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Extraction Chromatograph Separation Spark Source Mass Spectrometric Analysis of 14 Rare Earth Impurities in High Purity Rare Earth Oxide

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Abstract: An extraction chromatographic method of separating rare earth impurities from high purity Nd_2O_3, Sm_2O_3, Gd_2O_3, Er_2O_3, Dy_2O_3 and Yb_2O_3 was studied by using HCl-NH_4Cl as moving phase and P507 as stationary phase. After the impurities were enriched from the eluate by chelant-activated carbon, the active carbon was ashed and the ignited residue was used to prepare the sample electrode for spark source mass spectrometric determination. The impurities in 99.9999% rare earth oxide can be determined by the proposed method with recovery over 80%.

Keywords: Extraction chromatography, Rare earth element, Spark source mass spectrometry

1. Introduction

There still exist definite difficulties in analysing the rare earth (RE) impurities in 99.9999% multi-isotopic RE oxide (Nd, Sm, Gd, Er, Dy and Yb) directly with spark source mass spectrometry (SSMS), because the matrix seriously interferes the determination of the adjacent elements. In order to eliminate the matrix interference and improve the analytical sensitivity, it is necessary to carry out chemical separation. With mono (2-ethylhexyl) 2-ethylhexyl phosphonate (P507) containing resin as the stationary phase and HCl-NH_4Cl as the moving phase, the impurities can be separated in group or individually from the matrix after selecting appropriate separation conditions[1~3]. The matrix eluate is discarded and the impurities eluate is collected and absorbed on the chelant-active carbon column. With this method, the impurities can be concentrated up to 20 times and the sensitivity is greatly improved.

2. Experimental

2.1 Apparatus and Reagents

Superthermostat: Type CS-501, Chungking Experimental Equipment Works (China)

Spark source mass spectrometer: Type MS-702, Associated Electrical Industries LTD (England)

Scanning microphotometer: Type G Ⅱ (Germany)

Extraction chromatographic column: Φ16 × 1000 mm, with thermostatic pipe

Chelant-active carbon column: Φ8×100 mm

P507 resin: containing 55% P507, Shanghai Yuelong Nonferrous Metal Limited Company (China)

Active carbon: A. R., Beijing Guanghua Timber Mill (China)

Hydrochloric acid, Ammonium chloride, Sulfosalicylic acid and Hexamethylenetetraamine: A.R.

RE impurity standardized solution: 1 mg/mL

RE matrix standardized solution: 250 mg/mL

2.2 Preparation of chromatographic column

The column was packed with paste method. Clog some glass silk at the end of the column and stir the P507 resin evenly to gruel state and then pour the resin into the column about 900 mm. Stir the resin in the column with long glass rod in order to remove the bubble. With the resin sedimentating, new resin is added continuously into the column. When the column bed height is about 800 mm, the surplus resin is taken out from the column and the top of the bed is clogged tightly with some glass silk. The column is eluted with 1:1 HCl until there isn't Fe^{3+} in the eluate (detected with NH_4SCN) and then eluted with distilled water to neutrality. Then the column can be used.

2.3 Procedure of the separation of the resin column and Detection of rare earth elements

Adjust the mixed solution of RE matrix and adjacent elements to PH 2～4 and inject the solution into the column, controlling the column temperature about 50±5℃ and the sample injection rate at 0.2 mL · min^{-1} · cm^{-2}. When the mixed solution is on the same level with the column bed, rinse the beaker and the column wall with a little distilled water several times. After the rinsing solution is on the same level with the column bed, shut the clip and let the column balance about 5～10 hours.

Link the separating funnel filled definite acidity eluent with the column and control the elution flow rate at 1 mL · min^{-1} · cm^{-2}. The eluate is collected every 25 mL. Taking 15 mL out of the every 25 mL eluate, add 3～5 mL 10% sulfosalicylic acid (masking the interference elements, such as Fe, Al ect.) and 2～3 drops 0.5% xylenol orange indicator into the solution, then adjust the solution to red with 1:1 $NH_3 \cdot H_2O$ and then to yellow with 1:1 HCl and add two drops more 1:1 HCl. In the end, add 3 mL 10% hexamethylenetetraamine buffer and titrate the solution to brilliant yellow with 0.002 mol/L EDTA.

2.4 Concentration and Determination

The impurities eluate are mixed and adjusted to pH 7～8 and the internal standard element is added to it. And then, the trace RE impurities are absorbed on active carbon by passing through the chelant-active carbon column[4]. The active carbon with impurities is ashed and the ignited residue is ground evenly and pressed into "T" type electrode and determined in optimum SSMS parameters.

3. Results and Discussion

3.1 Chemical separation

The optimum separation acidity and matrix load capacity are selected by experiment. With those optimum conditions, each rare earth impurity is completely separated and the recovery is 90～110%.

3.1.1 Selection of elution acidity

The elution acidity influences the separation effect directly. With 200 mg RE oxide as matrix, adding respectively 1 mg other 14 rare earth elements (REE) as impurities, we have separated the REE with different acidity eluents and selected the optimum separation acidity. The result is shown in Table Ⅰ and elution curves are shown in Figure 1～7. Table Ⅱ～Ⅶ show the recovery and the blank area of each REE.

Table I Elution Acidity of Each REE in Different Matrix (HCl, mol/L+1 mol/L NH_4Cl)

REE	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Y	Er	Tm	Yb	Lu
Nd_2O_3	0.07	0.07	0.07	0.20	0.20	0.30	0.30	0.60	0.60	0.60	1.70	1.70	1.70	1.70	4.00
Sm_2O_3	0.07	0.07	0.07	0.07	0.30	0.30	0.60	0.60	0.60	0.60	1.70	1.70	1.70	1.70	4.00
Gd_2O_3	0.20	0.20	0.20	0.20	0.20	0.20	0.50	4.00	4.00	4.00	4.00	4.00	4.00	4.00	4.00
Dy_2O_3	0.07	0.07	0.07	0.20	0.30	0.30	0.30	0.50	0.60	0.70	0.70	1.70	1.70	1.70	4.00
Er_2O_3	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	0.60	/	1.20	4.00	4.00	4.00
Yb_2O_3	0.08	0.08	0.08	0.08	0.20	0.20	0.60	0.60	0.60	0.60	/	1.70	1.70	1.70	4.00

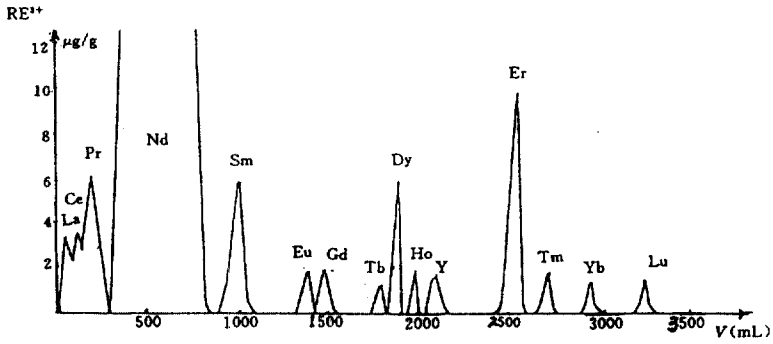

Fig. 1 Elution curve of rare earth elements in Nd_2O_3

Table II Recovery and Blank Area of Elements in Nd_2O_3

element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Y	Er	Tm	Yb	Lu
recovery(%)	125	137	137	91	135	73	93	69	101	61	73	130	59	50	65
elution volume(mL)	100	125	55	525	125	125	100	25	50	25	100	105	75	75	25
blank area (mL)	0	0	0	5	75	225	5	25	25	50	50	200	50	300	225

elution volume : 3300 mL, elution cycle : 132 h

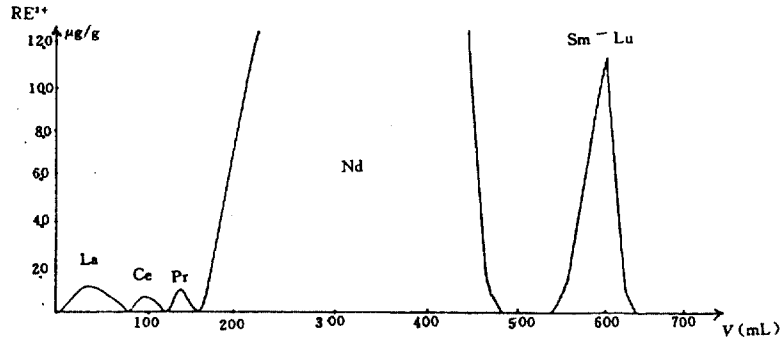

Fig. 2 Elution curve of groups separation of rare earth elements in Nd_2O_3

Table Ⅲ Elution Volume and Recovery of Groups Separation of REE in Nd_2O_3

element	La—Pr	Nd	Sm—Lu
recovery (%)	98	104	100
elution volume (mL)	162	309	76

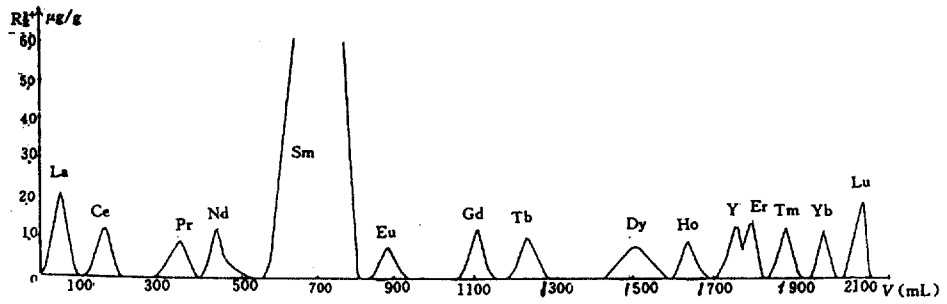

Fig. 3 Elution curve of rare earth elements in Sm_2O_3

Table Ⅳ Recovery and Blank Area of Elements in Sm_2O_3

element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Y	Er	Tm	Yb	Lu
recovery(%)	104	86	91	88	96	68	92	80	130	77	/	/	82	80	113
blank area(mL)	15	30	90	10	50	38	110	40	161	15	/	30	10	30	/
elution volume(mL)	75	90	135	145	200	110	60	84	155	67	/	140	100	130	90

elution cycle : 40 h, elution volume : 2700 mL

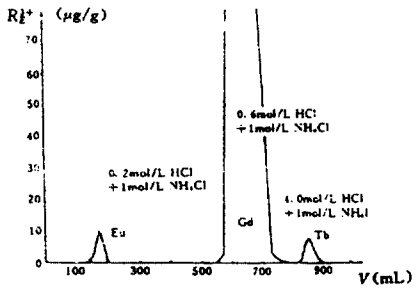

Fig. 4 Elution curve of adjacent elements in Gd_2O_3

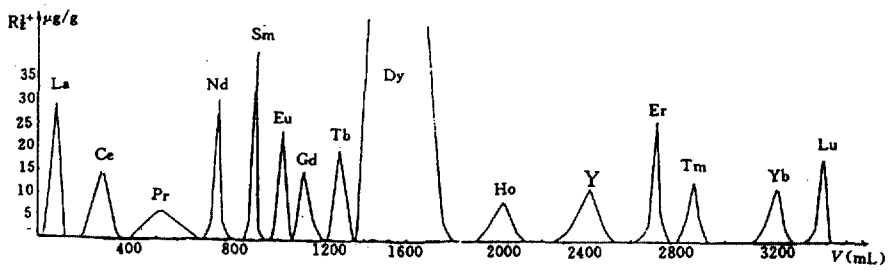

Fig. 5 Elution curve of rare earth element in Dy_2O_3

Table V Elution Volume and Blank Area of Element in Dy_2O_3

element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Y	Er	Tm	Yb	Lu
recovery(%)	115	108	94	94	104	108	97	96	97	97	97	99	93	99	103
blank area(mL)	82	82	32	106	44	5	65	5	90	25	81	63	78	75	/
elution volume(mL)	61	125	267	105	64	83	80	125	426	307	327	80	105	185	78

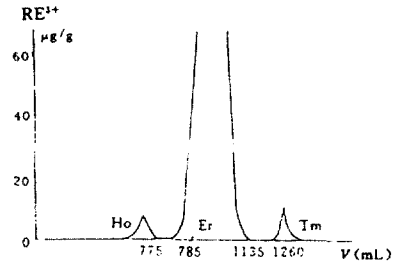

Fig. 6 Elution curve of adjacent elements in Er_2O_3

Table VI Elution volume and Blank Area of Ho—Er—Tm at Different Elution Acidity

HCl(mol/L) +1 mol/L NH_4Cl	Ho		
	recovery(%)	elution volume(mL)	blank area(mL)
0.5	94	1425	250
0.6	96	775	150
0.7	102	500	5
0.8	111	225	0
HCl(mol/L) +1 mol/L NH_4Cl	Tm		
	recovery(%)	elution volume(mL)	blank area(mL)
1.0	97	425	100
1.2	99	300	100
1.4	104	200	0

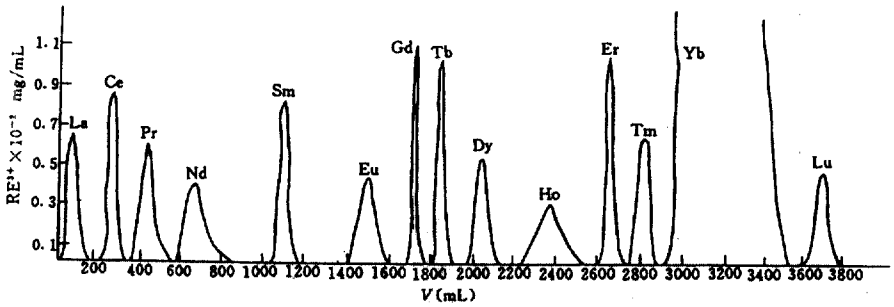

Fig. 7 Elution curve of rare earth elements in Yb_2O_3

Table Ⅶ Recovery and Blank Area of Rare Earth Elements in Yb_2O_3

element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
recovery(%)	89	80	80	93	84	82	98	96	99	80	87	80	97	68
blank area(mL)	68	40	20	100	200	100	40	100	120	100	20	60	40	/
elution volume(mL)	128	100	100	200	120	100	20	80	120	280	80	120	600	200

elution cycle: 50 h, elution volume: 3300 mL

3.1.2 Influence of matrix load capacity

The matrix load capacity (MLC) is an important factor of effecting the chromatographic efficiency. If the MLC is changed, the recovery and the elution volume will be changed in the meantime, which are shown in Table Ⅷ. From the Table, we can see that the REE will be separated completely if the MLC is below 250 mg.

Table Ⅷ Influence of Matrix Load Capacity

load capacity (Gd, mg)	Eu		Tb	
	recovery(%)	elution volume(mL)	recovery(%)	elution volume(mL)
20	112	650	117	1090
150	95	500	106	1050
250	100	1200	99	1000

3.2 Sample analysis

In the course of analysing a sample with SSMS, because the vacuum spark discharge in ion source comprises many complicated physical processes in producing ion current and the ionization efficiency of different element and the instrument transmission efficiency of different ion are not alike completely and the mass response of the photoplate is also different, the sensitivity of every element is inconsistent. The relative sensitivity factor is evaluated to correct the semiquantitative result by using the synthetic standard sample of similar substance. And then, the quantitative analytical result can be acquired.

We have analysed the trace RE impurities in 99.9999% RE oxide with the relative sensitivity factor method. The relative sensitivity factor and the relative standard deviation are listed in Table Ⅸ and the accuracy is shown in Table Ⅹ. Table Ⅺ shows the analytical result of the samples.

Table IX Relative Sensitivity Factor (R) and Relative Standard Deviation (RSD%)

element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
R	2.5	1.6	1.4	1.8	1.1	0.78	0.92	1.1	1.0	0.9	1.0	0.75	1.1	1.0
RSD%	7.8	14	15	22	10	29	23	11	11	13	7.4	12	14	11

Table X Recovery of Rare Earth Elements

element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
recovery(%)	83	105	112	76	76	104	108	93	92	88	97	102	72	119

Table XI Analytical Result of Samples (μg/g)

element	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
Nd_2O_3	<0.010	0.012	0.020	/	0.080	0.021	0.037	0.018	0.021	0.012	0.018	0.012	0.020	0.014
Sm_2O_3	0.010	0.060	0.020	0.18	/	0.026	0.12	0.012	0.034	0.030	0.023	0.012	0.066	0.013
Dy_2O_3	<0.010	0.015	0.010	0.040	0.040	0.020	0.050	0.010	/	0.013	0.037	0.021	0.040	0.013
Gd_2O_3	<0.026	<0.030	<0.026	<0.10	<0.11	0.055	/	0.030	0.11	<0.031	<0.095	<0.032	0.10	<0.033
Er_2O_3	<0.030	<0.038	<0.033	<0.065	<0.074	<0.069	<0.075	<0.038	<0.063	<0.039	/	0.12	<0.13	<0.04
Yb_2O_3	0.013	0.058	0.010	0.049	0.026	0.93	0.077	0.007	0.026	0.0076	0.018	0.016	/	0.013

Conclusions

This method which can eliminate the matrix interference satisfactorily solves the problem of reconcentrating ultra trace RE impurities in big volume eluate. The enrichment multiple is 10^3 and the recovery is up to 99%. Furthermore, comparing with extraction enrichment method, this method has the advantage of no preconcentration, simplicity and little contamination.

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