Separation and Determination of REEs and Y in Columbite-Tantalite Mineral by ICP-OES: A Rapid Approach

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INTRODUCTION

Rare earth elements (REEs) form a coherent group of elements of geochemical significance and their distribution in mineral samples is important in petrogenetic studies (1). The rare earth element geochemistry plays an important role in the interpretation of certain geological processes in which the REE distribution is influenced by magmatism and sedimentation (2-3). Inductively coupled plasma optical emission spectrometry (ICP-OES) is now a widely accepted method for the determination of REEs and Y due to its simplicity and the low cost of the instrumentation (4-6). However, a separation and pre-concentration of the REEs and Y is required to eliminate the spectral and background continuum interferences due to major matrix elements in the sample solution, especially if the concentration of the analytes in the mineral sample is very low.

Columbite and tantalite are refractory oxide minerals containing traces of U, Th, REEs, and Y. The major matrix elements in Nb-Ta rich samples hydrolyze on dissolution in a mineral acid. The trace level determination of REEs in mineral samples usually requires various dissolution and separation steps. These methods are rather time-consuming and require 2-3 working days for decomposition and group separation, in addition

ABSTRACT

A simple and rapid separation procedure is described for the determination of rare earth elements (REEs) and Y in Nb-Ta matrices by inductively coupled plasma-optical emission spectrometry (ICP-OES). In the proposed method, columbite-tantalite samples were fused with a 1:1 mixture of sodium dihydrogen orthophosphate and tetrasodium pyrophosphate and dissolved in distilled water. After disintegration of the melt, the solution was subjected to oxalate precipitation for separating the REEs from the major matrix-interfering elements. The accuracy of the method was evaluated by analyzing the international geo-standards IGS-33 Columbite and IGS-34 Tantalite, and comparing the REEs and Y recovery values of the present method with those obtained by the standardized fluoride separation procedure. The RSD of the method was found to be within 1-5% for the REEs by ICP-OES. The method was also applied to analyzing in-house Nb-Ta samples which showed comparable analytical results and considerable reduction in analysis time.

to using corrosive acids during the process.

Different authors have employed phosphate fluxes for the dissolution of refractory mineral phases (7-10). For the determination of REEs by ICP-OES, a simple separation from Nb, Ta, Fe, and Mn (major matrix elements) is required so that the analytes can be recovered quantita-

tively, while the concentration of the matrix elements should be below the tolerance level. Various group separation methods, such as precipitation as oxalate or fluoride, have been reported (11-13) for removing the major matrix elements. Hydrofluoric acid is used for the decomposition and separation of REEs in titanoniobate (14). Hydrofluoric acid alone and in combination with other mineral acids has been used for the dissolution of minerals for the solvent extraction of Nb and Ta in industrial samples. This dissolution requires high leaching temperatures and a high concentration of HF in the range of 70% (15). Hydrofluoric acid (40%) alone, however, is found to be unsatisfactory in decomposition. The REEs and Y were determined in IGS-33 Columbite and IGS-34 Tantalite samples (U.S. Institute of Geological Survey) after their separation as oxalate using Ca as the carrier (16). The quantitative recovery of heavy REEs is critical and a slight change in the conditions of precipitation results in low recovery. An ion exchange method was also reported for the separation of REEs in columbite-tantalite (11), but this process is time-consuming and unsuitable for routine analysis.

In this study and taking advantage of the solubility of the major matrix elements and the insolubility of the REEs and Y in oxalate precipitation, the REEs were decomposed and separated from the rest of the major elements in a single separation step. The columbite-tantalite mineral sample was fused with a 1:1 mixture of sodium dihydrogen

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orthophosphate and tetra-sodium pyrophosphate, then dissolved in distilled water. The pH was optimized, including the amount of Ca carrier to be used, sample solution aliquot, etc., as required for oxalate precipitation for the quantitative separation of the REEs and Y in a single step. The elements were determined by ICP-OES, at the same time reducing the concentration of the major matrix elements below their tolerance limits.

EXPERIMENTAL

Instrumentation

A Model JY Ultima-2 inductively coupled plasma optical emission spectrometer (ICP-OES) with a focal length of 1 m and a back-to-back grating of 4320 g/mm and 2400 g/mm was used for measurement of the emission intensity of the individual REEs (Horiba Jobin Yvon Corporation, Japan). The instrumental operating parameters are listed in Table I.

Standard and Reagents

The standard stock solutions of the REEs and Y were prepared from SpecPure® oxides (Johnson

Matthey, London, UK) by fusion with phosphate flux. The sodium di-hydrogen orthophosphate and tetra-sodium pyrophosphate used were of GR grade (E. Merck, Germany). All other reagents used were of AR/GR grade. Quartz boiling double-distilled water was used throughout this work.

Preparation of Standard Solutions

An amount of 0.20 g of each rare earth element and the Y oxides was weighed into separate platinum crucibles containing a total of 8 g of flux in 1:1 proportion. The content was fused on a burner for 5–10 minutes, cooled, dissolved in distilled water, and made up to 100-mL volume with distilled water to obtain a 2.0-mg/mL stock solution of the respective oxides. Then, 20 mL of the above solutions was diluted to 100 mL to give a 0.4 mg/mL concentration, and further diluted when required.

Preparation of Sample Solutions

Four grams each of sodium di-hydrogen phosphate monohydrate and tetra-sodium pyrophosphate were mixed well into a dry

platinum crucible (phosphate flux), heated slowly and then strongly on the flame for 2–5 minutes until a clear and nearly transparent melt of the condensed phosphate was formed. An accurately weighed 0.10/0.20 g mineral sample was added to the cooled phosphate flux, and heated again with intermittent stirring for fusion for about 10 to 15 minutes until complete decomposition. The contents were cooled and transferred into a 250-mL beaker containing distilled water and heated on a waterbath for dissolution of the fused melt. The crucible was removed from the beaker, washed thoroughly, and heated on a waterbath to clear the solution. The stock solution was then made up to 100-mL volume with distilled water.

Separation of REEs Using Proposed Procedure

A suitable aliquot (20 mL, 30 mL, 40 mL, or 100 mL) of this resultant stock solution prepared as above was placed into a 250-mL glass beaker, 50 mg of Ca was added as the carrier, plus 50 mL saturated oxalic acid solution. This solution was heated on a gas burner until start of boiling, then removed and kept on a hot waterbath for digestion of 25–30 minutes. This solution was filtered through a Whatman filter paper No. 540, the precipitate washed twice with 2% oxalic acid solution, and transferred to the original beaker using a fine jet of distilled water and HNO₃. The solution was evaporated to dryness with a few drops of HClO₄ in order to decompose the oxalate complexes of the REEs and Y. The residual mass was dissolved in dilute HCl and made up to 25-mL volume with double-distilled water for ICP-OES determination of the REEs and Y, using pure combined calibration standards of the REEs and Y, all doped with 50 mg calcium. The wavelengths and background points are listed in Table II.

TABLE I
Instrumental ICP-OES Operating Parameters

Instrument	Horiba JY Ultima-2
Radio Frequency Generator	40.68 MHz
Incident Power	1000 W
Reflected Power	< 5 W
Focal Length	1 meter
Wavelength Range	120–800 nm
Gratings	Dual back-to back gratings (4320 gv/mm & 2400 gv/mm)
Resolution	10 / 5 pm in first/second order
Plasma Argon	12 L/min
Auxilliary Argon	0.0 L/min
Nebulizer Argon	0.91 L/min
Humidifier	Yes
Nebulizer Pressure	2.45 Bar
Pump Speed	15%
Liquid Uptake Rate	0.91 mL/min

RESULTS AND DISCUSSION

The major matrix element composition of the Nb-Ta mineral samples under study was received from the Pandikimal areas, Jharsuguda district, Orissa, India, through the rare metal and rare earth group of our directorate, and is listed in Table III. The elements iron, manganese, niobium, tantalum, and titanium, being the strong emitters, give line-rich spectra in the plasma that will interfere in the subsequent analysis of the individual rare earth elements, predominantly, in the estimation of HREEs (2, 12, 18). Thus, the separation of REEs from all of these major matrix elements listed above is inevitable in almost all cases. In a conventional oxalate precipitation separation method of REEs and Y from nitric acid or HCl acid media, a close control of pH is required. Although the precipitation of REEs and Y as oxalates starts

at a pH closer to 2.0, the complete separation by precipitation of the lighter REEs (La and Ce) as oxalates occurs only at a pH close to 1.0. Hence, very close control of the pH at 1.0 is required for the quantitative recovery of all of the REEs and Y oxalates. Secondly, the quantity of calcium as the carrier required to bring down the trace quantities of the REE oxalate precipitates is also on the higher side, i.e., 200–250 mg. Due to this high amount of calcium present as the carrier, the solution cannot be used to feed directly into the plasma. Hence an R_2O_3 separation is again carried out to remove the excess amount of calcium from the test solution. Thus, the method takes sufficiently longer for complete separation of the REEs and Y from the matrix elements when using oxalate precipitation.

In the proposed method, the phosphate flux was used for the dissolution of the Nb-Ta mineral samples. For rapid separation of the REEs and Y from the major matrix elements in columbite-tantalite mineral, a modified approach of the well-established oxalate precipitation method with Ca as the carrier was used. Here,

optimization of the various parameters for the quantitative recovery of the REEs and Y from the major matrix elements in columbite-tantalite mineral was studied and is documented below;

Optimization of Parameters for Quantitative Recovery of REEs in CRM IGS-33

Effect of Flux Composition

The limitation of phosphate fluxes used for fusion is that they are less effective in dissolving silicate matrices (8). Columbite-tantalite samples normally contain <5% SiO_2 in mineral fractions. It was found that even (1+1) g of the recommended flux is sufficient to dissolve 0.1 g of the columbite-tantalite sample. However, the silica content tolerable is 5 mg which corresponds to the overall concentration of 5% SiO_2 in the sample (10, 11). The resultant melt easily disintegrates in water and provides a clear solution. However, as the silica content increases, the chances of silica hydrolyzing out of the solution increases. Hence, in order to obtain a clear and stable solution, 8 g of the flux (i.e., 4 g each) in 1:1 proportion was fixed

TABLE II
Wavelengths Used for REE Determination With Two Points Off – Peak Background Correction;

Element	Wavelength (nm)	Off-peak Background Correction Points (nm)	
		Left	Right
La	333.749	0.014	0.013
Ce	418.660	0.015	0.016
Pr	422.293	0.016	0.018
Nd	430.357	0.016	0.013
Sm	359.260	0.016	0.013
Eu	381.966	0.013	0.015
Gd	335.048	0.013	0.015
Tb	350.917	0.018	0.012
Dy	353.171	0.012	0.015
Ho	345.600	0.016	0.018
Er	349.910	0.012	0.012
Tm	346.221	0.012	0.012
Yb	328.937	0.017	0.014
Lu	261.542	0.014	0.011
Y	371.029	0.015	0.012

TABLE III
Major Matrix Element Composition

(a) Certified Reference Materials IGS-33 and IGS-34								
Sl.	Code	%Nb ₂ O ₅	%Ta ₂ O ₅	%SnO ₂	%WO ₃	%FeO(T)	%MnO	%TiO ₂
1	IGS-33	68.79	5.52	1.80	0.26	17.91	2.12	1.72
2	IGS-34	27.45	49.83	0.10	0.56	5.75	8.80	1.20
(b) In-house Nb-Ta Samples								
Sl.	Code	%Nb ₂ O ₅	%Ta ₂ O ₅	%SnO ₂	%WO ₃	%FeO(T)	%MnO	%TiO ₂
1	IHS-1	44.0	27.8	6.5	0.6	11.5	5.05	1.80
2	IHS-2	50.1	20.7	1.3	1.2	14.1	5.50	3.05
3	IHS-3	21.0	51.5	8.6	1.5	7.3	5.80	3.60
4	IHS-4	46.7	23.7	0.9	1.2	13.2	5.60	4.85
5	IHS-5	45.0	30.1	1.5	1.5	9.4	5.25	4.20

and is recommended for the efficient and complete fusion of all columbite-tantalite mineral samples. This procedure should also be considered in cases where prior knowledge of the sample matrix is not known (anticipating highest possible silica content in the mineral sample). Even when using a large quantity of flux, the high salt content of the solution does not pose a problem since it is removed during the oxalate precipitation of the REEs and Y and ensures removal of high TDS.

Effect of pH and Carrier Concentration

The phosphate complexes of REEs are comparatively stable and cannot easily get converted to oxalate complexes in cold conditions. However, by boiling the solution with saturated oxalic acid, the phosphate complexes of the REEs

easily convert to oxalate complexes. Recovery studies for REEs and Y from a phosphate medium using oxalate precipitation at various pHs and a carrier concentration show that the phosphate complexes of REEs are easily converted to oxalate complexes (see Table IV) (11, 17, 19). The results listed in Table V show that with a 25-mg Ca carrier concentration, the recovery of REEs is not quantitative. However, from a 50-mg Ca concentration and up, quantitative recoveries for all REEs were obtained. The greatest advantage of this phosphate flux used for fusion is that the resultant solution is acidic and exhibits a pH of ~1.0, which is ideal for carrying out oxalate precipitation. Hence, no pH adjustment is required, the results are quantitative, and there are no appreciable losses during the conversion of phosphate to oxalate complexes.

Effect of Solution Aliquot

From these studies it was observed that any suitable aliquot, i.e., 20 mL, 30 mL, 40 mL, or an entire 100 mL of this resultant stock solution prepared above could be subjected to the oxalate separation process with 50 mg of Ca carrier, resulting in the quantitative recovery of all REEs and Y. This indicates that any portion of the stock solution could be processed depending on the approximate concentration of REEs in the columbite-tantalite minerals (Table VI).

Determination of REEs and Y in the CRMs

Due to unavailability of certified values for individual REEs and Y in certified reference materials IGS-33 and IGS-34, the results obtained for these elements by the present method were compared with those obtained by using the well-established

Optimization of Parameters for the Quantitative Recovery in CRM IGS-33

TABLE IV : Effect of pH

pH	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm	Y ppm
Without pH adjustment	133	495	42	190	75	2.0	85	22	182	42	187	44	416	74	1050
pH=0.5	130	420	40	175	73	2.0	77	21	165	36	175	43	410	66	1010
pH=0.9	135	460	39	171	73	2.1	83	21	160	40	180	43	433	74	1040
pH=1.0	140	450	38	185	74	2.0	78	23	175	40	184	44	430	72	997
pH=1.5	137	475	36	175	74	2.0	69	26	161	38	176	42	420	70	1060
pH=2.0	121	385	38	170	70	2.0	69	23	160	38	177	41	415	68	990
pH= 1.0*	140	485	41	176	74	2.1	79	24	175	41	183	44	427	72	1045

*Values obtained by following normal oxalate precipitation at 1.0 pH adjustment with 250 mg Ca.

TABLE V : Effect of Amount of Carrier (Ca) Added

pH	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm	Y ppm
25 mg	75	240	15	100	38	<0.2	50	13	100	25	100	25	225	37	550
50 mg	133	495	42	190	75	2.0	85	22	182	42	187	44	416	74	1050
100 mg	137	485	41	175	73	2.0	83	24	175	44	188	43	415	75	1120
150 mg	138	490	38	179	74	2.0	80	23	177	41	200	45	432	75	1050
200 mg	137	480	40	195	76	2.1	81	25	176	43	188	46	428	73	1070
250 mg	139	485	39	184	72	2.0	83	22	174	40	175	42	430	74	1090

lished fluoride precipitation separation procedure. The results obtained by both methods were found to be within the experimental limits (see Table VII).

Determination of REEs and Y in In-house Nb-Ta Samples

Some in-house Nb-Ta mineral samples (from the RMRE group, Central Region, Nagpur) were analyzed by the present method as well as other existing standard procedures involving HF-H₂SO₄ acid

treatment, followed by fluoride precipitation separation. The results obtained by both methods are comparable and were well within the experimental limits (Table VIII). The proposed method is simple, rapid, and has been applied to the routine determination of REEs and Y in Nb-Ta samples. The RSD of the method was found to be within 1–5% (n=10) for the REEs and Y by ICP-OES.

CONCLUSION

The proposed method was applied to the rapid separation of REEs and Y in IGS-33 Columbite and IGS-34 Tantalite samples and is a modified approach to the well-established existing oxalate precipitation method. The method has the distinct advantages over the existing decomposition methods with regard to speed, simplicity, and applicability to columbite-tantalite samples.

TABLE VI
Effect of Sample Aliquot

pH	La ppm	Ce ppm	Pr ppm	Nd ppm	Sm ppm	Eu ppm	Gd ppm	Tb ppm	Dy ppm	Ho ppm	Er ppm	Tm ppm	Yb ppm	Lu ppm	Y ppm
20 mL	137	485	40	185	73	2.2	83	23	175	41	188	43	415	75	1120
30 mL	138	460	38	176	74	1.9	80	23	187	41	200	41	432	75	1050
40 mL	137	480	41	190	76	2.1	81	22	176	43	188	46	428	73	1055
100 mL	136	485	39	179	77	2.0	82	22	194	44	175	43	421	74	1065

TABLE VII
Determination of REEs and Y in CRM IGS-33 and IGS-34

Ele- ment	IGS-33		IGS-34	
	Present Method	Fluoride Precipitation	Present Method	Fluoride Precipitation
La	133	138	126	130
Ce	495	530	295	330
Pr	42	39	43	40
Nd	190	175	183	177
Sm	75	66	175	170
Eu	2.0	1.8	4.0	4.2
Gd	85	84	279	295
Tb	22	20	62	60
Dy	182	190	282	290
Ho	42	37	31	26
Er	187	185	72	75
Tm	44	47	14	12
Yb	416	440	102	104
Lu	74	70	16	14
Y	1050	1100	940	920

Present: Proposed separation method.
FP: Fluoride precipitation separation (Ref 11, 19).

TABLE VIII
Determination of REEs and Y in Real Nb-Ta Samples

Ele- ment	AMD-1		AMD-2		AMD-3		AMD-4		AMD-5	
	A	B	A	B	A	B	A	B	A	B
La	661	657	1270	1310	330	320	330	345	91	92
Ce	1710	1695	2520	2585	595	590	640	630	170	176
Pr	170	185	250	258	38	39	62	63	11	12
Nd	830	850	1165	1210	106	110	275	270	61	62
Sm	320	315	380	395	28	29	85	87	21	21
Eu	3.7	3.8	7.4	7.8	2.4	2.5	6.3	6.8	1.3	1.3
Gd	185	188	243	247	16	16	83	84	25	25
Tb	39	40	46	47	7	7	25	26	12	13
Dy	225	240	228	231	45	46	191	194	112	109
Ho	35	36	35	37	8	8	36	34	17	18
Er	119	124	128	130	27	28	118	121	59	58
Tm	30	31	30	32	6	6	25	25	12	12
Yb	305	319	310	318	58	61	240	254	85	93
Lu	49	51	58	58	10	11	40	41	13	14
Y	1740	1765	1100	1120	302	307	1165	1185	652	640

Method-A: HF-H₂SO₄ dissolution /Fluoride precipitation separation procedure (Ref.13, 19).

Method-B: Proposed phosphate decomposition method with modified oxalate precipitation separation.

The separation of REEs from the phosphate medium using the modified oxalate precipitation procedure with 50 mg of Ca as the carrier proves to be simple and fast, thus saving considerable analysis time. The method is eco-friendly, rapid, and suitable for the routine determination of REEs and Y in columbite-tantalite samples.

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