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ARTICLE

Study of Applicability of Ion Beam Analysis Method for Determination of Trace Elements in Structural Materials of Nuclear Reactor Facilities

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Analytical techniques using ion beams from a small electrostatic accelerator were considered for use in decommissioning. In particular, it was assumed that the technique would be utilized to understand the behavior of contaminating elements when structural materials of nuclear facilities are contaminated. The ion beam analysis method can obtain various types of information depending on the wavelength of light detected. For example, the IBIL method makes it possible to determine the chemical form of elements by observing light in the visible region. In this study, the IBIL spectra were obtained for a europium compound as a simulant, assuming contamination by MA. IBIL spectra of mixtures of two europium compounds with varying molar ratios were also obtained, and changes in the emission spectra were discussed.

KEYWORDS: IBA, IBIL, TCU-Tandem, decommissioning, rare earth element, fluorescence spectrum, allowed transitions, forbidden transition

I. Introduction

Ion beam analysis (IBA) techniques are widely used in various fields because they use accelerated ions with energies of several MeV as the excitation source and can measure very small amounts of samples nondestructively. Another advantage is that no pretreatment of the measurement sample is required. By capturing the various wavelengths of light emitted from the sample, it has the potential to not only identify the element, but also to obtain information on the chemical form of the element.

Reasonable handling and disposal of waste is essential for the efficient decommissioning of nuclear facilities, such as RI facilities, nuclear fuel facilities, reactor facilities, etc. In particular, it is important to consider disposal methods for concrete, which is a structural material and has a large volume of waste. If the surface of concrete is contaminated for some reason, contaminants may permeate and diffuse into the concrete, and the pollution types are RI, nuclear fuel, MA (Np, Am, Cm), etc. This infiltration behavior and diffusion phenomena vary greatly depending on the type and chemical form of the contaminant.

To correctly understand these behaviors, it is necessary to gain knowledge of the dynamics of the elements, including their trace concentrations. However, concrete originally contains many elements, and depending on the analytical method, it may be difficult to detect trace elements. In contrast, basic studies have been conducted using IBA for quantitative analysis of trace elements.[1)] Research utilizing ion beam analysis techniques, including the ion beam induced luminescence (IBIL) method, has been in the nuclear fuel cycle in recent years, and examples are given in References 2-10. In research on extractants for certain elements in nuclear fuel reprocessing, the IBIL method is being utilized along with EXAFS analysis methods using large-scale synchrotron radiation facilities to elucidate their structures.[3)] On the other hand, the IBIL method can be performed at small accelerator facilities, and if recognized as an effective means of obtaining information on chemical bonding states, it is expected to contribute greatly to the promotion of research and development.

The purpose of this study is to obtain emission spectra in the visible region from compounds with the same valence state using the IBIL method, and to investigate the electronic transitions responsible for the observed luminescence. Europium compounds were selected as surrogates for minor actinides (MA) due to their similar trivalent state and well-known luminescent properties. In particular, observation of the emission spectra of mixtures of two different compounds, and confirmation of differences in emission intensity, aim to provide fundamental data for future applications of the IBIL method.

II. Experimental

1. Experimental Equipment and IBIL Analyses

The 1.7 MV Pelletron Tandem Accelerator at the Atomic Energy Research Laboratory of Tokyo City University (TCU-Tandem[11)]) was used to carry out the experiments in this study. The beamline for beam analysis is equipped with detectors capable of particle induced x-ray emission (PIXE) analysis, particle induced γ-ray emission (PIGE) analysis, and IBIL analysis. The sample to be analyzed is measured in a vacuum chamber. **Figure 1** shows photographs of the analysis chamber and its inside. The spectrometer used for IBIL analysis is a high sensitivity high resolution spectrometer, Solid Lambda CCD UV-NIR (Carl Zeiss, Wavelength

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accuracy: 0.3 nm, Wavelength pixel pitch: 0.8 nm / pixel, FWHM: 3 nm). The target wavelength range of this spectrometer is from 190 to 1015 nm. The proton beam is formed by a 5 mm diameter carbon collimator and reaches the target.

The proton beam conditions for TCU-Tandem were set to a beam energy of 2.0 MeV and a beam current of about 2 nA. The beam spot size is 5mmφ. The solid angle of the irradiation target and the focusing lens is approximately 0.05 sr. In the IBIL measurement, the irradiation time was set to 6500 ms, and multiple sets of five consecutive measurements were performed on the same sample to eliminate noise.

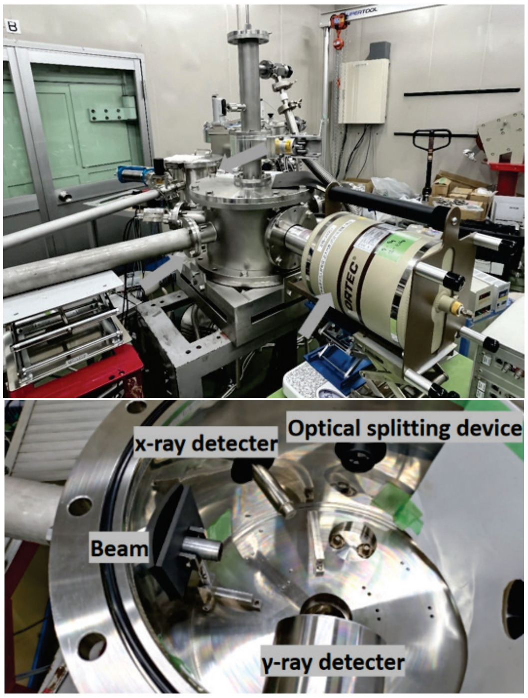

Fig. 1 Layout of the analysis chamber and its interior

2. Preparation of Samples

A trivalent europium compound, known from previous studies to emit at 615 nm, was selected as the measurement sample.[3)] The energy differences between the 4f orbital levels of trivalent europium are shown in **Table 1**. The electron configuration of Eu^{3+} is [Xe] $4f^6$. From this table, it can be seen that emission is observed in the wavelength region of about 500-800 nm in the transition from the $^5D_0$ level to the ^7F_x level. Europium is also known as a simulant for minor actinides. In this study, three Eu compounds, europium fluoride, europium acetate, and europium chloride, were selected as samples for analysis, and each compound was single compounds and molar mixtures of the two compounds were measured, as shown in **Table 2**. Powder samples were fixed to a sample holder with carbon tape and used as the analysis target.

III. Results and Discussion

1. IBIL Spectra of Single Compounds

Figure 2 shows the IBIL spectra of each of the Eu compounds alone. **Table 3** shows the wavelengths and energies of the detected peaks, with wavelengths corresponding to the energy gap of the 4f orbital in trivalent europium shown in Table 1 marked with inverted triangles and peaks that do not fit are marked with rhombic marks. The peaks marked with rhombic marks are considered to be due to forbidden transitions.

Table 1 Energy difference between 4f orbitals

Intermediate levels	Energy between levels (eV)	Wavelength (nm)
$^5D_0 \rightarrow {}^7F_0$	2.141	580
$^5D_0 \rightarrow {}^7F_1$	2.095	593
$^5D_0 \rightarrow {}^7F_2$	2.012	615
$^5D_0 \rightarrow {}^7F_3$	1.907	651
$^5D_0 \rightarrow {}^7F_4$	1.786	697
$^5D_0 \rightarrow {}^7F_5$	1.656	750
$^5D_0 \rightarrow {}^7F_6$	1.529	812

Table 2 Type and weight of Eu compounds

case	Weight (g)		
	EuF_3	$(CH_3COO)_3Eu$	$EuCl_3$
A1	0.214	0	0
A2	0.170	0	0.090
A3	0.130	0	0.165
A4	0.097	0	0.240
A5	0	0	0.419
B1	0	0.115	0
B2	0	0.321	0.087
B3	0	0.252	0.163
B4	0	0.169	0.243
B5	0	0	0.406

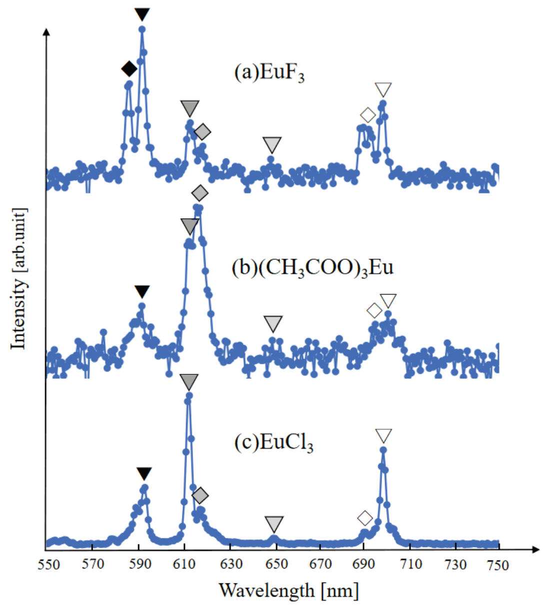

Fig. 2 IBIL spectra of different Eu compounds

In fluoride, relatively high intensity emission from forbidden transitions was observed at the wavelengths of 587 nm and 690 nm. In the acetate compound, high intensity luminescence was observed at 619 nm, which is characterized by a peak that is stronger than that of the forbidden transition. In chloride, the luminescence intensity is stronger than the other two compounds and the allowed transitions are dominant, so that the luminescence from the other transitions can hardly be confirmed.

2. IBIL Spectra of Mixtures

Figure 3 shows IBIL spectra of mixtures of europium fluoride and europium chloride in the proportions shown in Table 2, A1 to A5. Similarly, **Figure 4** shows the IBIL spectra of mixtures of europium acetate and europium chloride made in the proportions shown in Table 2, B1 to B5.

Table 3 Wavelength and energy of detected peaks

	Wavelength (nm)	Energy (eV)	
◆	587	2.115	
▼	**593**	2.095	$^5D_0 \rightarrow {}^7F_1$
▼	**615**	2.012	$^5D_0 \rightarrow {}^7F_2$
◆	619	2.001	
▼	**651**	1.907	$^5D_0 \rightarrow {}^7F_3$
◇	690	1.788	
▽	**697**	1.786	$^5D_0 \rightarrow {}^7F_4$

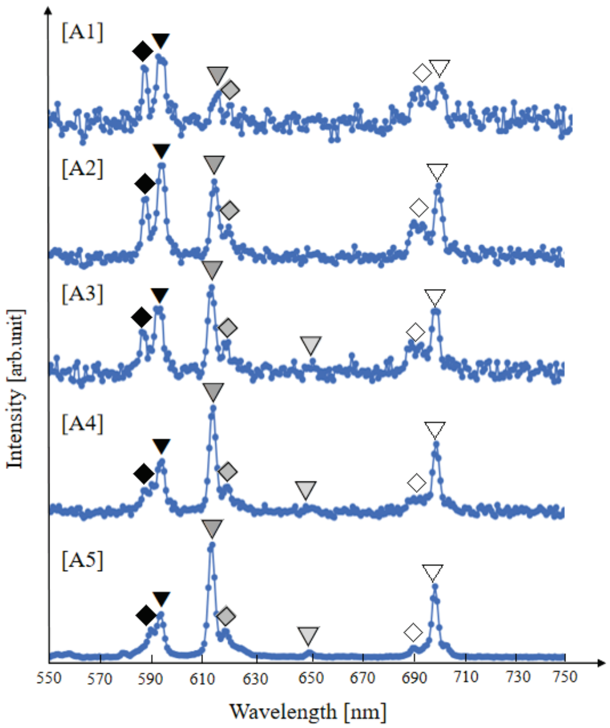

Fig. 3 IBIL spectra for mixtures with different molar ratios of EuF_3 and $EuCl_3$

From the results of the measurements of mixtures with varying molar ratios of the compounds, spectra corresponding to luminescence intensities were observed. In the present case, no change was observed in the wavelength of the high emission intensity, as expected, since the sample was a mixture of two different powdered compounds. Since the luminescence originating from the forbidden transition depends on what the compound is compounded with, understanding the details regarding this transition will provide important information when analyzing unknown compounds. In this study, three trivalent europium compounds with relatively easily observable luminescence were selected, and the focus was placed on their emission wavelengths to determine the electronic transitions responsible for the luminescence. This result can be effectively used for comparison in future measurements of different europium compounds or europium compounds with different valence.

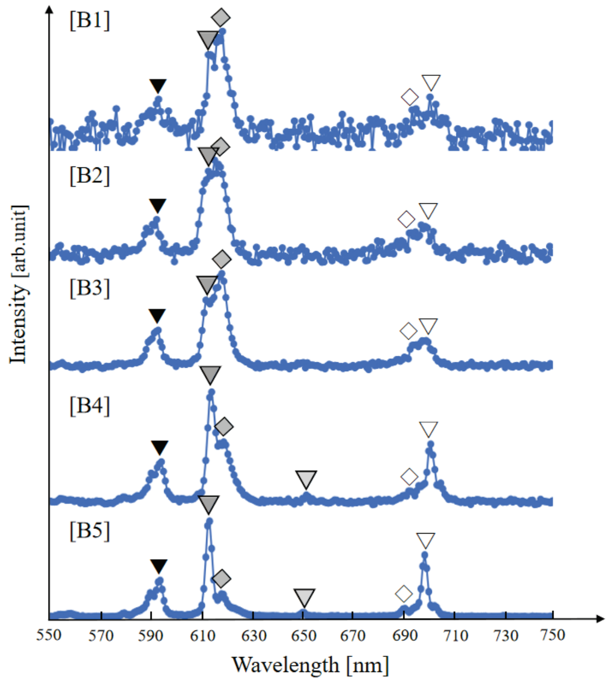

Fig. 4 IBIL spectra for mixtures with different molar ratios of $(CH_3COO)_3Eu$ and $EuCl_3$

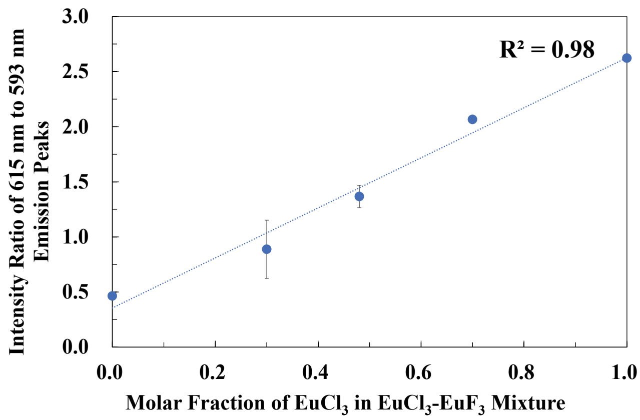

Fig. 5 Relationship between $EuCl_3$ molar fraction and the emission intensity ratio (615 nm / 593 nm)

Figure 5 presents the intensity ratio of the emission peaks at 593 nm and 615 nm as a function of the molar fraction of $EuCl_3$ in the $EuCl_3$-EuF_3 mixture. The 593 nm and 615 nm peaks were selected as representative emission features characteristic of EuF_3 and $EuCl_3$, respectively. The error bars in Fig. 5 represent three times the standard deviation (3σ) obtained from repeated measurements. A strong correlation was observed between the molar fraction and the emission intensity ratio, with a correlation coefficient of $R^2 = 0.98$. The result suggests that, by selecting characteristic emission peaks of each compound and comparing their relative intensities, the molar composition of such mixtures can be estimated.

IV. Conclusion

Basic research was conducted to examine the effectiveness of the IBA method, and in particular the IBIL method, as a method of elemental analysis during the decommissioning phase of nuclear facilities. The IBIL method is already being used as an effective method for clarifying the structure of extractants in the nuclear fuel cycle field, but there is a lack of information on the details of the emission spectra and the transition energy levels of each compound. In this study, the emission spectra of different europium compounds - used as surrogates for minor actinides (MA) - were compared. A mixture of these compounds was also prepared, and its emission spectrum was measured. By selecting characteristic emission peaks of each compound, it is demonstrated that a strong correlation ($R^2 = 0.98$) between the relative emission intensities and the molar composition of the $EuCl_3$-EuF_3 mixture. The result indicates that the molar ratio of the components can be estimated from their relative emission intensities. As such spectral data accumulate in the future, the effectiveness of the IBIL method is expected to be recognized more broadly, establishing a foundation for its application across various fields.

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