Solvent Extraction ICP-MS/MS Method for the Determination of REE Impurities in Ultra-high Purity Ce Chelates

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ABSTRACT

This paper describes a new method for the determination of trace rare earth elements (REEs) in cerium chelates of extremely high purity by triple quadrupole inductively coupled plasma mass spectrometry (ICP-MS/MS) after solvent extraction. Based on the outstanding performance of ICP-MS/MS, interferences on La, Pr, Tb, Gd, and Yb were reduced by 2~3 orders of magnitude in comparison with ICP-QMS. Further, chemical separation employing solvent extraction using Cyanex® 272 (bis(2,4,4-trimethylpentyl) phosphinic acid) was carried out, and about 99.95% of the Ce matrix, after being digested and oxidized to Ce⁴⁺ with KMnO₄, could be removed, with recoveries for all of the 14 REEs ranging from 92.8% to 103%. Key factors that influenced the separation effects, such as the extraction

acidity and time, the amount of KMnO₄, the back-extraction acidity and time, were systematically studied and optimized. The established new separation procedure showed great superiority over the reported EHEHP (2-ethylhexyl hydrogen-2-ethylhexyl-phosphonate) based method in terms of conciseness in operation, low acidity for back-extraction, and high matrix separation efficiency. Thus, with the combination of chemical and physical high efficiency separation of the matrix-induced interferences, truly interference-free determination was realized, together with high analytical sensitivity and detection limits (3 σ) for the 14 REEs ranging from 0.013~0.44 ng g⁻¹. The proposed new method was also verified by using three real samples for batch analysis of cerium chelates up to 7N purity.

is of great challenge. Due to the severe optical spectra interferences and relatively low sensitivity, inductively coupled plasma optical emission spectroscopy (ICP-OES) is not recommended for application in the direct analysis of samples with a purity over 4N (6-8); while for inductively coupled plasma quadrupole mass spectrometry (ICP-QMS), matrix Ce induced mass spectra interferences on La, Pr, Tb, Gd, and Dy make it impossible for the direct analysis of samples with a purity over 5N (9).

In recent years, a new inorganic mass technique, named triple quadrupole inductively coupled plasma mass spectrometry (ICP-MS/MS), has demonstrated to be a good choice for the direct analysis of REE samples with ultra-low impurity content (10). In comparison with ICP-QMS, the mass screening function of the additional quadrupole mass filter in front of the collision/reaction system can greatly increase the power of polyatomic interference elimination (11, 12), which was well proved by the direct analysis of 6N Nd₂O₃ and Sm₂O₃ (13, 14). However, for REE samples with an even higher purity as 7N, especially for cerium compounds, there has up to now been no data available using ICP-MS/MS for direct analysis.

Of course, when the instrumental resolution is not sufficient, chemical separation of the matrix is then necessary, and usually solid phase chromatographic separation or solvent extraction separation is mostly adopted for this purpose (15-17). By comparison, the latter

INTRODUCTION

The Chelate Precursor Doping Technique (CPDT) based on volatile rare earth element (REE) organic chelates is a promising technique for high-power-laser fiber preparation. In comparison with the traditional inorganic REE halides-based techniques (1, 2), it can realize element doping with higher concentrations. The tetrakis-(2,2,6,6-tetramethyl-3,5-heptanedionato) cerium(IV) chelate

(Ce(TMHD)₄) is a very effective gas phase doping source of cerium for the function of reducing the darkening effect and improving power stability (3), which is extremely important for the development of laser fibers capable of ultra-high energy transmission. In order to minimize the risk of energy loss caused by the long optical path of the fiber, the purity of the REE chelates is usually required to be as high as possible, thus techniques effective for the accurate determination of REE impurities at ultra-low levels are essential (4, 5).

It is well known that the determination of ultra-trace REE impurities in high-purity cerium compounds

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has the merits of better conciseness in operation, higher sample throughput and most importantly, enrichment ability for the analytes, which is particularly desirable for ultra-trace analysis due to improvement in analytical sensitivity. The reason for recommending solvent extraction in Ce matrix separation is that Ce(III) can be easily oxidized to Ce(IV), which shows a much stronger affinity with some phosphinic acidic extractants, typically EHEHP (2-ethylhexyl hydrogen-2-ethylhexylphosphonate), than the REE(III) impurities, thus high matrix separation efficiency can be easily obtained.

A perfect example for 6N purity CeO₂ analysis by ICP-QMS was reported by Li et al. (17), though mathematical correction was additionally needed for the elimination of residual mass interferences, and matrix separation efficiency up to 99.5% was accomplished. However, the EHEHP extractant also has a relatively strong affinity with heavy REE(III) ions, thus two back-extraction steps employing relatively high concentrations of acidic solutions were required for satisfactory recoveries of all of the REE analytes. In addition, the obtained back-extraction aqueous solution must be evaporated to small volumes for acidity reduction and analyte enrichment, which inevitably damages the conciseness of the whole analytical procedure. Fortunately, a relatively new acidic organophosphorous extractant, Cyanex 272 (bis(2,4,4-trimethylpentyl) phosphinic acid), had been developed to overcome the problem with EHEHP. Since it had much weaker affinity with heavy REE(III) ions, back-extraction might be carried out at lower concentrations of acidic solutions and at a reduced frequency (18, 19). For analytical use, Cyanex 272 has been applied to prepare adsorption resin mini-columns for on-line or off-line chromatographic separation of REE(III)

ions prior to ICP-OES or ICP-MS analysis of some REE oxides with a purity of 5N (20).

In this work, we aimed to develop a robust method for rapid, concise, high sensitive, and interference-free determination of ultra-trace REE impurities in Ce(TMHD)₄ with an extremely high purity of 7N. ICP-MS/MS was employed for analyte detection, while Cyanex 272 was adopted for solvent extraction separation of the matrix. To our knowledge, no similar work has been previously reported.

EXPERIMENTAL

Instrumentation

For this study, an Agilent® 8800 triple quadrupole ICP-MS (ICP-MS/MS) (Agilent Technologies, USA) was used, equipped with x-lens and Ni cones, a MicroMist glass concentric nebulizer, a Peltier-cooled quartz double-pass Scott-type spray chamber and a quartz torch with a 2.5 mm i.d. injector. The ICP-MS/MS also features a high matrix introduction (HMI) aerosol dilution device for reducing the total sample load into the plasma. The instrumental parameters are listed in Table I.

Reagents, Standard Solutions, and Equipment

Deionized water (18.2 MΩ·cm), obtained from an ELGA PURELAB Ultra water purification system (England), was used to prepare all solutions. Nitric acid (ultrapure grade, ULTREX®II, J. T. Baker, USA) was used to digest the samples. A multi-element standard stock solution containing 10 mg L⁻¹ of Y, La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, and a single-element standard stock solution containing 1000 mg L⁻¹ of Cs (National Center for Analysis and Testing of Nonferrous Metals and Electronic Materials, Beijing, P.R. China) were used to prepare the calibration standard solutions and the internal standard

solution by stepwise dilution with 2% (v/v) HNO₃. All utensils used for the solutions were made of PFA material and prior to use, they were soaked overnight in 30% nitric acid, then washed repeatedly with deionized water.

Cyanex 272 (90%, Cytec Industries Inc., Canada) was used as the extractant and cyclohexane (ultrapure grade, Sigma-Aldrich, Germany) was used as the diluent. Working solutions were prepared by mixing Cyanex 272 with cyclohexane to give about a 0.05 mol L⁻¹ concentration, and purified by repeated back-extraction with 10% (v/v) HNO₃. Acetic acid-acetate buffer solution (pH = 4), monochloroacetic acid buffer solution (pH = 3), and KMnO₄ solution (5.0 g L⁻¹) were prepared with analytical grade chemicals.

Ce(TMHD)₄ of 7N purity was homemade.

Sample Digestion

A 0.1000 g amount of high-purity Ce(TMHD)₄ was digested using 1.0 mL HNO₃ in a PFA closed vial at 120 °C for 30 minutes until a clean sample solution was obtained. After cooling, the solution was transferred to the volumetric flask and adjusted to 50 mL with 2% (v/v) HNO₃.

TABLE I
ICP-MS/MS
Operating Parameters

Parameters	Values
Plasma RF power	1550 W
Sampling depth	8.0 mm
Carrier gas flow rate	0.6 L min ⁻¹
Dilution gas flow rate	0.5 L min ⁻¹
Extract 1 voltage	0.0 V
Extract 2 voltage	-70.0 V
Omega voltage	8.0 V
Omega Bias voltage	-60.0 V
KED voltage	-10.0 V
Octopole bias voltage	2.0 V

Separation Procedure

An amount of 20 mL 0.05 mol L⁻¹ Cyanex 272 was placed into a 60 mL separating funnel, and a mixture of 20 mL of water (pH = 4) and 2 mL of KMnO₄ was added. Then 5 mL of sample solution was adjusted to pH = 4 with 2% (m/v) NaOH and 15 mL of buffer solution (pH = 4) before 2 mL of KMnO₄ solution was added. The sample solution was subsequently subjected to extraction for about 2 minutes, and the aqueous layer discarded. Finally, the organic layer was back-extracted with 10 mL 5% (v/v) HNO₃ for 5 minutes, and the aqueous solution collected for ICP-MS/MS determination.

Blanks were prepared in exactly the same way as is listed in the sample procedure.

RESULTS AND DISCUSSION

Typical Interferences with ICP-MS/MS for REE Determination

In our previous work (21), through a joint instrumental optimization of both the aerosol dilution based sample introduction system and the DRC™ (Dynamic Reaction Cell™) coupled MS/MS detection system of ICP-MS/MS, some typical overlapping and polyatomic interferences on La, Pr, Tb, Gd, and Yb were greatly reduced

by about 2~3 orders of magnitude in comparison with those in ICP-QMS; thus, the direct analysis of Ce compounds with 6N purity was feasible. In this work, a similar optimization of the instrument was carried out to obtain the optimal operation conditions, in particular La, Pr, Gd, and Yb were detected in O₂ mass-shift mode (the first quadrupole Q1 was set to the mass of M⁺ and the second quadrupole Q2 was set to the mass of MO⁺), while Tb was detected in NH₃ mass-shift (Q1 was set to the mass of Tb⁺ and Q2 was set to the mass of TbNH⁺). After that, the interference elimination effect was evaluated more deeply with elevated Ce matrix concentrations. As indicated in Table II, the interferences on Gd, Tb, and Yb at higher Ce matrix concentrations were not negligible and constructed the major obstacles for the direct analysis of Ce compounds over 7N purity, thus, matrix separation became necessary.

For other REEs without interferences, the He collision mode was still selected to achieve collision focusing effects for higher analytical sensitivity.

Matrix Separation by Cyanex 272 Extraction

Thus, chemical separation of the matrix by solvent extraction was conducted. A relatively new extrac-

tion reagent of Cyanex 272 was investigated for the first time, and was compared with EHEHP as reported in the literature (17). As an acidic extractant, the extraction of the metal ions with Cyanex 272 could be expressed as follows:

where [Ln^{m+}]_a is the concentration of the metal ion in the aqueous phase and [H₂A₂]_o is the concentration of Cyanex 272 in the organic phase. It is well known that metal ions with larger charge number (m⁺) had stronger affinity with the extractant. So, if the matrix Ce(III) was previously oxidized to Ce(IV), then by applying extraction and back-extraction at different acidity in sequence, high separation efficiency could be obtained; for example, at low acidity, both Ce(IV) and REE(III) in the aqueous solution could be easily extracted into the organic phase, then with an increase of the acidity to a proper value, only REE(III) could be back-extracted into the aqueous phase, while leaving Ce(IV) in the organic phase due to its much higher combining energy with Cyanex 272.

Effect of pH on Extraction of REE(III)s

As mentioned above, it was desirable for Cyanex 272 to operate at low acidic aqueous solutions for metal ion extraction and the extraction efficiency was pH-sensitive. Following the literature (17), the ratio of organic phase volume to aqueous phase volume was fixed at 1:1, and the extractant concentration in the organic phase was set at 0.05 mol L⁻¹. For a 10 ng L⁻¹ of REE solution, two different pH values of 3 (adjusted with the mono-chloro-acetic acid buffer solution) and 4 (adjusted with the acetate buffer solution) were tested for their effects on the extraction efficiencies. As the results in Figure 1 show, pH 4 was more effective for

TABLE II
Evaluation of Interference Elimination Effects
Under Optimized ICP-MS/MS Operating Conditions

Isotopes	O ₂ Mass-shift			NH ₃ Mass-shift		
	1280 ^a	640	320	1280	640	320
¹³⁹ La	0.052 ^b	0.032	0.014			
¹⁴¹ Pr	0.051	0.024	0.017			
¹⁶⁰ Gd	0.249	0.069	0.038			
¹⁵⁹ Tb	1.086	0.506	0.269	0.324	0.155	0.072
¹⁷² Yb	0.128	0.042	0.019			

^a Ce concentrations, mg L⁻¹.

^b The apparent concentrations of the analytes, µg L⁻¹.

guaranteeing that all the extraction efficiencies for the REEs were over 90%. Higher pH values were not tested since precipitation of the REEs would occur, so the optimal extraction acidity was set at pH 4.

Optimization of KMnO_4 Amount and Extraction Time

It was proved that KMnO_4 was the most effective oxidant for Ce^{3+} at the optimized extraction pH value of 4 (17). It was important to optimize the amount of KMnO_4 and the extraction time for a given sample amount in this work. Through experiments, we found that Cyanex 272 tended to react with KMnO_4 more easily than EHEHP, which would result in more MnO_2 solid particles (the reduction product) produced within a similar extraction duration. Consequently, emulsification would occur more easily at the organic/water interface, thus increasing the difficulty of phase separation and the risk of analyte loss (even up to 80%), therefore, a large amount of KMnO_4 for the concentration of Ce is not suitable for the separation. So, we conducted a series of exploratory experiments to avoid emulsification, such as appropriately reducing the dosage of KMnO_4 , strictly controlling the oscillation intensity, and shortening the extraction time as far as possible. It was found that for

a 0.1 g of sample, 10 mg amount of KMnO_4 at the extraction pH of 4 and extraction duration of 2 minutes by manually shaking the vial could increase not only the oxidation efficiency by more than 99.99% for Ce^{3+} , but also result in a complete extraction of both the Ce matrix and the REE analytes.

Optimization of Acidity and Time for Back-extraction

It is well known that heavy REEs are more difficult to back-extract than light REEs with phosphonic acid extractants. As stated in the literature (17), back-extraction with 10% (v/v) HNO_3 was required to be done twice for the recovery of all REEs over 90% when EHEHP was used as the extractant. Therefore, the whole analytical procedure

became more tedious and complicated, and the separation efficiency of the Ce matrix was reduced since more Ce^{4+} ions were simultaneously back-extracted.

In this work, different concentrations of HNO_3 solutions of 10 mL were investigated to observe their effects for all REEs. As seen in Figure 2, a single back-extraction with 5% (v/v) of HNO_3 was enough even for the complete back-extraction of all of the heavy REEs. And in order to prevent the reduction of Ce^{4+} by the organic substance under acidic conditions, the back-extraction time should, therefore, be as short as possible. It was found that manually shaking the vial for about 5 minutes was enough for a complete extraction of all of the analytes.

Fig. 1. Effect of pH values on the extraction efficiencies of REE(III)s.

Fig. 2. Effect of acidity on the back-extraction efficiencies of all REE analytes.

Matrix Separation Efficiency Evaluation

To assess the matrix separation efficiency, the concentration of Ce remaining in the aqueous phase after back-extraction was determined. The separation efficiency was defined as $(1 - (C_1 \times V_1 / C_0 \times V_0)) \times 100\%$, where C_1 was the remaining Ce concentration in the final back-extraction solution, V_1 was the volume of the final back-extraction aqueous solution (10 mL), C_0 was the original Ce concentration

in the aqueous solution prior to extraction, V_0 was the volume of the aqueous solution prior to extraction (5 mL). The results of repeated tests in Table III show much higher separation efficiencies obtained in this work than those reported in the literature with EHEHP (17). So, in combination with the strong function of ICP-MS/MS for polyatomic interference elimination, ultra-high matrix separation efficiencies would help realize a truly interference-free determination of all of the ultra-trace

REE impurities.

Method Evaluation and Real Sample Analysis

The validity of the proposed method was demonstrated by the separation and analysis of a spiked sample. A spiked test for the whole analytical procedure was carried out and the results for different spiked levels were satisfactory, as listed in Table IV. The limits of detection (LOD, 3σ) for all of the analytes were calculated as three times the standard deviation of 11 blank measurements, ranging from 0.013 to 0.44 ng g⁻¹ for the liquid solution (also listed in Table IV). The data suggests that the accuracy and precision are satisfactory and the quantification limits allow the determination of 14 REE impurities in 7N cerium chealate. Finally, the method was applied for the analysis of three Ce(TMHD)₄ samples, claimed of 99.99999% purity, and the results are listed in Table V.

CONCLUSION

The combination of chemical

TABLE III
Matrix Separation Efficiencies of Five Replicate Separations

Sample No.	Original Ce Concentrations $C_0/\text{mg L}^{-1}$	Remaining Ce Concentrations $C_1/\text{mg L}^{-1}$	Separation Efficiencies (%)
1	332.6	0.0832	99.95
2	332.8	0.0836	99.95
3	332.8	0.0954	99.94
4	332.5	0.0870	99.95
5	332.8	0.0846	99.95
Average	332.7	0.0868	99.95

TABLE IV
Recoveries of Spiked Test and Limits of Detection for the Method

Element	Spiked Recovery Test (%)		LOD/ng g ⁻¹
	1.0 $\mu\text{g L}^{-1}$	10.0 $\mu\text{g L}^{-1}$	
Y	98.3	96.5	0.24
La	92.8	93.6	0.042
Pr	95.5	98.2	0.18
Nd	94.6	95.2	0.33
Sm	97.8	94.8	0.30
Eu	96.9	103	0.19
Gd	97.8	98.6	0.44
Tb	98.6	96.8	0.13
Dy	97.9	100	0.11
Ho	97.9	99.8	0.24
Er	98.7	94.2	0.33
Tm	98.6	98.7	0.013
Yb	96.0	96.3	0.30
Lu	99.8	98.6	0.12

TABLE V
Real Sample Analysis (n = 3)

Element	Sample 1		Sample 2		Sample 3	
	Content ($\mu\text{g g}^{-1}$)	RSD (%)	Content ($\mu\text{g g}^{-1}$)	RSD (%)	Content ($\mu\text{g g}^{-1}$)	RSD (%)
Y	ND ^a	- ^b	ND	-	ND	-
La	ND	-	ND	-	ND	-
Pr	0.013	1.2	0.016	1.6	0.016	1.2
Nd	ND	-	0.012	2.3	0.012	2.4
Sm	ND	-	ND	-	ND	-
Eu	ND	-	ND	-	ND	-
Gd	0.015	0.7	0.023	2.8	0.020	2.4
Tb	0.029	1.3	0.029	1.8	0.030	2.6
Dy	ND	-	0.013	3.6	0.010	4.2
Ho	ND	-	ND	-	ND	-
Er	ND	-	ND	-	ND	-
Tm	ND	-	ND	-	ND	-
Yb	0.010	3.3	0.017	2.0	0.013	2.2
Lu	ND	-	ND	-	ND	-

^a Not Detected.

^b Not Calculated.

separation with triple quadrupole inductively coupled plasma mass spectrometry provided a high sensitive and truly interference-free method for the determination of REE impurities in Ce compounds with extremely high purity. The use of Cyanex 272, instead of EHEHP for the purpose of matrix Ce separation, possessed the merits of much higher separation efficiencies and more concise operation.

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REFERENCES

1. E. H. Sekiya, P. Barua, K. Saito, and A. J. Ikushima, *J. Non-Cryst. Solids* 4347(42-44), 354 (2008).
2. A. J. Boyland, A. S. Webb, S. Yoo, F. H. Mountfort, M. P. Kalita, R. J. Standish, J. K. Sahu, D. J. Richardson, and D. N. Payne, *J. Lightwave Technol.* 912(6), 29 (2011).
3. M. Engholm, P. Jelger, F. Laurell, and L. Norin, *Optics Lett.* 1285(8), 34 (2009).
4. Y. Xu, D. Chen, S. Li, L. Hu, and J. Tang, *J. Inorg. Mater.* 240(3), 30 (2015).
5. T. Shi, Z. Zhou, L. Ni, X. Xiao, H. Zhan, A. Zhang, and A. Lin, *Appl. Optics* 3191(15), 53 (2014).
6. G. Ruan, *Chin J. Inorg. Anal. Chem.* 15(4), 1 (2011).
7. S. Chen and Z. He, *Anal. Test. Technol. Instrum.* 217(4), 17 (2011).
8. J. Ning, *Chin. J. Spectrosc. Lab.* 947(2), 30 (2013).
9. N. Shitaba, N. Fudagawa, and M. Kubota, *Anal. Chem.* 636(6), 63 (1991).
10. L. Balcaen, E. Bolea-Fernandez, M. Resano, and F. Vanhaecke, *Anal. Chim. Acta* 7, 894 (2015).
11. S. D. Fernandez, N. Sugishama, and J. R. Encinar, and A. Sanz-Medel, *Anal. Chem.* 5851(14), 84 (2012).
12. W. Guo, L. L. Jin, S. H. Hu, and Q. H. Guo, *J. Agric. Food Chem.* 65, 3406 (2017).
13. J. Li, X. Wu, and Y. Zheng, *Journal of Instrumental Analysis* 32(4), 24 (2005).
14. W. Wu, H. Liu, and T. Zheng, *Chin. J. Anal. Chem.* 697(5), 43 (2015).
15. K. Kawabata, Y. Kishi, O. Kawaguchi, Y. Watanabe, and Y. Inoue, *Anal. Chem.* 2137(19), 63 (1991).
16. T. Duan, H. Li, J. Kang, and H. Chen, *Anal. Sci.* 921(6), 20 (2004).
17. B. Li, Y. Zhang, and M. Yin, *Analyst* 543(6), 122 (1997).
18. M. I. Saleh, M. F. Bari, and B. Saad, *Hydrometallurgy* 75(1), 63 (2002).
19. E. Kashi, R. Habibpour, H. Gorzin, and A. Maleki, *J. Rare Earths* 317(3), 36 (2018).
20. H. Matsuyama, A. Azis, M. Fujita, and M. Teramoto, *J. Chem. Eng. Jpn.* 126(1), 29 (1996).
21. Y. Zhang, Z. Pan, P. Jiao, J. Ju, T. He, and H. Cai, *J. Instrumental Analysis* 304(3), 38 (2019).