Inductively Coupled Plasma Atomic Emission Spectroscopy Method for Precise Determination of Trace Europium in Biological Fluid: A Technical Note

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ABSTRACT

An analysis method for europium (Eu) in liquid biological samples by inductively coupled plasma atomic emission spectroscopy (ICP-AES) was established. The signal-to-background (S/B) ratios of Eu at λ = 381.967 nm showed the steepest increase among the Eu characteristic wavelengths of 381.967 nm, 390.710 nm, 393.048 nm, 412.970 nm and 420.565 nm.

The calibration at λ = 381.967 nm also showed wide dynamic range of <10-500 μg/L with detection limit (DL) of 0.388 μg/L and quantitation limit (QL) of 1.30 μg/L. Percent recovery and reproducibility for Eu spikes added to rat urine matrix at a 20-fold dilution showed 94.2-102.3 % with a small % coefficient of variation (% CV) of 0.65-1.04% and achieved good precision and accuracy.

Eu compound is important chemical materials for the recent lighting industries to produce new type fluorescent lamps and becomes an occupational and environmental potential toxicant of concern, however its health impacts are still uncertain. The Eu analytical method by ICP-AES described in this technical note will help to further explore of Eu in biological fluid samples.

INTRODUCTION

Europium (Eu) is the most reactive rare earth elements (REEs) and has been utilized for the red phosphor in color television tubes since 1960s. Now, its main industrial use is a key ingredient in the new long-life low-energy mercury-free compact fluorescent lamps, (TV) and personal computer (PC) display panel [1]. Its compounds coated onto the interior surface of the lamp are stimulated to glow by high intensity discharge through the low pressure gas in the fluorescent lamp tube and produce the pleasant warmer...
color of the light [2]. Although REEs and other substitute materials are believed to be nontoxic and earth friendly, human health consequences of individual REEs are uncertain [3,4]. Thus, Eu can pose a potential environmental health hazard associated with the increasing electric waste of broken lamps, TV and PC. Electrical workers are expected from occasional exposure associated with industrial processes. Accordingly, analytical technique that provides trace Eu concentrations in biological materials is necessary to further explore of these concerns.

Inductively coupled plasma atomic emission spectroscopy (ICP-AES) was developed in the early 1960s and quickly became the preferred technique for routine trace element analysis. It allows the determination of trace element concentration of in liquid samples at the μg/L level [5]. This technical note describes a simple, rapid and accurate determination method of trace Eu in liquid samples.

MATERIALS and METHODS

Apparatus
An ICP-AES system of iCAP 6300 Thermo Fisher Scientific Inc., MA, USA (Figure 1) was used for Eu determination. The operating conditions were as follows: RF power at torch, 1150W; auxiliary gas flow rate 0.5 L/min; coolant gas flow rate, 12.0 L/min, nebulizer gas flow rate, 0.7 L/min and pump flow rate 50rpm.

Figure 1 Thermo Scientific iCAP 6300 ICP Spectrometer

Eu standard solution
Ultrapure water of 18 MΩ cm obtained using a WG240/260 water purifier (Water Still System, Yamato scientific Co., Ltd., Tokyo, Japan) was used to prepare standards and samples in the study. A calibration curve was constructed using solutions containing Eu at 0, 100, 200, 300 and 500 μg/L. The standards were prepared by dilution of a commercial 1.0mg Eu/ml (1000-ppm) Eu stock solution (code 151-04251, Lot KWP4512) from Wako Pure Chemical Industries, Ltd., Osaka, Japan.

Analytical Procedure
The characteristic wavelengths of Eu are 381.967 nm, 390.710 nm, 393.048 nm, 412.970 nm and 420.505 nm. To select the most sensitive method, the signal to background ratio (S/B ratio) was examined in Eu concentration range of 0-500 μg/L. A calibration line was constructed with five different concentrations of Eu (0, 100, 200, 300, and 500 μg/L). Detection limit (DL) and quantitation limit (QL) was defined as 3SD and 10SD above the mean of a blank background signal from ultrapure water, respectively. The spectrum of Eu standard solution (10 and 500 μg/L) was determined to confirm the dynamic range of the calibration.

Quality assurance
Rat urine was obtained from 9-week-old male Wistar rats (Japan SLC; Hamamatsu, Shizuoka, Japan) with mean body weights of 310 g. Urine matrix spike samples were analyzed to determine the effect of sample matrix on analytical accuracy. For this purpose, rat urine samples at a 20-fold dilution were spiked with Eu standard solution to provide 25-, 50- and 100- μg/L concentrations. Accuracy was evaluated using percent recovery, which was calculated by dividing the measured spiked sample concentration by the corresponding certificate value times 100. Reproducibility was evaluated using % coefficient of variation (% CV), obtained by dividing the standard deviation by the arithmetic mean concentration and then multiplying by 100.

Statistical analysis
The statistical analysis software StatView for Windows v. 5.0 from SAS Institute Inc. Cary, NC, USA and MS Excel 2000 for Windows were used for data entry and analysis.

RESULTS and DISCUSSION

Figure 2 shows the signal-to-background (S/B) ratios of Eu at λ=381.967, 390.710, 393.048, 412.970 and 420.505 nm in the concentration range of 0 to 500 μg/L. The steepest slope is seen at λ=381.967 nm.

Figure 3 shows the good effective linearity of Eu
calibration line at $\lambda=381.967$ nm with the equation: 

$$y = 138.6x$$

where $x$ is the Eu concentration ($\mu$g/L) and $y$ is the signal intensity.

Figure 4 shows the fluctuations of blank background signal around 15400 at $\lambda=381.967$ nm from 18 MΩ cm ultrapure water. The sample detection limit (DL) of 0.389 $\mu$g/L and quantitation limit (QL) of 1.30 $\mu$g/L was calculated by substituting mean+3SD and 10SD of a blank background signal from ultrapure water for $y$ values into the equation in figure 3, respectively.

Figure 5 shows the signal intensity spectrum at $\lambda=381.967$ nm from Eu standard solution of 10-$\mu$g/L (a) and 500-$\mu$g/L (b). As shown in this figure, peak spectrum can be visually recognized at $\lambda=381.967$ nm and the calibration dynamic range of <10-500 $\mu$g/L was confirmed by the peak signal intensity of figure 5 (a and b) and the equation in figure 3.

Table 1 shows the recovery of spiked Eu stan-
Figure 5  Peak signal at $\lambda=381.967$ nm from Eu standards solution of 10-$\mu$g/L (a) and 500-$\mu$g/L (b)

Table 1  Spike Recovery and Reproducibility from Rat Urine Matrix with 20-Fold Dilution ($n = 3$)

<table>
<thead>
<tr>
<th>Certificate value ($\mu$g/L)</th>
<th>Recovery (%)</th>
<th>CV (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>102.3</td>
<td>1.04</td>
</tr>
<tr>
<td>50</td>
<td>94.2</td>
<td>0.65</td>
</tr>
<tr>
<td>100</td>
<td>97.1</td>
<td>0.84</td>
</tr>
</tbody>
</table>
standard solutions from rat urine matrix in the 25- to 100 μg/L concentration range averaged 94.2±102.3%. The assay also showed good reproducibility with small % CVs of 0.65±1.04%.

Eu is a strategic element in electrical industries and there is a potential human health risk from exposure to Eu compounds. Although the ICP-AES technique is widely used for trace element analysis including REEs in biological samples [6-8], the Eu analysis by ICP-AES has been reported only in non-biological samples [9-12]. Our results of wide linear calibration dynamic range of <10-500 μg/L (with DL and QL <10 μg/L) and satisfactory recovery of spiked Eu from rat urine matrix (94.2±102.3%) with good reproducibility (% CVs of 0.65±1.04%) indicate that ICP-AES can be applied for Eu determination in biological samples.

Thus, it can be concluded that the established Eu analysis method in this technical note is satisfactory for measuring trace Eu in biological samples and will be useful for animal experiment, health screening for people at the risk of Eu exposure from the environment and occupational condition.

REFERENCES