

Real-time Quantitative Analysis of Mixed Lanthanides for an Assessment of Material Stream in Pyroprocessing

Young Taek Jee^a, Bong Young Kim^b, Jong-Il Yun^{a*}

^aDepartment of Nuclear and Quantum Engineering, KAIST, 291 Daehak-ro, Yuseong-gu, Daejeon, Korea

^bKorea Atomic Energy Research Institute, Yuseong-gu, Daejeon, Korea

*Corresponding author: jiyun@kaist.ac.kr

1. Introduction

As the design of sodium-cooled fast reactor (SFR) has been suggested as a next generation reactor, the development of pyroprocessing has been carrying out vigorously as one of the most promising fuel-recycling technology [1]. The recovered U and TRU should not contain any substances detrimental to the utilization of re-manufactured actinide nuclear fuel, and in order to guarantee the performance of this process, a continuous monitoring technique of material stream included in the process is desired.

In this research, four representative lanthanides, which are neutron-poisoning due to their extraordinarily high neutron capture cross sections, were quantitatively analyzed by using UV/Vis absorption and fluorescence spectra. To achieve a condition of continuous monitoring, spectroscopic techniques were employed for the *in-situ* analysis. The measured spectra were then immediately deconvoluted into reference spectra of each lanthanide [2], and by investigating deconvoluted spectra, quantitative analysis could be completed.

2. Methods and Results

2.1 Sample Preparation

In the condition of pyroprocessing process, oxidation or hydrolysis can be critical and should be avoided. Therefore, the sample was prepared in a glove box under high-purity argon atmosphere (99.9999 % Ar, concentrations of H₂O and O₂ < 1 ppm). Four chosen lanthanides were evenly mixed in a quartz cuvette cell containing LiCl-KCl molten eutectic at 773 K [3]. The furnace system maintaining the experimental temperature at 773 K has small optical quartz windows for *in-situ* analysis across the central laser beam axis [4]. The energy source was penetrated the sample through that central axis. Lastly, ICP-OES was utilized to double-check input amounts of lanthanides.

2.2 Measurements of Absorption and Fluorescence Spectra

Absorption spectra were measured with a spectrometer (Carl Zeiss) which covers a wide UV/Vis wavelength range with deuterium lamp. An excitation UV/Vis lamp and a combined collimator were placed across the central axis. The light beam produced from

the lamp penetrated through the sample and was collected by the collimator on the opposite side of the furnace. The system was optically optimized, and the transmitted light was delivered to the spectrophotometer through an optical fiber.

Fluorescence spectra could be obtained by exciting the sample with incident laser beam. The excitation source for this experiment was a 435 nm wavelength provided from optical parametric oscillator (OPO) tunable laser (OPOTEK, Vibrant 335). Spectra were recorded with an intensified charge coupled device (ICCD, Andor Technology) connected with a Czerny-Turner spectrometer (Andor Technology). The fluorescence generated from the sample was collected at another window located at the perpendicular direction to the central axis.

2.3 Measured and Deconvoluted Spectra

Firstly, the absorption spectrum of mixed Nd-Pr-Sm-Dy system was obtained as dotted line on Fig. 1. By utilizing constructed code for the deconvolution, the background of measured spectrum was automatically subtracted and four reference absorption spectra of input lanthanides with appropriate concentration ratio were calculated at the same time.

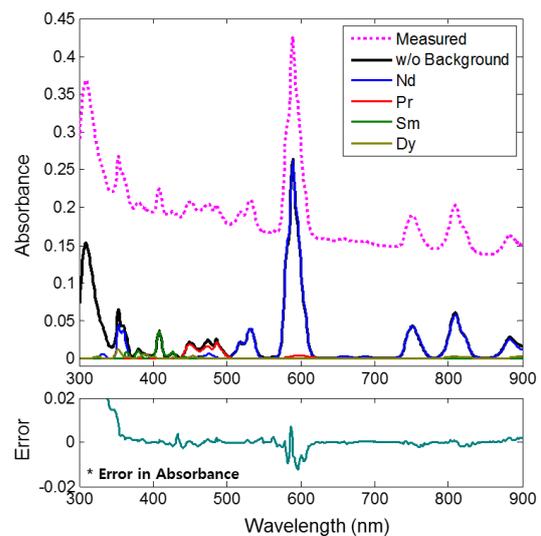


Fig. 1. Decoluted absorption spectrum of Nd-Pr-Sm-Dy mixed sample (above) and its error (below)

Based on the Beer-Lambert's law which refers to a linearly proportional relationship between absorbance and concentration, quantitative analysis of the given could be achieved by deconvoluting the measured mixed spectrum into reference spectra of individual lanthanides. Based on the deconvoluted spectra, it enabled to get the following results of input concentrations.

Table 1. Comparison between input concentrations and concentrations calculated by code

	Input Concentration [mol/L]	Concentration by code [mol/L]	Relative Error [%]
Nd(III)	0.024 ± 0.003	0.023 ± 0.005	4.2
Pr(III)	0.016 ± 0.002	0.014 ± 0.003	8.3
Sm(III)	0.015 ± 0.002	0.014 ± 0.004	5.5
Dy(III)	0.024 ± 0.004	0.022 ± 0.005	7.9

As represented in Table 1, relative errors calculated from the input concentration and the calculated concentration were less than 10 %. However, it reveals that the result by code was almost identical to the input concentrations when the uncertainties were taken into account. The graphical error shown in Fig. 1 was less than 0.01 absorbance along the entire range, and it yielded the maximum relative graphical error of 11 % at 430 nm where three lanthanides overlapped with very small absorbance. As a whole, the sum of mathematically deconvoluted spectra were almost identical to the experimentally obtained spectrum.

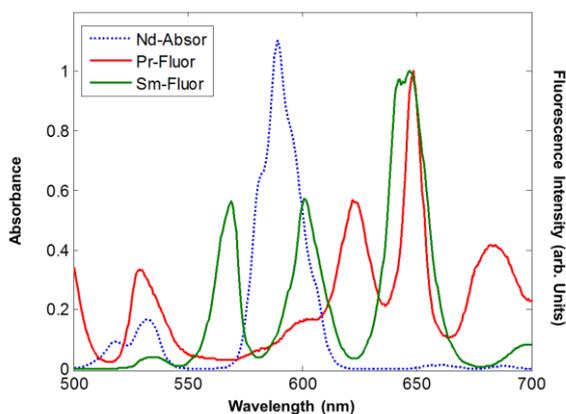


Fig. 2. Absorption spectrum of Nd (dotted) and fluorescence spectra of Pr and Sm (lined)

In addition to the investigation of absorption spectrum, fluorescence spectrum was also obtained. Quantitative analysis using fluorescence spectrum required much more research because of a complex energy transfer phenomenon which occurs in the mixed system when the absorption of one element influences

fluorescence of others. Thus, the fluorescence spectrum of mixed system could be contorted from the desired spectrum. However, in this research, by sectionalizing the calculating region into three by considering the absorption of input lanthanides, as shown in Fig. 2, the analysis using fluorescence spectrum could roughly and numerically reveal fluorescence energy transfer phenomenon. By dividing Fig. 2, three sections for the analysis were defined as follows: 300 nm ~ 580 nm, 580 nm ~ 610 nm, and 610 nm ~ 900 nm.

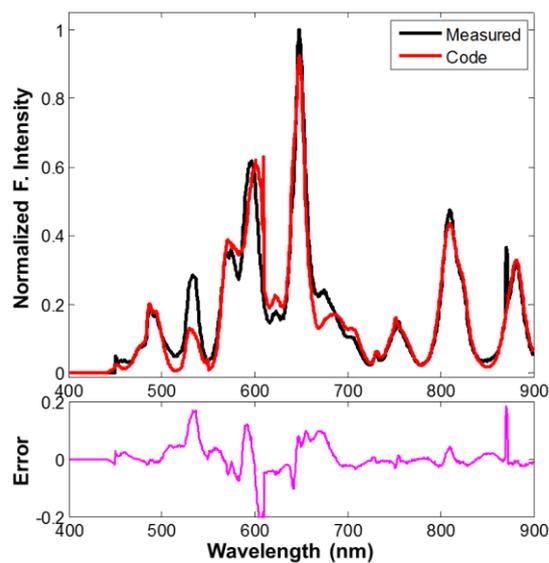


Fig. 3. Measured fluorescence spectrum and calculated fluorescence spectrum (above) and corresponding graphical error (below)

Table 2. Calculation of segmental contributions of the four lanthanides in the sample

	Section 1	Section 2	Section 3
Nd(III)	0.4151	4.0744	0.4329
Pr(III)	0.3085	0.1081	0.3612
Sm(III)	0.7860	0.1016	0.5410
Dy(III)	0.3073	0.2776	0.5292

From data shown in Fig. 3, it was found that a large absorption of fluorescence from Pr, Sm, and Dy occurred by Nd, and the reabsorption of fluorescence emission was estimated in Table 2. The numerical contribution of Nd at Section 2 was larger than those of Sections 1 and 3, while the numerical contributions of others at Section 2 showed just an opposite result. The difference between Section 2 and Sections 1 and 3 of Dy was smaller than other lanthanides because absorption and fluorescence characteristics of Dy were not as influential as others. The graphical error between the measured and the calculated spectra stayed within ~ 20 %, particularly at the segmented parts due to their discontinuities.

3. Conclusions

In this work, a computational tool for quantitative analysis of absorption and fluorescence spectra of lanthanides in high temperature LiCl-KCl molten eutectic has been successfully developed. The results produced from the code showed precise and reliable deconvolution of both absorption and fluorescence spectra for the Nd-Pr-Sm-Dy mixed lanthanide sample. The relative concentration errors obtained from the quantitative analysis of absorption spectrum were less than 10 %, and the qualitative analysis achieved with fluorescence spectrum revealed the fluorescence resonant energy transfer behavior in the mixed lanthanide samples.

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