

Original Paper

Determination of trace rare earth elements in natural water by electrothermal vaporization ICP-MS with pivaloyltrifluoroacetone as chemical modifier

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Abstract. A novel method based on gaseous compounds introduction into the plasma as their pivaloyltrifluoroacetone (PTA) chelates was developed for electrothermal vaporization inductively coupled plasma mass spectrometry determination of trace rare earth elements (REEs) in natural water. The factors affecting formation of the chelates and their vaporization behaviors were studied in detail. Under the optimized conditions, the limits of detection (3σ) of REEs for this method were from 0.20 to 0.91 ng L⁻¹, the relative standard deviations for 0.1 μg L⁻¹ REEs were 2.5–9.1% ($n=9$), and the linear ranges of calibration curve for REEs covered at least three orders of magnitude. The proposed method had been applied to the determination of trace REEs in water samples of Yangtze river, Han Shui river and East lake (Wuhan), and the recoveries for the spiked water samples were 93–105%.

Keywords: ETV-ICP-MS; rare earth elements; pivaloyltrifluoroacetone; chemical modifier; natural water.

Rare earth elements (REEs) have been widely used in industry, agriculture, medicine, and stockbreeding. More and more REEs are getting into environment

as a result. Their effect on environmental ecosystem has been the subject of continual attention. Sometimes, natural water system becomes the “source” and “influx” of metal ions among the cycle of environmental ecosystem. Especially, rare earth elements that have extremely similar chemical property but also have inner abundance difference among them are able to be a good tracer and to exert characterization function in the macroscopical and microcosmic process of natural water system [1]. Therefore, developing sensitive and accurate methods to determine REEs in natural water is necessary. There have been many analytical techniques used for the determination of REEs, neutron activation analysis (NAA) [2], inductively coupled plasma optical emission spectrometry (ICP-OES) [3–5], inductively coupled plasma mass spectrometry (ICP-MS) [6–12] and isotope dilution mass spectrometry (ID-MS) [13, 14] are the most popular ones. NAA has high sensitivity, satisfactory accuracy, without quantitative separation, non-destructive analysis for real samples. But it is difficult to determine all the REEs in samples. Moreover, due to time-consuming, complexity of operation, equipment and laboratory limitation, it is uneasy to be widely applied. ID-MS is a credible analytical technique for the determination of REEs, but expensive isotope must be added in pretreated samples and it is impossible to determine some rare earth elements of mono-isotope

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(such as Pr, Tb, Ho, Tm). REEs from trace content to minor component in samples could well be determined by ICP-OES with small matrix effect. But detection limit of them mostly lies in ng mL^{-1} , which is 2–3 magnitude orders poorer than ICP-MS. ICP-MS is usually the most favorable choice, due to its excellent analytical performance such as high sensitivity and selectivity, wide linear range, which make it to be an efficient determination technique for trace elements.

It should be pointed out that sample introduction technique exert a vital effect on analytical performance of ICP-MS. Contrasting with the conventional solution pneumatic nebulization introduction, electrothermal vaporization (ETV) introduction technique removes plentiful water component in drying stage. Therefore, oxygen and hydrogen source in some polyatomic ions were eliminated, and the isobaric interferences were minimized, distinct merits of high sampling efficiency and low sample consumption, detection limit was obviously improved, which has evoked much of interest and recognition of spacious analyst. ETV-ICP-MS was widely applied to determine trace elements in biological and environmental samples [15–18]. However, the very low sensitivities and severe memory effects would be encountered when the conventional ETV method was applied to determining refractory elements. It is because they are difficult to vaporize, and their more refractory carbides are often formed simultaneously during high temperature vaporization.

Fortunately, a lot of investigations indicated that the utilization of chemical modifiers, especially halogenating reagent is a very effective approach to solve the above problems. In our previous researches, fluorination assisted electrothermal vaporization technique with poly(tetrafluoroethylene) (PTFE) as chemical modifier has been studied extensively and it has been successfully applied to direct determination refractory elements in biological, environmental samples and high purity materials [19–22].

In recent years, considerably important development has been achieved in the exploration and application of organic chelating reagents as chemical modifiers in ETV-ICP-OES/MS. Tao and Kumamaru [23, 24] reported the vaporization of 8-hydroxyquinoline complexes of V, Cr, B, Nb, Zr and Al into ICP at about $1000\text{ }^{\circ}\text{C}$. Peng and Jiang [25] reported low temperature vaporization of La, Y, and Eu as their 1-phenyl-3-methyl-4-benzoylpyrazolone (PMBP) chelates in ETV-ICP-OES, the vaporization temperature used

was lower than $1200\text{ }^{\circ}\text{C}$. More recently, benzoylacetone (BZA) [26] and diethyldithiocarbamate (DDTC) [27] have also been used as chemical modifiers to the determination of Be, Co, Pd, Cd and platinum group elements for gaseous compound introduction by ETV-ICP-OES/MS. Some other organic chemical modifiers, such as EDTA, organic acids [28] and polyhydroxy compounds [29] have also been reported for ETV-ICP-MS determination of some metal elements in some standard materials.

These facts demonstrated that organic chelating reagents are another kind of effective chemical modifiers in the ETV-ICP-OES/MS. It is evident that organic reagent as chemical modifier may present the following advantages: (1) refractory elements can be vaporized at lower temperatures which is beneficial to prolong the lifetime of evaporator; (2) organic chelating reagents can be used both as chemical modifiers and as extracting reagents. Therefore, application range can be broadened and the analytical performances could be obviously improved by combining this technique with a chemical separation/pre-concentration procedure. Thus, the extensive research and exploitation of new organic reagent as chemical modifier may be a promising work.

Pivaloyltrifluoroacetone (PTA) is a fluorinated β -diketone which owns a trifluoromethyl in one end and a sterically crowded iso-butyl group in the other end. The special molecular structure enable the metal PTA chelates both have high volatility and good thermally stability. It was successfully used as derivative reagent in gas chromatography to separate metals [30–33].

In this work, a new method of ETV-ICP-MS using pivaloyltrifluoroacetone (PTA) as chemical modifier was developed for the determination of REEs in natural water. The factors affecting the chelate formation of REEs and PTA, the vaporization behaviors of the REE-PTA chelates were investigated in detail. The proposed method was applied to the analysis of trace REEs in natural water.

Experimental

Apparatus

To perform ETV-ICP-MS measurement, a modified commercially available WF-4C graphite furnace (Beijing Second Optics, China) as electrothermal vaporizer was used. The original silica windows at the two ends of the graphite furnace were removed and replaced by two PTFE cylinders, as which has been detailed in previous work [22], and one of them was connected to the injector tube of the

Table 1. Equipment and operating parameters

<i>ICP-MS plasma</i>	
RF power	1250 W
Outer gas flow rate	15 L min ⁻¹
Intermediate gas flow rate	0.9 L min ⁻¹
Carrier gas flow rate	0.6 L min ⁻¹
Sampling depth	7.0 mm
Sampler/skimmer diameter orifice	Nickel 1.0 mm/0.4 mm
<i>Data acquisition</i>	
Scanning mode	Time resolved analysis
Integration time	20 ms
Sweeps per reading	1
<i>ETV heating progress</i>	
Drying	100 °C, ramp 10 s, hold 10 s
Vaporization	1200 °C, hold 5 s
Sampling volume	10 µL

plasma torch. The transfer line consisted of a laboratory-built connecting interface and polyethylene tube (6 mm i.d.) with total length of 70 cm. Optimization of the ICP-MS instrument (Agilent 7500a, Hewlett-Packard) was performed with conventional nebulization method (PN-ICP-MS) prior to connecting with ETV device. And pyrolytically coated graphite tubes were used throughout the work. The operating parameters for ETV-ICP-MS were listed in Table 1.

Standard solution and reagents

The rare earth elements standard stock solutions (1 g L⁻¹) were prepared by dissolving the appropriate amount of their oxides in 1:1 (v/v) HNO₃, respectively, and diluted with 1% (v/v) HNO₃. The oxides employed were of suprapure grade. Multi-elements standard work solutions with concentrations of 0.1 and 1.0 ng mL⁻¹ were prepared from the stock solutions before use by stepwise dilution with 1% (v/v) dilute HNO₃.

0.5 mol L⁻¹ pivaloyltrifluoroacetone (PTA) was prepared by dissolving 4.80 g of PTA (Aldrich, 99%) in 50 mL of ethanol. All other chemicals were of analytical reagent grade at least. Milli-Q (Millipore, Bedford, MA, USA) ultrapure water was used throughout the experiments.

Sampling of natural water

Prior to use, all labware were cleaned sequentially with tap water, neutral detergent, distilled water, then soaked in nitric acid (1 + 1) for 48 h and cleaned with ultrapure water. Pore size 0.45 µm cellulose filter membrane was also soaked in nitric acid and cleaned with ultrapure water. The precleaned polyethylene bottles were used for sampling natural water, and then high-purity HNO₃ was added to keep the final acidity of natural water at about pH 2 after sampling. The natural water samples were taken at a depth of 1 m beneath the surface from Yangtze river (Wuhan) and Han Shui river (Wuhan), East lake (Wuhan) in June 2006. The samples were filtered through a millipore filter membrane and stored at temperature of about 4 °C.

Procedure

After a 5 mL mixed solution (pH 8.5 was adjusted by addition of 0.5 mol L⁻¹ sodium hydroxide and nitric acid) of 0.05 µg L⁻¹ REEs containing 0.1 mol L⁻¹ PTA were prepared, 0.5 mL CCl₄ was added to extract REE-PTA chelates. For optimizing conditions, 10 µL of organic phase was pipetted into the graphite furnace with a microsyringe after the plasma had stabilized. The sample inlet hole was

sealed with a graphite cylinder several seconds prior to the vaporization step. The gaseous analyte was carried into plasma source by the argon carrier gas, and the peak-hop transient mode of data acquisition was used to detect the ions selected and peak area for quantification with the on-board software.

For real sample analysis, 3.5 mL of filtered natural water sample was transferred into a 5-mL tube, then 1.0 mL of 0.5 M PTA was added. After the pH 8.5 of mixture solution was adjusted and fixed to 5.0 mL with milli-Q water, 0.5 mL CCl₄ was added to extract REE-PTA chelates by mechanical shaking for 5 min. The calibration standards with REEs concentration of 2.0, 5.0, 10.0, 50.0, 100.0, 300.0 ng L⁻¹, respectively were also subjected to the same pretreatment.

The above solution without the analytes addition was chosen as the blank solution, the blank solution was subjected to the same pretreatment and the blank values were determined. All experiments were carried out at room temperature and corrected against the blank, respectively.

Results and discussion

Effect of solution pH

It is well known that the pH of the solution was one of the important factors affecting the extraction and formation of chelates. The effect of solution pH on the signal intensity of analyte was examined, and Fig. 1 shows the effect of pH on the signal intensity of representative elements of La, Er, Dy and Ho. As can be seen, when the solution pH was less than 7, no signal of analyte or weak signal was observed. Maybe, an acidic medium is unfavorable to the PTA existing as enolic form, therefore REEs-PTA chelates could not be formed or were just partially formed. When the solution pH was increased up to pH 8, the maximum signal intensity was achieved and it keep constant up

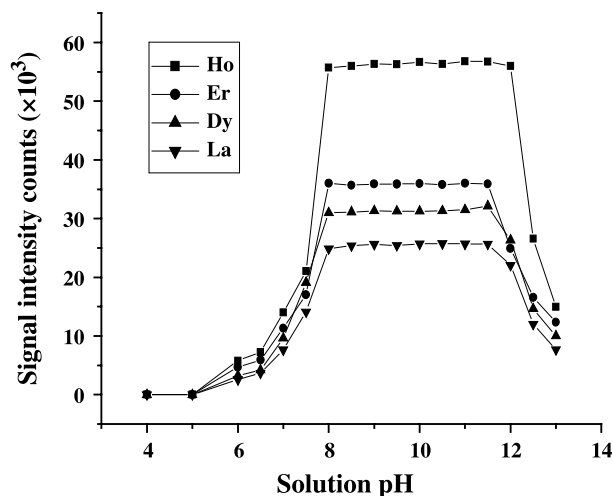


Fig. 1. Effect of pH on the signal intensity of La, Er, Dy and Ho ($C_{\text{REEs}} = 0.05 \mu\text{g L}^{-1}$, $C_{\text{PTA}} = 0.1 \text{ mol L}^{-1}$). Other conditions were listed in Table 1

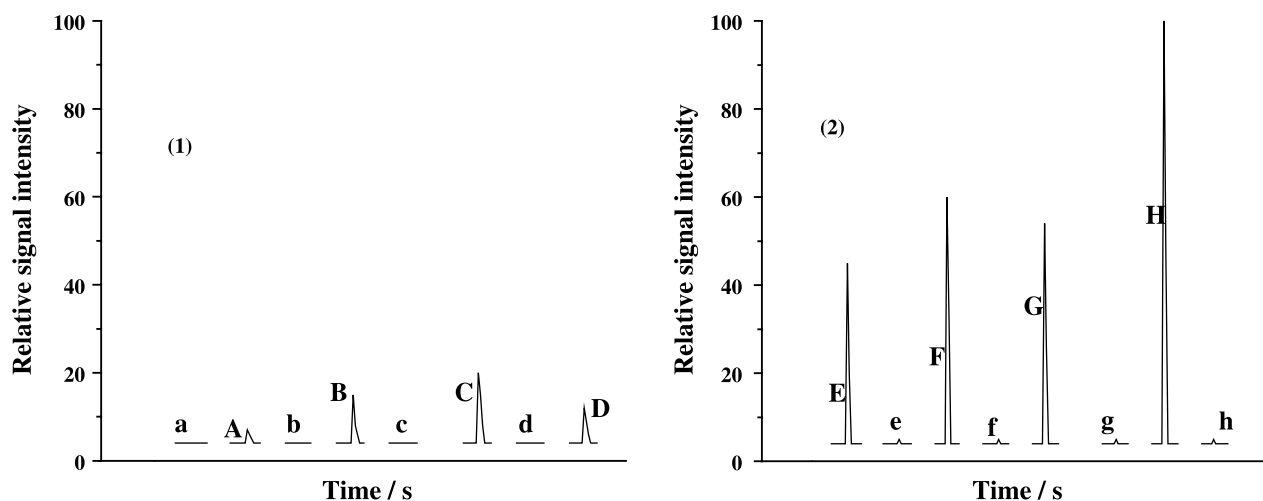


Fig. 2. (1) Signal profiles of La, Er, Dy and Ho vaporized at 1200 °C (*a, b, c, d*) and cleaned at 2500 °C (*A, B, C, D*) without PTA, respectively. (2) Signal profiles of La, Er, Dy and Ho vaporized at 1200 °C (*E, F, G, H*) with PTA as chemical modifier and residual signal profiles of La, Er, Dy and Ho at 2500 °C (*e, f, g, h*), respectively. ($C_{\text{Rees}} = 0.05 \mu\text{g L}^{-1}$, $C_{\text{PTA}} = 0.1 \text{ mol L}^{-1}$), Other conditions were listed in Table 1

to 11.5, which shows quantitative formation of REE-PTA chelates and quantitative extract by CCl_4 at wider pH range (8–11.5). When solution pH overran 11.5, the signal intensity of analyte began to decrease. This is probably due to the fact that the strong alkali media induce hydrolysis of PTA or and thus affecting the formation of REE-PTA chelates. Accordingly, pH 8.5 was selected as reactive solution media.

Vaporization behaviors of REE-PTA chelates in ETV

Thermogravimetric analysis indicates REE-PTA chelates have similar volatility and approach 100% weight loss in the temperature range 250–350 °C [33]. This implied that the REE-PTA chelates both have high volatility and good thermally stability. Thus, it is possible for the determination of trace amount of REEs by low temperature ETV-ICP-MS with PTA as chemical modifier. The effect of PTA as chemical modifier on the signal profiles of analyte in ETV-ICP-MS was observed. Fig. 2-(1) and (2) were the signal profiles of representative elements of La, Er, Dy and Ho in the absence and presence of PTA, respectively. As found in Fig. 2-(1), without PTA, no signal could be observed for analyte at the vaporization temperature of 1200 °C, weaker and wider signal profiles were recorded at the cleaning temperature of 2500 °C. On the contrary, as shown in Fig 2-(2), with the use of PTA as chemical modifier, more intense and sharper signal profiles for analyte were observed at vaporization temperature of 1200 °C, and no obvious memory signal was found at the cleaning temperature of

2500 °C, which means that REEs could be evaporated at 1200 °C completely. This signal enhancement and the vaporization temperature decrease of REEs in presence of PTA were attributed to the formation of volatile REE-PTA chelates, which improved the vaporization behaviors of analytes and increased the transport efficiency from the ETV to the plasma.

Choice of organic extracting solvent and extract phase ratio

The extract efficiency of conventional organic solvent such as tetrachloromethane, chloroform, toluene and cyclohexane were comparatively tested, and the experimental results are shown in Fig. 3. As could be

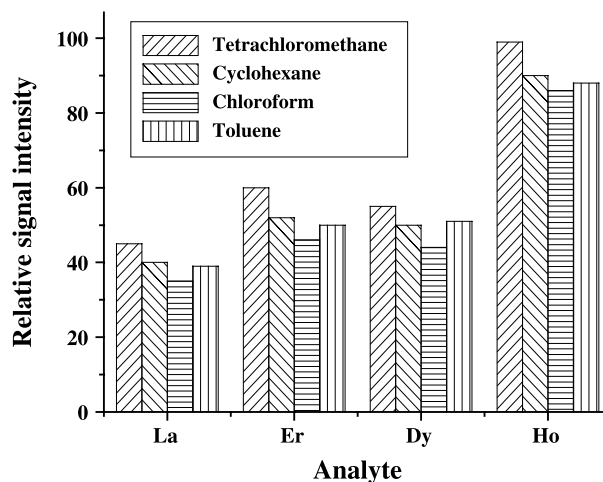


Fig. 3. Effect of the extracting solvent on the signal intensity of La, Er, Dy and Ho. Other conditions were listed in Table 1

seen, maximum signal can be attained with the use of tetrachloromethane as extract solvent. So tetrachloromethane was selected as extracting solvent in the following experiments.

In the conventional liquid–liquid extraction, the phase ratio between aqueous phase and organic phase is another factor affecting on the extract efficiency. With the use of tetrachloromethane as extract solvent, the effect of phase ratio on signal intensity of analyte was studied. When the phase ratio (V_w/V_o) is 10, chelates have been quantitatively extracted within 5 min by mechanical shaking. It is difficult to separate organic phase after the phase ratio exceeded 10. Therefore, in the further determination, the phase ratio is fixed at 10.

Effect of the amount of PTA on the signal intensity of analyte

As described in the section of vaporization behavior of REE-PTA chelates in ETV, in the presence of PTA, signal intensity of analyte was obviously increased. The amount of PTA will influence on the formation, extraction, vaporization of REE-PTA chelates, therefore, the effect of the amount of PTA on the signal intensity of analyte was examined. The experimental results shown in Fig. 4 indicates that the maximum signal intensity was obtained when the concentration of PTA was more than 0.05 mol L^{-1} and keep constant up to 0.2 mol L^{-1} . Considering that the co-existence

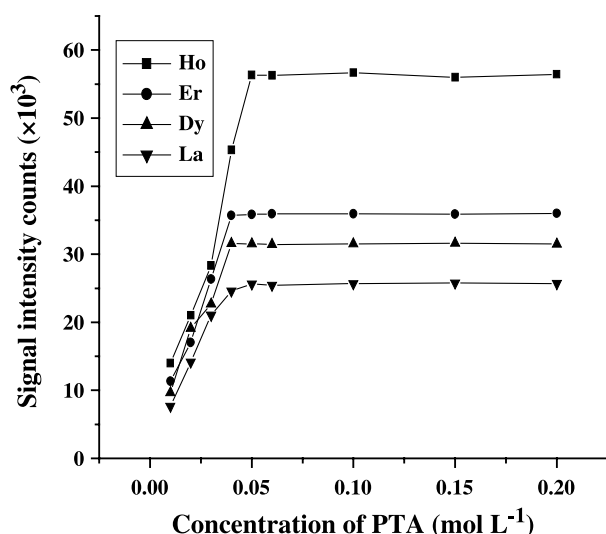


Fig. 4. Effect of PTA concentration on the signal intensity of La, Er, Dy and Ho ($0.05 \mu\text{g L}^{-1}$), Other condition were listed in Table 1

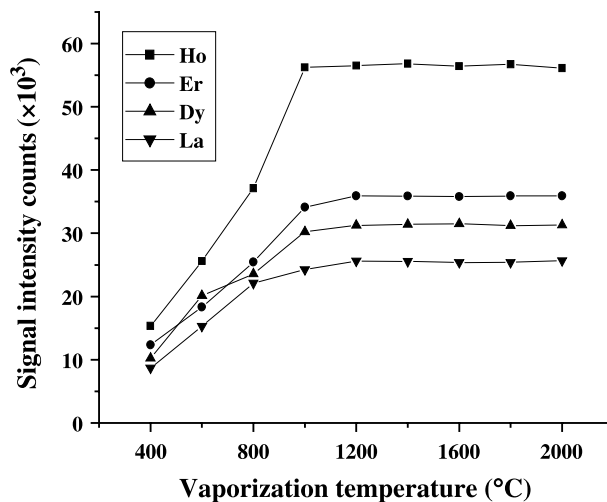


Fig. 5. Effect of the vaporization temperature on the signal intensity of La, Er, Dy and Ho, ($C_{\text{Rees}} = 0.05 \mu\text{g L}^{-1}$, $C_{\text{PTA}} = 0.1 \text{ mol L}^{-1}$), Other condition were listed in Table 1

ions may consume some PTA in real sample analysis, 0.1 mol L^{-1} PTA was used.

Effect of vaporization temperature and time

In order to ensure complete vaporization of REE-PTA chelates and no decomposition happened at a higher temperature, the choice of appropriate vaporization temperature is important. The effect of vaporization temperature on the signal intensity was studied and the experimental results are shown in Fig. 5. With the elevation of vaporization temperature, the signal intensity of analyte increased notably, and the maximum signal was obtained at 1000°C . These maximum signals remained constant with further increases of vaporization temperature up to 2000°C . Based on these results, vaporization temperature of 1200°C was chosen. Moreover, the effect of vaporization time on signal intensity was also investigated at a vaporization temperature of 1200°C . Maximum signal intensity was achieved after the vaporization time was greater than 4 s. A vaporization time of 5 s were selected in this work.

Effect of coexisting ions

The influences of coexisting metal ions, such as Na^+ , K^+ , Mg^{2+} , Ca^{2+} , Al^{3+} , Fe^{3+} , Cr^{3+} , Zn^{2+} , TiO^{2+} , Mn^{2+} , SiO_3^{2-} and Ba^{2+} were studied in this work. Solutions of $0.5 \mu\text{g L}^{-1}$ of REEs containing the corresponding interfering ions were prepared and operated according to the recommended procedure. The

amounts of tested coexisting elements which could be tolerated without interference occurring are as follows: Na^+ , K^+ and Mn^{2+} $1000 \mu\text{g mL}^{-1}$; Mg^{2+} , TiO^{2+} and Ca^{2+} $500 \mu\text{g mL}^{-1}$; Cr^{3+} , Zn^{2+} , Al^{3+} $200 \mu\text{g mL}^{-1}$; SiO_3^{2-} $100 \mu\text{g mL}^{-1}$; and Fe^{3+} , Ba^{2+} $10 \mu\text{g mL}^{-1}$ (results within $\pm 10\%$ error). The experimental results indicate good selectivity of this method.

Analytical performance

The analytical performance of the developed method was evaluated under the optimum operation conditions. The detection limit was defined as three times the standard deviation of background signal intensity in accordance with IUPAC recommendations. The relative detection limits, absolute detection limits and the relative standard deviations (RSDs) of the proposed method are listed in Table 2. Calibration graph of the analyte covered at least three orders of magnitude.

Recovery test

For evaluating accuracy of the method, the East lake water (Wuhan) spiked with 50.0 ng L^{-1} of Y, La, Ce, Pr, Nd, Sm, Eu, Gd, and 5.00 ng L^{-1} of Tb, Dy, Ho, Er, Tm, Yb, Lu were determined, and the recoveries are 93–105% for the spiked lake water.

Sample analysis

According to the established procedure, water samples of Han Shui river (Wuhan sect), East lake (Wuhan) and Yangtze river (Wuhan sect) were determined, and the analytical results were listed in Table 3.

Table 2. Analytical performance for ETV-ICP-MS

Element	Isotope	Detection limit (ng L^{-1})	Absolute detection limit (fg)	RSD (%) ($C = 0.1 \mu\text{g L}^{-1}$, $n = 9$)
Y	89	0.52	5.2	5.4
La	139	0.91	9.1	7.6
Ce	140	0.85	8.5	9.1
Pr	141	0.69	6.9	8.0
Nd	146	0.62	6.2	4.9
Sm	147	0.48	4.8	6.1
Eu	153	0.60	6.0	6.9
Gd	157	0.56	5.6	4.5
Tb	159	0.68	6.8	5.8
Dy	163	0.52	5.2	6.2
Ho	165	0.21	2.1	3.2
Er	166	0.26	2.6	4.3
Tm	169	0.22	2.2	2.5
Yb	172	0.20	2.0	3.0
Lu	175	0.29	2.9	3.5

Table 3. Determination results of REEs in water samples (ng L^{-1} , mean \pm S.D., $n = 3$)

Element	Isotope	Water samples		
		Han Shui river	East lake water	Yangtze river
Y	89	200 ± 7	218 ± 8	170 ± 9
La	139	118 ± 8	96.6 ± 8.6	51.0 ± 5.9
Ce	140	190 ± 14	87.9 ± 9.4	109 ± 9.9
Pr	141	12.4 ± 1.2	9.5 ± 0.8	10.7 ± 0.9
Nd	146	98.7 ± 2.2	143 ± 2	71.7 ± 1.7
Sm	147	18.2 ± 1.7	10.4 ± 1.4	14.8 ± 1.6
Eu	153	9.6 ± 1.2	5.4 ± 0.6	5.2 ± 0.5
Gd	157	14.1 ± 0.8	13.7 ± 0.6	16.6 ± 0.5
Tb	159	5.1 ± 0.6	7.2 ± 0.7	4.4 ± 0.4
Dy	163	15.7 ± 0.8	16.3 ± 0.9	17.3 ± 1.3
Ho	165	3.3 ± 0.2	3.0 ± 0.2	2.5 ± 0.2
Er	166	6.5 ± 0.6	7.2 ± 0.7	8.5 ± 0.5
Tm	169	3.2 ± 0.2	4.1 ± 0.2	5.5 ± 0.4
Yb	172	9.7 ± 0.7	7.3 ± 0.4	8.1 ± 0.34
Lu	175	2.1 ± 0.2	2.1 ± 0.2	2.3 ± 0.1

Conclusion

A novel method for determination of trace/ultratraces REEs in natural water by ETV-ICP-MS with the use of PTA as chemical modifier was developed in this work. The advantages of PTA used as chemical modifier could be summarized as follow: (1) not only effectively prohibits the formation of refractory carbides and eliminates the memory effect; (2) but also greatly promotes the vaporization efficiency and improve the analytical sensitivity due to the formation of the good thermal stable and volatile REE-PTA; (3) the lifetime of graphite tube could be prolonged because of lower vaporization temperature used; (4) PTA could be both as chemical modifier and as extracting reagent, therefore, it was easy to combine this technique with a chemical separation/preconcentration step; (5) This method could be applied to geochemistry investigation of natural water system.

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