Rare Earth Elements in Human Blood Serum as Determined by Inductively Coupled Plasma Mass Spectrometry

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The multielement determination of all rare earth elements in human blood serum by inductively coupled plasma mass spectrometry has been studied, where the blood serum sample was digested with nitric acid and perchloric acid, and then rare earth elements were preconcentrated by using the chelating resin prior to the determination. It was found that the concentrations of rare earth elements in human blood serum were at the ppt (10^{-12} g/ml) level.

In the previous paper,[1] we reported the determination of all rare earth elements (REEs) in human blood serum reference material (NIES No.4) issued from the National Institute for Environmental Studies (NIES), where ICP-MS (inductively coupled plasma mass spectrometry) was used for simultaneous multielement determination of REEs. In the study, the human blood serum sample was digested only with HNO_3, where the recoveries of REEs were in the range of 60-80%.[1] Thereafter, the digestion of blood serum was further investigated to obtain the improved recoveries of REEs, and it has been found that the more complete decomposition of the blood serum sample with use of both HNO_3 and $HClO_4$ provides the improved recoveries of REEs. Hence, the further study on the determination of all REEs in the human blood serum sample is reported in the present paper.

The human blood serum reference material (ca. 0.8 g), which was a freeze-dried sample, was put in a Teflon beaker, and 6 ml of conc. HNO_3 was added into it. After standing the solution overnight, the solution was heated at 100 °C for 6 h on a hot plate. Furthermore, 2 ml of conc. HNO_3 was added and heated at 150 °C for 2 h. After adding 2 ml of conc. HNO_3 and 1 ml of conc. $HClO_4$, the solution was heated again at 150 °C for 4 h almost to dryness until white fume appeared. This procedure was repeated 2-times. Finally, 0.76 ml of conc. HNO_3 and ca. 1 ml of pure water was added and heated at 110 °C for 1 h. Then, the final solution was diluted to 100 g with pure water, which was provided to the analysis solution in the following experiment. In the case of human blood serum, 10 ml of the blood serum sample was taken for analysis, and the same procedure mentioned above was performed for digestion.

In the chelating resin preconcentration of REEs, ca. 90 g of the analysis solution was first diluted to 300 ml with pure water. After adjusting to pH 6, 0.5 g of the chelating resin (Chelex 100 from Bio-Rad Laboratories, Richmond, CA, USA) was added to the solution, and it was stirred for 3 h. The chelating resin was collected on a glass filter. The resin was then rinsed with 10 ml of the 2 M ammonium acetate solution to reduce alkaline earth elements (Mg and Ca), which were partly adsorbed on the resin. Finally, REEs on the resin were eluted with 10 ml of 2 M HNO_3. The eluted solution was once evaporated to dryness in the evaporation chamber,[2] and the residue was dissolved with 2 ml of 0.1 M HNO_3, which contained the internal standard elements (10 ng/ml each of Rh and Re).

Table 1. Detection limits and blank values of REEs obtained by chelating resin preconcentraion and ICP-MS

Element	m/z	Detection limit	Blank value
La	139	0.1 pg/ml	14 pg/ml
Ce	140	0.2	28
Pr	141	0.1	3.1
Nd	146	0.5	10
Sm	147	0.6	3.1
Eu	151	0.2	<0.7
Gd	157	0.9	3
Tb	159	0.1	0.4
Dy	163	0.3	2.2
Ho	165	0.08	0.6
Er	166	0.2	1.8
Tm	169	0.08	0.4
Yb	174	0.4	1.9
Lu	175	0.07	0.5

The ICP-MS instrument of model SPQ 8000A from Seiko Instrument Co. (Tokyo) was used for the determination of REEs. The operating conditions of the ICP-MS instrument were almost similar to those in the previous paper.[1] The detection limits and blank values of REEs obtained by chelating resin preconcentration and ICP-MS are shown in Table 1.

The analytical results for REEs in the human blood serum reference material (NIES No.4) obtained in the present and previous works are summarized in Table 2, together with the recovery values. As is seen in Table 2, the recovery values of REEs in the chelating resin preconcentration were markedly improved in the present work, compared to those in the previous work.[1] Furthermore, it should be noted here that the recovery values for light REEs (La~Gd) are in general better than those for heavy REEs (Tb~Lu) in both of the two experiments. These results suggest that the residual organic compounds remained in the digested analysis solution, which may be amino acids and peptides produced after incomplete decomposition of blood serum proteins, influence the recovery values of REEs. It is also seen in Table 2 that the lower analytical values, except for Sm, Tm and Lu, were obtained in the present work rather than in the previous work. This may be attributed to the better recovery values obtained in the present work.

In Table 2, the concentrations of rare earth elements in human blood serum are shown on the personal basis for three persons (male). The observed value for Eu in human blood serum samples for all three persons was not obtained because of its too low concentration. It should be noticed here that the concentrations of rare earth elements in human blood serum were significantly lower than those in human blood serum

Table 2. Analytical results for REEs in human blood serum samples

Element	Human blood serum reference material (NIES No.4)				Human blood serum		
	Present work		Previous work [a]		Concentration		
	Concentration	Recovery [b]	Concentration	Recovery [b]	A	B	C
La	131 ±13 pg/ml	94.7±5.1 %	206 ±20 pg/ml	81.3±2.7 %	36.5 pg/ml	17.6 pg/ml	29.5 pg/ml
Ce	319 ±29	93.5±6.3	440 ±72	79.6±3.5	170	99	108
Pr	27.3± 3.0	88.1±2.4	42.3± 5.2	79.7±2.4	6.5	2.9	4.5
Nd	123 ±17	86.6±2.1	171 ±18	79.6±3.0	19.8	11.0	13.4
Sm	38.3± 3.4	84.1±2.7	35.9± 2.5	74.3±2.5	2.7	<1.0	<2.0
Eu	2.1[c]	85.0±2.2	3.1[c]	74.4±1.7	<0.2	<0.2	<0.2
Gd	28.0± 1.5	92.8±1.9	46.5± 1	73.4±0.8	<3.0	3.9	<3.0
Tb	6.6± 0.9	87.7±2.2	7.3 ± 0.8	74.2±1.2	0.5	0.5	0.8
Dy	33.6± 3.9	84.4±1.9	43.2± 6.2	75.0±0.7	5.2	3.1	2.0
Ho	6.3± 1.2	87.4±2.6	10.2± 0.6	73.6±0.9	1.0	0.8	0.4
Er	22.2± 2.7	85.4±2.1	31.2± 1.8	73.8±1.9	4.6	4.5	1.3
Tm	5.2± 1.4	85.8±1.4	5.1 ± 0.4	72.1±1.0	0.8	0.7	0.2
Yb	26.2± 2.8	84.3±2.0	44.7± 8.7	70.5±2.0	6.0	4.6	1.5
Lu	5.9± 1.6	83.7±1.1	5.6	67.2±2.5	0.8	0.9	0.2

[a] Cited from reference 1.

[b] Relative standard deviation of 3-times measurements (n = 3).

[c] Mean value of 2-times measurements.

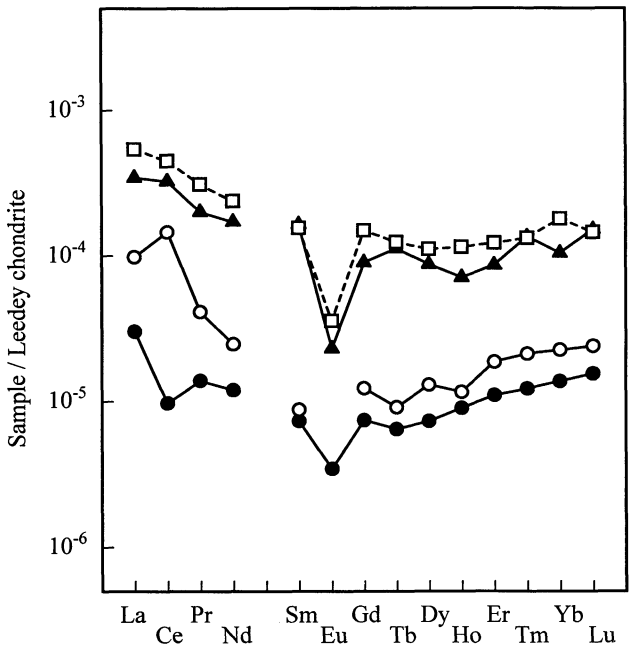

Figure 1. Rare earth element distribution patterns for human blood serum and seawater.

—○— human blood serum (mean values for 3 persons).
—▲— human blood serum reference material (present).
···□··· human blood serum reference material (Ref.1).
—●— coastal seawater (Ref.4).

reference material (NIES No.4). The determination of rare earth elements at such lower concentration level was possible because more complete sample decomposition and larger preconcentration factor were obtained in the present work, compared to those in the previous one.[1]

In Figure 1, the rare earth element distribution patterns are shown in terms of human blood serum, where the concentrations of rare earth elements were normalized by those in Leedey chondrite.[3] In Figure 1, the pattern for coastal seawater [4] is also shown for comparison. As is seen in Figure 1, human blood serum and seawater provide the similar REEs patterns, although the concentrations of rare earth elements are higher in the former than in the latter. It should be stressed here that only Eu anomaly is observed in the case of blood serum, while both Ce and Eu anomalies are observed in the case of seawater.

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