On-line Preconcentration of Rare Earth Element by FIA-ICP-AES

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A mini-column filled with Dowex 50x8 resin is developed and investigated for the analysis of trace level of rare earth element by ICP-AES. The column is installed between peristaltic pump and ICP-AES, and ng/ml level of rare earth element is analyzed directly by on-line FIA-ICP-AES. 6N hydrochloric acid is found to be an optimum concentration for stripping, and the optimum flow rates for loading and stripping are measured at 0.8 and 1.1 ml/min, respectively. Easily ionized elements from flux such as Na and K would be eliminated easily by 2N hydrochloric acid before stripping the rare earth element deposited on the resin. For an analysis of Sm, the absolute detection limit and linearity are found to be 0.9999, respectively. Less than 4% of reproducibility is observed for the analysis of Sm and Nd. The analytical result with NIST SRM 1633B is also found to be 20.3 ng/ml, which agrees well with the certified value.

Keywords ICP-AES, Flow injection analysis, Resin, Rare earth element

Rare earth elements (REEs) are widely used in electronic industry and optical glass industry. According to the development on the semiconductor and electronic industries, the more accurate and precise analytical methods for the analysis of trace element of rare earth elements are required. The analytical techniques developed for rare earth elements have to be sensitive and fast. In addition, rare earth elements in geological and environmental samples are very important to be analyzed.

In general, NAA (Neutron Activation Analysis), ID-MS (Isotope Dilution Mass Spectrometry), AAS (Atomic Absorption Spectrometry), and ICP-AES/MS (Inductively Coupled Plasma-Atomic Emission Spectrometer / Mass Spectrometer) have been used for analysis of rare earth elements. NAA1 is known to be sensitive technique, but it takes a long time and needs certain sample pretreatment to eliminate elements causing severe spectral interference2. Pr, Tb, Ho, and Tm could not be analyzed by ID-MS3 because those elements do not have isotope. Most of rare earth elements could be analyzed by AAS4,6 although AAS doesn't provide the sufficient sensitivity. ICP-AES/MS7,8 is known to be sensitive enough to analyze the trace level of rare earth element in various kinds of samples. Also it has several advantages such as a wide dynamic range, less interference effect, and ability to detect elements simultaneously as well as sequentially.

In general, the concentration level of rare earth element in sample is often found to be less than ng/ml. In this case, it is almost impossible to detect the ultra trace level of rare earth element directly by ICP-AES. Therefore, sample pretreatment is required to not only preconcentrate the ultra trace level of elements but also eliminate interference species. Flow injection analysis has been utilized for this purpose.

In this study, the simple and fast on-line preconcentration system for rare earth elements by ICP-AES are developed, and its analytical characteristics has been investigated. The trace levels of Sm and Nd are preconcentrated by on-line columns filled with cation exchange resin, anion exchange resin, or silica immobilized 8-hydroxyquinoline. The analytical performances for the columns are compared and reported.

Experimental

FIA used in this study consists of sample injection
port, peristaltic pump, and ion exchange column. Sample solution is injected into 10 port injection valve (VIVI Valco, USA) and 4-channel peristaltic pump (Gilson Miniplus 2, USA) is used to transfer sample solution. 1/16 inch O.D. of PTFE tubing is used for delivering sample solution. 1/4 inch O.D. and 5 cm length of PTFE tubing is filled with anion exchange resin, cation exchange resin, or silica immobilized 8-hydroxyquinoline. In order to eliminate the impurities, Dowex 1x8 and Dowex 50x8 are cleaned for 5 min. by Ultrasonic Cleaner, and washed by 2.0M nitric acid. 18 MΩ/cm of deionized water is obtained by using the water purification system (Barnstead Co., USA) and all acids are purified by sub-boiling system.

Inductively coupled plasma - Atomic Emission Spectrometer used in this study is built in our laboratory. The specification of ICP-AES is listed in Table 1. The optimized operating conditions of ICP-AES and FIA are also listed in Table 2.

Table 1. Specification of the FI-ICP-AES system

<table>
<thead>
<tr>
<th>Instruments</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>RF Power Supply</td>
<td>RFP 1CP16L</td>
</tr>
<tr>
<td>Monochromator</td>
<td>Spex 1000M</td>
</tr>
<tr>
<td>Focal Length</td>
<td>1.0 m</td>
</tr>
<tr>
<td>1800 grooves/mm</td>
<td>f-number 7.8</td>
</tr>
<tr>
<td>PWT</td>
<td>Hamamatsu R928</td>
</tr>
<tr>
<td>DAC/ADC Data acquisition</td>
<td>PCLAB-812PG (Advantech Ltd.)</td>
</tr>
<tr>
<td>10 Port Injection Valve</td>
<td>Valco. VMQ001</td>
</tr>
<tr>
<td>Peristaltic Pump</td>
<td>Gilson. Miniplus 2, 3</td>
</tr>
<tr>
<td>Computer</td>
<td>IBM-PC comparable</td>
</tr>
</tbody>
</table>

Table 2. Optimized operation conditions for ICP-AES

<table>
<thead>
<tr>
<th>Variables</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Coolant Argon Flow Rate</td>
<td>14 L/min</td>
</tr>
<tr>
<td>Nebulizer Gas Pressure</td>
<td>18 psi</td>
</tr>
<tr>
<td>RF Incident Power</td>
<td>1.0 kW</td>
</tr>
<tr>
<td>RF Reflected Power</td>
<td>&lt; 2 W</td>
</tr>
<tr>
<td>Nebulizer</td>
<td>Meinhard</td>
</tr>
<tr>
<td>Concentric</td>
<td></td>
</tr>
<tr>
<td>Observation Height above Load Coi</td>
<td>12 mm</td>
</tr>
</tbody>
</table>

As shown in Fig. 1, the mini-column of 1/4 inch-O.D. and 4 cm-length filled with ion exchangers is installed between 10 port injection valve and ICP torch. At first, an analytical sample is carried by deionized water and loaded in loop of 10 port injection valve. Consequently, the sample is loaded into analytical column for a preconcentration by switching from injection mode to loading mode as shown in Fig. 1.

![Fig. 1 Procedure of flow injection](image)

Results and Discussions

The Choice of Column

In this study, three kinds of analytical columns filled with Dowex 1x8, Dowex 50x8, and silica immobilized 8-hydroxyquinoline are tested for preconcentration of rare earth element. Firstly, 1 ppm Sm solution is loaded into column filled with Dowex 1x8 resin. And the mixed solution of acetic acid and nitric acid is used as a stripping solution. However, the reproducibility of preconcentration is less than 15%. Therefore, it is concluded that Dowex 1x8 resin is not adequate to preconcentrate rare earth element on line in ICP-AES. As same as the Dowex 1x8 resin, the 44.4% of recovery yield is observed by using silica immobilized 8-hydroxyquinoline. Contrary to the Dowex 1x8 resin and silica immobilized 8-hydroxyquinoline, 5% of reproducibility and 99% of recovery yield are obtained by using Dowex 50x8 resin. Throughout
the experiment, the Dowex 50x8 resin has been used to carry out a preconcentration of rare earth element.

**The Effect of HCl Concentration**

As expected, the distribution coefficients of rare earth elements in column are dependent on concentration of hydrochloric acid. According to Fig. 2, as the concentration of hydrochloric acid is increased from 1 to 6N, the observed emission intensity of Sm is rapidly increased. However, above 6N hydrochloric acid could not be used because of degradation of resin itself. Throughout the experiment, 6N hydrochloric acid is used as a stripping solution.

![Fig. 2 The effect on HCl concentration](image)

**The Effect of loading and stripping Solution Flow Rates**

In general, the slower the flow rate of sample loading solution, the more preconcentration. As shown in Fig. 3, as the flow rate of loading solution is decreased from 1.5 to 0.8 ml/min, the emission intensity is increased indicating more preconcentration at low flow rate of sample loading solution. When the flow rate is less than 0.8 ml/min, peak-broadening effect is dominant. The optimized flow rate of sample loading solution is found to be 0.8 ml/min. And the optimum flow rate of stripping solution is found to be 1.1 ml/min.

![Fig. 3 The effect on loading flow rate](image)

**Elimination of Easily Ionized Element**

The analytical samples including rare earth elements such as rocks, soils, and refractory samples, which are very hard to dissolve into liquid. In this case, the samples are usually dissolved by the method of alkali fusion. Due to the nature of flux such as Na₂CO₃ and K₂CO₃ added into analytical samples during sample preparation, the spectral and ionization interferences are expected when the sample solution is introduced directly into plasma.

Before stripping the deposited rare earth element by 6N hydrochloric acid, 2N hydrochloric acid has been used to eliminate easily ionized element such as K and Na. When 2N hydrochloric acid is introduced into column, the flow direction of hydrochloric acid is opposite to that of 6N hydrochloric acid for stripping. Otherwise the peak broadening is observed. As shown in Fig. 4, when the flow rate of 2N hydrochloric acid is 1.33 ml/min, K contaminated from flux is almost eliminated.

![Fig. 4 Removal of K by 2N HCl](image)

**Preconcentration of Sm and Nd**

2 ml, 4ml, and 6ml of 10 μg/ml Sm standard solution is injected and preconcentrated by minicolumn containing Dowex 50x8 resin. As shown in Fig. 5, the emission intensity of 100 μg/ml Sm introduced by concentric nebulizer continuously is
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about the same as that of 6 ml of 10 μg/ml Sm preconcentrated by the mini-column.

The reproducibility is found to be less than 4%. In Fig. 6, standard calibration curve is shown, and absolute detection limit and linearity are found to be and 0.9999, respectively. Fig. 7 illustrates the preconcentration of 2 and 4ml of 1 μg/ml-Nd solution. The emission intensities for 2 % HCl and 1 μg/ml of Nd solution introduced by concentric nebulizer are also shown in Fig. 7.

Fig. 6 Sm calibration curve

Analysis of NIST SRM

Sm in coal fly ash of NIST SRM 1633B is analyzed by on-line FIA-ICP-AES described above. The certified value of Sm in NIST SRM 1633B is originally 20 μg/ml, and then dissolved to the liquid with a final concentration of 20 ng/ml of Sm. 12 ml of dissolved solution of NIST SRM 1633B is loaded into mini-column, and stripped by 6N hydrochloric acid followed by 2N hydrochloric acid for elimination of easily ionized element. As shown in Fig. 8, 10 ng/ml of Sm standard solution is also injected to the mini-column, and the measured value is found to be 20.3 ng/ml.

In this study, the simple flow injection method for the analysis of a small amount of Sm with ng/ml level of concentration is constructed and characterized. A ng/ml level of rare earth element is analyzed directly by on-line FIA-ICP-AES. Dowex 50x8 resin is used for this purpose and the mini-column with the resin is installed between peristaltic pump and ICP-AES.

Fig. 6 Sm calibration curve

6N hydrochloric acid is found to be an optimum concentration for stripping, and the optimum flow rates for loading and stripping are measured at 0.8 and 1.1 ml/min, respectively. Easily ionized elements added in a process of fusion are also eliminated easily by 2N hydrochloric acid.

For an analysis of Sm, the absolute detection limit and linearity are found to be and 0.9999, respectively. Less than 4% of reproducibility is observed for the analysis of Sm and Nd. The analytical result with NIST SRM 1633B is also found to be 20.3 ng/ml and the concentration obtained agrees well with the certified value of 20 ng/ml. The further investigation has been doing in order to improve the analytical performances.

References