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# Development of an automatic pH-adjustment system for solid phase extraction prior to the determination of REEs in seawater by ICP-MS

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An automatic pH adjustment instrument was developed for solid phase extraction (SPE) of rare earth elements (REEs) using chelating resins. The automation of pH adjustment was carried out by using a spectrometer, an input/output (I/O) board, an automatic-switching valve, and a personal computer with LabVIEW® programming platform. Contactless monitoring of the pH was carried out by measuring the intensity of transmitted light at 550 nm that passed through a sample solution with an added pH-indicator, *i.e.* methyl red. A reagent for adjusting the pH, *i.e.* an aqueous ammonia solution, was sprayed into the sample solution using a nebuliser, which permitted the addition of a small amount of the reagent and the precise adjustment of the pH. The pH value of the sample was monitored by measuring the intensity of the transmitted light using the spectrometer, while the open-time of the valve to add the reagent was automatically controlled simultaneously with the measurement of the transmitted light. The precision of the pH adjustment was tested and confirmed by using a seawater sample. The blank values and detection limits of REEs were given as the analytical figures of merits. The usefulness of the present method was confirmed by analysing seawater samples from the Nikkawa Beach, the Kashima Bay, and the Ishigaki Island. The results of REEs in these samples were discussed with shale normalised REE distribution pattern.

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## Introduction

As defined by the International Union of Pure and Applied Chemistry (IUPAC), rare earth metals include the fifteen lanthanoids and other two chemically similar elements Sc and Y.[1] The synonym of rare earth metals, *i.e.* rare earth elements (REEs) are used in the present work. The present targeting REEs are, however, the 14 lanthanoids elements with exception of Pm all of whose isotopes are radioactive.

Due to their similar chemical and physical properties, the geochemical activities of REEs are generally similar to one another, which could be attributed to the fact that the electronic configurations of the REEs result in a particular trivalent positive oxidation state. On the other hand, fractionation of REEs occurred during the geochemical evolution, owing to the fact that the ionic radii of the REEs decrease slightly but steadily with the increase in atomic number for a given co-ordination number.[2] As a result, the distribution pattern of REEs is a good tracer for the source of a sample and a sensitive indicator of the environment. The REEs in seawater could serve as water-mass tracers to evaluate the marine geochemical cycle,[3] an objective of elemental budgets of the ocean,[4] and a bio-record for depositional environment.[5] The researches on REEs in seawater were also attractive along with Nd isotopes, which are a set of key trace elements and isotopes (TEIs) of the global GEOTRACES programme.[6,7] On the other hand, a Gd anomaly observed based on the distribution pattern of REEs was investigated as an indicator of anthropogenic impact on seawater and river water.[8–15]

Nowadays, inductively coupled plasma mass spectrometry (ICP-MS) is one of the most popular methods for elemental analysis.[16–19] Despite the fact that some modification of the introduction system could permit the direct introduction of a seawater sample into an ICP-MS instrument,[20–22] direct determination of REEs in most seawater samples is difficult because of their extremely low concentrations, which are generally at lower pg $mL^{-1}$ to fg $mL^{-1}$ level.

Solid phase extraction (SPE) techniques using chelating resins are often applied as the pretreatment of seawater samples to determine REEs,[23–42] with both purposes to remove the salt contents and to enrich the REEs in the samples. In SPE using chelating resins, the recoveries of REEs depend on the pH condition for adsorption. In most of the cases, the adsorption of REEs to the chelating resins was carried out at a neutral condition close to pH 6.[23,26–29,31,34–36,39,41,42] This fact could be explained by the adsorption of REEs to the chelating functional

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groups being stable only in a narrow pH range, with neither significant competition between $H^+$ and REE ions nor significant competition between $OH^-$ and chelating functional groups. Therefore, pH adjustment is an important step in SPE operations to ensure the recovery of REEs and the reproducibility of the results.

To the best of the present authors' knowledge, up to date, there is not an automatic pH adjustment instrument for preconcentration of REEs or other trace elements by SPE. In the present work, an automatic pH adjustment instrument was developed. Contactless monitoring of the sample pH was carried out by measuring the light intensity at the wavelength of the characteristic absorption of the pH indicator. The adjustment of the sample pH was performed by adding an aqueous ammonia solution into the sample using a nebuliser, which is usually used in ICP-MS. Controlling the quantity of the aqueous ammonia solution added into the sample was carried out by an electromagnetic valve. The usefulness of the present instrument was confirmed by analysing REEs in seawater samples.

## Experimental

### Instrumentation

An Agilent 7700x (Agilent Technologies) ICP-MS instrument was applied to the measurements of the REEs. The typical operating conditions for the ICP-MS are summarised in Table 1. Syringe driven chelating columns (SDCCs, NOBIAS CHELATE-PB1M) were purchased from Hitachi High-Technologies Corp. (Tokyo, Japan) and applied to the solid phase extraction of REEs from seawater samples. Measurements of the REEs were carried out using an automatic column changing system[29] after adsorption of REEs to the SDCCs, where an inert type liquid chromatography pump (LC-10Ai, Shimadzu Corp., Tokyo, Japan) was applied to passing 2 mol $L^{-1}$ $HNO_3$ through the SDCCs to elute REEs.

**Table 1** Typical operating conditions of ICP-MS instrument

| | |
|---|---|
| **Plasma conditions** | |
| Incident power | 1.55 kW |
| Coolant gas flow rate | Ar 15.0 L $min^{-1}$ |
| Auxiliary gas flow rate | Ar 0.90 L $min^{-1}$ |
| Sample gas flow rate | Ar 0.80 L $min^{-1}$ |
| Make-up gas flow rate | Ar 0.40 L $min^{-1}$ |
| Dilution gas mode | Off |
| Collision gas flow rate | He 3.00 mL $min^{-1}$ |
| **Sampling conditions** | |
| Sampling depth | 8 mm from load coil |
| **Nebuliser: MicroMist** | |
| Sample uptake rate | 1.0 mL $min^{-1}$(plunger pump) |
| **Spray chamber: Scott double path** | |
| Wall temperature | 2 °C |
| **Data acquisition** | |
| Peak pattern | Time resolved analysis |
| Data points | 1 point per peak |
| Integration time | 20 ms |

A tungsten halogen light source (LS-1-LL), a spectrometer (USB2000 + VIS-NIR), and a pair of optical fibres were purchased from Ocean Optics, Inc. (Dunedin, FL, USA), to construct the contactless pH monitoring system. An I/O board (NI USB-6009, National Instruments Japan Corp., Tokyo, Japan), an electromagnetic valve (LS067A040, ASCO Japan Co. Ltd, Tokyo, Japan), and a MicroMist nebuliser (Glass Expansion, West Melbourne Vic, Australia) were utilised to construct the aqueous ammonia solution injection system. A digital mass flow controller (SEC-500, HORIBA Ltd, Kyoto, Japan) was applied to the control of carrier gas for the nebuliser used in the aqueous ammonia solution injection system. A magnetic stirrer (lab disc white, IKA® Japan K.K., Osaka, Japan) and a Teflon coated stirring bar were used to homogenise the sample solution during pH adjustment. A pH meter (SevenEasy, METTLER TOLEDO, Tokyo, Japan) with an Inlab® 410 pH electrode (glass) was used to monitor the pH of the sample. An all-plastic pH electrode (AMANI-650, Warner Instruments, Hamden, CT, USA) was used, in comparison to the glass electrode, to check the blank values of REEs when an electrode was used.

### Chemicals and materials

Ultrapure grade nitric acid, acetic acid and an aqueous ammonia solution were purchased from Kanto Chemicals (Tokyo, Japan). Single REE standard solutions (1000 mg $L^{-1}$ each, for atomic absorbance spectrochemical analysis) for making the working calibration curves were purchased from Wako Pure Chemicals (Osaka, Japan). A standard solution of Ba was also purchased from Wako Pure Chemicals and was properly diluted followed by the analysis to check the polyatomic interference with Eu. Methyl red and ethanol were purchased from Wako Pure Chemicals to prepare a 1 mg $mL^{-1}$ methyl red solution in ethanol, which was used as the pH indicator.

A coastal seawater sample collected near the shore of the Nikkawa Beach (Kamisu, Ibaraki, Japan) was used for optimising the experimental conditions and to check the usefulness of the present instrument. Coastal seawater samples collected respectively from the Kashima Bay (Kashima, Ibaraki, Japan) and the Ishigaki Island (Ishigaki, Okinawa, Japan) were also analysed as the application of the present method. The seawater samples were filtered with a membrane filter (pore size 0.45 μm, Nihon Millipore Kogyo, Tokyo, Japan) immediately after sampling and acidified to approximately pH 1.0 with nitric acid. All bottles, test tubes and pipette tips used in the present experiment were soaked in 3 mol $L^{-1}$ nitric acid for a week and then rinsed three times with pure water, except for the transparent polyethylene terephthalate (PET) bottles, which were confirmed free of REE contaminations in advance. Pure water used throughout the present experiment was prepared by a Milli-Q purification system of model Element A-10 (Nihon Millipore Kogyo).

### Construction of the automatic pH adjustment system and the flow chart of the controlling programme

The construction of the pH adjustment instrument is illustrated in Fig. 1. As can be seen in Fig. 1, the sample (2) was stirred by a

 

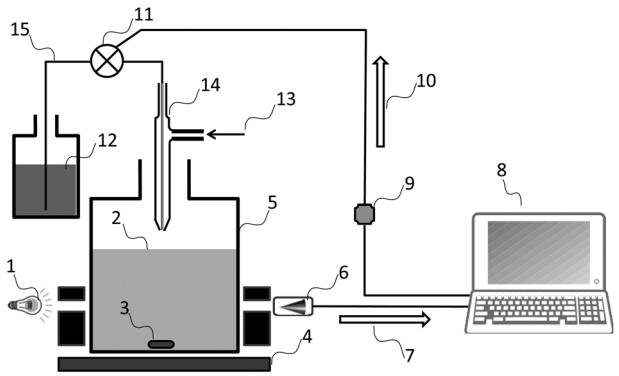


**Fig. 1** Construction of the pH adjustment instrument. (1) Light source; (2) sample; (3) stirring bar; (4) magnetic stirrer; (5) polypropylene sample bottle (transparent); (6) spectrometer; (7) transmitted light signal; (8) controlling computer; (9) I/O board; (10) open/close signal to the valve; (11) electromagnetic valve; (12) a 28% aqueous ammonia solution; (13) $N_2$ gas; 14, nebuliser; (15) nebuliser tube.

magnetic stirrer (4) with a stirring bar (3). The light passed through the sample was monitored by the spectrometer (6). Based on the signal intensity of the transmitted light (7), open/close signals (10) were sent to the electromagnetic valve (11). An aqueous ammonia solution (12) was added into the sample through the nebuliser (14) with the assistance of $N_2$ gas and the control of the electromagnetic valve (11). Measurement of the transmitted light and generation of open/close signals for the electromagnetic valve were carried out with a laboratory made programme based on LabVIEW® system design software. The flow chart of the programme for the present pH adjustment system is shown in Fig. 2. As seen from Fig. 2, the signal intensity of the transmitted light ($I_i$) was always monitored during the adjustment procedure. Based on the comparison of the $I_i$ with the objective signal intensity ($I_o$), the waiting time ($t$) and the valve position were automatically controlled. When the value of $I_i$ was larger than $I_o$, the counting number ($n$) increased by one until the value of $n$ reached five and the adjustment procedure ended. A typical adjustment time for 100 mL of seawater in 0.1 mol $L^{-1}$ $HNO_3$ was approximately five minutes, where 0.5 mL of acetic acid and 0.1 mL of the methyl red solution were added into the sample prior to the adjustment. The adjustment could be carried out in less than one minute by adding a proper amount of a 28% aqueous ammonia solution prior to the adjustment. The present system could be applied to the pretreatment of a sample volume from 20 mL to 100 mL.

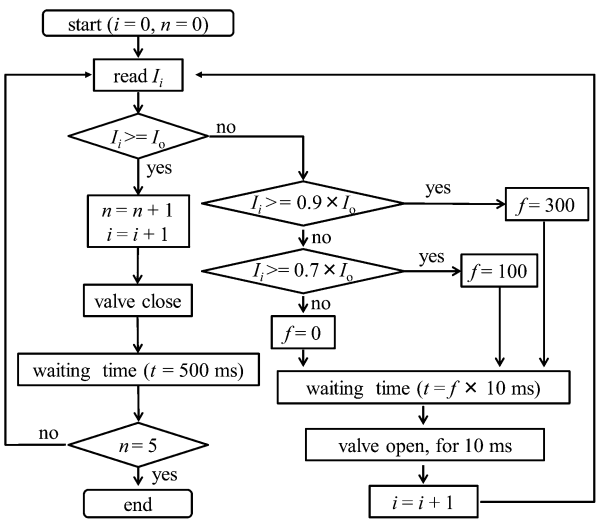


**Fig. 2** Flow chart of the controlling programme for the pH adjustment system. $I_i$ and $I_o$, the monitored and the objective signal intensities of the transmitted light.

### Procedures of SPE for measuring REEs in seawater

The SDCCs used for SPE were preserved in pure water after passing through 5 mL of 1 mol $L^{-1}$ ammonium acetate. Prior to loading the samples, 5 mL each of 3 mol $L^{-1}$ $HNO_3$ and pure water were passed through the SDCCs in succession for washing. After being adjusted to pH 6.0 using the pH adjustment system, each sample (50 mL) was loaded into one of the SDCCs using an all-plastic syringe at the flow rate of 5 mL $min^{-1}$. Loading of the sample to the SDCC was carried out with the assistance of a laboratory made multi-syringe pump. After loading the sample, 5 mL of pure water was passed through the SDCC to remove the residual seawater. Finally, the REEs adsorbed in the SDCC were eluted with approximately 0.4 mL of 2 mol $L^{-1}$ $HNO_3$ at the flow rate of 1 mL $min^{-1}$ and measured on-line with the ICP-MS, where the on-line measurements were carried out with the assist of an automatic column changing system.[29]

## Results and discussion

### Absorbance characteristics of the methyl red reagent

Taking into consideration the fact that the maximum recoveries for REEs by SPE using chelating resins were obtained around pH 6, the objective pH condition in the present work was set as pH 6.0. In order to avoid the contamination by inserting the pH electrode into the sample, monitoring of the pH was carried out by measuring the signal intensities of the transmitted light through the sample. Methyl red is a well known pH indicator, which changes the colour from red to yellow along with the pH change from 4 to 6. The usefulness of methyl red as the pH indicator for the present purpose was confirmed by measuring the signal intensity at the wavelength from 350 nm to 1000 nm to investigate the characteristic absorbance. The tests were carried out using 100 mL of seawater sample in 0.1 mol $L^{-1}$ $HNO_3$, into which 0.5 mL of acetic acid was added.

The spectrograms of the transmitted light passed through the samples are plotted in Fig. 3. As can be seen from Fig. 3, the spectrogram obtained with methyl red (dotted line) at alkaline condition was close to that obtained without methyl red (solid line) with slight absorbance around 450 nm. By contrast, the spectrogram obtained with methyl red at acidic condition showed significant absorbance in the range of 450 nm to 600 nm with the maximum absorbance at *ca.* 550 nm. These results indicate that the variation of the pH of the sample could be sensitively monitored by measuring the transmitted light at *ca.*

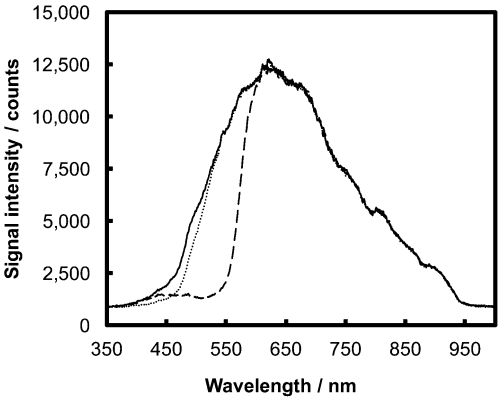


**Fig. 3** Spectrograms of the transmitted light through the sample. Solid line, without addition of methyl red; dashed line, with methyl red, pH 1.0; dotted line, with methyl red, pH 8.0.

550 nm. Therefore, the signal intensity of the transmitted light at 550 nm was monitored for the purpose of pH adjustment.

### Correlation between the signal intensity of the transmitted light at 550 nm and the pH of the sample

The correlation between the signal intensity of the transmitted light and the pH of the sample was investigated using 100 mL of a seawater sample in 0.1 mol $L^{-1}$ $HNO_3$, into which 0.1 mL of 1 mg $mL^{-1}$ methyl red and 0.5 mL of acetic acid were added. The pH of the sample was measured by the pH meter and was elevated by gradual addition of an aqueous ammonia solution; the signal intensity of the transmitted light at 550 nm was recorded for 17 points from approximately pH 0.7 to pH 8.2. The results are plotted in Fig. 4. These results indicate that there is a definite correlation between the signal intensity of the transmitted light and the pH of sample in the range between 4.7 and 6.4. Therefore, in the following experiments the objective signal intensity of the transmitted light at 550 nm was set as 5700 counts, corresponding to pH 6.0. Furthermore, the maximum signal intensity of the present light source was observed at 622 nm. In order to achieve a stable pH, the sample bottles were set to the automatic pH adjustment instrument and it was ensured that the signal intensity of the transmitted light at 622 nm was 12 600 counts.

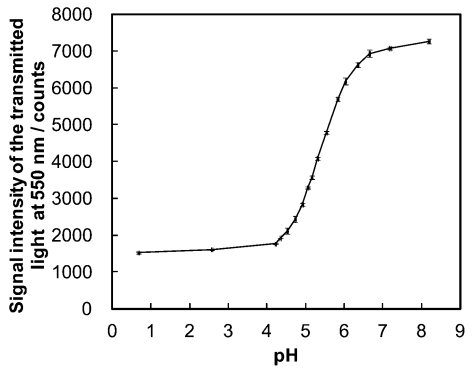


**Fig. 4** Correlation between the signal intensity of the transmitted light at 550 nm and the pH of the sample. Sample, 100 mL seawater; methyl red, 0.1 mL; bar, standard deviation of the average value of each point, $n = 3$.

### Operating conditions of the nebuliser and reproducibility of the pH obtained with the present instrument

The nebuliser for the addition of the aqueous ammonia solution was working at a flow rate of approximately 0.4 mL $min^{-1}$ using 0.80 L $min^{-1}$ $N_2$ as the carrier gas, which was optimized to get the highest flow rate of the aqueous ammonia solution. The time used for adjustment of the pH of a sample was recorded by the controlling programme, so that the consumed volume of the aqueous ammonia solution could be calculated.

In order to check the reproducibility of the pH obtained by the present instrument, 10 seawater samples were subjected to the pH adjustment. The pH values of the samples after pH adjustment were 5.9 (2 samples), 6.0 (4 samples), 6.1 (4 samples), respectively. These results indicate that pH adjustment using the present instrument was reproducible, which permitted a reproducible SPE operation for REEs' measurements in seawater to be obtained.

### Blank values in comparison with those obtained with the assist of pH electrodes

In the present work, contactless pH monitoring was carried out by measuring the signal intensity of the transmitted light at 550 nm with methyl red as the pH indicator. Contamination from pH measurement was expected to be much lower than that obtained with the assist of a pH electrode.

Blank tests were carried out using 0.1 mol $L^{-1}$ of $HNO_3$ solutions as the test samples. The pH adjustments were carried out by the present pH adjustment instrument, with the assist of a glass electrode, and with the assist of a plastic electrode. The SPE operations and the measurements were carried out in a similar way to the seawater samples. The results of the blank tests are summarised in Table 2.

It can be seen from Table 2 that the blank values obtained by the present method were in the range from 0.13 fg $mL^{-1}$ of Tm to 34.1 fg $mL^{-1}$ of Ce, which are adequately low for the measurement of REEs in natural seawater samples. By contrast, the blank values obtained with the assist of the glass electrode and the plastic one were in the ranges from 4.0 fg $mL^{-1}$ of Tm to 5750 fg $mL^{-1}$ of Ce and 1.9 fg $mL^{-1}$ of Tm to 422 000 fg $mL^{-1}$ of La, respectively. The blank value for each REE obtained with the present method was significantly lower than those obtained with the assist of the pH electrodes. These results confirmed that the contaminations of REEs were effectively controlled in the present method, which could be attributed to the fact that the methyl red reagent was almost free of REEs. Higher blank values of REEs on glass and plastic electrodes might be attributed to the electrolytes used in the electrodes.

### Analytical results of REEs in a seawater samples

The present method was applied to the analysis of REEs in coastal seawater samples collected from the Nikkawa Beach, the Kashima Bay, and the Ishigaki Island. The recovery values of REEs by the present method were tested by adding a mixed

 

**Table 2** Blank values obtained with the present method in comparison with those obtained with the assist of pH electrodes

| | | Blank value[a]/fg mL$^{-1}$ | | |
|---|---|---|---|---|
| Element | *m*/*z* | Present method[b] | Glass electrode | Plastic electrode |
| La | 139 | *25.2 ± 9.8* | 4220 ± 110 | 422 000 ± 2400 |
| Ce | 140 | *34.1 ± 13.4* | 5750 ± 120 | 1020 ± 20 |
| Pr | 141 | *3.01 ± 1.38* | 431 ± 13 | 28.9 ± 1.5 |
| Nd | 146 | *10.1 ± 4.5* | 1180 ± 30 | 94.1 ± 0.8 |
| Sm | 147 | *2.56 ± 1.56* | 53.2 ± 4.5 | 21.9 ± 3.9 |
| Eu | 153 | *0.44 ± 0.28* | 12.7 ± 1.2 | 9.6 ± 1.2 |
| Gd | 157 | *2.20 ± 1.14* | 143 ± 10 | 82.1 ± 3.9 |
| Tb | 159 | *0.29 ± 0.24* | 11.5 ± 0.9 | 4.6 ± 0.5 |
| Dy | 163 | *1.78 ± 0.73* | 70.6 ± 2.7 | 23.7 ± 0.9 |
| Ho | 165 | 0.29 ± 0.03 | 17.1 ± 0.6 | 5.6 ± 0.4 |
| Er | 166 | *1.03 ± 0.38* | 57.4 ± 4.2 | 17.3 ± 0.8 |
| Tm | 169 | 0.13 ± 0.03 | 4.0 ± 0.4 | 1.9 ± 0.3 |
| Yb | 172 | *1.26 ± 0.59* | 56.2 ± 0.3 | 15.2 ± 1.9 |
| Lu | 175 | 0.32 ± 0.07 | 9.2 ± 0.8 | 3.0 ± 0.3 |

[a] Mean ± standard deviation, $n = 3$. [b] The values given in italic font were lower than the respective detection limits in Table 3.

**Table 3** Analytical results of REEs in seawater sample from the Nikkawa Beach, recoveries, and detection limits

| | Concentration in a seawater sample/ pg mL$^{-1}$ | | | |
|---|---|---|---|---|
| Element | Observed[a] | Reported[a,b] | Recovery[a]/% | Detection limit/ pg mL$^{-1}$ |
| La | 4.34 ± 0.16 | 4.7 ± 0.3 | 97.9 ± 1.8 | 0.029 |
| Ce | 3.86 ± 0.23 | 3.8 ± 0.2 | 97.5 ± 2.6 | 0.040 |
| Pr | 0.79 ± 0.02 | 0.83 ± 0.04 | 97.0 ± 1.1 | 0.004 |
| Nd | 3.72 ± 0.15 | 4.2 ± 0.2 | 100.2 ± 1.6 | 0.014 |
| Sm | 0.91 ± 0.05 | 0.90 ± 0.07 | 99.0 ± 0.8 | 0.005 |
| Eu | 0.252 ± 0.014 | 0.25 ± 0.02 | 97.8 ± 2.2 | 0.0008 |
| Gd | 1.50 ± 0.08 | 1.46 ± 0.10 | 100.7 ± 1.8 | 0.0034 |
| Tb | 0.246 ± 0.012 | 0.25 ± 0.02 | 97.1 ± 1.8 | 0.0007 |
| Dy | 2.02 ± 0.11 | 1.86 ± 0.13 | 100.4 ± 2.2 | 0.0022 |
| Ho | 0.52 ± 0.02 | 0.49 ± 0.03 | 99.5 ± 1.9 | 0.00009 |
| Er | 1.74 ± 0.10 | 1.60 ± 0.06 | 97.8 ± 2.6 | 0.0012 |
| Tm | 0.26 ± 0.02 | 0.25 ± 0.02 | 96.7 ± 2.8 | 0.00008 |
| Yb | 1.75 ± 0.13 | 1.59 ± 0.11 | 97.5 ± 3.2 | 0.0018 |
| Lu | 0.30 ± 0.03 | 0.28 ± 0.02 | 97.5 ± 3.3 | 0.00022 |

[a] Mean ± standard deviation, $n = 4$. [b] Cited from ref. 43.

solution of REEs to obtain a spiked sample of the Nikkawa Beach seawater, in which the concentration of each REE was approximately 2-fold of that in the non-spiked sample.

The concentrations of REEs were calibrated using a 3-point calibration curve for each REE, which was made with the reagent blank and two standard solutions containing different concentrations of the REE. The correlation factor ($R^2$) of the calibration curve for each REE was better than 0.9999.

The standard solutions were made in 3 groups in the order of atomic numbers: group I, from La to Sm; group II, from Eu to Ho; group III, from Er to Lu. The polyatomic spectral interferences to each REE were investigated with the above standard solutions along with a solution of Ba (5 ng mL$^{-1}$ in 2 mol L$^{-1}$ $HNO_3$). The interference ratios of $MO^+/M^+$ for Ba, Pr, Nd, Sm, Nd, Eu, Gd, and Tb were in the range from 1.2% of $EuO^+/Eu^+$ to 2.9% of $PrO^+/Pr^+$, while the ratios for the other REEs were less than 0.1%. Therefore, corrections of the interferences of $^{137}Ba^{16}O$, $^{141}Pr^{16}O$, $^{143}Nd^{16}O$, $^{147}Sm^{16}O$, $^{149}Sm^{16}O$, $^{150}Nd^{16}O$, $^{153}Eu^{16}O$, $^{156}Gd^{16}O$, and $^{159}Tb^{16}O$ were carried out to the results of $^{153}Eu$, $^{157}Gd$, $^{159}Tb$, $^{163}Dy$, $^{165}Ho$, $^{166}Er$, $^{169}Tm$, $^{172}Yb$, and $^{175}Lu$, respectively.

The results of the REEs in the Nikkawa Beach seawater sample are summarised in Table 3, along with the reported value,[43] the recovery values, and the detection limits. The detection limits were calculated as 3-fold of standard deviation of the blank values obtained by the present method, as is summarised in Table 2. It can be seen from Table 3 that the recovery of all REEs were close to 100% with the standard deviations less than 3.3%. All of the observed values were obtained after blank value corrections and recovery value corrections.

It can be seen from Table 3 that the detection limit for each REE was low enough for the analysis of the present seawater sample. The present seawater sample was taken from the bottle that was previously used to determine REEs and to report the results in ref. 43. The concentrations of REEs in the present sample covered a range from 0.246 pg mL$^{-1}$ of Tb to 4.34 pg mL$^{-1}$ of La, and the observed value for each REE was coincident with the reported value taking into consideration the standard deviations of both values, which were the major sources of the uncertainties of the values. These results indicate that the present method is useful for the determination of REEs in a natural seawater sample.

The results of REEs in seawater samples from the Ishigaki Island and the Kashima Bay are summarised in Table 4, along with the spiked seawater samples with two levels of spikes. The results in Table 4 cover a concentration range from 0.074 pg mL$^{-1}$ of Eu in seawater from the Ishigaki Island to 25.5 pg mL$^{-1}$ of La in seawater from the Kashima Bay with Spike II. It can be seen that all of these results were obtained with good reproducibility. Furthermore, the result for each element in both spiked samples was in good agreement with the sum of the concentration in the spike and that in the non-spiked sample. These results further confirmed that the present method is effective for the determination of REEs in seawater samples.

## Shale normalised REE distribution pattern in seawater samples

Shale normalised REE distribution pattern is an effective approach to assess the features of REEs in water samples.[8–15] The results of REEs in the present samples were normalised to those in post-Archean Average Australian Shale[44] ($[REE]_{PAAS}$) and are plotted in Fig. 5 against the REEs based on atomic number.

It can be seen from Fig. 5 that all the three seawater samples showed generally smooth REE distribution patterns with relative enrichment of heavy REEs. The enrichment of heavy REEs in seawater samples could be attributed to the fact that the ion species of heavy REEs are more soluble in the solution than those of middle and light REEs.[44] Furthermore, significant Ce

**Table 4** Analytical results of REEs in seawater samples from the Ishigaki Island and the Kashima Bay

| | Concentration/pg mL$^{-1}$ | | | | | |
|---|---|---|---|---|---|---|
| Element | Ishigaki Island[a] | Kashima Bay[a] | Spike I | Kashima Bay with Spike I[a] | Spike II | Kashima Bay with Spike II[a] |
| La | 1.51 ± 0.03 | 4.20 ± 0.20 | 10.7 | 15.1 ± 0.4 | 21.0 | 25.5 ± 0.6 |
| Ce | 2.84 ± 0.05 | 2.73 ± 0.14 | 8.44 | 11.4 ± 0.3 | 16.5 | 19.6 ± 0.5 |
| Pr | 0.349 ± 0.008 | 0.70 ± 0.03 | 2.10 | 2.84 ± 0.07 | 4.10 | 4.87 ± 0.10 |
| Nd | 1.53 ± 0.05 | 3.33 ± 0.12 | 8.43 | 11.8 ± 0.2 | 16.5 | 19.8 ± 0.3 |
| Sm | 0.370 ± 0.008 | 0.78 ± 0.04 | 2.09 | 2.89 ± 0.09 | 4.09 | 4.90 ± 0.15 |
| Eu | 0.074 ± 0.004 | 0.195 ± 0.018 | 0.51 | 0.73 ± 0.04 | 1.00 | 1.24 ± 0.03 |
| Gd | 0.500 ± 0.023 | 1.99 ± 0.10 | 3.12 | 5.13 ± 0.16 | 6.09 | 8.13 ± 0.20 |
| Tb | 0.081 ± 0.003 | 0.207 ± 0.010 | 0.51 | 0.714 ± 0.016 | 1.00 | 1.20 ± 0.04 |
| Dy | 0.562 ± 0.023 | 1.55 ± 0.06 | 4.18 | 5.65 ± 0.12 | 8.17 | 9.57 ± 0.14 |
| Ho | 0.141 ± 0.008 | 0.413 ± 0.012 | 1.04 | 1.43 ± 0.05 | 2.03 | 2.40 ± 0.04 |
| Er | 0.488 ± 0.018 | 1.35 ± 0.05 | 3.17 | 4.47 ± 0.09 | 6.19 | 7.45 ± 0.09 |
| Tm | 0.082 ± 0.004 | 0.185 ± 0.007 | 1.05 | 1.22 ± 0.03 | 2.05 | 2.21 ± 0.03 |
| Yb | 0.532 ± 0.024 | 1.13 ± 0.05 | 3.17 | 4.30 ± 0.10 | 6.20 | 7.32 ± 0.12 |
| Lu | 0.085 ± 0.005 | 0.202 ± 0.008 | 0.52 | 0.741 ± 0.015 | 1.02 | 1.25 ± 0.02 |

[a] Mean ± standard deviation, $n = 4$.

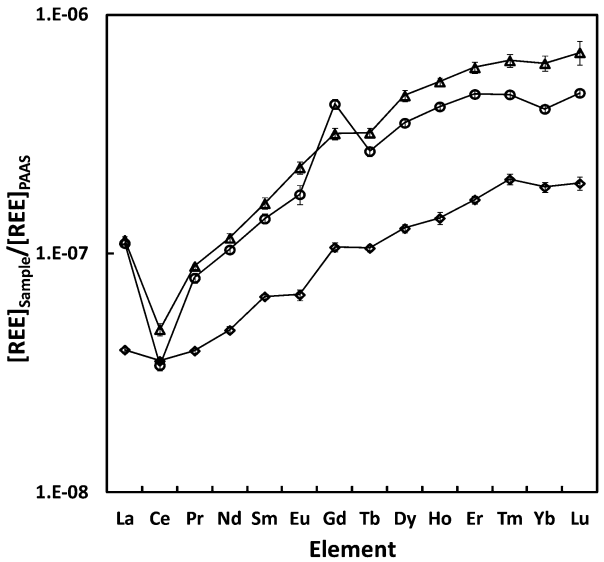


**Fig. 5** Shale normalised REE distribution pattern of seawater samples from the Nikkawa Beach, the Kashima Bay, and the Ishigaki Island. △, the Nikkawa Beach; ○, the Kashima Bay; ◇, the Ishigaki Island; bar, standard deviation, $n = 4$.

depletions could be observed for seawater samples from the Nikkawa Beach and the Kashima Bay. This phenomena could be attributed to the fact that Ce(IV) is much more stable but less soluble than Ce(III),[44] which resulted in the sedimentation of Ce as $CeO_2$ and resulted in the relative depletion of Ce in seawater samples. It is noted that the concentrations of REEs in the seawater sample from the Ishigaki Island were significantly lower than the other two samples, which could be attributed to the fact that the Ishigaki Island is located in the open ocean and is far from the continents, which is one of the major sources for REEs in seawater samples. The Ce depletion in the seawater sample from the Ishigaki Island was not significant, which might indicate that the concentration of Ce in this sample was extremely low and could not produce any more $CeO_2$ precipitate. Besides, the concentrations of Ce in the seawater samples from the Nikkawa Beach and the Kashima Bay were relatively close to that in the seawater sample from the Ishigaki Island, which was significantly different from other REEs. This fact also supports the above speculation about the lack of the Ce depletion in the seawater from the Ishigaki Island. The significant Gd enrichment in the seawater sample from the Kashima Bay could be attributed to the discharge of Gd compounds due to their medical use as MRI contrast reagents, which had been observed for seawaters and river waters from various countries.[8–15]

## Conclusions

An automatic pH adjustment instrument was developed for SPE of REEs using chelating resins. Contactless monitoring of the pH of a sample was carried out by monitoring the signal intensity of transmitted light at 550 nm with methyl red as the pH indicator. The adjustment of the pH of a sample was carried out by adding an aqueous ammonia solution into the sample to elevate the pH, where the amount of the aqueous ammonia solution was sensitively controlled by a nebuliser. The pH of the sample was precise and reproducible after pH adjustment using the present instrument. The blank values of REEs obtained using the present method were significantly lower than those obtained with the assist of pH electrodes and permitted the determination of REEs in natural seawater. The recoveries of the REEs were close to 100% with standard deviations less than 3.3%. The analytical results of a seawater sample confirmed that the present instrument and method are useful for the determination of REEs in natural seawater. The present method was applied to the determination of REEs in three seawater samples, which results were discussed using shale normalised REE distribution pattern.

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