High Sensitive and Prompt Discrimination of Luminescent Europium ß-Diketonates Using Electrospray Ionization Mass Spectrometry

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Europium complexes with six types of tris ß-diketones in the absence and presence of 1,10-phenanthroline were accurately analyzed qualitatively and quantitatively using both infusion electrospray ionization mass spectrometry (ESI-MS) and fluorescence spectrometry (FL), which is usually used as the analytical method. Detection limits for compounds extracted with acetonitrile were 1–100ppb corresponding to those by FL.

Europium ß-diketonates are used as red emitters in various fields such as organic electroluminescent devices, dyes for latent fingerprint detection, and labels for fluoroimmunoassay. Europium ß-diketonates have been analyzed often by FL.[1–7] Such FL analysis shows only similar emission spectra and featureless and broad excitation spectra for all compounds. Accordingly, qualitative analysis shows large errors. Furthermore, many analytical methods have been studied for accurate europium complex discrimination: europium ß-diketonates were identified by means of electron ionization and chemical ionization mass spectrometries.[8–11] However, extracting solvents were necessarily removed from samples before the mass spectrometry measurements and fixed europium complexes such as tris(naphtyltrifluoroacetonato)europium ($EuTFNB_3$) were hardly detected. Furthermore, X-ray analysis[12] could not determine a trace of the samples. In this study, we first report that infusion electrospray ionization mass spectrometry (infusion ESI-MS) analyzes promptly the europium ß-diketonates. This analytical method is suitable for both qualitative and quantitative analyses of europium ß-diketonates. Samples are six types of europium ß-diketonates: tris(pivaloyltrifluoroacetonato)europium ($EuPTA_3$), tris(benzoyltrifluoroacetonato)europium ($EuBFA_3$), tris(furoyltrifluoroacetonato)europium ($EuFTA_3$), tris(thenoyltrifluoroacetonato)europium ($EuTTA_3$), $EuTFNB_3$, and tris(2,2-dimethyl-6,6,7,7,8,8,8-heptafluoro-3,5-octanedionato) europium ($EuDMHFO_3$) in the absence and presence of 1,10-phenanthroline (phen).

Infusion ESI-MS analysis was performed using a micromass ZMD in Waters Alliance systems for discrimination of 12 samples and determination of detection limits. Acetonitrile was selected as solvent optimized for obtaining strongest peak intensities of both ESI-MS and FL for europium complexes in acetonitrile/water (10:0–5:5) and methanol/water (10:0–5:5).

Figure 1(a) shows the radical anion ($M^{\bullet-}$) of the neutral europium complex molecule (M), the adduct anion ($[M + (L - H)]^-$) by adding a deprotonated molecular anion ($[L - H]^-$) of a ligand molecule (L) to the M, and the $[L - H]^-$ mainly detected in ESI-MS spectra of negative ion mode of europium complexes with tris ß-diketones ($Eu(L - H)_3$).

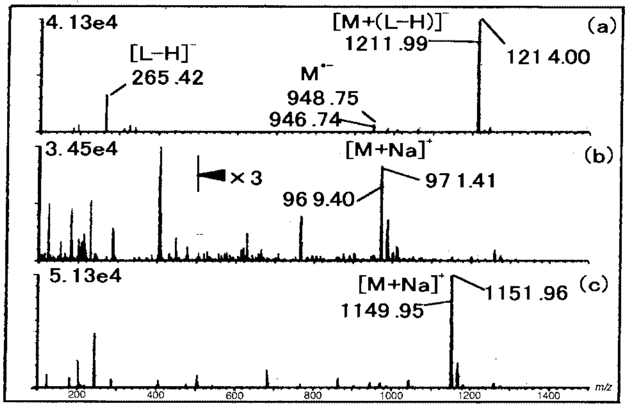

Figure 1. ESI-MS spectra of $EuTFNB_3$ in acetonitrile in negative ion mode (a), $EuTFNB_3$ in acetonitrile in positive ion mode (b), and $EuTFNB_3(phen)$ in positive ion mode (c) at 10 ppm. The ESI-MS conditions are shown in negative ion mode (or positive ion mode): electrospray capillary, 4.0 (3.5) kV; cone, 60 (40) V; source block temperature, 130 (130) °C; desolvation temperature, 400 (400) °C; multiplier, 650 (650) V; nitrogen gas, 420 (380) L/h.

Respective $M^{\bullet-}$ and $[M + (L - H)]^-$ were detected as a pair of peaks due to the europium isotope effect. ß-Diketone ligands were deprotonated to form $[L - H]^-$ as a peak. Six europium complex types, $Eu(L - H)_3$, were easily identified by confirming the three anions ($M^{\bullet-}$, $[M + (L - H)]^-$, and $[L - H]^-$). In the positive ion mode, the adduct cation ($[M + Na]^+$) was produced and detected mainly as a pair of peaks by addition of a sodium cation to the neutral europium complex molecule (M). The sodium cation was probably mixed from glass instruments into samples. Europium complexes $Eu(L - H)_3$ and $Eu(L - H)_3(phen)$, with tris-ß-diketones in the absence and presence of 1,10-phenanthroline, were promptly discriminated by corresponding cations $[M + Na]^+$ at *m/z* 971 and 969, and 1152 and 1150 in spectra of $EuTFNB_3$ and $EuTFNB_3(phen)$, respectively, as shown in Figures 1(b) and 1(c). However, FL analysis could not distinguish $Eu(L - H)_3$ and $Eu(L - H)_3(phen)$ nor $EuPTA_3$ and $EuDMHFO_3$ nor $EuTTA_3$ and $EuFTA_3$. Figure 2 shows the percentage of ESI-MS peak abundance of each cation in $[Eu(L - H)_3 + Na]^+$ and $[Eu(L - H)_3(phen) + Na]^+$ compared to the ratio of each component at 10 ppm of mixtures of $EuTFNB_3$ and $EuTFNB_3(phen)$ in acetonitrile. However, FL analysis could not detect each component of the mixtures. Therefore, ESI-MS analysis was more available to quantitative analysis of each component in complex mixtures such as $Eu(L - H)_3$ and

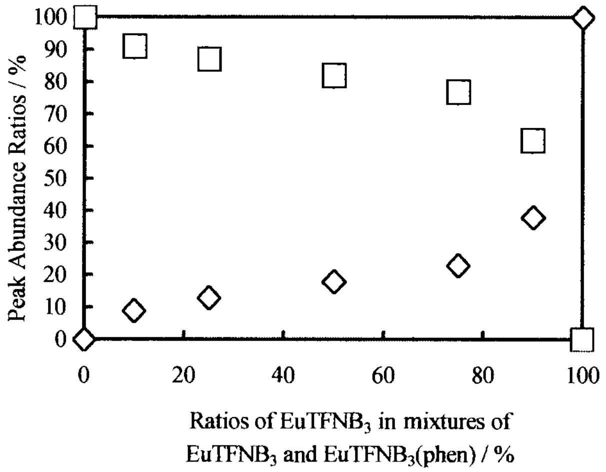

Figure 2. Percentage of ESI-MS peak abundance of $[\mathrm{EuTFNB_3} + \mathrm{Na}]^+$ (◇) and that of $[\mathrm{EuTFNB_3(phen)} + \mathrm{Na}]^+$ (□) in the two cations compared to the ratio of each component in 10 ppm mixtures of $\mathrm{EuTFNB_3}$ and $\mathrm{EuTFNB_3(phen)}$ in acetonitrile.

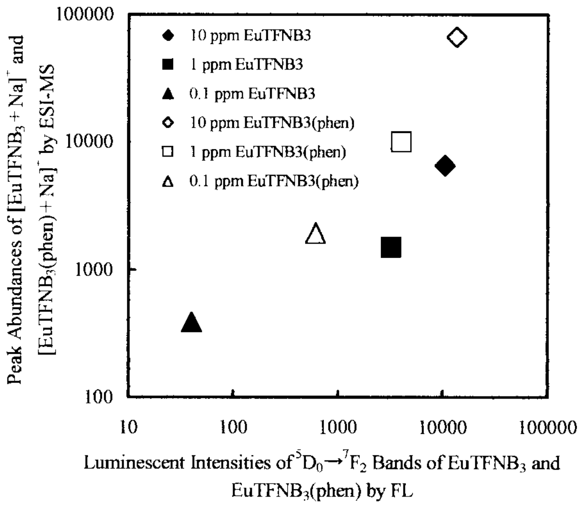

Figure 3. Detection sensitivity of $[\mathrm{EuTFNB_3} + \mathrm{Na}]^+$ and $[\mathrm{EuTFNB_3(phen)} + \mathrm{Na}]^+$ detected by ESI-MS in comparison to that of emission band from $^5D_0$ to $^7F_2$ by FL of $\mathrm{EuTFNB_3}$ and $\mathrm{EuTFNB_3(phen)}$ in the range of 0.1 to 10 ppm in acetonitrile. The ESI-MS conditions are the same as those shown in Figure 1. The FL was performed using a Hitachi F-4500 fluorescence spectrophotometer. $\mathrm{EuTFNB_3}$ and $\mathrm{EuTFNB_3(phen)}$ were excited at 332 and 330 nm, respectively.

$\mathrm{Eu(L\text{-}H)_3(phen)}$ than with FL analysis. Furthermore, detection limits of $[M]^{\bullet -}$, $[M + Na]^+$ of complexes $\mathrm{Eu(L - H)_3}$ and $[M + Na]^+$ of complexes $\mathrm{Eu(L - H)_3(phen)}$ in ESI-MS analysis were about 1–100 ppb. Figure 3 shows detection sensitivity of $[M + Na]^+$ detected by ESI-MS compared to that of the emission band from $^5D_0$ to $^7F_2$ at 611 nm by FL analysis of $\mathrm{EuTFNB_3}$ and $\mathrm{EuTFNB_3(phen)}$ in the range of 0.1 to 10 ppm in acetonitrile. The ESI-MS had higher detection sensitivities than FL for $\mathrm{EuTFNB_3}$ and $\mathrm{EuTFNB_3(phen)}$ in acetonitrile, although it had similar sensitivity for some other types of complexes. The intensities of the emission bands of $\mathrm{EuTFNB_3}$ and $\mathrm{EuTFNB_3(phen)}$ extremely decreased in the range of the low concentration below 1 ppm in acetonitrile, compared to the abundances of the $[M + Na]^+$ by ESI-MS. Therefore, infusion ESI-MS sensitively and promptly analyzed the luminescent europium ß-diketonates.

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