Determining Trace Rare-earth Oxides in High-purity Europium Oxide by Microsecond-pulsed and Continuous Direct-current Glow-discharge Mass Spectrometry

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ABSTRACT: Establishing the purities of rare-earth oxides is an important objective as they are extensively used in a variety of applications. Herein, we reported the development of mixing and secondary-cathode methods for the microsecond-pulsed and continuous direct-current glow-discharge mass spectrometric analyses of trace rare-earth-oxide contaminants present in europium oxide samples. Matrix effects were corrected for, results were calibrated using relative sensitivity factors derived from pure copper, and the accuracy of the method was validated using Eu_2O_3 certified reference materials, with relative deviations of less than 15% obtained for most analytes in both modes.

INTRODUCTION

High-purity rare-earth oxides, such as europium oxide (Eu_2O_3), are extensively employed as advanced ceramic materials and hydrogenous storage materials,¹ among others. The purity requirements of rare-earth oxides are specified in the first version of the “Catalogue of Demonstration Guide for Key New Materials” released by the Ministry of Industry and Information Technology of P. R. China. The mass fractions of rare-earth elements need to be known because they can considerably affect the properties of the material. Inductively coupled plasma mass spectrometry (ICP-MS) is the most common technique used to analyze trace rare-earth elements in high-purity rare-earth oxides.^{2,3} However, the required sample dissolution and separation steps are very time-consuming, while dilution and the use of high blank reagents can negatively affect detection limits. In addition, as a solution-sampling technique, complex hydrogen- and oxygen-based polyatomic spectral interference can severely hamper the analysis of some rare-earth elements; *i.e.*, $^{165}\text{Ho}^+$ is interfered with by $^{164}\text{DyH}^+$, $^{141}\text{Pr}^+$ is interfered with by $^{140}\text{CeH}^+$, and $^{169}\text{Tm}^+$ is interfered with by $^{168}\text{ErH}^+$ and $^{153}\text{Eu}^{16}\text{O}^+$. Therefore, a rapid, sensitive, and reliable analytical method for the analysis of trace rare-earth oxides (elements) in high-purity rare-earth oxides is of urgent need.

As a solid sampling technique, glow-discharge mass spectrometry (GD-MS) is a powerful tool for analyzing trace elements in high-purity materials;^{4,5} further, its simple sample pretreatment protocol significantly improves analysis efficiency. High sensitivities (~ 100 cps/ppb) result in very low detection limits (down to ng kg^{-1}) in solid materials. Moreover, the polyatomic interferences derived from hydrogen and oxygen are very low because a dry aerosol is used. In addition, the use of the high-resolution ($m/\Delta m > 10000$) mode eliminates most spectral interference. Therefore, GD-MS is well-suited to the analysis of trace rare-earth elements. Direct-current glow-discharge (dc-GD) and radio frequency glow-discharge (rf-GD) sources are the two commonly used GD sources,⁶ and both can be used in the continuous and pulsed modes.

The sample needs to be electrically conducting in the dc-GD system, as it serves as the cathode. Therefore, a challenge of this work involves preparing electrically conducting samples. Auxiliary conductors, such as high-purity metal powder or foil, are necessary when analyzing non-conductive materials. A secondary-cathode technique can be used for pin-shaped^{7,8} or plate-shaped^{9,10} solid samples. On the other hand, mixing with a high-purity conducting powder is always required for powdered samples,^{11,12} although the mixing procedure may lead to some elemental

contamination.

In addition to problems associated with sample conductivity, accurate quantitative analysis is also challenging, due to a lack of matrix-matched certified reference materials (CRMs) with known chemical compositions similar to that of the sample to be analyzed. Generally, standard relative sensitivity factors (StdRSFs),¹³ which are matrix-independent, are used to calibrate the acquired data. However, the use of StdRSFs still leads to relatively large uncertainties (of a factor of approximately two)^{14,15} in most cases, and matrix-matched RSFs are always needed to provide more accurate results. Synthetic pressed tablets^{5,16} and melting bulks¹⁵ are two commonly used types of metal calibration sample; however, calibration samples of melting bulks and pressed tablets of europium oxides are difficult to prepare because auxiliary conductors are required.

In this work, europium oxides were examined by microsecond-pulsed and continuous dc GD-MS, and mixing and secondary-cathode methods were established. Matrix effects were corrected for in order to calibrate the results using RSFs derived from pure copper, and the accuracy of the method was validated using Eu₂O₃ CRMs. Finally, a real europium oxide sample was examined and its relative purity determined.

EXPERIMENTAL

Mass spectrometer. An Element GD Plus (Thermo Fisher Scientific, USA) high-resolution double-focusing sector-field glow-discharge mass spectrometer, equipped with a fast-flow Grimm-type direct-current (dc) ion source, was used in this study. The ion source can be operated in both microsecond-pulsed and continuous modes. The instrument has three mass-resolution modes, namely low (LR), medium (MR), and high resolution (HR), with resolution values of approximately 400, 4000, and 10000, respectively. The sample is required to be electrically conducting in the ion source because the sample serves as the cathode in the GD system.

Reagents and samples. High-purity 22-mesh copper powder with a nominal purity of 99.999% was purchased from Alfa Aesar Corp. (Ward Hill, MA, USA). The powder was sieved in-house into two size ranges. The powder with grains 500–600 μm in size was used to prepare the calibration samples needed to calculate the RSFs of the rare-earth elements. The powder with grains less than 150 μm in size was used as the auxiliary conductor when preparing electrically conducting samples for GD-MS. Multi-element standard solutions of 17 rare-earth elements with mass fractions of 100 mg/kg were provided by the National Institute of Metrology (NIM), P.R. China. The impurity constituents of GBW02902 europium oxide CRMs were used for validation purposes. A sample of high-purity Eu₂O₃ with a nominal purity of more than 99.999% was purchased from Alfa Aesar (Tianjing, China).

Fig. 1 High-purity copper secondary cathode (A) before and (B) after GD-MS sputtering.

Table 1. Optimized Values of the Discharge Parameters Used in Direct-current GD-MS

Discharge Parameter	Microsecond-pulsed	Continuous
Discharge voltage (V)	1000	1200V
Discharge current (mA)	30	55
Discharge gas flow (mL min ⁻¹)	505	430
Pulsed duration (μs)	70	ND ^[a]
Pulsed frequency (Hz)	2000	ND ^[a]

^[a] No data.

Sample preparation. The calibration samples used to determine RSFs were prepared by doping high-purity copper powder with rare-earth standard solutions. Details of the preparation procedure are reported elsewhere.^{5,15} The mixing and secondary-cathode methods were used to directly analyze the non-conducting Eu₂O₃. In the mixing method, mixtures, each with an optimal Cu/Eu₂O₃ mass ratio of 4:1, were prepared by mechanical mixing. Tablets of the mixtures were prepared by pressing each homogenized powder in a filling ring (i.d.=12 mm; o.d.=25 mm; height=1.2 mm) using a pressing machine (SYP-30TS, Shanghai, China) with a pressure of 30 MPa for a hold time of 20 s. In the secondary-cathode method, a 20 mm-thick cylindrical high-purity (>99.999%) copper block with a 5 mm-diameter hole was custom-made by China New Metal Co., Ltd. (Beijing, China). The surface was cleaned by grinding with a lapping machine (LaboPol-5, Struers, USA) and then ultrasonically cleaned using deionized water and ethanol. The Eu₂O₃ sample was loaded by pressing at 0.5 MPa with a pressure lever for a hold time of approximately 20 s, as shown in Fig. 1.

Glow-discharge mass spectrometry. Based on a previous study,¹⁷ GD-MS was performed in the microsecond-pulsed and dc modes when the mixing method was used, while only the microsecond-pulsed mode was used with the secondary-cathode method. The discharge parameters were optimized for high intensity and sufficient ¹⁵¹Eu analytical stability. The optimal values of the discharge parameters in the microsecond-pulsed and continuous dc modes are summarized in Table 1. Each experiment was carried out six times in succession, with the average value

Fig. 2 Mixing method: ^{151}Eu signal intensity at medium resolution (MR) as functions of time and the mass ratio of high-purity Cu to Eu_2O_3 in the continuous dc mode.

Fig. 3 Secondary-cathode method: ^{151}Eu signal intensity at medium resolution (MR) as functions of time and the secondary cathode hole diameter in the microsecond-pulsed mode.

Table 2. Limits of Quantification (LoQ) of Rare-earth Oxides Using the Mixing and Secondary-cathode Methods

Oxide	LoQ, mg/kg		Oxide	LoQ, mg/kg	
	Mixing	Secondary Cathode		Mixing	Secondary Cathode
Y_2O_3	0.17	0.005	Tb_4O_7	0.002	0.001
La_2O_3	0.012	0.002	Dy_2O_3	0.001	0.001
CeO_2	0.79	0.041	Ho_2O_3	0.012	0.004
Pr_6O_{11}	0.081	0.002	Er_2O_3	0.007	0.001
Nd_2O_3	0.35	0.016	Tm_2O_3	0.003	0.001
Sm_2O_3	0.11	0.020	Yb_2O_3	0.007	0.019
Gd_2O_3	0.030	0.022	Lu_2O_3	0.001	0.001
SUM	1.6	0.14			

reported. The mass fraction of each rare-earth element was calculated using the following equation:

$$\frac{C_x}{C_{\text{Eu}_2\text{O}_3}} = \left(\frac{I_x}{I_{\text{Eu}}} - \frac{I_x}{I_{\text{Cu}}} \cdot R \right) \times \frac{\text{RSF}_{x/\text{Cu}}}{\text{RSF}_{\text{Eu}/\text{Cu}}} \cdot \frac{M_{\text{Eu}}}{M_{\text{Eu}_2\text{O}_3}}$$

where $C_x/C_{\text{Eu}_2\text{O}_3}$ is the mass fraction of the element in Eu_2O_3 ; I_x/I_{Eu} , I_x/I_{Cu} , and R are the ion beam ratio (IBR) of element x to Eu

derived from the mixture, the IBR of element x to Cu derived from the auxiliary Cu conductor, and the IBR of Cu to Eu from the mixture, respectively; and M is the molecular/atomic weight. The mass fraction of element x is multiplied by the ratio of the molecular mass of the oxide to the element, in the case of an oxide.

RESULTS AND DISCUSSION

Optimizing the mass ratio in the mixing method and the hole diameter in the secondary-cathode method. The mass ratio of high-purity copper powder to Eu_2O_3 was optimized to obtain high sensitivity and good stability in the mixing method; the intensities of the ^{151}Eu signals from 1:1, 2:1, 3:1, 4:1, and 5:1 mixture at MR (Fig. 2). In view of both sensitivity and stability, a 4:1 Cu/ Eu_2O_3 mass ratio was determined to be optimal, with a ^{151}Eu sensitivity of approximately 7×10^9 cps and a relative standard deviation (RSD) of less than 1%. The diameter of the hole was also optimized in the secondary-cathode method by comparing the intensity, ^{151}Eu stability, and equilibrium time, as shown in Fig. 3. More of the Eu_2O_3 sample is exposed to the GD ion source with increasing hole diameter, resulting in a more-intense ^{151}Eu signal; however, less of the Cu conductor is exposed to the GD ion source, which increases the equilibrium time. A diameter of 5 mm was determined to be optimal, with a ^{151}Eu sensitivity of approximately 5×10^9 cps, an RSD of less than 1%, and an equilibrium time of approximately 25 min. Even though the equilibrium time associated with the secondary cathode with the 5 mm hole was much longer than that with the 3 mm hole (approximately 2–3 min), the intensity of the ^{151}Eu signal was more than one order of magnitude higher than that observed with the 3 mm hole, for which the sensitivity was approximately 2×10^8 cps.

Limits of quantification (LoQ) of rare-earth oxides determined by the mixing and secondary-cathode methods.

The LoQs of rare-earth oxides were determined statistically for the mixing and secondary-cathode methods using the 10s-criterion, as summarized in Table 2. The LoQ of most oxides were approximately one order of magnitude lower using the secondary-cathode method compared to those obtained using the mixing method, due to the lower blanks in the high-purity copper secondary cathode. The mass fractions of most rare-earth elements were less than 0.003 mg/kg in the high-purity copper secondary cathode, with the exception of Ce (0.005), Gd (0.004), Sm (0.003), and Yb (0.003). The LoQ across all oxides were 1.6 mg/kg and 0.14 mg/kg for the mixing and secondary-cathode methods, respectively. Hence, europium oxides with relative purities of more than 99.999% and 99.9999% can be measured and identified by the mixing and secondary-cathode methods, respectively.

Matrix effects in microsecond-pulsed and continuous dc GD-MS. In order to better calibrate the acquired data using the RSFs derived from pure Cu, which are relatively easy to obtain, the effects of the GD-MS matrix in the microsecond-pulsed and

Fig. 4 Matrix effects in the continuous dc mode: Pr-to-Cu ion beam ratios (IBRs) of different mixtures of doped copper (high-purity copper doped with 10 mg/kg rare-earth standard solutions) in high-purity Eu_2O_3 in the continuous dc mode at medium resolution (MR). Error bars represent standard deviations (SDs; $n = 6$).

Fig. 5 Matrix effects in the microsecond-pulsed mode: Pr-to-Cu ion beam ratios (IBRs) of different mixtures of doped copper (high-purity copper doped with 10 mg/kg rare-earth standard solutions) in high-purity Eu_2O_3 in the microsecond-pulsed mode at medium resolution (MR). Error bars represent standard deviations (SDs; $n = 6$).

continuous dc modes were investigated. High-purity Cu powder samples doped with 10 mg/kg elemental rare-earth standard solutions were prepared and are referred to as “doped copper” powder in this work. High-purity Eu_2O_3 , for which the mass fractions of all rare-earth elements were very low (<0.1 mg/kg), was used. Mixtures of “doped copper” and high-purity Eu_2O_3 with mass ratios of 2:1, 3:1, 4:1, and N:0 (doped Cu only) were prepared. The rare-earth element in each of the various mixtures had the same mass fraction relative to Cu (the rare-earth elements in Eu_2O_3 can be ignored); hence the matrix effect can be studied by comparing the IBRs of the rare-earth elements relative to Cu.

An optimized discharge current of 55 mA was used in the continuous dc mode when the 2:1, 3:1, and 4:1 mixture were examined, with a ^{63}Cu sensitivity of approximately 7×10^9 cps determined at MR for the 4:1 mixture. The Pr-to-Cu IBRs, as examples, in the various mixtures are compared in Fig. 4, which shows that the IBR of Pr in the N:0 sample at 55 mA is twice that

of the 4:1 mixture, thereby confirming the presence of a marked matrix effect. This observation is attributable to variations in the real-time discharge voltage, which was 589 V at 55 mA when analyzing the 4:1 mixture, but 1081 V when analyzing the N:0 sample. The Pr sputtering efficiency is enhanced at a higher discharge voltage, leading to a distinct IBR discrepancy. The results obtained for the mixtures were calibrated using the RSFs determined using the N:0 calibration sample at a current of 35 mA. The IBRs for Pr in the 4:1 mixture and the N:0 sample agree well at 35 mA. The real-time voltage and current were approximately 800 V and 33.6 mA, respectively, at 35 mA; the voltage was higher and the current was lower than those observed at 55 mA when the 4:1 mixture was analyzed. The opposite effect resulted in good agreement. In other words, the matrix effect was corrected for by optimizing the discharge parameters. Accurate values can be obtained in the dc mode when calibrated using RSFs measured at 35 mA (other parameters listed in Table 1) using the N:0 sample.

The same discharge parameters were used to analyze the various mixtures in the pulsed mode. The Pr-to-Cu IBRs were in good agreement to within uncertainty intervals, even though the IBR of the 4:1 sample appeared to be 15% higher than that of the N:0 sample, as shown in Fig. 5. This slight difference may be due to differences in real-time discharge currents. The real-time current was approximately 12 mA when the N:0 sample was analyzed, whereas it was approximately 26 mA for the 4:1 mixture. The higher current enhances both sputtering efficiency and ionization efficiency. Actually, the Eu-to-Cu IBR of the 4:1 sample was also approximately 15% higher than that of the N:0 sample; hence, the Pr-to-Eu IBR of the 4:1 sample was close to that of the N:0 sample. In other words, the values measured in the pulsed mode can be calibrated using RSFs measured with N:0 calibration samples possessing the same parameters as the 4:1 sample.

Validating and comparing the mixing and secondary-cathode methods.

GBW02902 europium oxide CRMs containing 14 rare-earth impurities were used to validate the two methods, with the optimal mass ratio of 4:1 used in the continuous dc mode with the mixing method. The results calibrated using RSFs determined at 35 mA, 45 mA, and 55 mA, as well as the standard RSFs provided by the spectrometer manufacturer, are summarized in Table 3, with the average values of six replicates and their standard deviations (SDs) reported. The SDs were obtained by combining the IBR and RSF RSDs. Relative deviations ($D/\%$) were calculated using the equation: $D = (C_{\text{measured}} - C_{\text{certified}}) / C_{\text{certified}} \times 100\%$. Table 3 reveals that the results calibrated using RSFs at 35 mA best match the certified values, with relative deviations of less than 15% for most oxides; relative deviations of 30% and 45% were determined at 45 mA and 55 mA, respectively, which is ascribable to the matrix effect. It is noteworthy that the results calibrated using the StdRSFs are in good agreement with the certified values, with relative deviations of less than 20%. Therefore, from the perspective of simplicity, calibration using the StdRSFs is greatly advantageous when an accuracy of $\pm 20\%$ is acceptable.

Table 3. Data Acquired in the Continuous DC Mode Using the Mixing Method with Certified Values

Oxide	Mass fraction (mg/kg) ^[a]					D ₁ ^[c] /%	D ₂ ^[c] /%	D ₃ ^[c] /%	D ₄ ^[c] /%
	Certified	RSF-35 mA ^[b]	RSF-45 mA ^[b]	RSF-55 mA ^[b]	StdRSF ^[b]				
Y ₂ O ₃	17.2±1.0	16.9±2.4	20.7±2.9	24.1±3.4	16.2	-1.5	20.1	40.2	-5.9
La ₂ O ₃	12.8±1.2	14.3±2.0	15.3±2.2	16.5±2.4	10.5	12.1	19.3	29.2	-17.6
CeO ₂	3.4±0.4	3.9±0.5	4.1±0.5	4.2±0.5	2.8	15.0	19.7	23.9	-16.8
Pr ₆ O ₁₁	15.2±1.5	12.3±1.8	13.5±2.0	17.1±2.5	15.6	-19.1	-11.1	12.2	2.9
Nd ₂ O ₃	11.8±0.6	10.2±1.4	11.3±1.6	13.0±1.8	9.8	-13.8	-4.2	10.6	-16.7
Sm ₂ O ₃	15.3±1.8	15.2±2.2	16.6±2.4	18.8±2.7	13.2	-0.9	8.4	23.1	-13.6
Gd ₂ O ₃	16.8±1.3	16.2±2.1	18.2±2.3	22.6±2.9	15.0	-3.5	8.5	34.2	-10.9
Tb ₄ O ₇	12.2±1.0	11.3±1.3	12.5±1.4	15.6±1.8	10.8	-7.3	2.5	27.8	-11.5
Dy ₂ O ₃	11.3±0.6	11.1±1.0	12.2±1.1	13.5±1.2	10.2	-2.2	7.7	19.0	-10.1
Ho ₂ O ₃	15.0±1.0	13.3±1.3	14.9±1.4	18.3±1.8	13.9	-11.0	-0.6	21.8	-7.5
Er ₂ O ₃	12.6±1.1	12.6±1.2	13.9±1.3	15.6±1.5	12.2	0.3	10.7	24.0	-2.8
Tm ₂ O ₃	10.2±0.7	10.3±0.8	11.5±0.9	13.7±1.1	9.2	1.3	12.9	34.4	-9.8
Yb ₂ O ₃	16.3±0.6	18.6±1.5	20.8±1.6	22.1±1.7	13.2	14.0	27.5	35.5	-18.8
Lu ₂ O ₃	11.6±0.8	11.7±0.7	12.7±0.7	14.7±0.8	11.0	1.1	9.5	26.7	-5.3

^[a] Mean ± SD (n=6); ^[b] measured values calibrated using RSFs at different discharge currents; ^[c] D₁, D₂, D₃, and D₄ are relative deviations between certified and measured values calibrated using RSFs at 35 mA, 45 mA, and 55 mA, and StdRSFs, respectively.

Table 4. Data Acquired in the Microsecond-pulsed Mode Using the Mixing and Secondary-cathode Methods with Certified Values

Oxide	Mass fraction(mg/kg) ^[a]					D _{M1} ^[d] /%	D _{M2} ^[d] /%	D _{S1} ^[e] /%	D _{S2} ^[e] /%
	Certified	M-RSF ^[b]	M-StdRSF ^[b]	S-RSF ^[c]	S-StdRSF ^[c]				
Y ₂ O ₃	17.2±1.0	17.1±1.6	20.7	17.9±1.7	23.4	-0.4	20.3	4.3	36.0
La ₂ O ₃	12.8±1.2	13.8±1.3	18.8	13.7±1.3	16.7	7.5	47.1	6.8	30.6
CeO ₂	3.4±0.4	4.1±0.4	3.9	4.4±0.4	4.2	19.2	15.4	30.0	22.3
Pr ₆ O ₁₁	15.2±1.5	15.1±1.5	15.9	16.4±1.6	17.5	-0.3	4.9	7.8	15.1
Nd ₂ O ₃	11.8±0.6	12.8±1.2	15.4	13.8±1.3	17.2	8.7	30.2	16.8	45.5
Sm ₂ O ₃	15.3±1.8	16.8±1.6	19.2	17.7±1.7	19.2	9.7	25.3	15.7	25.3
Gd ₂ O ₃	16.8±1.3	17.2±1.5	21.2	19.1±1.7	27.0	2.5	25.9	13.9	60.9
Tb ₄ O ₇	12.2±1.0	12.1±0.9	13.7	13.5±1.0	16.2	-0.6	12.0	10.9	32.8
Dy ₂ O ₃	11.3±0.6	11.0±0.7	14.1	12.4±0.7	15.8	-2.5	24.5	9.7	40.2
Ho ₂ O ₃	15.0±1.0	13.2±0.9	17.8	14.5±1.0	20.1	-11.8	18.8	-3.5	34.1
Er ₂ O ₃	12.6±1.1	12.4±0.8	14.0	13.6±0.9	16.1	-1.5	11.0	8.0	27.9
Tm ₂ O ₃	10.2±0.7	9.9±0.5	12.2	10.5±0.6	13.5	-2.8	20.1	2.9	32.6
Yb ₂ O ₃	16.3±0.6	18.7±1.0	22.1	17.9±1.0	15.8	14.5	35.6	9.9	-3.0
Lu ₂ O ₃	11.6±0.8	10.3±0.4	13.3	11.7±0.4	15.8	-11.0	15.0	0.6	36.2

^[a] Mean ± SD (n=6); ^[b] measured values using the mixing method calibrated using the RSFs in this work and StdRSFs, respectively; ^[c] measured values using the secondary-cathode method calibrated using RSFs in this work and StdRSFs, respectively; ^[d] D_{M1} and D_{M2} are relative deviations between certified and measured values using the mixing method calibrated using RSFs in this work and StdRSFs, respectively; ^[e] D_{S1} and D_{S2} are relative deviations between certified and measured values using the secondary-cathode method calibrated using RSFs in this work and StdRSFs, respectively.

Table 5. Mass Fractions (mean ± 2SD) of Rare-earth Oxides in a Europium Oxide Sample, mg/kg

Oxide	Mass fraction	Oxide	Mass fraction
Y ₂ O ₃	1.7±0.5	Tb ₄ O ₇	<0.001
La ₂ O ₃	<0.002	Dy ₂ O ₃	<0.001
CeO ₂	0.40±0.16	Ho ₂ O ₃	<0.004
Pr ₆ O ₁₁	3.1±0.7	Er ₂ O ₃	0.23±0.09
Nd ₂ O ₃	2.5±0.5	Tm ₂ O ₃	<0.001
Sm ₂ O ₃	7.9±2.4	Yb ₂ O ₃	<0.019
Gd ₂ O ₃	3.4±1.3	Lu ₂ O ₃	0.12±0.04

Both, the mixing and secondary-cathode methods, were used in the microsecond-pulsed mode. The RSFs of the rare-earth elements in the microsecond-pulsed mode with the optimized parameters listed in Table 4 were measured using the calibration samples, the details of which are found elsewhere.¹⁸ The results obtained using the RSFs and StdRSFs were compared; the measured values calibrated using the RSFs in this work are in good agreement with the certified values for the mixing and secondary-

cathode methods, with relative deviations of less than 15% determined for most elements. However, the results calibrated using the StdRSFs exhibit poor accuracies, with relative deviations of up to 40% and 50% for the mixing and secondary-cathode methods, respectively, which is probably ascribable to the fact that the StdRSFs were determined in the dc mode, rather than in the pulsed mode.

Europium oxide sample analysis. In view of its lower LoQs, the secondary-cathode method was used to analyze a europium oxide sample, with the results calibrated using the RSFs determined in this work. The results for the 14 rare-earth oxides are summarized in Table 5. The sum of the mass fractions of all rare-earth oxides was determined to be 19.3 ± 2.9 mg/kg (mean ± 2SD); hence the relative purity of the Eu₂O₃ sample is 99.9981 ± 0.0003 %. According to the Chinese National Standard Terms of Rare Earths (GB/T 15676-2015), this Eu₂O₃ sample was confirmed to be a high-purity rare-earth oxide (>99.99%).

CONCLUSIONS

We developed mixing and secondary-cathode methods for the microsecond-pulsed and continuous direct-current glow-discharge mass spectrometric analyses of trace rare-earth oxides present in europium oxide samples. A 4:1 mass ratio of high-purity copper to Eu_2O_3 was determined to be optimal for the mixing method, while a 5 mm-diameter hole was optimal for the secondary-cathode method. LoQs of the order of 10^{-9} were determined for the secondary-cathode method, which are approximately one order of magnitude lower than those obtained using the mixing method. A pronounced matrix effect was observed in the continuous dc mode, but it was sufficiently low to be ignored in the microsecond-pulsed mode. The matrix effect is probably the result of real-time variations in the values of the discharge parameters in various matrix samples, and was corrected for after optimizing the discharge parameters. The accuracies of the methods were validated using Eu_2O_3 CRMs; RSF calibration led to good agreement with the certified values, with relative deviations of less than 15% for most elements. The results calibrated using StdRSFs were also in good agreement with the certified values when the continuous dc mode was used, with relative deviations of less than 20%, whereas, StdRSF calibration in the microsecond-pulsed mode resulted in poor accuracies, with relative deviations of up to 40% and 50% for the mixing and secondary-cathode methods, respectively.

In summary, the pulsed mode is advantageous over the continuous dc mode in terms of qualification limits and sample quantities because the secondary-cathode method, which exhibits lower LoQs for smaller sample amounts, can be used in this mode. On the other hand, the continuous dc mode provides superior accuracies when calibrated using StdRSFs, while the dc and pulsed modes provide similar accuracies when calibrated using the RSFs determined in this work, regardless of which method (mixing or secondary-cathode) was used.

Finally, the 14 rare-earth oxides in a Eu_2O_3 sample were determined, with the relative purity of the sample found to be $99.9981 \pm 0.0003\%$, which meets the product standard of a high-purity rare-earth oxide.

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Notes

The authors declare no competing financial interest.

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