Pergamon

0039-9140(94)E0115-8

Talanta, Vol. 41, No. 11, pp. 1807–1813, 1994

0039-9140/94 $7.00 + 0.00

EXTRACTIVE CHROMATOGRAPHIC SEPARATION AND INDUCTIVELY COUPLED PLASMA ATOMIC EMISSION SPECTROMETRIC DETERMINATION OF TRACE IMPURITIES IN HIGH PURITY EUROPIUM OXIDE

Xiao-Jin Yang
China Institute of Atomic Energy, P.O. Box 275-93, Beijing 102413, China

(*Received* 29 *December* 1993. *Revised* 28 *March* 1994. *Accepted* 4 *April* 1994)

Summary—An easily applicable separation method has been developed for the accurate and simultaneous determination of trace amounts of Al, Ca, Co, Cr, Cu, Mg, Mn, Ni, Pb and Zn in high purity europium oxide by inductively coupled plasma atomic emission spectrometry (ICP-AES) combined with extraction chromatography. Spectral interferences and europium matrix effects were examined. The chromatographic separation procedure was carried out with a di-(2-ethylhexyl) phosphoric acid (HDEHP)-Levextrel resin as the stationary phase, which retained the matrix europium, and dilute nitric acid as the mobile phase, which eluted the analyte of interest. The effect of nitric acid concentration on the adsorption of europium and the analyte ions on the resin, the eluting behaviour of these elements on the chromatographic column, and the capacity of the resin for europium oxide were investigated. The quantitative limits for determination (10 σ), based on a 0.5-g amount of europium oxide, are between 0.36 μg/g for Mn and 6.4 μg/g for Pb. The method was applied to two spiked samples and a high purity europium oxide certified reference material. Results were obtained for recoveries of 93.2–112% and precision of 4–13%, expressed as the relative standard deviation and excellent agreement with the certified value with a relative error of <4%.

Rare earth elements (REEs) are increasingly being used for many different high technology applications such as laser, optical fibres, X-ray films, luminous materials and superconductors. For instance, europium oxide of the highest purity is used as raw material, *e.g.* phosphor powder $Y_2O_3:Eu^{3+}$ and $Y_2O_2:Eu^{3+}$ used in tricolour tubes, and in the production of microelectronic systems. Current production of REEs puts specific requirements on the analytical process, and they have to conform to a high degree of purity necessitating exact quality control requirements. For example, the content of copper, lead and nickel in europium oxide used as phosphor powder needs to be controlled and should not exceed 5, 10 and 10 μg/g, respectively. Hence, analytical methods capable of measuring impurities at μg/g or sub-μg/g levels in high-purity europium oxide are increasingly required. Determination by different methods should be discussed from the point of view of at least one of the following: low detection limits, accuracy and precision, expense and length of analysis (duration).

It is well known that atomic adsorption spectrometry (AAS) is very effective in determining trace elements. However, it has been reported[1,2] that the direct determination of trace elements at the μg/g level in high-purity europium oxide by AAS is very difficult and even impossible. In order to eliminate the interferences and matrix effects, the solvent extraction separation of Cu, Pb, Ni and Fe from europium oxide using ammonium pyrrolidinedithiocabamate (APDC)-isobutyl methyl ketone (IBMK) prior to AAS measurement was introduced[1] and, as a result, the detection limits obtained were much improved.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) has been widely applied for the determination of impurities in pure rare earth oxides[3–6] owing to its potential advantages of low detection limits, good precision and wide dynamic ranges of calibration. However, the ICP emission spectra of many REEs are very complex and, as a result, the complexity of the spectra makes the ICP-AES technique less selective in spite of its high power of detection owing to an incidental overlap of the spectra.[7–9] The application of the ICP-AES method is limited by the extraordinary line-richness of europium as well as other matrices. Liao *et al.*[10] showed that the direct determination of trace impurities in high purity rare earth by ICP-AES is very difficult and the chemical separation and enrichment of analyte is necessary. They determined trace amounts of Co, Cr, Cu, Fe, Mo, Ni and Zn in high-purity europium oxide using APDC-IBMK solvent extraction followed by ICP-AES determination. However, as APDC is only effective for transition metal ions, while not effective for the complexation of aluminium, alkalis and alkaline-earth metal ions, this solvent extraction method is not applicable simultaneously for these elements.

Di-(2-ethylhexyl) phosphloric acid (HDEHP) is a very effective extractant for REEs[11] and has been widely applied in extraction chromatography for separation of REEs.[12–15] Extraction chromatography has higher separation efficiency and less manipulation than solvent extraction. In extraction chromatography, Levextrel resin[16,17] should be mentioned. This is a type of extractant–support combination in which the support material is a styrene–divinylbenzene-based copolymers, which have a high surface area and high affinity for organic extractants. Owing to the highly cross-linked nature of the organic copolymers materials in Levextrel resin, HDEHP–Levextrel resin has been extensively applied to extraction chromatographic separation of REEs.[18–20] In our previous work, the combination of extraction chromatography using Levextrel resin with ICP detection has been successfully applied to the determination of trace impurities in high-purity uranium[21,22] and scandium oxide.[23,24] The aim of the present work is to develop a HDEHP–Levextrel resin chromatographic separation procedure combined with the widely available ICP atomic emission spectrometry which enables one to determine simultaneously the trace amounts of aluminium, alkaline earth and some transition metals impurities at the μg/g level in high purity europium oxide.

EXPERIMENTAL

Reagents

Deionized, distilled water and 'GR' grade nitric acid were used for preparing the solutions. Standard stock solution (1 mg/ml) of individual elements were prepared by dissolving the high purity or spectral purity metals, oxides or salts in a purified 'GR' grade nitric acid. These stock solutions of each element were diluted to obtain a set of calibration standards which contained the concentration range 0.004–10 μg/ml in 0.1*M* HNO_3.

Europium oxide (99.999%), supplied by Changchun Research Institute of Applied Chemistry (Changchun, China), was used as a base matrix for the studies of spectral interference and matrix effects, capacity, adsorption and elution behaviour and the recovery tests. A 10 mg/ml of europium oxide solution was prepared. EDTA standard solutions (0.0002, 0.005, 0.05 and 0.1*M*), Xylenol Orange solution (0.5%, w/v) as the indicator and acetic acid–sodium acetate buffer solution (pH 5.5) were prepared for the determination of europium by complexometry.[25] HDEHP–Levextrel resin (60–75 mesh, HDEHP loading: 40–50%, w/v) was obtained from Beijing Research Institute of Chemical Engineering and Metallurgy.

Apparatus and conditions

The ICP-AES determination was carried out on an ARL 3580 combined sequential-simultaneous ICP instrument. The vacuum spectrometer was equipped with 26 fixed channels and used a concave grating in a Paschen–Runge mounting. The instrumental facilities and operating conditions used in this work are summarized in Table 1. A DEC PDP 11/23+ computer controlled all instrument functions.

Distribution ratio measurements

The distribution ratios (D) of europium and impurity elements under study between the resin and an aqueous solution were determined by a batch technique. Batches of air-dried resin (1.0 g) were placed in 50-ml polyethylene bottles, followed by addition of 1 ml of impurity elements solution (50 μg/ml) and 4 ml of europium oxide solution (10 mg/ml). Appropriate concentrations of dilute nitric acid were added to give a final volume of 25 ml. The bottle was shaken until equilibrium was attained. The suspension was then filtered with dry filter paper and the remaining europium and metal concentrations in the solution were determined by EDTA titration[25] and ICP-AES, respectively. The D values were calculated from

$$D = [(C_i - C_e)/C_e]V/W,$$

where C_i and C_e are the concentration of the solution initially and after equilibrium, respectively, and V and W are the volume (ml) of the solution and weight (g) of the resin used, respectively.

Table 1. Instrumentation and operating conditions for ICP-AES

ICP spectrometer	ARL 3580
RF generator:	
Frequency	27.12 *MHz*
Forward power	1.2 *kW*
Reflected power	<5 *W*
Argon flow rate:	
Coolant gas	12 *l/min*
Plasma gas	0.8 *l/min*
Carrier gas	1 *l/min*
Observation height	15 *mm* above load coil
Nebulizer	Meinhard TR-30-A$_3$ concentric glass nebulizer
Sample uptake rate	1.5 *ml/min*
Stabilization time	20 *sec*
Signal integration time	10 *sec*
Integration cycle	2
Wavelength (*nm*):	
Al	308.215
Ca	317.933
Co	228.616
Cr	267.716
Cu	324.754
Mg	279.079
Mn	257.610
Ni	231.604
Pb	220.350
Zn	213.856

Preparation of chromatographic column

HDEHP–Levextrel resin (5 and 12 g) were soaked in water overnight and then packed into glass columns (10 mm I.D.) with a sintered-glass plate at the bottom to give a bed height of 92 and 230 mm, which were prepared for breakthrough study and sample separation, respectively. A small amount of PTFE fibres was placed at the top of the resin in the column so as not to disturb the resin during passage of sample solution and eluent. Before using the column, the resin was eluted with 3M hydrochloric acid to remove any residual impurities in the resin. Before loading, the resin column was pre-equilibrated with 0.1M nitric acid.

Adsorption and breakthrough capacity measurements

The adsorption capacity of the resin for europium oxide was determined at 0.1M HNO_3 medium. Solution (5 ml) containing 80 mg europium oxide was added to 200 mg of resin and then shaken until equilibrium. The suspension was filtered and rinsed with water. The remaining europium in the solution was determined and the europium oxide difference was the static adsorption capacity.

A breakthrough study was performed with europium in 0.1M nitric acid. The solution of 5 mg/ml europium oxide was passed through the column at a given flow rate until the concentration of europium in the effluent was in agreement with that in the feed solution. Then, the column was washed with 0.1M nitric acid until no europium was detected in the effluent. Afterwards, the europium retained on the resin was eluted with 3M hydrochloric acid and collected and adjusted to pH 5.5 followed by determination as described above, and the determined value of the content of europium was the breakthrough capacity.

Procedure for column separation

A given volume (2–5 ml) of 0.1M nitric acid solution containing europium and impurity elements was loaded on the column and then dilute nitric acid was passed through the column. The effluents were fractionated into 5 ml portions and the concentration of impurity elements was determined by ICP-AES. For europium retained on the column, 3M hydrochloric acid was used as eluent and the europium eluated was determined.

ICP-AES measurement

All sample and standard solutions were made up to 0.1M nitric acid. The ICP-AES measurements were carried out using the facilities and conditions summarized in Table 1. The linear regression calibration data of standard solutions were reproducible and the correlative coefficients were all over 0.9990.

RESULTS AND DISCUSSION

Spectral interference and matrix effects

In terms of the wavelength tables of ICP emission,[26] it can be seen that for the prominent lines of Cu I 324.754 and 327.396 nm, the emission lines of Eu I 324.732, 324.755 and 327.277 nm will cause interferences, which was experimentally verified in this study, as shown in Fig. 1, which is a schematic representation of the spectral scans of solutions containing (a) Cu (2 μg/ml) as analyte and (b) Cu (2 μg/ml) and europium oxide (2 mg/ml) mixture.

The effect of the matrix europium concentration on the emission intensity of the elements was also investigated. This was done by aspirating solutions containing 2 μg/ml of analytes and various concentrations of europium oxide (10–2000 μg/ml) into the plasma and measuring

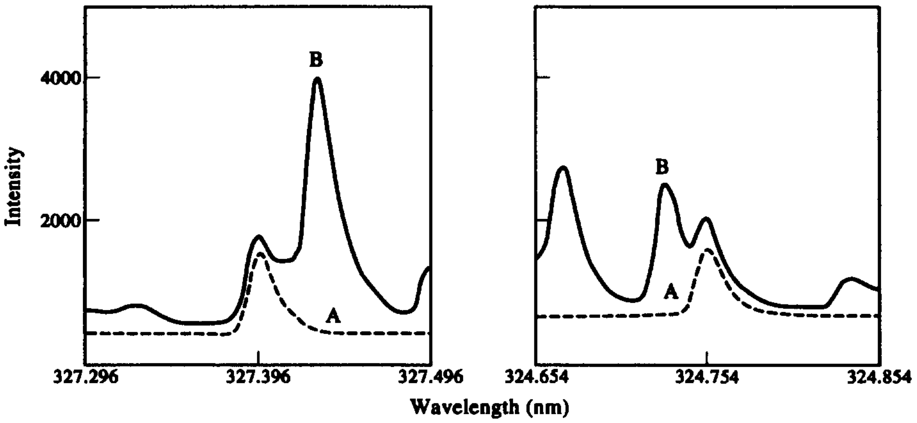

Fig. 1. Wavelength scans in the vicinity of the Cu I 327.396 and 324.754 nm lines. (A) 2 μg/ml Cu and (B) 2 μg/ml Cu + 2000 μg/ml Eu_2O_3.

the peak emission and the background intensities at the wavelength used for the analyte determinations. The results demonstrated that with increasing matrix europium concentration, the intensity at the background positions for all of the elements under study showed a considerable growth, whereas the peak emission signal even increased a little, but in contrast, decreased for some elements such as Co, Ni and Ca. The tolerance limit for europium oxide, if significant matrix effects are to be avoided, is 200 μg/ml. Hence, separation of analytes from the matrix europium prior to ICP-AES measurement should be a very effective method to avoid spectral interferences and matrix effects and improve detectability.

Adsorption and distribution of europium and impurity elements

Zhou and Wang[27] measured the distribution ratio of europium between 0.5*M* HDEHP–kerosene and aqueous solution as a function of concentration of nitric acid (0.1–1*M*). In this work, the adsorption of europium and impurity elements on the HDEHP–Levextrel resin was tested in the range of 0.1–1*M* nitric acid. The results (Fig. 2) show that the plot of $\log D_{Eu} - \log [HNO_3]$ is linear with a slope of approximately -3, which is in agreement with that of the solvent extraction system.[27] Therefore, the adsorption reaction can be written as

$$\underset{\text{(aqueous phase)}}{Eu^{3+}} + \underset{\text{(resin phase)}}{n\,(HR)_2} \rightleftharpoons \underset{\text{(resin phase)}}{Eu(HR_2)_3(HR_2)_{n-3}} + \underset{\text{(aqueous phase)}}{3H^+},$$

where $(HR)_2$ denotes the dimer of HDEHP in the neutral form and $Eu(HR_2)_3(HR_2)_{n-3}$ is the complex of HDEHP with Eu(III) ion ($n \leqslant 3$).

From Fig. 2, it can also be seen that negligible adsorption was obtained for Al, Pb and Cu, suggesting that complexes were not formed between HDEHP and these elements. Other elements under study with the exception of Fe showed a similar behaviour with these three elements.

Adsorption capacity and breakthrough curve

In the utilization of a chromatographic column, the breakthrough capacity is an important parameter. The capacity of the resin is one of the factors that determine how much

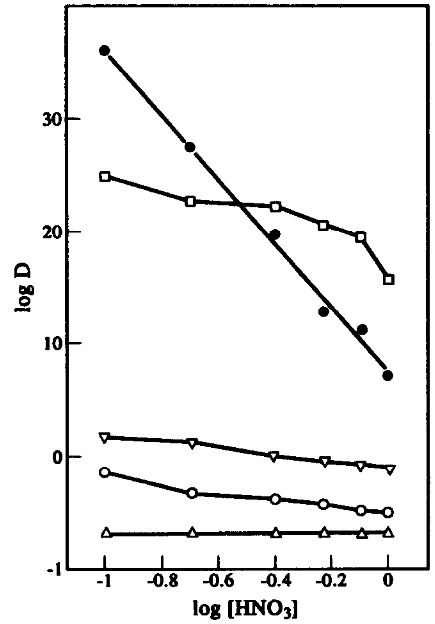

Fig. 2. Distribution ratio of europium and impurity elements between the aqueous solution and the HDEHP–Levextrel resin. (●) Eu, (□) Fe, (▽) Al, (○) Pb and (△) Cu.

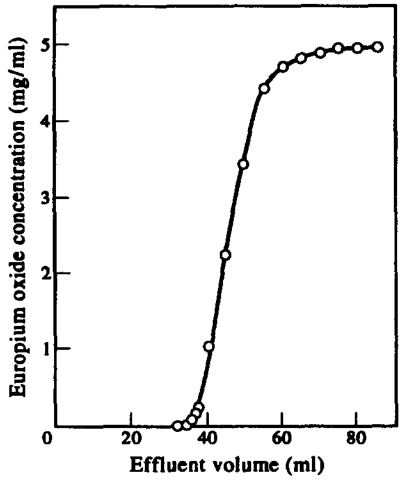

Fig. 3. Breakthrough curve for europium on the resin column (10 mm I.D. × 92 mm bed height). Resin, 40–50% (w/w) HDEHP, 60–75 mesh; concentration of europium oxide, 5 mg/ml in 0.1*M* nitric acid; flow rate: 0.25 ml/min.

resin will be needed for the quantitative separation of impurities from a given amount of analysed sample taken. First, the static adsorption capacity of the resin for europium was measured and the value was found to be 63.8 mg Eu/g dry resin. Then, the breakthrough study was carried out and the breakthrough curve for europium in 0.1*M* nitric acid at a flow rate of 0.25 ml/min is shown in Fig. 3. The breakthrough capacity was 47.6 mg Eu/g dry resin. Therefore, it could be concluded that for a mass of 0.5 g europium oxide, 12 g of the resin in a column of internal diameter 10 mm to give a bed height of 230 mm was sufficient for the separation purpose.

Column separation

In extraction chromatography numerous extraction and back-extraction steps will occur in the course of elution. Consequently, a chromatographic system involves multi-separation steps and as a result, the separation efficiency is superior to the solvent extraction system. Thus, from the extraction chromatography feature and the distribution and adsorption data, it could be concluded that the separation of trace amounts of impurity elements, except for iron, from a large amount of europium can be achieved simply by elution with diluted nitric acid using HDEHP–Levextrel resin as stationary phase. Examples of the elution curves for impurity elements and europium are shown in Fig. 4. It was found that iron was retained on the column during the elution process. The separation of μg amounts of impurity elements, except for iron, from 0.5 g of europium oxide was easily performed by elution with 0.1*M* nitric acid; 0.5 g europium oxide was completely retained on the column and 20 ml of 0.1*M* nitric acid was sufficient to eluate the analyte ions, and the elution peaks of all the elements were sharp. The europium retained on the column was stripped with 30 ml of 3*M* hydrochloric acid followed by washing with 50 ml water so that the resin was regenerated.

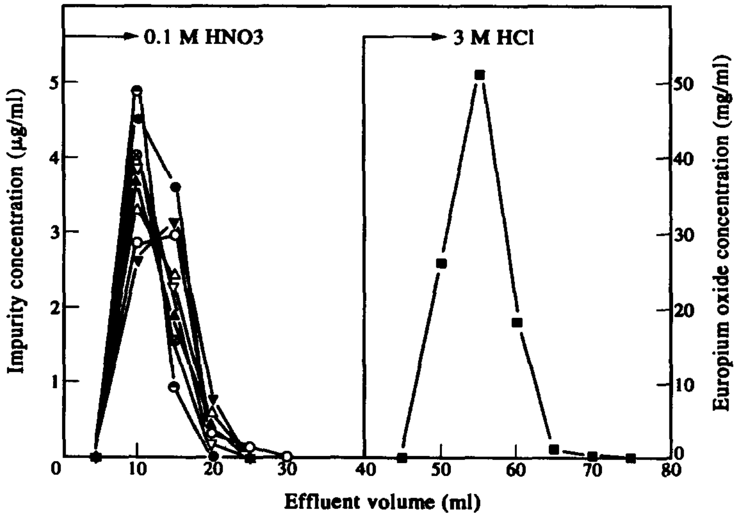

Fig. 4. Elution curves for impurity elements and europium on a HDEHP–Levextrel resin column (10 mm I.D. × 230 height). (○) Al, (●) Ca, (◒) Cu, (⊗) Ni, (▽) Mn, (▲) Co, (△) Pb, (▼) Zn and (■) Eu. Loading, 25 μg of impurities and 0.5 g of europium oxide; flow rate: 0.8 and 0.5 ml/min for 0.1*M* nitric acid and 3*M* hydrochloric acid, respectively.

The eluate was analysed for europium and the concentration of europium in the eluate was found to be <5 μg/ml for a freshly prepared and regenerated column. Hence the matrix effects and the spectral interferences were completely eliminated after the separation in terms of the above studies of spectral interference and matrix effects.

The effect of flow rate was examined. The flow rate was varied from 0.2 to 1.5 ml/min. A flow rate of 0.2–0.8 ml/min for 0.1*M* nitric acid did not affect the elution of impurities and the retention of europium and 0.5 ml/min flow rate for europium stripping remained suitable.

Regarding the life of the resin in the column, no significant bleeding of the extractant HDEHP from the column was observed by analysing the content of P in the effluents. In addition, it has been reported[28] that the performance of the column had been stable for 60 separations.

Procedure for the analysis of samples

A sample of europium oxide (0.3–0.5 g) was accurately weighed into a beaker and dissolved in 3 ml purified concentrated nitric acid by gentle warming. After complete dissolution of the sample, the solution was evaporated nearly to dryness to remove the excess nitric acid and then the residue dissolved in 5 ml water. The solution was adjusted to 0.1*M* nitric acid and then loaded on the top of a resin column previously pre-equilibrated with 0.1*M* nitric acid. The impurity elements were eluted with 20 ml of 0.1 nitric acid at the flow rate of 0.8 ml/min, whereas europium was adsorbed on the resin. The first 5 ml effluent was discarded and the following 20 ml effluent containing the analyte ions was collected and analysed by ICP-AES using the operating conditions defined in Table 1.

Detection limits

In order to evaluate the blank concentration and the detection limits, replicate blank procedures were carried out. For each impurity element, no sample was taken, but all the other steps were the same as the procedure for the analysis of the sample. The blanks were 'total blank', including the dissolution acid, the resin, the elution blanks and the contamination during the sample dissolution, separation and determination. The detection limit, defined by the instrument's software, was calculated as the concentration giving twice times the standard deviation (σ) of the blank solution prepared as above. In order to provide a realistic estimate of the lowest levels of detectability, the limits of quantitative determination (LQD), calculated from 10 σ, were employed and expressed in μg/g of europium oxide. The detection limits and the LQD values for each element in μg/g with respect to europium oxide are given in Table 2.

Table 2. Detection limits and the limits of quantitative determination (LQD)

Element	Detection limit (2σ) (*μg/ml*)	LQD (10 σ) *μg/ml*	*μg/g**
Al	0.014	0.069	2.8
Ca	0.015	0.073	2.9
Co	0.005	0.023	0.92
Cr	0.003	0.013	0.52
Cu	0.002	0.011	0.44
Mg	0.016	0.079	3.2
Mn	0.0018	0.009	0.36
Ni	0.01	0.048	1.9
Pb	0.032	0.16	6.4
Zn	0.0039	0.02	0.78

*Calculated for 0.5 g of sample in 20-ml volume of the sample solution.

Accuracy and precision

First, the proposed method was applied to the analysis of spiked samples, and the recovery factors of each element were calculated. The spiked samples were prepared by weighing 0.2 g of high-purity europium oxide (99.999%), to which a given amount of each element was added. The subsequent procedure for analysis

Table 3. Recovery of impurities added to high-purity europium oxide and relative standard deviation (RSD) by the proposed method

Element	Amount (μg) Present	Added	Found	Recovery (%)	Precision as RSD (%)*
Al	2.0	2	4.20	110	13
		15	16.75	98.3	9
Ca	1.27	2	3.52	112	12
		15	15.95	97.9	10
Co	<0.2	2	1.94	97.0	7
		15	16.0	107	5
Cr	<0.1	2	2.10	105	8
		15	16.5	110	7
Cu	0.22	2	2.38	108	8
		15	16.5	108	6
Mn	<0.1	2	2.03	101	6
		15	16.25	108	4
Ni	0.18	2	2.22	102	10
		15	16.35	108	7
Pb	0.20	2	2.38	109	12
		15	14.18	93.2	11
Zn	0.20	2	2.26	103	9
		15	15.1	98.7	7

*Based on six separate determinations of the spiked samples.

Table 4. Determination of impurities in a high-purity europium oxide certified reference material (GBW 02902)

Impurity	Determined value* ($\mu g/g$)	Certified value ± SD ($\mu g/g$)
Al_2O_3	16.3 ± 2.1	—†
CaO	13.4 ± 0.86	13.0 ± 1.1
CoO	<1.2	—†
Cr_2O_3	<0.8	—†
CuO	6.88 ± 0.38	6.7 ± 0.2
MnO	<0.5	—†
NiO	9.97 ± 0.95	9.6 ± 0.8
PbO_2	7.89 ± 0.65	8.0 ± 0.3
ZnO	15.3 ± 0.84	15.6 ± 2.3

*Mean ± SD of three parallel determinations.
†No certified value.

was described as above. The results obtained are summarized in Table 3. The recoveries ranged from 93.2 to 112% and the relative standard deviation (RSD) was 4–13% even at the μg level. Furthermore, the accuracy of the proposed method was evaluated by the analysis of a high-purity europium oxide certified reference material (GBW 02902). The results, given in Table 4, are statistically indistinguishable from the certified values for the impurity elements. The precision of the determination, expressed as RSD, is better than 13%.

CONCLUSION

The extraction chromatography with HDEHP–Levextrel resin column combined with ICP-AES technique has been effectively applied to the simultaneous determination of trace amounts of aluminium, alkaline earth and some transition metal impurities in high purity europium oxide. The separation of trace analytes from a large amount of europium matrix can be achieved simply by elution with dilute nitric acid and was found to be rapid and highly efficient, but was limited to iron. The ICP-AES determination after separation is free of interferences from the europium matrix and the detection limits were improved. The proposed analytical methodology permits the determination of trace amounts of impurities in high purity europium oxide with very satisfactory levels of precision and accuracy. The proposed procedure could be extended to other high purity rare earth oxides and be used for quality control purposes as long as the analyte is not absorbed on the resin, whereas the matrix is absorbed.

REFERENCES

1. S. Mo and B. Yuan, *Fenxi Huaxue*, 1982, **10**, 482.
2. V. Spevackova, K. Kratzer and M. Cejchanova, *J. Anal. Atom. Spectrosc.*, 1991, **6**, 673.
3. M. I. Rucandio, *Anal. Chim. Acta*, 1992, **264**, 333.
4. S. M. Marathe, S. S. Biswas, P. B. Patil and P. S. Murty, *Mikrochim. Acta*, 1992, **109**, 261.
5. S. Velichkov, N. Daskalova, N. Krasnobaeva and P. Slavova, *ICP Inf. Newslett.*, 1991, **16**, 571.
6. N.-C. Ru, W.-M. Chang, Z.-C. Jiang and Y.-E. Zeng, *Spectrochim. Acta*, 1983, **38B**, 175.
7. R. K. Winge, V. A. Fassel, V. J. Peterson and M. A. Floyd, *ICP Atomic Emission Spectroscopy*, p. 7. Elsevier, Amsterdam, 1985.
8. P. W. J. M. Boumans, J. A. Tielrooy and F. J. M. J. Maessen. *Spectrochim. Acta*, 1988, **43B**, 173.
9. P. W. J. M. Boumans, Z. Z. He, J. J. A. M. Vrakking, J. A. Tielrooy and F. J. M. J. Maessen, *Spectrochim. Acta*, 1989, **44B**, 31.
10. Z. H. Liao, J. X. Zheng and Z. G. Jiang, *Rare Earth* (in Chinese), 1988, **12**(5), 19.
11. I. H. Qureshi, L. T. McClendon and P. D. Lafleur, *Radiochem. Acta*, 1969, **12**, 107.
12. E. Cerrai and C. Testa, *J. Chromatog.*, 1962, **8**, 232.
13. R. J. Sochacka and S. Siekierski, *J. Chromatog.*, 1964, **16**, 376.
14. E. Cerrai, C. Testa and C. Triulzi, *Energia Nucleare (Milan)*, 1962, **9**(4), 193.
15. H. Herrman, H. Grosse-Ruyken and V. A. Chalkin, *J. Chromatog.*, 1973, **87**, 351.
16. R. Kroebel and A. Meyer, *Ger. Offen.*, 2162951 (1973).
17. H. W. Kauczor, *Hydrometallurgy*, 1978, **3**, 65.
18. F. You, *Fenxi Huaxue*, 1983, **11**, 379.
19. W. J. Yin, W. H. Yia, Y. Y. Shen, L. Y. Wang and J. Zhang, *Rare Metals* (in Chinese), 1981, **5**(6), 1.
20. R. Blumberg, *Hydrometallurgy*, 1979, **4**, 389.
21. J. S. Guan, X. J. Yang, B. H . Gao and Y. M. Liu, *Atom. Energy Sci. Technol.*, 1993, **27**, 42.
22. X. J. Yang and J. S. Guan, *Anal. Chim. Acta*, 1993, **274**, 237.
23. X. J. Yang, J. S. Guan and T. J. Shen, *Anal. Chim. Acta*, 1993, **277**, 157.
24. X. J. Yang and J. S. Guan, *Anal. Chim. Acta*, 1993, **279**, 261.
25. C. M. Liu, S. Z. Ci and S. Q. Liang, *Rare Metals*, 1984, **8**(2), 50.
26. P. W. J. M. Boumans, *Line Coincidence Tables for ICP-AES*, Vol. 1, 2nd Edn. Pergamon Press, New York, 1989.
27. J. Z. Zhou and D. X. Wang, *Nucl. Chem. Radiochem.* (in Chinese), 1979, **1**, 57.
28. Y. B. Zhi and J. Y. Bai, *Rare Metals* (in Chinese), 1983, 7(2), 42.