



Highly sensitive detection of neodymium ion in small amount of spent nuclear fuel samples using novel fluorescent macrocyclic hexadentate polyaminocarboxylate probe in capillary electrophoresis-laser-induced fluorescence detection

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ABSTRACT

A rapid and high-sensitive detection method for the total concentration of Nd ion (total Nd) in a small amount of a spent nuclear fuel sample is urgently required since the precise quantification of total Nd ion makes it possible for burnup (degree of fuel consumption) to be determined. In this work, a capillary electrophoresis-laser-induced fluorescent detection method (CE-LIF) is proposed for the analysis of total Nd in a spent fuel sample solution, with the use of a newly synthesized metal fluorescent probe which has a fluorescein and a macrocyclic hexadentate chelating group, FTC-ABNOTA, for lanthanide (Ln) ions. Ln ions were derivatized to form a strongly fluorescent complex with the probe to suppress the quenching of the ligand-centered emission. The detection of Ln complexes in the CE-LIF indicated that the interaction between Ln ions and the FTC-ABNOTA was strong enough not to dissociate during migration. The mutual separation among the Ln-FTC-ABNOTA complexes in CE-LIF was achieved by pH control providing a dynamic ternary complexation (DTC) with hydroxide ions. Using the DTC separation mode, a high resolution of Nd from other Ln ions with high resolution of 1.3–1.9 and a theoretical plate number of 68,000, and a very low detection limit of 22 pM (3.2 ppt, 0.11 attomole amount basis) were successfully obtained. A simulated spent fuel sample containing various metal ions was examined in this method with a good quantification result of 102.1% recovery obtained even with a large excess of U.

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1. Introduction

Estimating the composition of various nuclides in radioactive waste is of great importance with respect to safe disposal. In the case of high-level radioactive waste, burnup (degree of fuel consumption) in a spent nuclear fuel sample, which is a major source of the waste, provides basic information with respect to the radionuclide composition. While the precise measurement of the burnup by the determination of several specific nuclides is extremely laborious, the Neodymium-148 method [1] is widely accepted as a standard method for measuring burnup. The method involves the determination of several specific nuclides with the fission product ¹⁴⁸Nd, the burnup monitor, determined using mass spectrometry (MS) (inductively coupled plasma (ICP)- and thermal ionization (TI)-MS) after an ion-exchange separation process of the spent

nuclear fuel sample using a column packed with anion-exchange resin. This method, however, has several drawbacks. (1) It is time-consuming: it takes almost two weeks to complete all the processes, including the isolation of Nd from the sample containing ¹⁴⁸Sm to avoid isobaric interference and the MS measurement. (2) It requires too much handling of a rather large amount of the radioactive sample and eluent: the manual handling of milliliters of the radioactive sample exposes technicians to the risk of radiation, and the method inevitably involves the production of a large amount of radioactive waste, including the eluent used for ion-exchange. (3) It is extremely costly: this is largely due to the large amount of running time for the MS detection. A new determination method of ¹⁴⁸Nd is needed for measuring burnup, one which is simple, safe, fast, requires only a small amount of sample and can be run at a low cost.

It was recently reported that the total concentration of Nd (total Nd) is highly correlated to that of ¹⁴⁸Nd, within 3% error of burnup; that is, by measuring the total Nd in spent nuclear fuel, it is possible to determine the burnup [2]. In this paper, we proposed a

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capillary electrophoresis-laser induced fluorescent detection (CE-LIF) method for the determination of total Nd in spent nuclear fuel samples using a newly synthesized emissive metal probe. The advantages of the CE-LIF are that it allows for the analysis to be completed within a short time frame (generally within 30 min) yet the separation efficiency is high, only 20–100 μL of the sample is needed, the running cost is low, and it has high sensitivity and selectivity for fluorescent chemical compounds. Besides these distinct advantages, the ease with which the analysis operation can be automated, means that it would be possible to remotely control using robot operations, and avoid the risks to human health that come with exposure to nuclear fuel and waste.

With respect to CE for the separation and detection of lanthanide ions (Ln), there are many reports in the literature [3–7]. While indirect UV detection was employed in most of them, their detection limits were on μM levels (ppm–sub ppm). While the total amount of Nd ions in spent nuclear fuel samples is at the ppm level, dilution must be at exactly the right proportion to suppress the matrix effect and radiation exposure. A sample with a concentration in the range of sub-low ppb levels of Nd ions is frequently used in practical measurements. Thus, a detection limit at ppt level ($S/N = 3$) is necessary for precise quantification ($S/N = 10$). The most sensitive CE-UV detection technique for Ln ions is the electrokinetic supercharging (EKS) reported by Hirokawa and co-workers [8], an on-capillary concentration technique which combines electrokinetic injections and transient isotachopheresis. When using this EKS technique, the detection limit of ppt levels for Ln ions (6.7 ppt, 0.04 nM for Er) was successfully achieved. However, it is difficult to apply this technique to real radioactive spent nuclear fuel samples. The electrokinetic injection used in this technique limits its application to low-conductivity samples, making it impossible to work with sample solutions of nuclear waste, which generally contain 1–4 M nitric acid to dissolve all metals. Because of the large excess of various metal ions typically contained in waste samples (see Section 2), serious interference is also anticipated by unselective indirect UV detection, which detects all metal ions. It was decided that the CE-UV detection technique is not suitable for use with spent nuclear fuel samples with regard to sensitivity and sample treatment, even though it satisfies all the other requirements.

Another approach to CE was reported by Saito and co-workers after carrying out a series of studies on metal probes in CE-LIF for heavy metal ions [9–12]. Fluorescent probes, composed with a fluorophore (fluorescein), a chelating moiety (polyaminocarboxylate) and a spacer between them, were synthesized according to the following considerations. (1) A chelating moiety which strongly binds to the target metal ions was selected so that no dissociation takes place from the probe complex to the free probe and the free metal ion during migration. (2) A spacer was added to the probe chemical structure to avoid the quenching of the ligand-centered fluorescence due to the paramagnetic and heavy atom effect. It is well known that most Ln ions, including Nd, quench ligand-centered emissions through complexation. It was found that the quenching effect was significantly suppressed when allowing a distance of 8–12 Å between the two moieties [9]. (3) To separate bulky metal complexes from each other, new separation modes were developed: a dynamic ternary complexation (DTC) mode [10,12–15] and an ion association complex separation mode [9]. For Ln ions, it was reported that a hexadentate acyclic probe, FTC-ABEDTA (FTC, fluorescein-thiocarbamyl; AB, aminobenzyl; EDTA, ethylenediaminetetraacetic acid), which satisfied all the above mentioned requirements, provided very high sensitivity without quenching, resulting in a detection limit of 91 pM [12]. The separation of almost all the Ln ions except Sm–Pr was complete using the DTC mode with the simultaneous addition of iminodiacetic acid (IDA) and citric acid (Cit) to the separation buffer. These agents for ternary complexation bound to the residual coordination sites in the mother

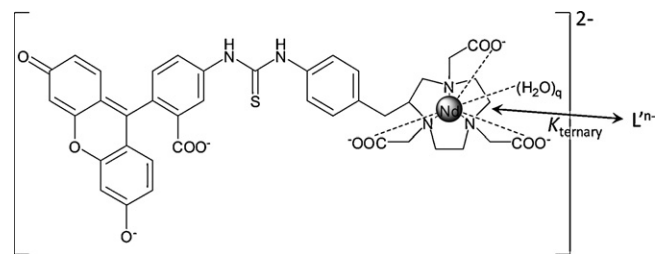


Fig. 1. Chemical structure of Nd-FTC-ABNOTA complex and ternary complex formation with $\text{L}^{\text{n}-}$.

Ln-FTC-ABEDTA complexes, with their center Ln ion dependent different charge densities providing high resolution. Our preliminary applications of this probe to a simulated spent fuel sample revealed that the Nd ion could be detected, but the poor resolution of Nd–Pr and Nd–Sm ($R_s = 0.9$) did not allow for a precise analysis due to the similar concentration levels of Pr and Sm, which coexist with Nd in spent fuel samples (see Section 2). In addition, analysis took over 20 min (Nd was detected at 23 min). With respect to other fluorenescent probes [9,11], the kinetically labile complexes which a tetradentate probe formed with lanthanide ions in our unpublished results suggest the tetradentate probe is unsuitable for the DTC separation of Ln ions. Likewise, the octadentate probes appear likely to be unsuitable due to the almost coordinative-saturated complexes they form.

Our goal in this study was to establish a new CE-LIF method for the detection of Nd in a spent fuel sample with high sensitivity at ppt levels, with a selectivity with R_s near 1.5 and an analysis time within a 10 minute framework when working with a small sample volume of 50 μL . To achieve this, a macrocyclic hexadentate fluorescent probe, FTC-ABNOTA (ABNOTA = aminobenzyl-triazacyclononane-triacetic acid), was newly synthesized (the chemical structure is shown in Fig. 1). The introduction of a macrocyclic hexadentate chelating structure, NOTA, as a substitute for EDTA in the FTC-ABEDTA probe meant that different separation patterns were expected. The Ln–EDTA structure in the FTC-ABEDTA complexes has 2–3 residual coordination sites [16,17] (the coordination number and the denticity of Ln and EDTA is 8–9 and 6, respectively) and singly negative charge ($[\text{Ln}^{3+}\text{-EDTA}^{4-}]^-$). In the case of the Ln–NOTA structure, it has 2–3 residual coordination sites (NOTA is a hexadentate) but no charge ($[\text{Ln}^{3+}\text{-NOTA}^{3+}]^0$). For metal–FTC-ABEDTA complexes, several effective agents for ternary complexation in the DTC mode have been found, such as IDA [12,14], cit [12], carbonate [15], dipicolate [14] and hydroxide anions [10] at mM level to bind to the residual coordination sites. In the case of FTC-ABNOTA, then, larger ternary complex formation constants for Ln–NOTA structure than Ln–EDTA were expected, since the uncharged Ln–NOTA structure would avoid the electrostatic repulsion between the mother Ln complex and the anionic agent for ternary complexation compared with Ln–EDTA. This means more choices of agents for ternary complexation are expected in the DTC mode.

2. Experimental

2.1. Chemicals

All certified metal standard solutions (1000 ppm in nitric acid or hydrochloric acid, for atomic spectrometry) were purchased from Kanto Kagaku (Japan). With respect to standard solution of U, a multi-element standard solution for ICP-MS measurement, containing 10 $\mu\text{g}/\text{cm}^3$ each of Be, Al, V, Cr, Mn, Co, Ni, Cu, Zn, As, Se, Mo, Cd, Sb, Ti, Pb, Th and U purchased from Accu Standard (CT, USA) was employed after the isolation of U

according to a method previously reported [18]. The concentration of the U standard solution of 4.76 ppm in 1 M nitric acid was determined by ICP-MS. As the reagents for the synthesis of FTC-ABNOTA, fluorescein isothiocyanate isomer I (FITC-I, >98% purity, <1.5% content of the isomer II) purchased from Fluka (Buchs, Switzerland), 2-S-(4-aminobenzyl)-1,4,7-triazacyclononane-1,4,7-triacetic acid (ABNOTA, >94% purity) purchased from Macrocyclics (Dallas, TX, USA), were dissolved in acetone (analytical grade, Kanto Kagaku, Tokyo, Japan) or deionized water. The stock solution of FITC-I was stored at -4°C in the dark to prevent it from decomposing. The reagent, CyDTA, employed for the masking of metal ions in the separation buffer, was purchased from Dojindo (Japan). As candidates of agents for DTC separation, IDA, sodium bicarbonate, disodium hydrogen phosphate and citric acid monohydrate purchased from Wako Pure Chemical Industries (Japan) were dissolved in deionized water (over $18.2\text{ M}\Omega$ prepared from Arium 611D (Sartorius, Gottingen, Germany)) prepared as appropriate concentrations. All the stock solutions were stored in PTFE (polytetrafluoroethylene) bottles to prevent contamination with metal ions.

2.2. Synthesis of FTC-ABNOTA

The probe was synthesized in accordance with the method described in previous reports [9,10]. The procedure is described briefly as follows. A 2.5 mL of 10 mM FITC-I was mixed with 25 mL of 1 mM ABNOTA and 22.5 mL of deionized water in the presence of 10 mM malate–NaOH buffer for 6 h. The reaction mixture was fractionated by RP-HPLC. The obtained solution was acidified with drop-wise concentrated HCl at pH 2.5. After 30 min standing, the resulting orange powder precipitate was filtered and dried. The yield was 20.1%. Found: C, 56.42; H, 5.13; N, 7.98%, 0.24% error. Calc. for $\text{C}_{40}\text{H}_{39}\text{N}_5\text{O}_{11}\text{S}(\text{H}_2\text{O}\cdot\text{HCl})$. MS (ESI(–)): m/z 796.2302 ($[\text{M}-\text{H}]^-$), 0.96 ppm error; isotopic abundance error, 0.07%. δ_{H} (300 MHz, d_6 -DMSO) 10.62 (1 H, s), 10.18 (2 H, s), 8.25 (1 H, s), 7.90 (1 H, d, $^3J_{\text{HH}} = 8.7$ Hz), 7.53 (2 H, d, $^3J_{\text{HH}} = 8.1$ Hz), 7.23 (3 H, m), 6.60 (2 H, m), 6.60 (2 H, m), 3.63 (2 H, d, $^3J_{\text{HH}} = 6.0$ Hz), 3.54 (3 H, m), 3.00 (10 H, m), 2.90 (6 H, m). The stock solution of FTC-ABNOTA was prepared by simply dissolving the powder in deionized water.

2.3. Apparatus

The CE setup used in this study was assembled from different parts. High voltage was supplied by the HCZE-30P model purchased from Matsusada Precision (Shiga, Japan). The LIF detection system employed was the ZETALIF evolution (Picometrics, Ramonville, France) equipped with a Model 163-M12 25 mW argon laser (Spectra-Physics, CA, USA). A Lambda 1010 model UV/vis spectrophotometric detector was employed. We used a bare fused-silica capillary tube (with an inner diameter of 50 μm and an outer diameter of 375 μm ; a total length of 60.0 cm and effective length to the detection window of 47 cm) obtained from Scientific Glass Engineering (Austin, TX). New capillary tubes were pretreated by rinsing with a 1 M solution of NaOH for 20 min and deionized water for 20 min followed by rinsing with separation buffer for 10 min. Between each run, the capillary was flushed by the separation buffer for 10 min. All the carrier buffers and rinsing solutions for use in the capillaries were exchanged under reduced pressure by a vacuum pump.

2.4. Measurement of mobility

Since no marker of electroosmotic flow (EOF) could be observed with LIF detection methods, the UV/vis detection of ethanol markers at 215–230 nm was employed to measure the EOF rate. The

Table 1
Elemental composition in a simulated spent nuclear fuel sample.

Element	Concentration (ppb)	Element	Concentration (ppb)	Element	Concentration (ppb)
U	238	Pd	6.0	Rb	1.25
Nd	14.0	La	4.3	Gd	0.70
Zr	12.8	Pr	3.9	Cd	0.45
Mo	11.4	Sm	2.9	Eu	0.45
Ce	8.4	Sr	2.2	Ag	0.35
Ru	8.2	Te	1.75	Sn	0.25
Cs	7.6	Rh	1.45	Se	0.20
Ba	7.1	Y	1.45	Br	0.05

mobility value of the probe and the metal–probe complex was determined using the following equation:

$$\mu_{\text{complex}} = \frac{L_t L_d}{Vt} - \frac{L_t L_d}{Vt_{\text{EOF}}} \quad (1)$$

where L_t and L_d are the total and the effective capillary lengths, V is the applied voltage, and t and t_{EOF} are the detection times of the EOF marker and the probe complexes. The mobility measurement was replicated for three times (relative standard deviation (RSD) values of migration time were within 2–4%).

2.5. Simulated spent nuclear fuel sample preparation

The elemental composition in a simulated sample was calculated using an isotope generation and depletion code ORIGEN2 as a PWR spent fuel sample with a burnup of 45 GWd/t and a cooling time of about 20 years [19]. Appropriate amounts of each metal standard solution of 1000 ppm were mixed to obtain the calculated composition. The mixed solution was diluted to 10.0 mL of 4.0 M nitric acid, and evaporated to dryness. The resulting solid, the uranium fuel sample, was dissolved in 10.0 mL of 4.0 M nitric acid. After the filtration of the insoluble residue using a 0.45- μm membrane filter, the sample solution was diluted by a factor of 20,000 with 1.0 M nitric acid. The composition of the diluted simulation sample solution is summarized in Table 1.

2.6. Typical procedure

Solutions of FTC-ABNOTA and borate buffer were added to the sample solution. The concentrations of the mixed solutions were typically 2–55 μM and 1 mM for the probe and borate at pH 9.6–9.8, respectively. For simulated samples, FITC-I of 10 μM was added to the sample solution as an internal standard. The sample solutions were prepared in 20–100 μL polypropylene vials purchased from Agilent. After 1 min, the resulting sample solution was hydrodynamically injected into the capillary from the cathodic end with an injection height differential of $\Delta 5$ cm for 36 s (resulting in an estimated injection volume of 5 nL calculated using the Hagen–Poiseuille equation). A constant separation voltage of 20 kV was then applied (resulting in a typical current 38–42 μA). A separation buffer was 12 mM borate ($\text{H}_3\text{BO}_3\text{-NaOH}$) at pH 9.60 including 25 μM CyDTA. Since it has been reported that a large tailing peak of contaminant calcium was successfully decreased with the addition of CyDTA in the buffer [12], CyDTA was employed as a contamination blocking agent. The voltage of the photomultiplier and the power of the Ar laser in the LIF detection system were set at 580 V and 8 mW, respectively. The temperature was set at 293 K by air cooling.

3. Results and discussion

3.1. Pre-capillary derivatization kinetics

When Ln ions form complexes with FTC-ABNOTA during the pre-capillary derivatization step, the degree of advancement of the complexation of near 100% is desirable for quantitative determination. All the Ln ions were obviously able to form FTC-ABNOTA complexes at the equilibrium state, since very high stability constants for the Ln–NOTA complexes are reported as $10^{13.17}$ – $10^{15.35}$ M⁻¹ [20]. With respect to the formation kinetics, the reaction time for quantitative reaction was estimated, with assumption that the reaction rate of Ln–FTC-ABNOTA is similar to that of Ln–NOTA. The estimation of the reaction time is crucial when quantitatively obtaining the derivatized complex, since slow complexation kinetics can extend the analysis time significantly. Brucher and Sherry reported details of the kinetics of Ln–NOTA complexes [21]. The rate law is expressed in the following equation.

$$\frac{d[\text{Ln-NOTA}]}{dt} = -\frac{d[\text{Ln}]}{dt} = \frac{k_{\text{OH}}[\text{OH}^-]K^*[\text{Ln}]}{1 + K^*[\text{Ln}]} [\text{NOTA}]_0 \quad (2)$$

where $[\text{NOTA}]_0$, K^* and k_{OH} represents total NOTA concentration, a parameter characterizing the formation of an intermediate and a rate constant depending on $[\text{OH}^-]$, respectively. The values of K^* and k_{OH} were given as 1171 M⁻¹ and 7.1×10^7 M⁻¹ s⁻¹ for Gd³⁺ [18]. Assuming that the value of $[\text{Ln}]$ and $[\text{NOTA}]_0$ are 10^{-6} – 10^{-11} M and 5 μM in our case, and using $1 \gg K^*[\text{Ln}]$ into Eq. (2), yields

$$\frac{d[\text{Ln-NOTA}]}{dt} = -k_{\text{OH}}[\text{OH}^-]K^*[\text{L}]_0[\text{Ln}] = k_{\text{obs}}[\text{Ln}] \quad (3)$$

Accordingly, the formation rate of Ln–NOTA is represented as a pseudo-first order reaction of Ln ion with an apparent rate constant, k_{obs} , of 16.8 s⁻¹ at pH 9.6. If that is the case, it takes only 0.4 s for a reaction rate of 99.9%. According to the Eigen–Tamm mechanism, more negatively charged ligands form complexes more quickly due to their ability to form an outer-sphere complex [22]. It could be assumed that the complexation rate of Ln–FTC-ABNOTA was faster than that of Ln–NOTA since NOTA and FTC-ABNOTA were doubly and quadruply charged, respectively, at pH 9.6. Therefore, a mixing time of 1 min in a typical procedure can be assumed for quantitative derivatization. In fact, no change in the peak area or the height of Ln ions in CE-LIF was observed for different derivatization times (1 min–1 h), and the recovery of the spiked Ln ions at various FTC-ABNOTA concentrations (5–22 μM) remained consistently close to 100%. This indicates the quantitative complexation of the Ln–FTC-ABNOTA was completed within 1 min.

3.2. CE-LIF without agents for ternary complexation

When the Ln–FTC-ABNOTA complexes were applied to capillary zone electrophoresis (CZE), the peaks of the complexes were detected with LIF detection (Fig. 2). This suggests that Ln–FTC-ABNOTA complexes were emissive and inert enough to survive during migration. However, when La- or Ce–FTC-ABNOTA complexes were injected, no peak and a small peak were observed for the La or Ce ion, respectively. This indicates that both complexes decomposed to free metal ion and probe, that is, they were labile in the dissociation process during separation. Brucher and Sherry investigated the dissociation kinetics of Ln–NOTA complexes. Their conclusion that the Ln–NOTA complexes were largely inert, reached after considering their dissociation rate constants (the half-lives for Ce, Gd and Er complexes were calculated as 7.7, 23.1 and 71.3 h at pH 8–10), was inconsistent with our results. This can be explained by the existence of other reaction paths, such as the ligand-exchange reaction and base-assisted dissociation. In this case, a base-assisted dissociation process most probably takes

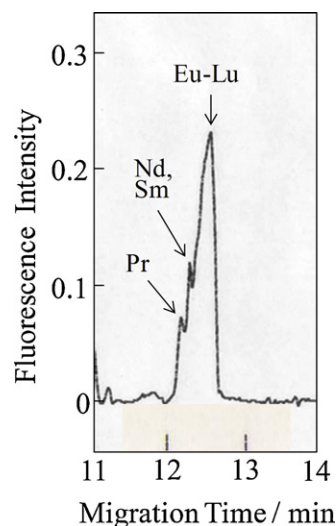


Fig. 2. Typical electropherogram of Ln–FTC-ABNOTA complex. Sample, $[\text{Ln}] = 50$ nM, $[\text{FTC-ABNOTA}] = 5$ μM , $[\text{borate}] = 1.0$ mM (pH 9.6). Separation buffer, $[\text{phosphate}] = 40$ mM (pH 8.04), $[\text{CyDTA}] = 25$ μM .

place, since the hydroxide ion works as an agent for ternary complexation in slightly basic solutions (see next section), which means hydroxide anion nucleophilically attacks the center Ln ions in the mother Ln–probe complex.

With respect to the separation among Ln ions, very poor resolution was observed using the phosphate buffer at pH 8.04 (Fig. 2). This strongly suggested that each Ln–FTC-ABNOTA complexes has almost the same electrophoretic mobility due to their similar sizes and charges in the chemical structures. The phosphate buffer did not work as an agent for ternary complexation to improve the resolution.

3.3. Separation of lanthanide ions by dynamic ternary complexation mode

The DTC mode was applied in order to separate Ln–FTC-ABNOTA complexes from each other. When the agent for ternary complexation, IDA, cit and carbonate were employed, somewhat higher resolution than CZE was obtained (data not shown). Those agents easily formed ternary complexes with Ln–FTC-ABNOTA at lower concentrations (IDA ≤ 3 mM) than in the case of Ln–FTC-ABEDTA (IDA ≤ 5.5 mM). This seems to be attributable to the higher affinity of the agents for ternary complexation to noncharged Ln–NOTA structures than Ln–EDTA structures. However, the incomplete separation of Nd indicated that the stability constants for ternary complex formation are so similar among Ln ions that high resolution cannot be obtained.

The highest resolution was obtained when a borate buffer was employed as the separation buffer. Although the dependence of electrophoretic mobility on the borate buffer concentration was determined, the mobility was independent of borate concentrations in the range of 4–120 mM (-2.17 to -2.28×10^{-4} and -2.58 to -2.62×10^{-4} cm² V⁻¹ s⁻¹ for Nd and Gd, respectively). On the other hand, it was found that the mobility of the complexes significantly depended on the pH value (Fig. 3). In Fig. 3, a low borate concentration (1 mM) in the separation buffer was employed in order to avoid even a small effect of borate on mobility through ternary complex formation and not to cause high electric current during migration with the addition of NaClO₄ for a constant ionic strength of 0.1. When the pH value increased from 8.3 to 10.5, the mobility dramatically decreased, with the highest resolution obtained at pH 9.60 (Fig. 4). This strongly suggests that the

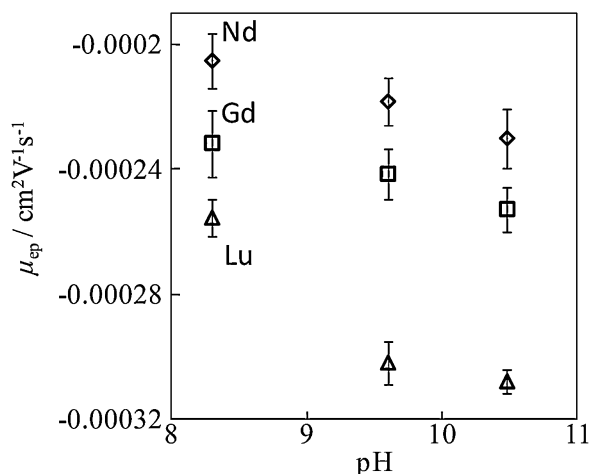


Fig. 3. Dependence of the mobility on pH. Sample, $[\text{Nd}] = [\text{Gd}] = [\text{Lu}] = 40 \mu\text{M}$, $[\text{FTC-ABNOTA}] = 0.2 \text{ mM}$, $[\text{borate}] = 1.0 \text{ mM}$, pH 9.0. Separation buffer, $[\text{borate}] = 1.0 \text{ mM}$ at various pH values, $I = 0.1 \text{ M}$ (NaClO_4).

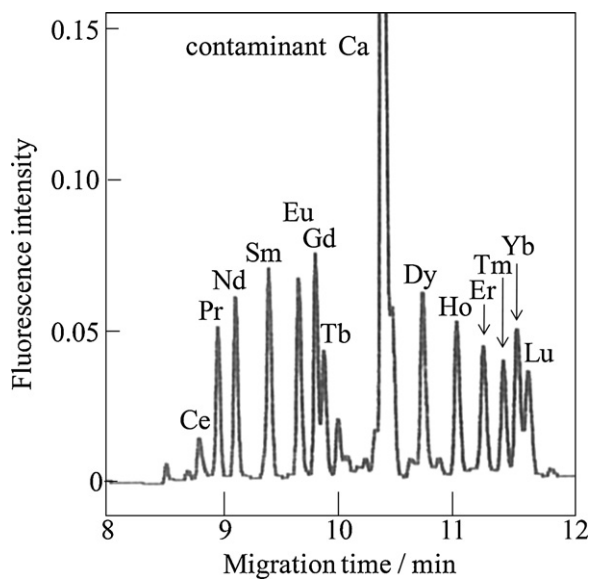


Fig. 4. Typical electropherogram for Ln-FTC-ABNOTA complexes. Sample, $[\text{Ln}^{3+}] = 5 \text{ nM}$, $[\text{FTC-ABNOTA}] = 2 \mu\text{M}$. Separation buffer, $[\text{borate}] = 12 \text{ mM}$ (pH 9.60), $[\text{CyDTA}] = 25 \mu\text{M}$.

hydroxide ion forms a ternary complex with the mother complex ($[\text{Nd}^{3+} - \text{FTC-ABNOTA}^{5-} - \text{OH}^-]^{3-}$). Since the ternary complex formation of Ln-polyaminocarboxylate complex with hydroxide ion was reported for Eu-EDTA(OH^-), -CyDTA(OH^-) complexes around pH 9–11.5 [16], ternary complex reaction at 8–10 for Ln-FTC-ABNOTA was very likely. It was also found that the ternary complex formation with the hydroxide ion was effective in the case of transition metal ion complexes with FTC-ABEDTA at highly alkaline conditions with pH 12.3 [10]. The observed migration order of atomic number is reasonable, since the higher charge density on the heavier Ln ion by lanthanide contraction can be expected to provide a higher stability constant of the ternary complex between the Ln-FTC-ABNOTA and hydroxide ion, resulting in a more negatively charged species.

Reasonable resolution between Pr-Nd and Nd-Sm for determination of Nd was obtained as $R_s = 1.3$ and 1.9, respectively (the theoretical plate number obtained was 6.8×10^4). In addition, the short migration time required, within 12 min (9.1 min for the Nd

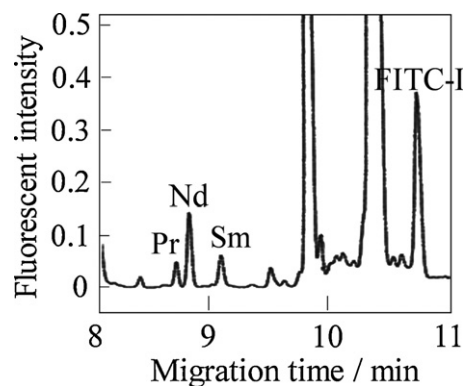


Fig. 5. Typical electropherogram for a simulated spent nuclear fuel sample including 14 ppb of Nd. Sample, $[\text{FTC-ABNOTA}] = 55 \mu\text{M}$, $[\text{FITC-I}] = 50 \text{ nM}$, the composition of metal ions is the same in Table 1. Other conditions are the same as those in Fig. 4.

ion), makes the rapid analysis of spent nuclear fuel samples possible.

3.4. Calibration curve, detection limit, and quantification of Nd in a simulated spent nuclear fuel sample

Under the optimal separation conditions (12 mM of borate at pH 9.60), the quantitative performance of the Nd ion was assessed. Linearity was obtained in the range of 0.5–100 ppb (3.5 nM–0.7 μM) with a correlation coefficient of $R^2 = 0.9993$ ($N = 7$). The RSD ($N = 5$) of the peak area and the detection time of Nd (14 ppb) were 3.07% and 1.07%, respectively. The detection limit of Nd determined by 3σ of blank was 3.2 ppt (22 pM, 0.11 attomole as a mass detection limit). The quantification limit of 10.7 ppt based on 10σ was sufficient for sub ppb of Nd in the real sample. When adding a large excess amount of U (2.38 ppm), which can be assumed to be in the form of UO_2^{2+} , to a sample including Nd (7.31 ppb), no peak of U was observed and the recovery of Nd was 100.8%. This suggests that UO_2^{2+} formed a labile complex with FTC-ABNOTA, and there was no interference from U.

This CE-LIF method was applied to the simulated sample. Pr and Sm were well separated from Nd (Fig. 5). The determined value of Nd was 14.3 ± 0.68 ppb with RSD 4.82%, which was consistent with the prepared concentration value of 14.0 ppb with 102.1% recovery. As a result of spiking the solution with 5 ppb Nd to the simulated sample, 101.5% recovery was successfully achieved.

4. Conclusions

The usefulness of CE-LIF using a fluorescent metal probe was demonstrated for the determination of Nd in a spent nuclear fuel sample with a large excess of U. The significantly shorter analysis time (within 15 min) than the ASTM standard method (two weeks) is the biggest advantage of this CE-LIF technique. It is also characterized by its ability to achieve highly efficient separation and highly sensitive detection. In addition, the sample volume needed and the waste volume caused by measurements are very small; less than 1 ml of the separation buffer waste after 10 analysis runs and 50 μL of a fuel waste in a sample vial. The total volume of the waste solution is less than that of the conventional method by a factor of 10. In terms of disposable supplies, only the fused silica capillary and some 1.5 mL microvials were discharged (the capillary was amenable to over 100 runs). Obviously, this is a significant minimization of emission of radioactive waste due to analysis procedure. In addition, no operation

training is necessary to use this method since no delicate handlings of materials or equipment is required. Among the other methods used for the determination of total Nd, such as inductively coupled plasma atomic emission spectroscopy (ICP-AES) and atomic absorption spectroscopy (AAS) with general detection limits of 0.2–2 ppb, our CE-LIF method is the one which allows for the rapid determination and the minimization of radioactive-contamination.

Although there are few examples of CE methods which have practical applications for the determination of ultratrace heavy metal ions, this method is a powerful candidate for use with real samples due to its simplicity, robustness, sensitivity and selectivity. The recent development of on-capillary concentration techniques [23], one of which was applicable to even high conductivity samples [24], should be acknowledged. The combination of our probe system with on-capillary concentration techniques may provide a higher sensitivity and robustness. Our future experiments will focus on applying CE-LIF using metal probes to real nuclear fuel samples, validating the method and automatizing it with robot operation. Also, since the determination of actinide ions in fuel samples is of great importance and interest, we will focus on developing new metal probes selective to actinide ions.

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