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METALLURGY OF RARE AND NOBLE METALS

Separation and Preconcentration of Impurities in Rare-Earth-Based Materials for Spectrometric Methods

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Abstract—The efficiency of using rare earth metals largely depends on their impurity composition, which affects the structure and properties of materials. Before the analytical control of materials based on rare earth elements (REEs) and the starting materials for their production, the task is to determine both macrocomponents with high accuracy and impurities with high sensitivity, correctness, and precision. To determine the impurities in REE-based materials in the range from 10^{-5} to 5.0 wt %, a complex of methods of atomic emission and mass spectral analysis is frequently used. However, the analysis of REE-based materials, even using these modern highly sensitive methods, is a difficult task due to spectral and matrix interferences. Therefore, different separation/preconcentration procedures are needed to determine both rare earth and non-rare-earth impurities. This article reviews publications of preconcentration methods for spectral and mass spectral methods of analysis of materials based on REEs and some other analytical methods. It is shown that the most common approaches are liquid extraction and chromatography. Sorption, cloud-point extraction, and precipitation are also used. There is no universal approach. Each method discussed in this article has its advantages and limitations. The analytical completion of the method confirms the effectiveness of the selected separation/preconcentration method in each specific case.

Keywords: rare earth elements, separation, preconcentration, spectral analysis, inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma atomic emission spectrometry (ICP-AES)

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INTRODUCTION

Rare earth metals are widely used in industries connected with electronics, nuclear engineering, and phosphor materials [1–3]. Impurity elements noticeably affect the properties of materials based on rare earth elements (REEs). Therefore, sensitive, multielement, and reliable methods are required to determine rare earth impurities (REIs) and non-rare-earth impurities (NREIs) to meet the needs for quality control of promising functional materials based on REEs.

The application of solid-state highly sensitive methods (for example, mass spectrometry with different ionization sources) for quantitative analysis is frequently complicated because of the absence of reliable calibration and control samples despite ultimate analytical performance in terms of sensitivity. Therefore, technologies combining high-temperature atomization sources and sample dissolution have been actively implemented in recent decades.

However, these methods (inductively coupled plasma mass spectrometry (ICP-MS) and atomic emission spectrometry (ICP-AES)) have limitations connected with matrix and interelement influence, which is the most typical of REEs having multiline spectra [4, 5]. The required sensitivity and selectivity cannot be reached without preliminary extraction and preconcentration of impurities.

Spectral overlaps at ICP-AES of REE-based materials constitute a significant problem discussed in a large number of works [6–13]. It was shown in [11–13] that the presence of line interferences in REEs results in a noticeable worsening of detection limits of required elements (Na, Ca, Ni, Fe, Co, Cr, Cd, etc.). Dilution of sample solutions, use of comparison elements, and introduction of additives did not give correct results when the content of impurities was lower than 10^{-3}–10^{-2} wt %. In this case, in the analysis of sample solutions, it is proposed to use calibration solutions with a composition close to the analyzed one and preliminary separation of the matrix to take into account and minimize spectral interferences of the matrix element [11–13].

The main limitations of ICP-MS are the matrix effect and interference from polyatomic ions [14–23]. The matrix effect can be compensated by using an internal standard because the intensity of the analytical signal of its element and analyte of interest decreases simultaneously with an increase in matrix element concentration [24, 25]. However, the interference problem can limit the analytical possibilities of ICP-MS for many REE-based materials, especially high-purity ones. For example, the authors of [23] developed the method of REI, Ba, and Pb determination in Gd-based contrast agents used in magnetic resonance imaging with contrast enhancement as well as in gadolinium oxide used as a precursor. Since in ICP-MS of Gd-based substances $^{n}Gd^{16}O^{+}$ and $^{n}Gd^{16}O^{1}H^{+}$ polyatomic interferences are observed, which interfere with the determination of Tm, Yb, and Lu, a part of the study was devoted to the investigation of the possibility of their calculation. However, it was impossible to solve the problem of detecting low concentrations of these elements even with a higher resolution.

The given examples are far from being an exhaustive set of publications devoted to the problems in determining target impurities in ICP-AES and ICP-MS. Therefore, it appears to be relevant to review methods and approaches to separation of the matrix and/or preconcentration of rare earth and non-rare-earth impurities concerning the analysis of rare earth metals and materials based on them. This work summarizes the trends in this area with an emphasis on the methods of spectral and mass spectral analysis.

PRECONCENTRATION OF RARE EARTH IMPURITIES

There are many ways to preconcentrate impurities in rare earth materials [26–58]. Procedures based on liquid and liquid-solid-phase extraction, sorption, and coprecipitation are used. Each approach has its own features. Extraction and preconcentration of REEs from rare earth matrices are especially interesting. This is connected with the fact that REEs have similar chemical and physicochemical properties. Even trace amounts of REEs can significantly change the functional characteristics of materials. Table 1 presents summarized information on the application of REE extraction methods combined with spectrometric methods of analysis; below, we will consider them in more detail.

Chromatographic methods are the most widely used for group preconcentration or separation of REIs from the base element owing to their high efficiency and separation rate. They allow one to separate ions with close chemical properties, including REEs. The separation of these ions by common chemical methods is extremely complicated. As seen in Table 1, works are mainly devoted to the determination of impurity elements in different REE oxides, including high-purity ones; ICP-AES and ICP-MS are used. In this case, it is the separation of impurity elements from the analyzed base that makes it possible to solve frequently occurring problems associated with spectral interferences.

Liquid-solid chromatography [26–44] is based on the separation of the liquid (sample solution) and solid (sorbent) phases, after which impurities are extracted when eluted with a suitable solvent (as a rule, diluted inorganic acids in case of REIs). Organic solvents can also be used as eluents for the subsequent ICP-MS or ICP-AES analysis combined with a special input system. α-Hydroxyisobutyric acid (α-HIBA) is one of the effective eluents for the separation of individual REEs [26]. In recent years, chromatography with chelate resins as a stationary phase has attracted growing attention for separation and preconcentration of REIs. The following substances are used: 2-ethylhexyl hydrogenethylhexy phosphonate (EHEHP) [28, 29], 2-ethylhexyl hydrogen 2-ethylhexyl phosphonate (commercial name P507) [32–41], 2-ethylhexyl hydrogen 2-ethylhexylphosphonate (PC-88A) [42], Amberite XAD-7HP resin [44]. Ion exchange resins Dowex AG 1W [48] and Dowex 50W-X8 [52] are also applied.

Thus, the authors of [28, 29] analyzed high-purity Gd_2O_3 and metal Yb by ICP-MS spectroscopy after chromatographic separation with EHEHP. The use of EHEHP in Gd_2O_3 analysis eliminated interferences of GdH, GdO, and GdOH in Tb, Tm, Yb, and Lu [28]. The limits of REE determination were 0.002–0.05 μg/g; the accuracy was 1.0–7.5%. The developed approach made the analysis of high-purity (99.99–99.9999%) Gd_2O_3 possible. Thus, the isobar interferences of atomic and molecular ions due to the matrix element were effectively eliminated.

The authors of [19–21, 30] carried out a number of studies on the determination of trace amounts of REE impurities in a high-purity rare earth matrix, combining high-performance liquid chromatography (HPLC) followed by ICP-MS analysis.

Sorbents used in preconcentration systems for REI determination can be modified chemically by means of complexing reagents [30, 31]. For example, the authors of [11] developed a type of resin impregnated with solvent (ionic liquid) IL-SIR to improve liquid-solid-phase extraction of metal ions based on imidazolium type. In this study, [C8mim] [PF6] containing Cyanex923 was immobilized on XAD-7 resin, which promoted an increase in mass transfer efficiency, i.e., reducing the time of establishing equilibrium from 40 to 20 min, increasing the efficiency of extraction from 29 to 80%. In addition, the new IL-SIR allowed one to conduct efficient separation of Y(III) from Sc(III), Ho(III), Er(III), and Yb(III) by adding a water-solu-

Table 1. Preconcentration procedures for the determination of rare earth impurities using spectrometric techniques

Base	Analyte	Features of the approach	Method	Characteristics of method	Ref.
La_2O_3 and Gd_2O_3	La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	Lanthanum oxide (0.1 g) and gadolinium oxide (0.1 g) were dissolved in 100 mL of HNO_3 (0.1 M). Hydroxyisobutyric acid was chosen as the eluent for Gd_2O_3, which made it possible to separate all rare earth elements completely. It was mentioned that lactic acid incompletely separates Gd, Eu, and Sm. Lactic acid was used as an eluent for La_2O_3	ICP-MS	DL = 1–5 pg/mL $S_r < 5\%$	[26]
La_2O_3	Ce, Pr, Nd, Sm	Chromatographic separation of Ce and impurity elements with La. Hydrogen 2-ethylhexyl in phosphinic acid 2-ethylhexyl ester was used as the stationary phase, and inorganic acid (HNO_3) was used as the mobile phase	ICP-MS	ED = 95–102%	[27]
La_2O_3	Sc, Y, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Gd, Ho, Er, Tm, Yb, Lu	Elements were separated by HPLC. Sodium laurylsulfonate 0.01 mol/L with pH of 2.9 was used as a phase modifier. Both samples and standards were filtered through a porous membrane of 0.2 mm. The volume injected for each determination was 100 mL	ICP-MS	DL = 0.5–12.3 ng/L $S_r = 2–5\%$	[20]
Nd_2O_3	Sc, Y, Ce, Pr, La, Sm, Eu, Tb, Dy, Gd, Ho, Er, Tm, Yb, Lu	Elements were separated by HPLC. Sodium laurylsulfonate 0.01 mol/L with a pH of 2.9 was used as a phase modifier. Both samples and standards were filtered through a porous membrane of 0.2 mm. The volume injected for each determination was 100 mL	ICP-MS	DL = 0.5–10.3 ng/L $S_r = 1.88–4.67\%$	[21]
Gd_2O_3	Y, La, Ce, Pr, Nd, Sm, Eu, Tb, Dy, Ho, Er, Tm, Yb, Lu	Gd_2O_3 powder (10 mg) was decomposed in 4 mL of HNO_3 (6.2%). The solution was transferred into a volumetric flask of 10 mL, a Re internal standard was added (1 mg), and the mixture was brought to volume with water. The matrix effect of Gd_2O_3 on signals of REE impurities (Y, La, Ce, Pr, Nd 146, Sm, Eu, Dy, Ho, and Er) was leveled by the internal standardization of Re. Gd_2O_3 sample (10 mg) was decomposed in 2 mL of HCl (50%) and evaporated to dryness. The dried residue was dissolved by heating with 10 mL of HCl (1%) and cooled for subsequent chromatographic separation and ICP-MS analysis. Thus, interferences of GdH, GdO, and $GdOH_n$ (n = 1–3) spectra on Tb, Tm, Yb, and Lu were eliminated by extraction chromatographic separation with 2-ethylhexylhydrogen-2-ethylhexyphosphonate (EHEHP)	ICP-MS	DL = 0.005–0.017 ng/mL (0.002–0.05 μg/g) $S_r = 1.0–7.5\%$	[28]
Sm_2O_3	La, Ce, Pr, Nd, Eu, Gd, Tb, Lu, Y, Dy, Ho, Er, Tm, and Yb	Sm_2O_3 (0.1 g) was decomposed in a mixture of ultrapure water (10 mL) and HNO_3 (2 mL) at $t = 80°C$, and H_2O_2 (0.5 mL) was simultaneously added La, Ce, Pr, Nd, Eu, Gd, Tb, Lu, and Y were determined without a separation stage because of the absence of interferences, but In was added as an internal standard. Dy, Ho, Er, Tm, and Yb were determined after almost complete removal of the Sm matrix (its residue is from 0.006 to 0.053 μg/L depending on the isotope) by chromatographic extraction separation with EHEHP. It was eluted with 4 mol/L HCl. A small amount of Tb remained in the eluted Dy, but this did not affect the result	ICP-MS	DL = 0.01–0.07 μg/g $S_r < 5\%$	[29]

Table 1. (Contd.)

Base	Analyte	Features of the approach	Method	Characteristics of method	Ref.
Sm_2O_3	16 REEs	Separation of REIs from the base was conducted by HPLC with subsequent ICP-MS analysis. The authors used reverse phase liquid chromatography; sodium lauryl sulfonate was used as a modifier	ICP-MS	$DL_{La} = 0.2$ (La) pg/mL $DL_{Gd} = 8$ pg/mL $S_r = 0.9–1.5\%$ $n = 5$	[30]
Pr_2O_3	14 REEs (Sc, Y, La, etc.)	The impurities were separated by HPLC. A solution of sodium laurylsulfonate (0.01 mol/L, pH = 2.9) was used as a phase modifier. The elution time of each trace element was determined with a UV-Vis detector operating at 655 nm by means of an Arsenazo III	ICP-MS	DL = 0.5–12.3 ng/L $S_r = 3–5\%$ $n = 5$	[19]
Sc, Er, Tm, Yb, and Y oxides	Y	Liquid-solid-phase extraction of yttrium from REEs by a resin impregnated with a solvent (ionic liquid) combined with a complexation method. This method increases the efficiency of mass transfer, i.e., reduces the time to establish equilibrium from 40 to 20 min and increases the extraction efficiency from 29 to 80%	ICP-MS	No data	[31]
Eu_2O_3	14 REEs	Liquid-solid-phase chromatography using P507 resin	ICP-MS	DL = 0.005–0.021 g/L $S_r = 1.4–8.1\%$	[32]
CeO	Sc, Y, Nd, Pr, La, Sm, Eu, Tb, Dy, Gd, Ho, Er, Tm, Yb, Lu	HPLC technology combined with ICP-AES with electrothermal evaporation. 2-ethylhexylhydrogen 2-ethylhexylphosphonate resin (P507) was used as the stationary phase and dilute nitric acid was used as the mobile phase. It was found that REE impurities (Pr–Lu) can be efficiently eluted using EDTA	ICP-AES	DL = 0.8 (Yb)–36 (Nd) μg/L	[33]
La_2O_3	Sc, Y, Nd, Pr, Ce, Sm, Eu, Tb, Dy, Gd, Ho, Er, Tm, Yb, Lu	Separation of REEs from a matrix was conducted using P507 resin as the stationary phase and dilute nitric acid as the mobile phase. It was observed that the use of EDTA as eluent allows efficient eluting of REE impurities from the HPLC column	ICP-AES	DL = 0.8 (Yb)–48 (Ce) μg/L ED = 90–105%	[34]
High-purity Dy_2O_3	REEs	REE impurities were preconcentrated by ion chromatography using P507 resin as a stationary phase and $HCl–NH_4Cl$ solution as eluent	ICP-AES	No data	[35]
Lu_2O_3	14 REEs	Impurities were separated by HPLC using P507 resin in hydrochloric acid system	ICP-AES	ED = 81.4–116% $S_r = 1.68–6.0\%$	[36]
High-purity (99.99%) Eu_2O_3	Ce, Pr, Sm, Gd, and Dy,	Impurities were extracted from europium oxide by HPLC using P507 extraction resin	ICP-AES	ED = 88–105% $S_r < 10\%$ (impurity content in Eu_2O_3 5 μg/L)	[37]
Eu_2O_3	14 REEs	Two-stage separation was used. Firstly, REEs were separated by chromatography using P507 resin as the stationary phase and dilute HCl as eluent. Secondly, non-rare-earth elements were separated from the sample using a cation exchanger	ICP-AES	DL = 0.02–7.0 μg/L ED = 84–112% $S_r \leq 13\%$	[38]
Gd_2O_3 5 N purity grade	14 REEs	Chromatographic separation with P507. The separation period was relatively short: 3.5 h	Spectrography	DL = 1.2 μg/L	[39]

Table 1. (Contd.)

Base	Analyte	Features of the approach	Method	Characteristics of method	Ref.
Nd_2O_3	14 REEs	Chromatographic separation with P507 resin. A mixture of hydrochloric acid and ammonium chloride was used as the eluent	Spark MS	No data	[40]
Sm_2O_3, Eu_2O_3 Gd_2O_3 99.9999–99.99999%	14 REEs	According to the HPLC technology with an REE as the stationary phase, P507 was eluted with a solution of HCl + NH_4Cl and 4 M HCl. The separation time was 10–14 h	ICP-AES	ED = 67–133% S_r = 6.4–18.4%	[41]
Tb	La, Nd, Sm	Chromatographic separation of REEs was performed using a column filled with polymer resin with 2-ethylexyl hydrogen 2-ethylhexyl phosphonate (PC-88A). Trace amounts of La, Nd, and Sm were separated from large terbium concentrations by eluting with 1M HCl	ICP-AES	ED = 98.2–100.5% $S_r \leq 2\%$	[42]
Monazite	Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Y	Heavy REEs were separated from light ones by extraction using 0.22 M bis-(2-ethyl hexyl) hydrogen phosphate (GDEHP). Reextraction of heavy REEs is achieved by means of 4 M HCl in the presence of tributyl phosphate (TBP)	ICP-AES	S_r = 1–7% $n = 4$	[43]
Aqueous solution containing 100 ppm Ba, La, Eu, Y, and Tb	La, Eu, Tb, Y	Chromatographic extraction of REEs was performed. Amberite XAD-7HP resin was used as the stationary phase and D2EHPA was used as the solvent. Each REE was successfully separated by elution with a 0.1–1.0 N HCl solution at a rate of 1.6 to 2.6 mL/min	ICP-AES	No data	[44]
Monazite leaching solution	Sm, Gd	The separation of Sm and Gd was studied in a continuous system on a micropilot installation. 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester diluted in 1 M solution of isododecane was used as an extractant	ICP-AES	No data	[45]
Monazite sand	La, Ce	A liquid extraction method was used with N-phenyl-(1,2-methanofullerene C60)61-formohydroxamic acid (PMFFA). Monazite sand (0.5 g) was dissolved in a mixture of HCl and $HClO_4$ (1 : 1) and brought to a volume of 250 mL with distilled water. Then, for the extraction of lanthanum, an aliquot (10 mL) was taken and extracted with PMFFA in chloroform. The pH value of the aqueous layer was then raised to 9.5 with buffer, and Ce(IV) was extracted. Reextraction of La(III) and Ce(IV) was carried out with 0.5 M HNO_3	ICP-AES	DL = 0.5 ng/mL S_r = 1.7–1.8%	[46]
Solutions Y(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III)	Lu	It was reported for the first time about a new synergistic system of combined ionic liquids of ammonia and phosphonium types—[P66614][EHEHP] and [N1888][BTMPP]—which exhibits a pronounced synergistic effect in the extraction of Lu(III). Extracted Lu(III) in this system can be completely removed using hydrochloric acid. New synergistic extraction makes it possible to separate heavy lanthanides, which is of theoretical and practical importance	No data	No data	[47]

Table 1. (Contd.)

Base	Analyte	Features of the approach	Method	Characteristics of method	Ref.
Monazite, xenotime	Sc, Y, La, Ce, Nd, Sm, Eu, Tb, Yb, Dy, Ho, Er, Tm, Lu	To remove a matrix from a sample (xenotime or monazite), its leaching solution was dried on a stove at *t* = 120°C for 4 h. Then, the precipitant was dissolved in 2 mL of HNO_3 (7 M) and passed through a Dowex AG 1W column (×8). The eluent—15 mL of 0.5 mol/L HNO_3 and 20 mL of 0.5 mol/L HCl—was passed through the column. Then, the solution was evaporated and dissolved in 5 mL of HNO_3 (0.5 mol/L). After cooling, the precipitant was transferred to a 25 mL volumetric flask for analysis	ICP-AES	DL = 0.3–50 μg/L	[48]
Monazite sand	La	Liquid extraction. The synthesized calix[4]resorcinarene-hydroxamic acid (C4RAHA) exhibits a high affinity for La(III) in the presence of large amounts of associated metal ions. The binding of lanthanum to C4RAHA in a ratio of 4 : 1 (metal : ligand) was performed for the first time. Quantitative La(III) extraction of C4RAHA was carried out in ethyl acetate in the pH range of 7.5–8.0	ICP-AES	DL = 6.35 ppb S_r = 1.9%	[49]
Monazite	Sc	Sc(III) complex was concentrated using cloud-point extraction with nonionic surfactant Triton X-100 (pH = 5.5). Sc(III) ions formed complexes with 2-amino-4-(*m*-tolyazo)pyridine-3-ol (ATAP) in an aqueous medium. After separation of phases at *t* = 45°C, the phase enriched with surfactants was dried and the residual phase was dissolved in 0.5 mL of dimethylformamide	Spectrophotometry	DL = 0.12 ng/mL S_r = 1.10%	[50]
REE monazite concentrate	Sm, Pr, Nd	Selective extraction of Sm(III), Pr(III), and Nd(III) from REE monazite concentrate using Cyanex 921 as an extractant and Chrome azurol S as a dye. To eliminate spectral interferences, cerium and europium were previously extracted from the sample. Cerium was extracted from raw solution using 15% tributyl phosphate in *n*-hexane as a diluent at a ratio of organic and aqueous phases O : A = 1 : 3 and a contact time of 15 min at room temperature. Eu was separated from the obtained cerium-free REE raffinate using a combined method of chemical reduction–precipitation. Sm(III), Pr(III), and Nd(III) were extracted from the remaining aqueous solution of REEs (free of Ce and Eu) by shaking equal volumes (50 mL) of the aqueous and organic phases in a rocking thermostat (GFL 3031, Germany) for 15 min at *T* = 298 K (25°C ± 2°C)	ICP-AES, spectrophotometry	No data	[51]
Concentrate containing (%) 44 Ce, 23 La, 16.94 Nd, and 5.91 Pr	Pr	Pr(III) was extracted from an REE concentrate using Dowex 50W-X8 cationic ion exchange resin. An EDTA solution with a concentration of 0.015 mol/L was used for elution	Spectrophotometry	DL = 100 mg/L	[52]

Table 1. (Contd.)

Base	Analyte	Features of the approach	Method	Characteristics of method	Ref.
NdFeB leaching solution	Dy	A new sorbent based on mesoporous silicon oxide was developed for the dysprosium separation by liquid-solid-phase extraction in an acid medium with pH 2.0	ICP-AES	No data	[53]
Solution of chloride leaching of monazite with composition, ppm: 781 La, 119 Pr, 333 Nd	La	Separation of La from Pr and Nd was conducted by liquid extraction. Among the extraction agents studied by the authors (Cyanex 272, D2EHPA, PC-88A, and Cyanex 301), Cyanex 272 demonstrated the best degree of REE extraction. Hydrolysis of Cyanex 272 positively affected the separation of La from Pr and Nd. A 1 M HCl solution was used as the eluent	ICP-AES	ED = 4.9% (La), 96.6% (Pr), and 98.7% (Nd)	[54]
Hydroxide cake after leaching of Egyptian monazite	La, Nd	Liquid extraction was conducted from nitric acid aqueous solutions using a mixture of two neutral extractants—trioctylphosphine oxide (TOPO) and trialkylphosphine oxide (TRPO)—in kerosene	ICP-AES	ED = 83.5–88%	[55]
Synthetic aqueous solution of REE mixture	Tb	The sorption method was used. To reach pH ~ 1, HNO_3 or NaOH was added to 10–2000 mL of the analyzed solution. The obtained solution was heated in a sand bath for 1 h and then filtered through a thick paper filter. NaOH solution was added to the filtrate to reach pH ~ 7; after that, a borate buffer with pH 8.25 was introduced, and its concentration in the final solution should be 2.5×10^{-4} M. The obtained solution was passed through a cartridge filled with 0.6 g of sorbent using a peristaltic pump with a flow rate of 3 mL/min. Then, 50 mL of bidistilled water was passed at the same rate. Dried clinoptilolite–Tb(III) sample was calcined in a muffle furnace at $t = 500$°C for 2.5 h and cooled in a desiccator to room temperature. Then, the phosphor luminescence was measured at $\lambda = 545$ nm	Luminescent method	DL = 1 ng/mL ED = 90–108% $S_r = 0.78$–6.2%	[56]
REE concentrate	Eu	Combination of chemical reduction and precipitation. This process consists of two stages: reduction in which a solution of Eu(III) chloride is passed through a column of zinc particles and precipitation of the obtained Eu(II) chloride in an inert medium using a sulfate salt	Spectrophotometry	ED = 91%	[57]
Monazite filtrate	Eu, La, U	Sorption separation of elements using PAM-AA-K ((polyacrylamide-acrylic acid)-kaolin) new sorbent obtained by polymerization of kaolin by gamma radiation	ICP-AES	ED = 94.6% (Eu) and 91.6% (La)	[58]

Characteristics of method: DL—determination limit, ED—extraction degree, S_r—relative standard deviation, n—the number of parallel measurements.

ble complexing agent. Thus, liquid-solid-phase extraction with IL-SIR combined with the method of complexation can be considered as an effective strategy to increase the efficiency of mass transfer and selectivity of extraction based on ionic liquid.

The studies are relevant in creating new sorbents to extract REEs by liquid-solid-phase chromatography. Thus, the authors of [53] developed a new sorbent based on mesoporous silicon oxide and obtained by ion imprinting technology for the selective extraction of dysprosium with liquid-solid-phase chromatography in acidic media. New studies can be expected on the development of ecological solutions for selective preconcentration of REIs in the analysis of REE-based materials.

Liquid extraction is widely used for preconcentration and separation of REIs in REE-based materials. In this method, an analyte is distributed between two immiscible liquid phases (usually aqueous and organic). Before the analysis with spectral methods, as a rule, re-extraction of the released substances from the organic phase into the aqueous one is conducted (most often using dilute solutions of hydrochloric or nitric acids). However, measurement directly from the organic phase is also possible. Liquid extraction of La(III) from geological samples, including monazite sand, was carried out in [49] using calix[4]resorcinarene-hydroxamic acid (C4RAHA) in ethyl acetate, which exhibits a high affinity for La(III). The extract is injected directly into an inductively coupled plasma spectrometer, which greatly increases the sensitivity of the analysis.

When liquid extraction is used, separation and preconcentration are characterized by a high extraction factor. As seen in Table 1, in recent years, liquid extraction has found application in the analysis of REE ores [45–51, 54, 55] and is rarely used in the analysis of oxides of individual REEs. For example, the authors of [54] separated La from Pr and Nd (with subsequent determination by the ICP-AES method), and La and Nd were extracted from monazite in [55].

As seen in Table 1, the following extractants for separating REIs from a rare earth base in the analysis of rare earth ores have been widely used recently: bis-(2-ethyl hexyl) hydrogen phosphate (HDEHP) [43], 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester [45], N-phenyl-(1,2-methanofullerene C60)61-formohydroxamic acid (PMFFA) [46], calix[4]resorcinarene hydroxamic acid (C4RAHA) [49], Cyanex 921 [51], Cyanex 272, D2EHPA, PC88A, and Cyanex 301 [54], trioctylphosphine oxide (TOPO) and trialkylphosphine oxide (TRPO) in kerosene [55]. Liquid extraction has some drawbacks such as the necessity of using a large number of organic solvents, a multistage process, and the formation of wastes harmful to the environment.

Cloud-point extraction by nonionic surfactants (NSA) at a cloud point temperature is an effective preconcentration method that can be used to extract REIs from REE-based materials [50]. Compared with conventional extraction by organic solvents, cloud-point extraction is characterized by increased preconcentration coefficients and operational safety owing to the low flammability of nonionic surfactants. Taking into account the toxicity of most organic solvents, cloud-point extraction is considered as a “green” alternative to traditional liquid extraction. In [50], a spectrophotometric technique was developed using cloud-point extraction of trace amounts of scandium from monazite into the modified micellar phase Triton X-100. The use of spectrophotometric determination in this method is dictated by the very small volume of the phase obtained after extraction and the use of organic reagents to dissolve the analyzed phase, which complicates the analysis by ICP-MS or ICP-AES.

In addition to the methods for REI separation listed above, deposition is also applied when using ICP-MS and ICP-AES. As seen in Table 1, this method is mainly used to analyze ores and concentrates of REEs. The main requirement for this method is that the precipitant must be easily separated from the matrix solution. This can be performed by filtration, centrifugation, and sediment washing. In addition, the precipitant should be pure and readily available. This method is simple, and different analyte ions can be preconcentrated and separated from the matrix simultaneously.

Various inorganic or organic precipitating substances are used precipitation of REEs. For example, in [57], the separation of europium from a mixture of REEs was conducted in two stages. The first stage was the reduction of europium with metal zinc to its bivalent oxidation state. The second stage included the precipitation of the resulting Eu(II) chloride using a sulfate salt in an inert medium, while other rare earth sulfates remained in the solution. The precipitated Eu(II) sulfate was allowed to settle, and the residual Eu content in precipitant was determined by the spectrophotometric method. The disadvantages of this method include the complexity and duration of the process.

A few works describe the application of sorption methods for preconcentration/separation of REIs before the analysis of REE-based materials. For example, the authors of [56] proposed a sorption-luminescence method of terbium determination in natural Transcarpathian clinoptilolite without the use of synthetic organic compounds and toxic solvents. Optimal conditions of preparation of luminophore are sorption of Tb(III) on zeolite in a borate buffer solution with pH 8.25 and subsequent calcination of clinoptilolite–Tb(III) samples at $t = 500°C$. To excite luminescence, beams with the wavelength λ = 220 nm were used. The luminescence intensity at λ = 545 nm was chosen as an analytical parameter for quantitative estimation of terbium. The determined Tb(III) concentration range is from 3 to 1140 ng/mL. The proposed method can be used to determine the terbium content in the presence of many REEs, including the determination of trace amounts of terbium ions in synthetic aqueous solutions and intermetallic compounds. In this case, the use of the single-element method is justified because the selective extraction of only one component is conducted. On the basis of the region of determined values, ICP-AES and ICP-MS can also be applied in this combined technique.

Work [58] is devoted to the modification of kaolin (natural clay) using radiation polymerization to obtain a polyacrylamide–acrylic acid–kaolin composition for sorption of lanthanum (light REE), europium (heavy REE), and uranium from monazite ore. The studies were conducted with different sorbent weights (0.1 and 0.2 g). The degree of extraction for Eu^{3+}, La^{3+}, and UO_2^{2+} was 94.6, 91.6, and 73.4%, respectively. The mechanism of sorption of lanthanum and europium ions on the PAM-AA-K sorbent is mainly in the form of $Ln(OH)^{2+}$, and it is in the form of UO_2^{2+} for uranium. The concentration of each element was measured by ICP-AES.

On the basis of the given studies, it can be concluded that group preconcentration of REIs followed by multicomponent analysis is widely used for REE oxides as precursors for obtaining materials based on them. This approach is suitable to estimate "academic purity" [59] and control correctness in determining the target purity by individual impurities. Methods of individual preconcentration and single-element methods are used for the selective evaluation of a small amount of elements.

PRECONCENTRATION OF NON-RARE-EARTH IMPURITIES

Besides rare earth impurities, an important role in the purity of REE-based materials is taken by non-rare-earth impurities (NREIs). For example, in the manufacture of phosphors and optical ceramics, high-purity rare earth oxides are used, and critical impurities are colored ions Fe, Ni, Cr, Co, Cu, V, Mn, etc., as well as some lanthanides [5, 11–13]. The properties of such materials deteriorate significantly even at a content of these impurities above 10^{-5} wt %. However, determining the low concentrations of these elements by ICP-MC and ICP-AES is a complicated task because of matrix and spectral phenomena. Therefore, combined methods of analysis are used to find NREIs.

Table 2 summarizes information on the application of methods of NREI extraction combined with spectrometric methods of analysis. As is seen, preconcentration is more frequently used for the subsequent ICP-AES analysis which has good characteristics for the determination of impurities in pure REE oxides: low determination limits, high accuracy, and a broad dynamic range of determined concentrations. Nevertheless, emission spectra of many REEs are complex, which limits the selectivity of this method owing to spectrum overlapping. However, ICP-AES and ICP-MS are widely used for this purpose in combination with preliminary separation/preconcentration of analytes. It was shown in [73] that direct determination of trace impurities in high-purity rare earth elements by ICP-AES is complicated, and chemical separation and preconcentration of analytes are required. The authors determined trace amounts of Co, Cr, Cu, Fe, Mo, Ni, and Zn in high-purity europium oxide by means of liquid extraction with APDC-IBMK solvent followed by ICP-AES analysis. However, since APDC is useful only for transition metal ions and is not effective for complex formation with aluminum, alkali, and alkaline earth metal ions, this extraction method is inapplicable for simultaneous extraction of these elements.

More versatile and frequently found in articles is the method of liquid-solid-phase chromatography [60–69]. The following sorbents are used for the group chromatographic separation of rare earth impurities from a rare earth matrix: di-(2-ethylhexyl)phosphoric acid (HDEHP) [60, 61], TOPO-Levextrel [62], XAD-16 resin [63], P507 resin [64, 69], and silica gel with activated carbon [65, 67, 68].

Coprecipitation is also used to extract NREIs. A technique described in [13] is developed for the analysis of pure Y_2O_3 by ICP-AES with preconcentration of impurities from a nitrate solution of the sample by coprecipitation with a trace amount of yttrium hydroxide. The main advantages of the developed technique of analysis are a wide range of simultaneously determined impurities (28 elements) and the use of available reagents (H_2O, HNO_3, NH_3 aqueous solution).

Sorption is a promising method of NREI preconcentration in REE-based materials. This is one of the modern approaches to cleaning the analytical signal of the desired elements in such complex and multicomponent objects. Thus, the efficiency of polymer thioether sulfur- and nitrogen-containing sorbents for separating As, Bi, Sb, Cu, and Te from a rare earth matrix with subsequent arc spectral analysis was demonstrated in [73].

Table 2. Preconcentration procedures for the determination of non-rare-earth impurities using spectrometric techniques

Base	Analyte	Features of the approach	Method	Characteristics of method	Ref.
Y_2O_3	Al, As, Be, Bi, Co, Cr, Cu, Fe, Ga, Ge, In, Mo, Pb, Sb, Se, Si, Sn, Te, Ti, V, W, Er, Tm, Dy, Ho, Lu, Sc, Yb	Impurities were preconcentrated from a nitrate sample solution containing a trace amount of yttrium hydroxide. Analytical weighed portion (0.5 g) was dissolved in diluted HNO_3 (5.5 mL) with a ratio of 1 : 5. A small part of yttrium was precipitated as $Y(OH)_3$ by adding an NH_3 solution (0.01%) to the prepared $Y(NO_3)_3$ solution. The obtained suspension was shaken several times and then centrifuged with a speed of 4000 min^{-1} for 20 min. Then the precipitate was separated by decantation and dissolved in 0.1 mL of diluted HNO_3 (1 : 10). The solution above the precipitate remaining after centrifugation was used to assess the degree of extraction of impurities and to conduct a control experiment	ICP-AES, Atomic absorption spectrometry	DL = 10^{-7}–10^{-4} wt % The value of the relative combined standard uncertainty of the results is 0.05–0.15	[13]
Dissolved chlorides of La, Ce, Pr, Nd, Sm, and some transition elements (Al, Ca, Fe, and Zn) in distilled and ionized water	La, Ce, Pr, Nd, and Sm, Al, Ca, Fe, and Zn	Liquid-solid-phase chromatography was conducted using resin impregnated with di-(2-ethyl hexyl)phosphoric acid (D2EHPA) as the stationary phase. The process included three stages: (1) loading the column with a loading solution where La and some impurities are adsorbed on the stationary phase, while other impurities are eluted from the column; (2) eluting only La; (3) restoration of the resin with a concentrated solution of hydrochloric acid. Optimal conditions of separation at room temperature are the following: resin layer height of 180 mm, diameter of 25 mm; eluent for La of 1800 mL of 0.15 M HCl solution; flow rate of 1 mL/min	ICP-AES	ED_{La} = 90%	[60]
Eu_2O_3 (purity of 99.999%)	Al, Ca, Co, Cr, Cu, Mg, Mn, Ni, Pb, and Zn	Europium oxide sample (0.3–0.5 g) was dissolved in concentrated HNO_3 (3 mL) under heating and evaporated almost to dryness to remove excess nitric acid; the obtained residue was dissolved in water (5 mL). The solution was adjusted to 0.1 M HNO_3 and then loaded onto the top of a column of di-(2-ethyl hexyl)phosphoric acid (HDEHP)-Levextrel resin previously equilibrated with 0.1 M HNO_3. Impurity elements were eluted to 20 mL of 0.1 M HNO_3 solution at a flow rate of 0.8 mL/min. Europium was adsorbed on the resin	ICP-AES	DL = 0.0018–0.016/0.00–0.079 μg/mL S_r = 4–13%	[61]

Table 2. (Contd.)

Base	Analyte	Features of the approach	Method	Characteristics of method	Ref.
Sc_2O_3 (purity of 99.99–99.9995%)	Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mn, Ni, Pb, Sn, Sr, Ti, V, Zn	Chromatographic separation using TOPO-Levextrel resin. Scandium oxide sample (0.1 g) was dissolved in HNO_3 (1.5 mL) by heating on a hot plate until it was completely dissolved. The solution was then evaporated almost to dryness to remove excess acid, and the residue was dissolved in 1 M HNO_3 (3 mL). The solution was passed through a chromatographic column preliminarily equilibrated with 1 M HNO_3. Scandium was extracted using TOPO in the stationary phase, and impurities were eluted with 30 mL of 1 M HNO_3 at a flow rate of 1 mL/mm. The solution (30 mL) containing the analytes was collected in a glass vessel and concentrated to 2 mL in 1 M HNO_3; then, the analysis was performed	ICP-AES	DL = 0.0006–0.15/0.08–4.0 μg/mL S_r = 16%	[62]
Gd	Ag, B, Cd, Dy, Eu, Sm	Extraction chromatography was conducted using 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (PC-88A) as the mobile phase and XAD-16 resin as the stationary phase. The best eluent for separation of Eu and Sm in the Gd matrix is 0.3 M HNO_3; for Ag, B, and Cd, it is 0.1 M HNO_3; and Dy is quantitatively extracted by 4 M HNO_3	ICP-MS	DL = 0.6–3.0 ng/mL ED (Ag, B, and Cd) = 90–104% ED (Eu, Gd, and Sm) = 100–102% S_r = 1.0–15.4%	[63]
High-purity Tb_4O_7	Ca, Cu, Mg, Mn, Ni, Si, La, Ce, Pr, Nd, Sm, Eu, and Gd	HPLC using P507 resin. Successful separation of micro concentrations of Cu and Gd from Tb matrix was performed by elution with dilute nitric acid for 25 min	ICP-AES	DL = 0.4–4.0 g/L ED = 78–105%	[64]
High-purity La_2O_3	Non-rare-earth metals	For preconcentration of NREI, the chromatographic method was used. Silica gel with activated carbon was chosen as a sorbent, and sodium diethyldithiocarbamate (NaDDTC) was chosen as a chelating agent	ICP-AES	DL at a level of 10^{-3} μg/mL S_r = 2.3–5.0% $n = 7$	[65]
Zr–U–Er alloy	Al, Ca, Co, Cr, Cu, Fe, Mg, Mn, Mo, Ni, Ph, Sn, Ta, Ti, V, Y, Zn, and Er	Chromatographic separation with tributyl phosphate	ICP-AES	ED = 94–108% S_r = 0.2–2.1% $n = 8$	[66]
Eu_2O_3	Al, Cr, Cu, Fe, Pb, V, and Zn	Preconcentration was performed using a microcolumn with activated carbon and silica gel. Al, Cr, Cu, Fe, Pb, V, and Zn were preconcentrated in a buffer solution at pH 4.6; then the elution was carried out with nitric acid with a concentration of 4.5 mol/L	ICP-AES	DL at a level of μg/g	[67]

Table 2. (Contd.)

Base	Analyte	Features of the approach	Method	Characteristics of method	Ref.
High-purity La_2O_3 and Eu_2O_3	Al, Cr, Cu, Fe, Pb, V, Zn	Impurities were preconcentrated using silica-carbon gel as an adsorbent and sodium diethyldithiocarbamate (NaDDTC) as a chelating agent	ICP-AES	DL at a level of ng/mL $S_r = 2.3–5.0\%$	[68]
La_2O_3	8 NREIs	HPLC was performed using 2-ethylhexyl hydrogen 2-ethylhexylphosphonate (P507) chelating resin as the stationary phase and dilute nitric acid as the mobile one. It was found that the use of HNO_3 with pH = 1.7 provides efficient elution of NREIs from the HPLC column while La remains on the column. Experimental results demonstrate that La and NREIs can be separated in 15 min	ICP-AES	ED = 90–110%	[69]
Er, Eu, Dy and their compounds	Zr, Nb, Mo, Hf, Ta, W, and Te	Zr, Nb, Mo, Hf, Ta, W, and Te were extracted from hydrochloric acid media (6 M HCl) using 0.1 M TOFO solution in dichloroethane with subsequent re-extraction with 0.1 M solution of oxalic acid	ICP-MS	DL = $n \cdot 10^{-8} – n \cdot 10^{-6}$ wt %	[70]
Monazite sand	Th	Liquid extraction was used for the separation and preconcentration of trace amounts of thorium by means of N-phenylbenzo-18-crown-6-hydroxamic acid (PBCA). Thorium was extracted from a dichloromethane solution of PBCHA at pH = 4.5. The extract was directly injected into the plasma to measure the Th content	ICP-AES	DL = 4.6–13.85 ng/mL $S_r = 1.12–1.18\%$	[71]
Eu_2O_3	18 NREIs (Cu, Pb, Co, Ni, REEs)	Eu(III) was reduced to Eu(II) by zinc powder. In a buffer solution with pH = 5, the impurities were separated from the europium by extraction with 1-phenyl-1-3-methyl-4-benzoyl-1-5-pyrazolone (PMBP). This method can be applied to determine the fluorescent purity of europium oxide	ICP-AES	DL = 0.0075–0.75 μg/g ED = 80–125% $S_r < 25\%$	[72]
Y, Gd, Nd, Eu, Sc, and their oxides	As, Bi, Sb, Cu, Te	Group preconcentration of As, Bi, Sb, Cu, and Te was carried out using S,N-containing heterochain polymeric sorbent. To choose the conditions of sorption concentration, the kinetics of sorption and the dependence of the degree of extraction of impurities on the acidity of the solution were studied. Graphite powder was used as a collector in the analysis of rare earth oxides because of the relative simplicity of its emission spectrum and versatility	Arc atomic emission spectrometry	DL = $n \cdot 10^{-5}$ wt %	[73]

CONCLUSIONS

This review demonstrates that, to eliminate interferences strongly limiting analytical possibilities of spectrometric methods of analysis, methods of separation and preconcentration of impurities are widely used. Liquid extraction and liquid-solid-phase chromatography are the most widespread methods for studying REE-based materials equivalently allowing one to extract the impurities and subsequently determine them by the spectral method of analysis. Precipitation, sorption, and complex formation are also successfully used. The use of preconcentration, undoubtedly, makes it possible to eliminate the problem of the interfering influence of the matrix and, in most cases, to reduce the limits of determination. However, this time-consuming procedure requires highly qualified analysts.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

REFERENCES

1. Li, D., Li, Y., Pan, D., Zhang, Z., and Choi, C.J., Prospect and status of iron-based rare-earth-free permanent magnetic materials, *J. Magn. Magn. Mater.,* 2019, vol. 4691, pp. 535–544.
2. Baranovskaya, V.B., Karpov, Yu.A., Petrova, K.V., and Korotkova, N.A., Actual trends in the application of rare-earth metals and their compounds in the production of magnetic and luminescent materials: A review, *Russ. J. Non-Ferrous Met.,* 2021, vol. 62, no. 1, pp. 10–31.
3. Ritter, S.K., A whole new world for rare earths. How the technologically important metals rose from obscurity to ubiquity, *Chem. Eng. News,* 2017, vol. 95, no. 34, pp. 30–34.
4. Petrova, K.V., Baranovskaya, V.B., and Korotkova, N.A., Direct inductively coupled plasma optical emission spectrometry for analysis of waste samarium–cobalt magnets, *Arabian J. Chem.,* 2022, vol. 15, no. 1, p. 103501.
5. Korotkova, N.A., Petrova, K.V., and Baranovskaya, V.B., Analysis of cerium oxide by mass-spectral and atomic-emission methods with inductively-coupled plasma, *J. Anal. Chem.,* 2021, vol. 76, no. 12, pp. 1–12.
6. Marathe, S.M., Biswas, S.S., Patil, P.B., and Murty, P., An ICP-AES method for the determination of heavy rare earth elements (Eu–Lu) in high purity yttrium oxide, *Microchim. Acta,* 1992, vol. 109, no. 5, pp. 261–268.
7. Li, J.Y., Yang, J., and Dong, Z.R., *Determination of 14 rare earth elements in high purity europium oxide by ICP-AES*, *Spectrosc. Spectral Anal. (Beijing, China),* 1995, pp. 71–74.
8. Dong, R. and Xin, R., ICP-AES determination of Coexisting rare-earth impurities in high-purity europium oxide, *Phys. Test. Chem. Anal., Part B,* 2004, vol. 40, no. 3, pp. 135–137.
9. Biswas, S.S., Sethumadhavan, A., and Murty, P.S., Determination of Y, Sm, Eu, Gd, Dy, Ho, Er in high purity terbium oxide by ICP-AES, *Microchim. Acta,* 1991, vol. 103, no. 1, pp. 71–77.
10. Cai, B., Hu, B., and Jiang, Z., Direct determination of trace rare earth elements in high purity Y_2O_3 using fluorination assisted electrothermal vaporization inductively coupled plasma atomic emission spectrometry with slurry sampling, *Fresenius' J. Anal. Chem.,* 2000, vol. 367, no. 3, pp. 259–263.
11. Evdokimov, I.I. and Pimenov, V.G., Determination of impurities in optical ceramics and its precursors by atomic spectrometry, *Vestn. Nizhegorod. Univ. im. N.I. Lobachevskogo,* 2013, no. 4 (1), pp. 98–102.
12. Evdokimov, I.I. and Pimenov, V.G., Determination of impurities in high-purity neodymium-doped yttrium oxide nano-powders by inductively coupled plasma atomic emission spectrometry, *Anal. Kontrol,* 2013, vol. 17, no. 2, pp. 170–176.
13. Evdokimov, I.I. and Pimenov, V.G., Analysis of yttrium oxide by inductively coupled plasma atomic emission spectrometry and coprecipitation of impurities, *Zavod. Lab., Diagn. Mater.,* 2016, vol. 82, no. 9, pp. 5–12.
14. Javis, K.E., Gray, A.L., and Houk, R.S., *Handbook of Inductively Coupled Plasma Mass Spectrometry,* Glasgow: Blackie, 1992.
15. Becker, J.S. and Dietze, H.J., State-of-the-art in inorganic mass spectrometry for analysis of high-purity materials, *Int. J. Mass Spectrom.,* 2003, vol. 228, nos. 2–3, pp. 127–150.
16. Day, J.A., Caruso, J.A., Becker, J.S., and Dietze, H.-J., Application of capillary electrophoresis interfaced to double focusing sector field ICP-MS for nuclide abundance determination of lanthanides produced via spallation reactions in an irradiated tantalum target, *J. Anal. At. Spectrom.,* 2000, vol. 15, pp. 1343–1348.
17. Kozono, S., Takahashi, S., and Haraguchi, H., Determination of boron in high-purity tantalum materials by on-line matrix separation/inductively coupled plasma mass spectrometry, *Analyst,* 2002, vol. 127, pp. 930–934.
18. Zhang, X.Q., Yi, Y., Liu, Y.L., Li, X., Liu, J.L., Jiang, Y.M., and Su, Y.Q., Direct determination of rare earth impurities in high purity erbium oxide dissolved in nitric acid by inductively coupled plasma mass spectrometry, *Anal. Chim. Acta,* 2006, vol. 555, pp. 57–62.
19. Pedreira, W.R., Sarkis, J.E.S., Rodrigues, C., Tomiyoshi, I.A., and Queiroz, C.A., Determination of trace amounts of rare earth elements in highly pure praseodymium oxide by double focusing inductively coupled plasma mass spectrometry and high-performance liquid chromatography, *J. Alloys Compd.,* 2001, vol. 49, pp. 323–324.

20. Pedreira, W.R., Sarkis, J.E.S., Rodrigues, C., Tomiyoshi, I.A., Queiroz, C.A., Queiroz, C.A., and Abrão, A., Determination of trace amounts of rare earth elements in high pure lanthanum oxide by sector field inductively coupled plasma mass spectrometry (HR ICP-MS) and high-performance liquid chromatography (HPLC) techniques, *J. Alloys Compd.,* 2002, vol. 344, pp. 17–20.
21. Pedreira, W.R., Sarkis, J.E.S., Queiroz, C.A., Rodrigues, C. Tomiyoshi, I.A. and Abrão, A., Determination of trace amounts of rare-earth elements in highly pure neodymium oxide by sector field inductively coupled plasma mass spectrometry (ICP-SFMS) and high-performance liquid chromatography (HPLC) techniques, *J. Solid State Chem.,* 2003, vol. 171, pp. 3–6.
22. Balaram, V., Strategies to overcome interferences in elemental and isotopic geochemical analysis by quadrupole inductively coupled plasma mass spectrometry: A critical evaluation of the recent developments, *Rapid Commun. Mass Spectrom.,* 2021, vol. 35, pp. 1–29.
23. Douraied, B.S. and Jean-Alix, B., Determination of rare earth elements in gadolinium-based contrast agents by ICP-MS, *Talanta,* 2021, vol. 221, p. 121589.
24. Shabani, M.B. and Masuda, A., Sample introduction by on-line two-stage solvent extraction and back-extraction to eliminate matrix interference and to enhance sensitivity in the determination of rare earth elements with inductively coupled plasma mass spectrometry, *Anal. Chem.,* 1991, vol. 63, pp. 2099–2105.
25. Adrian, A.A., Amman Inductively coupled plasma mass spectrometry (ICP MS): A versatile tool, *J. Mass Spectrom.,* 2007, vol. 42, pp. 419–427.
26. Kawabata, K., Kishi, Y., Kawaguchi, O., Watanabe, Y., and Inoue, Y., Determination of rare-earth elements by inductively coupled plasma mass spectrometry with ion chromatography, *Anal. Chem.,* 1991, vol. 63, no. 19, pp. 2137–2140.
27. Qin, S., Jiang, Z., Hu, B., Qin, Y., and Hu, S., HPLC combined with ICP-MS for the determination of trace amounts of rare earth impurities in high-purity La_2O_3 by using 2-ethylhexyl hydrogen-2ethylhexylphosphonate resin as a stationary phase, *Fresenius' J. Anal. Chem.,* 2000, vol. 367, no. 3, pp. 250–253.
28. Cao, X., Yin, M., and Li, B., Determination of rare earth impurities in high purity gadolinium oxide by inductively coupled plasma mass spectrometry after 2-ethylhexylhydrogen-ethylhexy phosphonate extraction chromatographic separation, *Talanta,* 1999, vol. 48, no. 3, pp. 517–525.
29. Zhang, X., Liu, J., Yi, Y., Liu, Y., Li, X., Su, Y., and Lin, P., Determination of rare earth impurities in high purity samarium oxide using inductively coupled plasma mass spectrometry after extraction chromatographic separation, *Int. J. Mass Spectrom.,* 2007, vol. 260, no. 1, pp. 57–66.
30. Pedreira, W.R., Queiroz, C.A., Abrao, A., Rocha, S.M., Vasconcellos, M.E., Boaventura, G.R., and Pimentel, M.M., Trace amounts of rare earth elements in high purity samarium oxide by sector field inductively coupled plasma mass spectrometry after separation by HPLC, *J. Alloys Compd.,* 2006, vol. 418, nos. 1–2, pp. 247–250.
31. Sun, X., Peng, B., Ji, Y., Chen, J., and Li, D., The solid-liquid extraction of yttrium from rare earths by solvent (ionic liquid) impregnated resin coupled with complexing method, *Sep. Purif. Technol.,* 2008, vol. 63, no. 1, pp. 61–68.
32. Yin, M., Li, B., Zhang, Y., and Cao, X.D., *Determination of rare earths impurities in high purity Eu_2O_3 by ICP-MS*, *Anal. Lab.-Beijing,* 1999, vol. 18, pp. 1–6.
33. Qin, S., Bin, H., Yongchao, Q., Wanjau, R., and Zucheng, J., Determination of trace rare earth impurities in high-purity cerium oxide by using electrothermal vaporization ICP-AES after HPLC separation with 2-ethylhexylhydrogen 2ethylhexylphosphonate resin as the stationary phase, *J. Anal. At. Spectrom.,* 2000, vol. 15, pp. 1413–1416.
34. Shuai, Q., Qin, Y., Hu, B., Xiong, H., and Jiang, Z., Determination of rare earth impurities in high-purity lanthanum oxide using electrothermal vaporization/ICP-AES after HPLC separation, *Anal. Sci.,* 2000, vol. 16, pp. 957–961.
35. Zishu, W., Xiyun, S., and Lijun, L.P., Extraction chromatographic separation and spark source mass spectrometric determination of 14 rare earth impurities in extra-pure Dy_2O_3, *J. Instrum. Anal.,* 1995, no. 4, pp. 06–09.
36. Xinjun, Z. and Yongfeng, Z.M.Z., The determination of 14 kinds of rare-earth element as impurity in high pure lutetium oxide by means of P507 chromatographic separation and ICP-AES, *Uranium Geol.,* 1998, no. 1, pp. 6–10.
37. Lu, Y.Q., Cao, Y.-Q., Wang, L.-H., and Xin, R.-X., Analysis of rare earth elements in high purity europium oxide, *Rare Met.,* 2005, vol. 24, no. 3, pp. 216–220.
38. Jinying, L., Binghua, G., and Jingsu, G., Determination of 14 rare earth impurities in high purity europium oxide by axis-view ICP-AES with chromatographic separation, *Rock Miner. Anal.,* 1994, vol. 3, pp. 21–28.
39. Zhiguang, W., Changqing, W., and Xing, W., Chemical preconcentration spectrographic determination of 14 rare earth impurities in 5N Gd_2O_3, *Anal. Lab.,* 1998, vol. 1, p. 1.
40. Xigun, S., Zishu, W., and Furong, H., Determination of fourteen rare earths impurities in high purity Nd_2O_3 by P(507) extraction chromatography separation-spark source mass spectrometry, *J. Chin. Mass Spectrom. Soc.,* 1996, vol. 1, p. 1.
41. Li, W., Peng, C., Yuan, P., Qi, W., Kuang, Z., and Xu, C., Determination of 14 rare earth impurities in Sm_2O_3, Eu_2O_3 and Gd_2O_3 of ultra-high purity by extraction chromatography atomic emission spectrometry, *J. Instrum. Anal.,* 1998, vol. 1, pp. 18–21.
42. Kobayashi, S., Wakui, Y., Kanesato, M., Matsunaga, H., and Suzuki, T.M., Chromatographic separation and inductively coupled plasma atomic emission spectrometric determination of the rare earth metals contained in terbium, *Anal. Chim. Acta,* 1992, vol. 262, no. 1, pp. 161–166.

43. Premadas, A. and Khorge, C.R., Solvent extraction separation of heavy rare earth elements from light rare earth elements and thorium: ICP-AES determination of REEs and yttrium in monazite mineral, *At. Spectrosc.,* 2006, vol. 27, no. 5, pp. 170–177.

44. Kim, J.-G., Separation of heavy rare earth elements with extraction chromatography, *Curr. Nanosci.,* 2014, vol. 10, pp. 11–15.

45. Miranda, P. and Zinner, L.B., Separation of samarium and gadolinium solutions by solvent extraction, *J. Alloys Compd.,* 1997, vol. 249, nos. 1–2, pp. 116–118.

46. Agrawal, Y.K., Liquid-liquid extraction, separation, preconcentration, and ICP AES determination of lanthanum and cerium with N-Phenyl-(1,2-methanofullerene C60)61-formohydroxamic acid, *Fullerenes, Nanotubes, Carbon Nanostruct.,* 2004, vol. 12, no. 3, pp. 545–570.

47. Zhao, Z., Lyu, H., Guo, X., Dong, Y., Wang, Y., and Sun, X., The synergistic extraction by combined ammonium and phosphonium type ionic liquids for rare earth elements separation, *Hydrometallurgy,* 2017, vol. 174, pp. 234–247.

48. Hastiawan, I., Bings, N.H., and Broekaert, J.A.C., Development and optimization of pre-concentration procedure of rare-earth elements (REEs) in their minerals, using microwave - assisted sample dissolution for ICP-atomic emission spectrometric detection, *Procedia Chem.,* 2015, vol. 17, pp. 93–98.

49. Jain, V.K., Pillap, S.G., and Mandal, H.C., Liquid-liquid extraction, preconcentration and transport studies of lanthanum(III) with calix [4]resorcinarene-hydroxamic acid (C4RAHA), *J. Chil. Chem. Soc.,* 2007, vol. 52, no. 2, pp. 1177–1181.

50. Amin, A.S., Kassem, M.A., and Moalla, S.M.N., Determination of scandium in monazite and environmental samples using cloud point extraction coupled with a spectrophotometric technique, *RSC Adv.,* 2016, vol. 6, p. 73797.

51. Guirguis, L., Orabi, A., and Mohamed, B., Extraction and derivative spectrophotometric assay of Sm(III), Pr(III) and Nd(III) from REEs monazite concentrate, *Int. J. Environ. Anal. Chem.,* 2019, no. 6, pp. 1–20.

52. Abdou, A.A., Abdelfattah, N.A., and Weheish, H.L., Development of a procedure for spectrophotometric determination of Pr(III) from rare earth elements (REEs) concentrate, *SN Appl. Sci.,* 2019, vol. 1, no. 5, pp. 1–9.

53. Zheng, X., En-li, L., Zhang, F., Yan, Y., and Pan, J., Efficient adsorption and separation of dysprosium from NdFeB magnets in an acidic system by ion imprinted mesoporous silica sealed in a dialysis bag, *Green Chem.,* 2016, vol. 18, no. 18, pp. 5031–5040.

54. Banda, R., Jeon, H.S., and Lee, M.S., Solvent extraction separation of La from chloride solution containing Pr and Nd with Cyanex 272, *Hydrometallurgy,* 2012, vol. 121, pp. 74–80.

55. El-Nadi, Y.A., Lanthanum and neodymium from Egyptian monazite: synergistic extractive separation using organophosphorus reagents, *Hydrometallurgy,* 2012, vol. 119, pp. 23–29.

56. Vasylechko, V.O., Gryshchouk, G.V., Zakordonskiy, V.P., Vasylechko, L.O., Schmidt, M., Leshchack, I.M., Kalychak, Ya.M., and Bagday, S.R., Sorption-luminescence method for determination of terbium using Transcarpathian clinoptilolite, *Talanta,* 2017, vol. 174, pp. 486–492.

57. Rabie, K.A., Sayed, S.A., Lasheen, T.A., and Salama, I.E., Europium separation from a middle rare earths concentrate derived from Egyptian black sand monazite, *Hydrometallurgy,* 2007, vol. 86, nos. 3–4, pp. 121–130.

58. Metwally, S.S., Hassan, R.S., El-Masry, E.H., and Borai, E.H., Gamma-induced radiation polymerization of kaolin composite for sorption of lanthanum, europium and uranium ions from low-grade monazite leachate, *J. Radioanal. Nucl. Chem.,* 2018, vol. 315, no. 1, pp. 39–49.

59. Karpov, Yu.A., Churbanov, M.F., Baranovskaya, V.B., Lazukina, O.P., and Petrova, K.V., High pure substances—prototypes of elements of periodic table, *Pure Appl. Chem.,* 2020, vol. 92, no. 8, pp. 1357–1366.

60. Lee, G.S., Uchikoshi, M., Mimura, K., and Isshiki, M., Separation of major impurities Ce, Pr, Nd, Sm, Al, Ca, Fe, and Zn from La using bis (2-ethylhexyl) phosphoric acid (D2EHPA)-impregnated resin in a hydrochloric acid medium, *Sep. Purif. Technol.,* 2010, vol. 71, no. 2, pp. 186–191.

61. Yang, X.J., Extractive chromatographic separation and inductively coupled plasma atomic emission spectrometric determination of trace impurities in high purity europium oxide, *Talanta,* 1994, vol. 41, no. 11, pp. 1807–1813.

62. Yang, X.J. and Guan, J.S., End-on viewed inductively coupled plasma for the determination of trace impurities in high-purity scandium oxide by extraction chromatography, *Anal. Chim. Acta,* 1993, vol. 279, no. 2, pp. 261–272.

63. Choi, K.S., Lee, C.H., Kim, J.G., Kim, W.H., and Kang, J.G., Separating Ag, B, Cd, Dy, Eu, and Sm in a Gd matrix using 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester extraction chromatography for ICP analysis, *Talanta,* 2007, vol. 71, no. 2, pp. 662–667.

64. Ruth, W., Zu-cheng, J., Bin, H., Yong-chao, Q., Ying-liang, W., and Xia-shi, Z., Simultaneous determination of trace rare earth elements and other elements in high purity terbium oxide (Tb_4O_7) by ICP-AES after HPLC separation using P507 resin, *Wuhan Univ. J. Nat. Sci.,* 2002, vol. 7, no. 2, pp. 212–216.

65. Hongnian, J., Lian, L., Zhenhuan, L., and Zucheng, J., Determination of trace non rare earth metals in high purity lanthanum oxide by ICP AES with preconcentration on active carbon silica gel microcolumn in a flow injection system, *J. Anal. Sci.,* 1996, vol. 12, p. 03.

66. Hou, L., Wang, S., and Li, J., Determination of 17 trace impurity elements and erbium Zr–U–Er alloy by chromatographic separation with tributyl phosphate and ICP-AES, *Spectrosc. Spectral Anal. (Beijing, China),* 1996, no. 3, pp. 5–8.

67. Zucheng, J.H.J., Determination of trace non rare earth elements in high purity rare earth oxides by ICP AES, *J. Wuxi Univ. Light Ind.,* 1999, no. 1, p. 5.

68. Ji, H., Liao, Z., Sun, J.-G., and Jiang, Z., Study and application of a method for the determination of metallic elements by ICP-AES with preconcentration on an active carbon-silica gel microcolumn in a FI system, *Fresenius' J. Anal. Chem.,* 1998, vol. 360, no. 6, pp. 721–723.

69. Wanjau, R., Jiang, Z.-C., Hu, B., and Shuai, Q., Determination of non-rare earth impurities in high purity lanthanum oxide by inductively coupled plasma atomic emission spectrometry after HPLC separation using P507 resin, *Chin. J. Rare Earths,* 2001, vol. 19, no. 4, pp. 299–303.

70. Karandashev, V.K., Zhernokleeva, K.V., Turanov, A.N., Baranovskaya, V.B., and Karpov, Yu.A., Determination of admixtures of high-melting metals in rare-earth metals and their compounds, *J. Anal. Chem.,* 2012, vol. 67, no. 4, pp. 340–348.

71. Agrawal, Y.K. and Vora, S.B., Selective extraction and separation of thorium from monazite using N-phenylbenzo-18-crown-6-hydroxamic acid, *Microchim. Acta,* 2003, vol. 142, no. 4, pp. 255–261.

72. Jiafeng, W. and Zhengmin, Z., Determination of impurities in high purity europium oxide by inductively coupled plasma-atomic emission spectrometry after reduction-extraction separation, *Metall. Anal.,* 1998, vol. 18, pp. 1–5.

73. Koshel', E.S., Baranovskaya, V.B., and Doronina, M.S., Arc atomic emission analysis of rare earth metals and their oxides with preliminary sorption concentration of impurities, *Zavod. Lab., Diagn. Mater.,* 2018, vol. 84, no. 11, pp. 9–14.

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