Determination of Rare Earth Elements and Yttrium in Geological Materials by Inductively Coupled Plasma Atomic Emission Spectrometry Using Cu-DDTC as Coprecipitative Carrier

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INTRODUCTION

Rare earth elements (REEs) and yttrium (Y) find varied applications in different fields such as for lasers, phosphors, magnetic bubble memory films, fiber optics, superconductors, and nuclear reactor materials. REEs constitute one of the most important groups of trace elements in geochemical studies. The degree of REE fractionation in rocks or minerals acts as petrogenetic indicator to understand the evolution of igneous rocks which involves processes such as partial melting of crustal or mantle materials, fractional crystallization, and/or mixing of magmas (1-3). Thus simple, rapid, and accurate methods for REE and Y determination are needed to handle large quantities of samples taken up during a geochemical survey.

Neutron activation analysis (NAA) and isotope dilution mass spectrometry (IDMS) are the principal reference techniques to determine traces of REEs in geological samples (4). These methods are time-consuming and involve complicated experimental procedures at nuclear reactor facilities. Inductively coupled plasma mass spectrometry (ICP-MS) is a highly sensitive technique for REE determination. However, these instruments are very expensive, and the technique suffers from isobaric spectral interferences.

ABSTRACT

A rapid, simple, and precise method for the determination of trace rare earth elements (REEs) and Y in complex geological samples by inductively coupled plasma atomic emission spectrometry (ICP-AES) is described. The REEs and Y as a group were separated and pre-concentrated using copper diethyldithiocarbamate (Cu-DDTC) as coprecipitative carrier. Variables such as the optimum pH, amount of carrier concentration, and quantity of DDTC were optimized for the quantitative recovery of the analyte of interest. Using the proposed procedure, the REEs and Y were separated from Ca, Mg, Ba, Cr, Mo, Nb, and Ta. The method was validated by analyzing standard reference materials AC-E Granite and SY-4 Syenite. The method was found to be precise with a RSD $\leq 10\%$. The developed method was applied to the determination of REEs and Y in complex geological samples having varying matrices.

Inductively coupled plasma atomic emission spectrometry (ICP-AES) is the commonly used technique for the determination of trace REEs. It offers multi-element detection capabilities over a wide concentration range with relatively low detection limits, high levels of precision and accuracy, rapid analytical procedures, and excellent calibration linearity (5). The technique is also free from chemical

interferences. However, it is generally recognized that a substantial part of the detection power of ICP-AES may be lost if the sample contains major elements with rich line spectra. Elements such as uranium, barium, zirconium, etc., interfere seriously in the determination of REEs. Moreover, REEs are found at trace to ultra-trace levels in geological samples and since most of the matrix elements interfere with REE determination owing to the spectral overlaps and background continuum interferences (6), a prior separation and preconcentration from the rest of the matrix is essential. This further increases the sensitivity of the technique.

A number of separation and preconcentration methods have been successfully applied in the group separation and determination of REEs in various alloys, rocks, and geological materials (7). Liquid-liquid extraction utilizes preferable distribution of the analyte from the aqueous phase to the organic phase. However, this requires large quantities of hazardous and costly organic solvents. Methods involving chelating resins and solid phase extraction procedures are selective to the analytes of interest but are time-consuming and require sophisticated glassware as well as desorption of the elements from the solid support. On-line methods such as flow injection analysis offer freedom from contamination (8,9). Co-precipitation is the simplest and also a fast preconcentration procedure. This allows the quantitative precipitation of the metal ion of

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interest by the addition of a co-precipitant. Since many matrix elements co-precipitate along with the analytes, this process can be minimized by selecting suitable conditions during precipitation and subsequent washing of the resulting precipitate. The effect of interfering elements can be minimized by measuring the emission intensity at selected wavelengths.

Sodium diethyldithiocarbamate, ($C_5H_{10}NS_2Na$), Na-DDTC, is a known chelating agent for many metal ions, especially heavy metals and mercury. The reagent is readily soluble in water but much less soluble in organic solvents and is generally used with masking agents like EDTA and KCN, to enhance its selectivity at a particular pH. However, the compounds of metals with DDTC are insoluble in water since they are uncharged. The complexes decompose readily under highly acidic conditions into diethylamine and carbon disulphide leaving the analyte of interest free for analysis by a suitable technique (10). Na-DDTC was used in the separation and ICP-AES determination of trace elements including Zr and Hf in water samples (11). Na-DDTC has also been used in the determination of elements such as As(III), Bi, Sb(III) Se(IV), Te(IV), Ti(III), and V(V).

The present investigation reports the determination of REEs and Y in geological materials by ICP-AES after a simple and fast co-precipitative separation and pre-concentration of these elements as a group with copper diethyldithiocarbamate. The method was validated with the analysis of two international standard reference materials: AC-E Granite and SY-4 Syenite. The same method was also applied to the analysis of geological samples collected during a uranium exploration. The analytical results were compared with the values obtained by the well-established activated charcoal separation of

REEs and Y as their fluorides and subsequent determination by ICP-AES (14).

EXPERIMENTAL

Instrumental

All emission intensity measurements were performed using the Model Ultima2 ICP-AES, radial view (Horiba Jobin Yvon, France), equipped with a crystal-controlled RF generator of 40.68 MHz and a monochromator (focal length 1 m), employing ruled back-to-back grating of 4320 and 2400 grooves/mm. The sample introduction system had a concentric glass nebulizer and cyclonic spray chamber incorporated with a sheath gas device. Background corrections were applied wherever necessary. The instrumental parameters used are listed in Table I. All pH adjustments were made using a digital pH meter consisting of a glass electrode with an automatic temperature control (Systronics, India).

Reagents and Standard Solutions

The reagents used for the preparation of the samples and standards were of AR/GR grade. All single-element REEs and Y (as oxides) of 1 mg/mL standard stock solutions were made by dissolving Spec-Pure® rare earth oxides (Johnson and Matthey, UK) in nitric acid,

except for CeO_2 which was dissolved in a mixture of HNO_3 and H_2O_2 .

Multi-element calibration standard solutions were prepared by dilution of the stock solutions with Milli-Q™ water (Millipore Corporation, Bedford, MA, USA), keeping the final acidity at 3% (v/v) HNO_3 . Na-DDTC (Fisher Scientific, India) was used as received. The copper solution (10 mg/mL) was prepared by dissolving pure metal in sub-boiled HNO_3 .

Sample Pretreatment

Sample Decomposition

Geological samples (1.0 g) were treated with 5 mL of HF (40%) and 3 mL HNO_3 . The evaporation process was repeated three times. Then the contents were dissolved in 20 mL of 1:1 HNO_3 and transferred to a glass beaker.

Co-precipitation

To the above solution, 2 mg Cu was added and the pH adjusted to 6 with the digital pH meter using dilute ammonia/nitric acid solutions. Then 50 mg of crystalline sodium diethyldithiocarbamate (Na-DDTC) was added while stirring. This solution was kept standing for 10 minutes with continuous stirring. The dark brown precipitate of Cu-DDTC loaded with the analytes was filtered through a Whatman 541 filter paper. After washing the pre-

TABLE I
Instrumental Specifications and Operating Conditions of ICP-AES

Parameters	Specifications
Monochromator Mounting	Czerny-Turner
Order of Measurement	First order
First Order Resolution (180–420 nm)	0.005 nm
Power Applied	1 kW
Plasma Gas	Argon
Plasma Gas Flow Rate	12 L/min
Sheath Gas Flow Rate	0.2 L/min
Nebulizer Gas Flow Rate	0.5 L/min

precipitate thoroughly with distilled water, it was carefully transferred to a beaker with a fine jet of water. The filter paper was also rinsed with a few drops of HNO_3 to ensure the complete transfer of the precipitate. The precipitate was dissolved in 2–3 mL of HNO_3 by boiling thoroughly and then evaporated to incipient dryness. The clear solution was diluted to 25 mL final volume after maintaining 5% (v/v) acidity with nitric acid. However, it was found that the above precipitate, if needed, can be made up to 10 mL final volume. The elemental determinations were carried out by aspirating the solution into the ICP-AES at the selected wavelengths with minimum inter-elemental interferences.

RESULTS AND DISCUSSION

Preliminary experiments were started with co-precipitation of europium and its determination by flame atomic absorption spectrometry (FAAS). The results obtained were encouraging. Thus a synthetic mixture of REEs (La-Lu, Y) was pre-

pared, and the above procedure applied by separating the elements and analyzing them by ICP-AES at the specified wavelengths. The results are presented in Table II.

Effect of pH on Co-precipitation

The pH for co-precipitation was optimized by varying it from 1–10. However, it was observed that the recovery was negligible below pH 5 for all elements. However, quantitative recovery of all elements was obtained from pH 6 onwards. Hence, the pH of 6 was chosen for all further studies. Co-precipitation of the metal ions on the collectors can be attributed to several mechanisms such as adsorption, where the charge on the surface can attract ions in solution of opposite charge or through occlusion during which the ions are embedded within the precipitate formed. Co-crystallization of the analyte along with the carrier precipitate has also been suggested as the mechanism for co-precipitation (12). The major disadvantage of co-precipitation is that the precipitate,

which is present at a high mass-to-metal ratio, can be a major source of contamination. Further, the precipitate has to be dissolved before being analyzed by a suitable technique. However, during our experiment the Cu-DDTC bearing the analyte of interest was easily soluble in nitric acid. The solution so obtained was directly aspirated into the plasma through a nebulizer capillary.

Effect of Carrier Concentration and Amount of Na-DDTC

In order to optimize the concentration of the co-precipitative carrier, the amount of Cu was varied from 0.5 to 5.0 mg. It was found that 2 mg of Cu was enough to carry out effective co-precipitation of all REEs and Y. No quantifiable interference was observed due to the excess Cu (0.08 mg/mL) present in the sample.

The amount of Na-DDTC required was optimized by varying it from 10–100 mg. However, 50 mg of Na-DDTC was found suitable for the quantitative recovery of the analyte of interest.

Effect of Concomitant Elements

The introduction of easily ionizable elements like calcium and magnesium can cause matrix effects in ICP-AES since they are generally found in large quantities in samples such as seawater, sediments, and rocks (13). Rare earth elements at the 1 $\mu\text{g/mL}$ level were co-precipitated and analyzed by ICP-AES in the presence of major matrix elements such as Ca, Mg, Al, and Fe (100 $\mu\text{g/mL}$), and Ti and Mn (50 $\mu\text{g/mL}$), in order to estimate the effect of these concomitant elements in the geological samples. Generally, these major elements are present in silicate rock on the order of 1–10% and 0.1–1.0% by weight, respectively. On analysis it was found that Ca and Mg were not co-precipitated at the adopted pH level of 6. Hence, this co-precipita-

TABLE II
Analytical Results Obtained for Synthetic Mixture of REEs and Y
(wavelengths given in parentheses)

Element (Wavelength: nm)	Added ($\mu\text{g/mL}$)	Found ($\mu\text{g/mL}$)	(%) Recovery	RSD (%)
La (333.749)	0.80	0.78	98	8
Ce (418.660)	0.64	0.60	94	8
Pr (422.293)	0.80	0.74	93	10
Nd (430.357)	2.00	1.81	91	7
Sm (359.260)	0.80	0.74	93	8
Eu (381.966)	0.08	0.08	100	5
Gd (342.247)	0.40	0.38	95	6
Tb (350.917)	0.40	0.38	95	9
Dy (353.170)	0.20	0.19	95	8
Ho (345.600)	0.08	0.08	100	9
Er (349.910)	0.50	0.47	94	9
Tm (346.220)	0.20	0.19	95	9
Yb (328.937)	0.04	0.04	100	6
Lu (261.542)	0.02	0.02	100	8
Y (371.029)	0.08	0.08	100	5

tion could be of use for determining trace REEs in normal geological matrices. Trace elements like Ba, Cd, Co, Cr, Mo, Ni, Nb, Pb, Sr, Ta, V, Zn, and Zr at the concentration level of 10 µg/mL were added to a synthetic mixture of REEs (1 µg/mL). No quantifiable interference was observed at the wavelengths used. Further, Ba, Sr, Mo, Nb, Ta, and Cr were not co-precipitated. It can be seen that these results further enhance the utility of the proposed method in the determination of REEs and Y even at trace levels in matrices rich in the above elements.

Method Validation

A set of two certified reference materials, AC-E (Granite, Centre

National De La Recherche Scientifique, France) and SY-4 (Syenite, CANMET, Canada), containing sizable amounts of the analytes of interest, were selected and analyzed for evaluation of the effectiveness of the proposed methodology. Table III lists the values obtained with the present method which are in good agreement with the certified values.

Application to Real Geological Samples

The proposed method (PM) was also applied to the ICP-AES determination of REEs and Y in several rock samples received during an exploration for atomic minerals. The data from this analysis were compared with the values obtained

by separation and preconcentration of these elements as their fluorides on activated charcoal (14). The results of the present method (PM) and the fluoride precipitation-activated charcoal method (FPM) are listed in Table IV. The entire process of the proposed co-precipitation and separation method takes less than one hour for a batch of 10 samples which includes the time required for preparation of the standards for calibration. Hence, the present method is rapid compared to other rare earth element separation methods such as solvent extraction and solid phase extraction which are generally and routinely adopted.

TABLE III
Comparison of Results Obtained for CRMs, AC-E (Granite) & SY-4 (Syenite) (values in µg/g)

CRM	Comparison	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
AC-E																
	Value Obtained	56	150	19	85	22	1.9	24	5	30	6	16	2	16.4	2.4	190
	Certified Value	59	154	22.2	92	24.2	2	26	4.8	29	6.5	17.7	2.6	17.4	2.4	184
SY-4																
	Value Obtained	56	119	13	53	11	1.9	13	<3	18	4	13	2.0	13.9	2.0	120
	Certified Value	58	122	15	57	12.7	2	14	2.6	18.2	4.3	14.2	2.3	14.8	2.1	119

TABLE IV
Comparison of Results Obtained for REEs and Y in Geological Samples by Proposed Method (PM) and Fluoride Precipitation-Activated Charcoal Method (FPM) (values in µg/g)

Sample	Comparison	La	Ce	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	Y
AMD-1																
	P.M.	100	280	30	110	20	1.0	20	4	14	3	4	<1	3.1	<1.0	89
	F.P.M0	115	290	35	130	26	1.1	23	4	15	3	5	<1	3.4	<1.0	81
AMD-2																
	P.M.	35	90	<10	39	<10	<1	9	<3	12	3	6	<1	6.0	<1.0	90
	F.P.M	37	97	12	43	<10	<1	10	<3	13	3	8	<1	7.1	<1.0	91
AMD-3																
	P.M.	30	72	<10	30	<10	1.1	<5	<3	4	<3	<3	<1	2.5	<1.0	38
	F.P.M	32	80	<10	35	<10	1.2	5	<3	5	<3	3	<1	3.0	<1.0	36

CONCLUSION

The proposed procedure using copper diethyldithiocarbamate (Cu-DDTC) co-precipitation, separation, and preconcentration is simple, rapid, and accurate for the determination of rare earth elements (REEs) and yttrium (Y) in geological samples by inductively coupled plasma atomic emission spectrometry (ICP-AES).

The procedure is precise with a $\leq 10\%$ RSD for triplicate determinations of various rare earth elements and yttrium. This method can be applied on a routine basis for the determination of trace REEs and Y in samples with complex matrices and especially rich in Ca, Mg, Ba, Mo, Cr, Nb, and Ta since the preconcentration procedure excludes these elements. The method does not require large quantities of organic solvents, thus is environmentally friendly, and demonstrates the significance and effectiveness of coprecipitation.

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