of U(VI) and nitric acid was achieved using the fabricated multi-channel microfluidic chip. The instrumental arrangement is illustrated in Fig. 3. Light from the source was split into two beams via a bifurcated optical fiber, with each branch inserted into the self-aligning channels corresponding to the 2 mm and 10 mm optical paths on the chip. Two separate collection fibers were inserted into the opposing channels to guide the

transmitted light to the spectrometers. The 2 mm path was coupled to the NIR spectrometer for nitric acid quantification, while the 10 mm path was coupled to the UV-Vis spectrometer for U(VI) quantification. Spectral acquisition from both spectrometers was synchronized, and the data were displayed as a composite spectrogram.

Fig. 3 Integration of the multichannel chip with the optical system: (a) Schematic and (b) photograph of the setup

Experimental Procedure

The experimental protocol for simultaneous measurement was as follows. The chip was positioned on a custom stage, and fiber optic connectors were securely inserted into the self-aligning channels (Fig. 4). A 50 µL aliquot of the sample solution was pipetted into the injection port, filling the entire microchannel and optical paths (total volume: 25 µL) to ensure consistent measurements. This volume also provided sufficient flushing to prevent cross-contamination between samples. After spectral data acquisition, the solution was expelled into a waste container. This process was repeated for all samples. This streamlined procedure, requiring only pipetting and injection, is particularly advantageous for glovebox operations. It obviates the cumbersome steps associated with cuvette-based methods, such as cell cleaning and waste handling, thereby significantly increasing analytical throughput while minimizing sample consumption (Table 1).

Fig. 4 (a) Slide photograph of the multichannel chip on a stage; (b) Top photograph of the optical path on the chip

Table 1 Comparison of sample consumption between the two measurement methods

Method	Cuvette	Microfluidic chip
2 mm pathlength	2000 µL	25 µL
10 mm pathlength	3500 µL	25 µL
Total (µL)	**5500**	**25**

Chemometric Analysis

U(VI) and nitric acid exhibit characteristic absorption peaks in the visible (Vis) and near-infrared (NIR) regions, respectively. Significant spectral interference between these species precludes the use of univariate calibration. Consequently, multivariate calibration models based on partial least squares regression (PLSR) were developed for simultaneous analysis. The theoretical principles of PLSR are detailed in other literature [15, 16]. A training set comprising samples with varying concentrations of U(VI) and nitric acid was prepared. Spectral

data acquired on the microfluidic chip were used to construct and validate the models using Unscrambler 11.0 software.

Results and Discussion

Optical Performance and Calibration of the On-Chip System

To validate the optical performance of the custom-designed chip, which differs from conventional cuvettes, the absorption spectra of pure U(VI) solutions were measured. U(VI) standard solutions (0.5 g/L, 1.0 g/L, 5.0 g/L, 10.0 g/L, 20.0 g/L, 50.0 g/L, 80.0 g/L, and 100.0 g/L in a constant HNO_3 matrix) were analyzed to verify response stability and linearity.

Fig. 5 (a,b,c) Plot of absorbance measurement (in absorbance units, A.U.) vs. concentration of U(VI) with 3 different optical paths (a. 2 mm; b. 5 mm; c. 10 mm); (d) The linear relationship between absorbance and concentrations of U(VI)

As shown in Fig. 5, the spectral absorption intensity systematically increased with U(VI) concentration across all three optical path lengths. Calibration curves were established from the characteristic U(VI) absorption peak at 414 nm, demonstrating excellent linearity ($R^2 > 0.99$) for each path length. The molar extinction coefficients derived from the on-chip measurements were benchmarked against literature values (Table 2). The coefficients were in good agreement, with the 10 mm path length yielding the closest match; minor deviations were attributed to differences in solution acidity and instrumental conditions.

Table 2 Molar extinction coefficients of U(VI)

λ (nm)	Literature values ($L \cdot mol^{-1} \cdot cm^{-1}$)	2 mm path ($L \cdot mol^{-1} \cdot cm^{-1}$)	5 mm path ($L \cdot mol^{-1} \cdot cm^{-1}$)	10 mm path ($L \cdot mol^{-1} \cdot cm^{-1}$)
414	12.3	11.8	12.0	12.2

The stability of the on-chip measurements was assessed using a 40 g/L Ni^{2+} solution. Following the introduction of the solution into the chip, the absorption spectrum was continuously monitored for a 48-hour period, with data acquired at 10-minute intervals. Fig. 6 illustrates the resulting absorption spectra, wherein hundreds of individual scans acquired over the duration are nearly perfectly superimposed.

Fig. 6 Stability test for the chip

To quantify the signal stability, the relative standard deviations (RSD) of the absorbance at four discrete wavelengths were calculated. All determined RSD

values were below 3% (Table 3), validating the exceptional stability of the on-chip spectral analysis.

Table 3 Stability of on-chip measurements

λ (nm)	Average absorbance	RSD (48h)
400	0.85	2.1%
500	0.62	1.8%
600	0.41	2.3%
700	0.28	2.5%

Simultaneous Determination of U(VI) and Nitric Acid

A calibration set of 31 samples for U(VI) (0–81.77 g/L) and nitric acid (0.1–4.0 mol/L) was prepared. The detailed composition of the samples is presented in Table 4 .

Table 4 Concentration of the mixed sample

Sample	U(VI) (g/L)	HNO_3 (mol/L)	Sample	U(VI) (g/L)	HNO_3 (mol/L)
1	0.00	0.1	17	40.00	2.2
2	0.50	0.5	18	45.00	2.4
...	...	...	...	...	...

Spectra of all samples were acquired under identical conditions using deionized water as the blank (Fig. 7). As observed, the samples with U(VI) concentrations of 60.00, 65.0, and 81.77 g/L exhibited absorbance saturation and were therefore excluded from the calibration set. Consequently, chemometric models were developed using a training set of 23 samples for U(VI) and 26 samples for HNO_3. Five independent samples were used for external validation of each model. Based on the absorption spectra of U(VI) and nitric acid, the optimal wavelength ranges of 390–448 nm and 1560–1805 nm were selected to develop their respective calibration models.

Fig. 7 UV-Vis-NIR spectrum of U(VI) and HNO_3

Table 5 Modeling parameters of U(VI) and HNO_3

Component	λ (nm)	Factors	SEC	SEP	R^2
U(VI)	390–448	6	1.2 g/L	1.5 g/L	0.998
HNO_3	1560–1805	4	0.08 mol/L	0.10 mol/L	0.995

The U(VI) model demonstrated robust performance, characterized by low standard errors of calibration (SEC) and prediction (SEP), and a high coefficient

of regression (R^2) (Table 5). A t-test comparing predicted and reference values yielded a t-statistic of 0.31 ($p > 0.05$), confirming no significant difference and validating the model' s predictive accuracy. Similarly, the HNO_3 model exhibited excellent performance with low SEC/SEP values and a high coefficient of regression. The corresponding t-test ($T = 0.18$, $p > 0.05$) further corroborated the model' s robustness. The detailed results are presented in Table 6.

The analytical software can load both models simultaneously, enabling real-time, on-line analysis and concentration readout for both components.

Table 6 Prediction results of U(VI) and HNO_3

U(VI) Reference (g/L)	U(VI) Prediction (g/L)	Relative bias	HNO_3 Reference (mol/L)	HNO_3 Prediction (mol/L)	Relative bias
10.2	10.1	-0.6%	1.02	1.01	-0.6%
25.5	25.4	-0.3%	2.05	1.98	-3.6%
...	...	...	...	...	...

t-test: $|T| = 0.31 < T(0.05,4) = 2.78$ $|T| = 0.18 < T(0.05,4) = 2.77$

Conclusions

We have demonstrated a PMMA-based microfluidic chip that integrates multiple path lengths and fiber-guided spectroscopy for the simultaneous determination of U(VI) and nitric acid in nuclear reprocessing liquors. The chip demonstrated robust performance, with calibration curves exhibiting excellent linearity and stability. The molar extinction coefficient for U(VI) measured on-chip was consistent with literature values, affirming the accuracy of the approach.

By coupling on-chip Vis-NIR spectroscopy with PLSR, we achieved simultaneous determination of U(VI) and nitric acid. This approach lowers the limit of detection for U(VI) by an order of magnitude compared to previous techniques, which are constrained by a single, compromise path length.

The microfluidic platform offers decisive advantages over traditional cuvette-based analysis, including operational simplicity, drastic reduction in reagent consumption, and radioactive waste generation. These features make it particularly suitable for automated analysis within gloveboxes, leading to a substantial improvement in analytical throughput for nuclear fuel reprocessing applications.

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Conflicts of Interest

There are no conflicts to declare.

Data Availability

The authors confirm that the data supporting the findings of this study are available within the article.

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Note: Figure translations are in progress. See original paper for figures.