

Determination of trace rare earth impurities in high-purity cerium oxide by using electrothermal vaporization ICP-AES after HPLC separation with 2-ethylhexyl hydrogen 2-ethylhexylphosphonate resin as the stationary phase

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A method is proposed to determine trace rare earth impurities in high-purity CeO₂ by HPLC combined with electrothermal vaporization inductively coupled plasma atomic emission spectrometry (ETV-ICP-AES). The chromatographic retention behaviours of the matrix (Ce) and rare earth impurities were studied using 2-ethylhexyl hydrogen 2-ethylhexylphosphonate (P507) resin as the stationary phase and dilute nitric acid as the mobile phase. It was found that the matrix (Ce) can be separated quantitatively with dilute nitric acid as the mobile phase, and the rare earth impurities (Pr–Lu) can be eluted effectively by use of EDTA as an eluent. The experimental results show that a favorable separation between the matrix (Ce) and rare earth impurities (Pr–Lu) can be obtained within 60 min. The method proposed has been applied to determine 14 rare earth impurities in high-purity CeO₂ with satisfactory results.

The applications of high-purity rare earth oxides in high-tech fields depend not only on the characteristics of the basic substances, but also on the purity of compounds. As the demand for high purity rare earth compounds is increasing, the development of a new analytical method for the determination of trace impurities in REE compounds is required.

It is well known that inductively coupled plasma atomic emission spectrometry (ICP-AES) has been widely applied to the determination of trace impurities in high-purity REE^{1,2} due to its good performance in the aspects of simultaneous multi-element capability, a wide dynamic range and high sample throughput. However, the analysis of high-purity cerium oxide by ICP-AES suffers from two problems: (1) spectral interference and matrix effect; and (2) insufficient sensitivity. It can only be used for direct determination of trace rare earth impurities in 99.9% high-purity cerium oxide. Therefore, a separation and preconcentration step prior to the analysis of high-purity cerium oxide is essential.³ Methods reported in the literatures for separation of REE included liquid–liquid extraction,^{4,5} solid–liquid extraction⁶ and column chromatography,^{7,8} among which column chromatography has been applied widely in the separation of rare earth elements.^{9,10} It has been demonstrated that 2-ethylhexyl hydrogen 2-ethylhexylphosphonate (P507) chelating resin is an excellent column material for REE separation with inorganic acid as the mobile phase.¹¹ However, in most cases it was used in conventional chromatography with an open column.^{12–14} According to our knowledge, few papers have been reported on the utilization of P507 as stationary phase in HPLC. In a previous report,¹⁵ a P507-HPLC combined with ICP-MS was used for the determination of trace rare earth impurities in high-purity lanthanum oxide with satisfactory results. Compared with an open column, the HPLC column has some advantages such as short separation time, low reagent consumption and simple operation. However, it should be indicated that heavier REE cannot be eluted completely from a P507-HPLC column when using inorganic acid as the mobile phase, because the HPLC system cannot tolerate high acidity.

Electrothermal vaporization (ETV), as a means of sample introduction technique for ICP-AES, provides many attractive

features, such as small amounts of sample required, low absolute detection limits and low matrix interference. The fluorination-assisted ETV-ICP-AES has been applied successfully to the determination of rare earth and refractory elements in biological, environmental and high purity materials by using polytetrafluoroethylene (PTFE) emulsion as a fluorinating reagent.^{16–18}

The aim of this work is to develop an effective method for the separation and determination of trace rare earth impurities in high-purity CeO₂ by combination of a P507-HPLC separation with the highly sensitive ETV-ICP-AES determination.

Experimental

Apparatus

The HPLC system consisted of two Model LC-10AD pumps (Shimadzu, Kyoto, Japan), a Model 7125 injector (Rheodyne, Cotati, CA, USA) with a 100 µl loop and a Model CTO-10AC column oven (Shimadzu, Kyoto, Japan). Unless otherwise mentioned, the instrument was operated under the following conditions: eluent flow rate 1.0 ml min⁻¹, column oven temperature 40 °C, and sampling volume 100 µl. A stainless-steel column of 4.6 mm id × 150 mm packed with 2-ethylhexyl hydrogen 2-ethylhexylphosphonate (P507) resin (Shanghai Yuelong Chemical Factory, Shanghai, China, 120–140 mesh) was used as the separation column. All mobile phase solutions should be filtered through 0.45 µm membranes (Tianjing Filter Factory, Tianjing, China) and degassed by a Model AS2060 ultrasonic cleaner (Tianjing Autoscience Instrumental Factory, Tianjing, China) before use.

The inductively coupled plasma source system and the graphite furnace sample introduction device used in this study were identical with that reported previously.¹⁸ A commercial 27 ± 3 MHz argon ICP source (Beijing Broadcast Instrument Factory, Beijing, China) with a 2 kW plasma generator was interfaced to a PGS-2 plane grating spectrograph with a 2400 grooves mm⁻¹ (Carl Zeiss, Jena Germany). The evolved compounds were swept into the plasma excitation source through a concentric glass tube with three openings connected

Table 1 The operating parameters for ETV-ICP-AES

Incident power/kW	1.1
Carrier gas/l min ⁻¹	0.3
Auxiliary carrier gas/l min ⁻¹	0.7
Coolant gas/l min ⁻¹	16
Entrance slit width/ μ m	20
Drying temperature/ $^{\circ}$ C	100; ramp 10 s, hold 20 s
Ashing temperature/ $^{\circ}$ C	1000; ramp 10 s, hold 20 s
Vaporization temperature/ $^{\circ}$ C	2400, 4 s
Signal record time/s	10
Sample volume/ μ l	50

with plastic tube (4 mm id) by two flows of carrier gas.¹⁸ The operating conditions for ETV-ICP-AES are listed in Table 1.

Reagents

Stock solutions of 1 mg ml⁻¹ REE were purchased from the National Center for Analysis and Testing of Steel Materials (Beijing, China). A 60% w/v PTFE slurry (viscosity $7-15 \times 10^{-3}$ Pa s) was purchased from the Shanghai Institute of Organic Chemistry (Shanghai, China). Analytical-reagent grade chemicals were used in all experiments. Doubly distilled water was used throughout.

Procedure

P507 resin was immersed in 1:1 (v/v) hydrochloric acid for 2 h in order to remove Fe³⁺, then filtered and washed with doubly distilled water until Cl⁻ could not be detected. After being dried, the P507 resin was packed into a chromatographic column by the dry packing technique. The packed column was successively washed and equilibrated with doubly distilled water for later use. Under the HPLC operation conditions as described above, 100 μ l of the standard mixture solution of REE was injected into the HPLC system. La was first eluted with pH 1.3 nitric acid, then the matrix (Ce) was eluted with pH 1.2 nitric acid, and finally REE impurities (Pr–Lu) were eluted with 25 mmol l⁻¹ EDTA. The fractions were added to 0.2 ml of 60% PTFE and measured by ETV-ICP-AES, and the elution curve was plotted based on these results.

Results and discussion

Effect of acidity of mobile phase on the separation of matrix

The acidity of the mobile phase obviously influences the separation of the matrix from rare earth impurities. Usually,

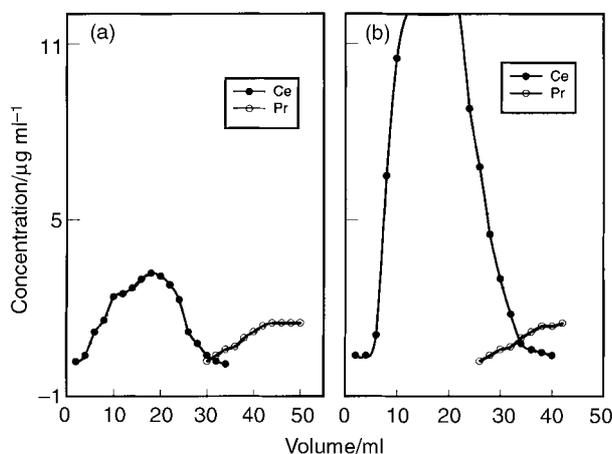


Fig. 1 Effect of acidity of mobile phase on the separation of Ce and Pr: mobile phase, pH 1.2 HNO₃; temperature, 40 $^{\circ}$ C; flow rate, 1.0 ml min⁻¹; injection, 100 μ l; concentration of Pr, 100 μ g ml⁻¹; concentration of Ce, (a) 100 μ g ml⁻¹, (b) 10 mg ml⁻¹.

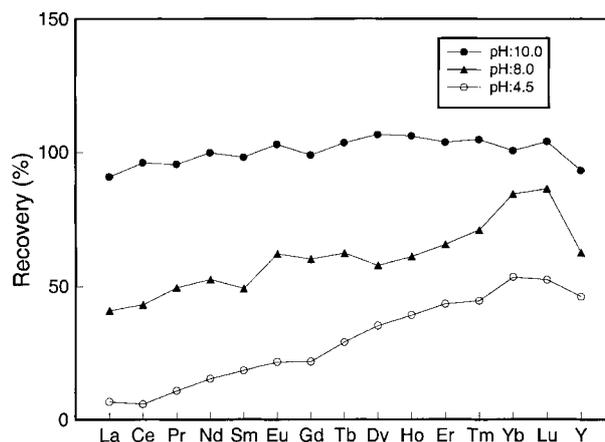


Fig. 2 Effect of acidity of EDTA: temperature, 40 $^{\circ}$ C; flow rate, 1.0 ml min⁻¹; concentration of EDTA, 25 mmol l⁻¹; concentration of REE, 10 μ g ml⁻¹; injection, 100 μ l.

the chromatographic retention time of REE in the P507 column is increased with an increase in the numbers of atoms. Therefore, the separation of REE impurities from the Ce matrix depends on the separation of Ce–La and Ce–Pr. Previous studies¹⁵ showed that an efficient separation of La and Ce could be achieved with a mobile phase of pH 1.3 nitric acid even when the ratio of Ce/La was as high as 100:1.

Fig. 1 shows the effect of acidity of the mobile phase on the separation of Ce and Pr. As can be seen, a nearly complete separation of Ce and Pr can be achieved with a mobile phase of pH 1.2 nitric acid when the ratio of Ce/Pr is 1:1 [Fig. 1(a)]. However, with a higher ratio of Ce/Pr, a much wider peak of Ce was observed and the appearance time of the chromatographic peak of Pr decreased; a partial peak overlap in elution curves for these two elements was observed. Fig. 1(b) shows the elution curves for Ce and Pr with a ratio of 100:1. In order to remove the matrix Ce as completely as possible and at the same time retain Pr on the column as much as possible, the effect of eluent volume on the remaining Ce and the retention amounts of Pr in the P507 chromatographic column was investigated. The results indicated that more than 99.9% of the matrix Ce can be removed using an elution volume varying from 26 ml to 34 ml, and at the same time the recoveries of Pr was more than 85%. Therefore, a pH 1.2 mobile phase and an elution time of 30 min were chosen for the separation of the Ce matrix. Under these conditions, 99.96% of Ce could be removed and 96.3% of Pr could be retained on the column. No obvious influence of

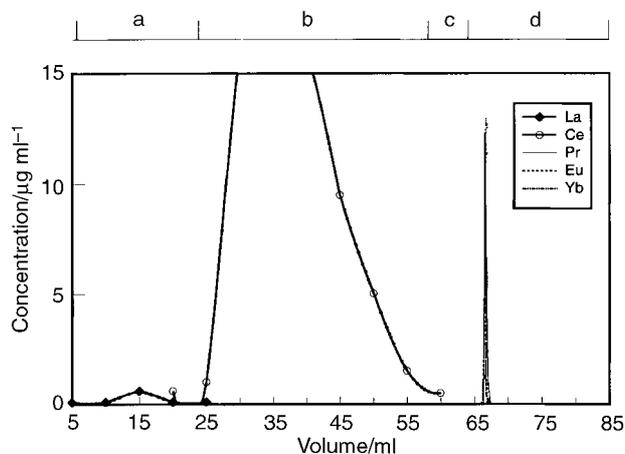


Fig. 3 The elution curve of the matrix Ce and the REE impurities: mobile phase, a, pH 1.3 HNO₃, b, pH 1.2 HNO₃, c, H₂O, d, 25 mmol l⁻¹ EDTA; concentration of Ce, 20 mg ml⁻¹ and La, Pr, Eu and Yb, 20 μ g ml⁻¹; temperature, 40 $^{\circ}$ C; flow rate, 1.0 ml min⁻¹; injection, 100 μ l.

Table 2 Comparison of analytical performance between HPLC column and open column

	Open column ¹⁶		HPLC column
	Ho	Er	La
Matrix element	Ho	Er	La
Analytes	14 REEs	14 REEs	14 REEs
Resin weight/g	100	100	1.2
Elution matrix volume/ml	1800	640	30
Elution impurities volume/ml	—	—	0.5
Separation time/h	10	8	1
Operation	Complex		Simple, no contamination

Table 3 The analytical results of REEs in CeO₂

	Ce-98-9/ $\mu\text{g g}^{-1a}$		Ce-991125/ $\mu\text{g g}^{-1b}$	
	Determined value ^c	Indicative value	Determined value ^c	Indicative value
La ₂ O ₃	0.4	0.5	42	40
Pr ₆ O ₁₁	0.6	0.4	1.0	1.2
Nd ₂ O ₃	0.2	<0.4	0.9	0.8
Sm ₂ O ₃	0.3	0.2	0.7	0.8
Eu ₂ O ₃	0.4	0.3	1.2	1.4
Gd ₂ O ₃	0.1	0.2	0.6	—
Tb ₄ O ₇	—	<0.2	0.4	—
Dy ₂ O ₃	2.0	1.5	2.5	2.0
Ho ₂ O ₃	0.5	0.6	0.6	0.6
Er ₂ O ₃	2.4	2.2	0.5	0.4
Tm ₂ O ₃	—	<0.2	—	<0.02
Yb ₂ O ₃	0.1	<0.2	0.2	0.1
Lu ₂ O ₃	—	<0.2	0.5	0.3
Y ₂ O ₃	0.1	<0.2	7	6

^aSample and the indicative values were supplied by Institute of Rare Earth Elements and Metal Material of Hunan. ^bSample and the indicative values were supplied by Jiahua Company Limited of New Material of Jiangyin. ^cDetermined value was the mean of three analysis.

any remaining Ce on the determination of REE impurities was observed.

The elution of rare earth impurities

EDTA was used as an eluent for the purpose of faster elution of rare earth impurities (Pr–Lu) from the P507-HPLC column. As is known, EDTA reacts with REE ions, and their complex stable constants are in the range of 16.4–19.8 (Pr–Lu). The acidity effect of EDTA will influence the reaction between EDTA and REE. The recoveries of REE under different acidity conditions of EDTA solution are shown in Fig. 2. The results show that with a pH of 4.5, the rare earth impurities could not be eluted quantitatively, and the recoveries of REE were less than 50%. However, the recoveries of REE improves with a decrease of acidity of EDTA. When EDTA of pH 10 was used, a complete elution of analytes was obtained, and the recoveries of REE were more than 90%. A pH 10 EDTA solution was chosen to elute rare earth impurities.

Using a pH 10 solution, the effect of the mobile phase concentration on the elution of Nd, Er, Tb and Yb was explored. The results show that the chromatographic retentions of Nd, Er, Tb and Yb decrease with an increase of concentration of EDTA from 5 to 50 mmol l⁻¹; furthermore, the eluent volume decreases. A complete elution of rare earth impurities can be achieved under the conditions of 0.5 ml EDTA with a concentration of 25–50 mmol l⁻¹. In this work, a concentration of 25 mmol l⁻¹ of EDTA was chosen for further studies.

Effect of EDTA amount on the determination of REEs

It was reported in the literature¹⁶ that an ashing temperature of 1200 °C could be used for the fluorinating electrothermal vaporization-ICP-AES determination of rare earth elements. In order to eliminate the organic matrices (EDTA) in the

furnace, an ashing temperature of 1000 °C was chosen. The results showed that no obvious influence was observed under the experimental conditions, when the concentration of EDTA was increased up to 50 mmol l⁻¹. As an EDTA concentration of 25 mmol l⁻¹ was used, the effect of EDTA could be neglected.

Comparison of separation performance

Fig. 3 shows the elution curves of the matrix Ce and the impurities of REE. A good separation of rare earth impurities from the Ce matrix can be achieved under the optimal conditions. A comparison of the separation performance between the P507-HPLC column and the conventional P507 open column is given in Table 2. It can be seen that the HPLC column has some advantages in the separation of Ce and rare earth impurities over the reported open column method,¹⁴ especially for separation speed, reagents and resin consumption, and operation convenience.

Detection limits and sample analysis

The detection limits are defined as the analyte concentration yielding a signal equal to 3 times the standard deviation of the background noise. Under the optimum experimental conditions, the detection limits of 14 REE are in the range of 0.8(Yb)–36(Nd) ng ml⁻¹.

The proposed method has been applied to the determination of trace amounts of rare earth impurities in high-purity CeO₂. A 0.1 g high purity CeO₂ sample was weighed and dissolved in 2 ml HNO₃ and 0.5 ml H₂O₂ by heating. The solution was diluted to 1 ml with doubly distilled water. A 50 μl portion of the solution was injected into the HPLC system, which was operated as described above. The fractions collected were determined by fluorination-assisted ETV-ICP-AES. The ana-

lytical results are given in Table 3. The agreement with the reference values was satisfactory.

Conclusions

HPLC combined with fluorination-assisted ETV-ICP-AES is an effective method for the determination of trace amounts of impurities in high-purity CeO₂. The results show that a selective separation of the Ce matrix can be obtained by using P507 resin as the stationary phase and dilute HNO₃ as the mobile phase. The analytes (Pr–Lu) remaining on the column can be quantitatively eluted by EDTA reagent. A successful combination of HPLC and ETV-ICP-AES has been achieved due to the fact that the elution volume needed was very small. Compared with a conventional open column method and conventional ICP-AES, this system provides some advantages in separation speed, operating convenience, low sample/reagent consumption and high absolute sensitivity. The results also indicated that the ETV-ICP-AES coupled with HPLC is suitable for the determination of high-purity rare earth materials.

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