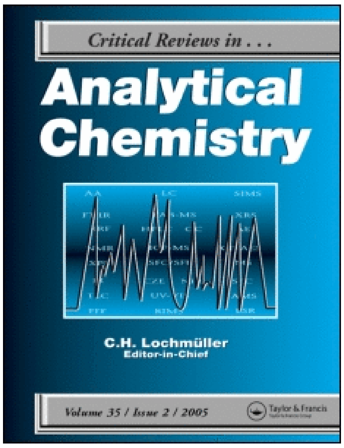

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T. Prasada Rao; V. M. Biju

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Trace Determination of Lanthanides in Metallurgical, Environmental, and Geological Samples

T. Prasada Rao and V. M. Biju*

Regional Research Laboratory (CSIR), Trivandrum -695 019, India

ABBREVIATIONS: REE, rare earth elements; **MAS,** molecular absorption spectrometry; **AAS,** atomic absorption spectrometry; **GFAAS,** graphite furnace atomic absorption spectrometry; **ETAAS,** electrothermal AAS; **EDXRF,** energy-dispersive X-ray fluorescence spectrometry; **TRXRF,** Total reflectance XRF **NAA,** Neutron activation analysis; **ICP-AES,** inductively coupled plasma atomic emission spectrometry; **ICPMS;** inductively coupled plasma mass spectrometry; **HPLC,** high-performance liquid chromatography; **IC,** ion chromatography; **SSMS,** spark source mass spectrometry; **PIXE,** particle-induced X-ray emission; **FES,** flame emission spectrometry; **DCPAES,** direct current plasma atomic emission spectrometry; **SIMS,** secondary ion mass spectrometry; **IDMS,** isotope dilution mass spectrometry; **SEM,** scanning electron microscopy; **EPMA** electron probe microanalysis.

I. INTRODUCTION

The presence of the alloying elements in aluminium brings down its electrical conductivity sharply. Rare earth elements (REE) have low solid solubility and similar electronic structure to that of aluminium. In addition, REE forms intermetallics with some of the alloying elements present in Al matrix. This results in strengthening of Al matrix without affecting ductility and little decrease in conductivity.[1-2] Similarly, REE additions to steel have a strong influence on sulfur and or sulfides.[3] This results in cleaner steels with the alteration of the shape and distribution of sulfides and oxysulfides.[4] High-purity individual lanthanides are used increasingly as major components in lasers, phosphors, magnetic bubble memory films, refractive index lenses, fiber optics, and superconductors.[5,6] Recent innovations in the area of phosphors are trichromatic and superdeluxe lamps. Both of them employ RE ions such as Eu^{2+}, Eu^{3+}, Ce^{3+}, amd Tb^{3+} as activators in an oxide, aluminate, or borate lattice. Although RE-based superconductors are well known, their importance became greatly enhanced after the discovery of the high-temperature superconductors with rare earth and cupric oxide as major constituents.[7]

The role of trace REE in environment is not clear, as there are conflicting reports such as (1) reports from China indicating that RE is used as nutrients for getting higher yields;[8] (2) toxicity of Nd salts in mice increased in the order: chloride < propionate < acetate < 3-sulfonicotinate < sulfate < nitrate;[9] and (3) terbium group elements have lesser toxicity other than REE above or below them in the periodic table.[10]

The abundance of REE in geological objects like rocks and minerals for elucidating petrogenesis and in the evaluation of the coefficients of partitioning of REE between various minerals and melts received major impetus with the availability of various powerful analytical techniques.[11,12]

Quantitative analytical techniques are required to determine REE accurately and rapidly with sufficient sensitivity for the determination in metallurgical, environmental, and geological samples. This requirement has led to major technological advances in the development of analytical instrumentation. On the other hand, the rapid studies made in analytical techniques resulted in the increased sensitivity and quick analysis of individual REE than ever before. Only one review article on metallurgical applications[13] and a few on geological applications[14-19] are available

*Address for correspondence: Fax +91-471-491712/490186] E.mail:rao@csrrltrd.ren.nic.in

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so far. Hence, the review of various procedures developed for the determination of REE in metallurgical, environmental, and geological samples since 1980 is very appropriate. These procedures have been summarized in Tables 1 to 5.

II. ANALYTICAL TECHNIQUES

A. MAS

All lanthanides have similar absorption spectra when they are reacted with a chromegenic agent. Hence, it is difficult to determine the lanthanides when they are present together. However, the presence of lanthanides in combination with non-rare earth elements in alloys, electronic materials, and environmental samples could be estimated accurately. Thus, a particular lanthanide at trace level can be determined in Al alloys,[33,46,55-57,73] Mg alloys,[42,47,50,51] silver alloy,[25] nickel alloys,[24,32,55] Ti alloys[41], Cu based alloys,[30,60] zirconium alloys,[52] and in steels and castiron.[27,31,87] Yttrium in $YBa_2Cu_3O_x$[146] and garnet crystals,[118] neodymium in Nd:YAG, europium in phosphors, neodymium and erbium in laser glasses[117] and silicate glasses,[134] and few lanthanides in ZrO_2 refractory materials,[121] magnesium chromite,[108] and rare earth mixtures[107,125,127,129,169,170] could be determined by using MAS. Only two procedures for the determination of lanthanum and Gadolineum in waste water[188] and urine,[194] respectively, were described among applications to the environmental samples. MAS procedures are developed, despite its limitations mentioned in the beginning for the determination of geological samples,[241,243,247,255] minerals,[231,235,264,294] and ores.[261]

B. Fluorimetry

Fluorimetry has similar limitations as that of MAS with regard to determination of individual lanthanides in mixtures. Still a few procedures are described for the determination of cerium in low alloy steels,[35] europium in semiconductor germanium,[26] and in high purity rare earth oxides[124] and a few lanthanides in environmental samples such as natural waters[191,207] and feces.[196] Sensitive fluorimetric procedures are described for the determination of one or two particular lanthanides in geological samples,[285,286,304] rocks,[253,258,260] minerals,[251,299] and ores.[240]

C. AAS

Flame atomic absorption, however, provides successive determination of lanthanides but is not sensitive and has been used only scarcely. Traces of yttrium in alloys,[48,53] steels,[54,58] neodymium in YAG,[103] and Y in $YBa_2Cu_2O_x$[155,156] and few lanthanides in rocks,[303] and in ores[326] have been determined using nitrous oxide-acetylene flame in flame AAS.

D. GFAAS

GFAAS such as flame AAS is useful for singular element determination of REE but is more sensitive. However, unlike flame AAS, the interference due to matrix is pronounced and is not that popular for the determination of lanthanides in metallurgical and geological samples. Yttrium, sammarium, and dysprosium in misch metal,[85] europium in RE metals,[130] and Y in YBa_2Cu_3Ox superconductors[154] were determined by GFAAS. GFAAS procedures were described for the determination of lanthanum in food and water[186] and ytterbium in seawater samples.[197,198] Lanthanides present in geological samples,[339,378] rocks,[237,246,254,314] minerals,[245,363] soils,[242] and blast furnace slags[484] were determined by GFAAS. Sengupta[429] described a unique simultaneous multielement GFAAS of individual lanthanides in six geological reference materials.

E. Spectrography

Both DC and AC spectrographic techniques were used for the simultaneous determination of few lanthanides in chromium alloys,[59] RE-rich alloys,[61] cobalt-based alloys,[78] Mg alloys,[91] steels,[26,75] electronic materials,[106,116,128,136] and high-purity RE oxides.[159,177] In addition, trace amounts

TABLE 1
Determination of Lanthanides in Metallurgical Samples

S.No.	Elements	Matrix	Analysis technique	Reactions conditions	Sensitivity/ Limit of detection	Ref.
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	La	$LaNi_4Cu$ alloys	AC-Oscillopolarography	pH 4.6, Titration with EDTA	-	20
2	La	La-Ni alloy	"	pH 5.6, EDTA titration	-	21
3	La	$La\text{-}Ni_{4.5}\text{-}Sn_{0.5}$ alloy	"	pH 5.8, EDTA titration	-	22
4	La	Fe-2OCr-5Al alloys	SIMS	-	-	23
5	Ce	Ni alloy	MAS	pH 11.5, Tetrabromopyrocatechin, $\lambda max = 540$ nm	-	24
6	Ce	Ag alloy	MAS	$\lambda max = 380$ nm	$\varepsilon = 1.2 x 10^3$	25
7	Ce	Steels	Spectrography	-	0.01-0.08% Ce	26
8	Ce	Steel and cast iron	MAS	$\lambda max = 330$ nm	0.001-0.2% Ce	27
9	Ce	Ce-Fe alloy	Enthalpimetry	-	-	28
10	Ce	Al-Ce alloy	X-ray spectrometry	Irradiated for 40s in a flux of - 10^8 n $cm^{-1}s^{-1}$	0.01-0.1% Ce	29
11	Ce	Brasses	MAS	$\lambda max = 350$ nm	0.01-0.1% Ce	30
12	Ce	Fe & steels	MAS	o-Tolidine, $\lambda max = 440$ nm	0.01-0.05% Ce	31

TABLE 1 continued

13	Ce	Ni-Cr alloys	MAS	Dibromo-p-nitrochlorophosphonazo, $\lambda max = 640$ nm	-	32
14	Ce	Al alloys	MAS	Tribromoarsenazo	$\varepsilon = 1.27x10^5$ l $mol^{-1}cm^{-1}$	33
15	Ce	Steel, Fe & Al	Radioassay	-	-	34
16	Ce	Steel	FIA-spectrofluorimetry	$\lambda exci = 260$ nm $\lambda em = 350$ nm	upto 7 ppm	35
17	Pr	Al metal, steels and alloys	MAS	Bromopyrogallol red	1-20 μg/25 ml	36
18	Pr	Al metal	MAS	5,7-dichlorooxine, Rhodamine 6G	$\varepsilon = 1.83x10^5$ l $mol^{-1}cm^{-1}$	37
19	Nd	Al metal	MAS	5,7-dichlorooxine, Rhodamine 6G	$\varepsilon = 1.36x10^5$ l $mol^{-1}cm^{-1}$	38
20	Nd	Fe-Nd-B alloys	DCPAES	-	28-31% Nd	39
21	Nd	Nd-Fe-B alloys	WDXRF	W target, Nd La lines	-	40
22	Nd	Ti alloys	MAS	$\lambda max = 645$ nm	0.01-0.16% of Nd, $\varepsilon = 8.1x10^4$ l $mol^{-1}cm^{-1}$	41
23	Nd	Mg alloys	DMAS	Fifth derivative	0.005-0.5% of Nd	42
24	Eu	Eu-Co-B alloys	Polarography	-	-	43
25	Dy	RE-Fe alloys	ICPAES	-	-	44
26	Lu	Allloyed wires & foils	NAA	-	-	45
27	Y	Al alloys	MAS	Arsenazo III, $\lambda max =$ 670 nm	2-5% Y	46
28	Y	Mg alloys	MAS	Bromophosphanazo-PB 0.04-0.12 M HCl	5-40 μg of Y/25 ml	47
29	Y	Ni or Co alloys	AAS	0.2-2% Y, 20-130 ppm	-	48

30	Y	Ni base alloys	ICPAES	360.07 nm	10-2000 ppm	49
31	Y	Mg-Y alloys	MAS	Chromotropic acid	$\varepsilon = 8.33 \times 10^{4}$ l $mol^{-1}cm^{-1}$	50
32	Y	RE-Mg alloys	MAS	Thymol blue, pH 1.8 λmax = 740 nm	30-80 μg of Y	51
33	Y	Zr alloys	MAS	Arsenazo I, pH 7.7-7.8	0.2-3 ppm	52
34	Y	Mg Cr, Ni or Ti alloy	AAS	-	100 ppm - 1% Y	53
35	Y	Steels	AAS	-	-	54
36	Y	Ni base alloys	MAS	p-nitrochloro-phosphonazo	13-20 μg of Y	55
37	Y	Ti alloys	ICPAES	-	-	56
38	Y	Cr-Ni alloys & steel	WDXRF	-	0.001-0.1% Y	57
39	Y	Steel	GFAAS	-	-	58
40	La & Y	Cr alloys	DC arc spectrograph	317.3 or 326.5 nm	0.1-1.0% La or Y	59
41	Ce & Ce group RE	Cu based alloys	MAS	p-nitrochloropho-sphonaze, λmax =680 nm	-	60
42	Ce, La, Pr, Nd &Sm	RE alloys	Spectrograph	-	-	61
43	Ce, La, Pr, Nd, Sm, Y & Lu	Ce based alloys	NAA	-	1000, 100, 1500, 2000, 1700, 750 & 4000 μg	62
44	Ce, La, Pr, Sm & Nd	Mg-Nd alloys	ICPAES	-	-	63
45	Ce, Pr, Sm & La	Nd-Fe-B alloys	ICPAES	Gradient elution with α-hydroxy isobutyric acid	0.05, 0.09, 0.05 & 0.01%	64

TABLE 1 continued

46	Ce, La, Pr & Nd	Al alloy	ICPAES	413.7, 398.8, 414.3 & 401.2	0.05 & 0.01%	65
47	Ce, Sm, Y	RE-Co magnets	ICPAES	-	-	66
48	Ce, La, Pr & Nd	Nd-Fe-B alloy	ICPAES	-	-	67
49	Ce, La, Pr, Nd & Sm	RE-Al alloys	XRF	-	-	68
50	Ce, La & Y	Steels & Ni alloys	ICPAES	413.76, 408.07 & 360.07 nm	-	69
51	Ce & Sm	Permanent magnet alloys	ICPAES	413.7 & 359.2 nm	5-30% Ce or Sm	70
52	Ce, La, Pr, Nd & Y	Si-Al alloys	ICPAES	-	-	71
53	Ce, La, Pr & Nd	Steels	"	-	upto 40µg/L, Detection limits are in the range 5-36 µg/L	72
54	Ce, La, Pr & Nd	RE-Al alloys	MAS	Chlorophosphonazo III	-	73
55	CE & La	Steel	ICPAES & XRF	413.7 & 433.3 nm	-	74
56	Ce, Y, La & Dy	Steel	Spectrography	-	0.001-1.0%	75
57	Ce & La	Cast iron	WDXRF	-	3-60 & 3-30 ppm of Ce &La	76
58	Ce, La & Y	Steels	ICPAES	-	-	77
59	Ce, Pr, Sm, Gd, Dy &Er	Co-based alloys	Spectrography	-	-	78

60	Ce, La & Y	Cast iron	EDXRF	-	10 & 9 ppm for La & Ce	79
61	Ce, La, Nd & Pr	Ni &Fe based alloys	ICPAES	-	-	80
62	Ce, La, Pr, Nd, Sm &Eu	Carbon steel	"	-	-	81
63	Sm, La, Eu, Ho & Yb	Steel	NAA	Fe matrix was removed by extraction into isopropylketone	-	82
64	Sm, Gd, Dy & Nd	RE alloys	DMAS	-	-	83
65	Sm & Gd	Magnetic alloys	XRF	-	-	84
66	Y, Sm & Dy	Misch metal	GF AAS	-	0.6, 0.86 and 0.17 ng	85
67	REE	Steel	ICPAES	Extracted with benzyl phenyl hydroxylamine	-	86
68	REE	Cast iron	MAS	Solid liquid extraction with diethyl dithiocarbamate	-	87
69	REE	Steels	ICPAES	-	0.0003-0.0009% of REE	88
70	REE	Al	"	-	1-75 ppb	89
71	REE	Co based alloys	MAS	Ion-exchange chromatographic separation	-	90
72	REE	Mg-Y alloys	Spectrography	-	-	91
73	REE	Steels	XRF	Coprecipitation as fluorides	1 ppm	92

TABLE 1 continued

74	REE	Steels	NAA	-	1 ppb - 10ppm	93
75	REE	Steels	MAS	Liquid chromatographic separation	-	94
76	REE	Ferrous alloys	AES	-	0.5-20%	95
77	REE	Cu alloys	ICPAES	-	-	96
78	REE	Steels	NAA	Ion-exchange separation	-	97
79	REE	Al alloy	ICPAES	-	<84 ng/g	98
80	REE	Mg alloy	IC	PAR as post column reagent-	0.01 ppm	99

TABLE 2
Determination of Lanthanides in Electronic Materials

Sl.No.	Elements	Matrrix	Analysis technique	Reaction conditions	Sensitivity/ Limit of detection	Reference
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	La	Semiconductor grade Si	NAA	-	6.5 ppb	100
2	La	Pb-Zr-Titanate ceramics	WDXRF	$L\alpha_1$ line	-	101
3	La	lanthanum doped Ba titanate	ICPAES	-	-	102
4	La	RE concentrate	AES	441.8 nm	0.8 ppm of La	103
5	La	Superconductor materials	IC	Anion exchange separation	upto 100 ppm	104
6	Ce	Ba-Sr-niobate crystals	XRF	$L\beta_1$, line	-	105
7	Ce	Zn WO_4 monocrystal	Spectrography	-	-	106
8	Ce	Mixed RE	MAS	Oxidation of methyl organge	0-1 ppm	107
9	Ce	Mg chromite	MAS	8.5-9.0	0.5-4.5 ppm	108
10	Ce	Zirconia based ceramic materials	ICPAES	318.286 & 328.471nm	93 & 84 ppb	109
11	Nd	YAG crystals	Optical microscope	-	-	110
12	Nd	Nd-Y-Al-borate crystals	ICPAES	-	0.4 ppm	111
13	Nd	La tungstate crystals	"	-	-	112
14	Nd	YAG	AAS	-	2 ppm	113
15	Nd	YAG	XRF	-	10 ppm	114

TABLE 2 continued

16	Nd	YAG	nondestructive MAS	-	-	115
17	Nd	Titanate ceramics	Spectrography	-	-	116
18	Nd	Laser glasses	MAS	795.5 nm	-	117
19	Nd	YAG	MAS	588.3 nm	5 ppm	118
20	Nd	YAG	EDXRF	-	-	119
21	Sm	Co-Sm thin film	XRF	-	-	120
22	Sm	ZrO_2	MAS	pH 7.0-7.9, Arsenazo I	10-35% of Sm_2O_3	121
23	Sm	Sm-Co thin film	XRF	-	38.03% of Sm	122
24	Sm	Sm-Co magnetic powders	XRF	-	-	123
25	Eu	La, Pr &Dy oxides	Luminescence	TTA, Dibenzo-18-crown-6	10^{-11} - 10^{-6} M	124
26	Eu	RE oxides	MAS	Reduction of molybdo phosphoric acid	-	125
27	Eu	Ge semiconductor	Luminescence	pH5-6, Benzoyltrifluoro acetone, TOPO	0.5 ppb	126
28	Eu	RE oxides	MAS	Extraction of molybdenum blue into isopentanol	2-50 ppm	127
29	Eu	Phosphor	DC arc spectrography	268.0 nm	-	128
30	Eu	Re oxides	FIA-MAS	Methylene blue	3-25 ppm	129
31	Eu	RE metals	GFAAS	-	144 ppb	130
32	Eu	Red phosphor	MAS	Dibromocarboxy arsenazo	0.04-1 ppm	131
33	Gd	Co-Gd thin films	XRF	-	-	132

34	Dy	Tb-Dy-Fe films	EDXRF	-	-	133
35	Er	Silicate glassses	MAS	377.5 nm	-	134
36	Er	Optical fibres	ICPAES	337.276 nm	31 ppb	135
37	Yb	Thin films of silica	Laser emission spectrography	369.4 nm	0.01% Yb	136
38	Y	$YaBa_2Cu_3O_{8-x}$	ICPAES	371.030 nm	1-50 mg/L	137
39	Y	"	EDXRF	-	-	138
40	Y	"	PIXE	-	-	139
41	Y	Bi(Pb,Y)SrCaCuO	ICPAES	371.04 nm	-	140
42	Y	Y-Ba-Cu-oxide film	XRF	-	-	141
43	Y	"	ICPAES	-	1500 ppm	142
44	Y	"	XRF	-	-	143
45	Y	"	EDXRF	-	-	144
46	Y	Y-Ba-Cu oxide	NAA	-	-	145
47	Y	"	MAS	Arsenazo III, pH4.7	-	146
48	Y	"	AAS	597.2 nm	5-50 ppm	147
49	Y	Y-Ba-Cu oxide	NAA	-	11-13% Y	148
50	Y	"	EDXRF	-	-	149
51	Y	"	EDXRF & PIXE	-	70 ng	150
52	Y	"	EDXRF	-	-	151
53	Y	"	RBS	-	-	152
54	Y	"	ICPAES	321.609 & 324.228 nm	-	153
55	Y	"	ETAAS	-	-	154

TABLE 2 continued

56	Y	"	MAS	Arsenazo III, λmax = 650 nm	-	155
57	Y	"	AAS	-	35-200 ppm	156
58	Y	Ceramics	EDXRF	-	-	157
59	La, Nd, Sm, Ce & Y	Pr	ICPAES	-	7.1, 13, 17.5, 10.1 & 0.73 μg/g	158
60	La, Ce, Nd, Sm, Eu & Gd	Re_2O_3	XRF	-	-	159
61	La, Gd, Sm, Pr, Dy & Nd	Nd-Fe-B magnet	XRF	-	-	160
62	La, Ce, Pr, Nd, Sm & Gd	Permanent magnet	ICPAES	-	-	161
63	La & Y	Y-Ba-Cu oxide or Ba(Sr)-La-Cu oxide	XRF	-	-	162
64	La & Y	"	Amperometry	pH 3.5-6.0	64% La, 13% Y	163
65	La & Y	"	ICPAES	-	-	164
66	Ce, Nd, Lu, Er &Ho	YAG crystals	ICPAES	-	-	165
67	Ce & Y	Ceria & Yttria mixtures	XRF	-	15-88% & 12-85%	166
68	Ce & Y	Ce-Y-Ba-Cu oxide	XRF	-	-	167
69	Ce, Sm, E, Gd &Dy	U	ICPAES	-	-	168
70	Dy, Ho & Er	RE_2O_3	HDMAS	Second order derivative	0.001-0.2%	169
71	Dy & Y	RE_2O_3	HDMAS	Fourth order derivative	-	170

72	Dy, Eu, Gd & Sm	U	ICPAES	-	0.02 ppm for Dy & Eu, 0.05 ppm for Gd	171
73	Eu & Yb	RE	SWP	-	0.1 ppm for Sm	172
74	Lu, Sm & Y	Garnet films	ICPAES	291.14, 442.43 & 371.03 nm	-	173
75	REE	High purity RE	LC-ICPAES	pH 4.22, 1 M ammonium lactate	upto 500 ppm	174
76	REE	High purity U	NAA	After extraction with 4-(1-butylpentyl) pyridine	-	175
77	REE	High purity Ti	ICPAES	-	-	176
78	REE	Crude Y_2O_3	Spectrography	-	0.03-3%	177
79	REE	High purity Yb_2O_3	ICPAES	-	-	178
80	REE	High purity Europia	XRF	-	<1 µg	179
81	REE	Y, La, Gd & Yb matrices	ICPAES	-	2-80 ppb	180
82	REE	High purity Zn	ICPAES	FIA preconcentration on microcolumn	ppblevel	181
83	REE	Niobate-Tantalate	ICPAES		0.14-9.9 ppb	182
84	REE	Garnets	Laser ablation ICPMS	-	0.1-1 µg/g	183

TABLE 3
Determination of Lanthanides in Environmental Samples

Sl.No.	Elements	Matrix	Analysis technique	Reaction conditions	Sensitivity/ Limit of detection	Reference
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	La	Seawater	NAA	-	-	184
2	La	Coal dust particulates	NAA	-	-	185
3	La	Food & Water	GFAAS	-	7.8 ng	186
4	La	Natural waters	FIA-ICPAES	-	0.7 ppm	187
5	La	Waste water	MAS	-	-	188
6	La	Cement dust particulates	Isotope dilution Analysis	-	1.75-44 μg	189
7	Ce	ICPP reprocessing solutions	ICPAES	-	upto 5 g/L	190
8	Ce	Natural water	Flourimetry	2 M HCl, λex = 256 & λem = 358 nm	0.5 ppb 0.7 ppm	191
9	Ce	River sediments	ICPAES	-	-	192
10	Ce	Seawater	NAA	-	-	193
11	Gd	Urine	MAS	2-(3,5-dichloro-2-pyridylazo)-5-dimethylamino phenol λmax = 592 nm	-	194
12	Er	Natural waters	ETAAS	-	-	195
13	Tb	Faeces	Fluorimetry	pH 11.9, sulphosalycilic acid, λex = 320 & λem=545 nm	-	196

14	Yb	Seawater	GFAAS	Preconcentration on $Fe(OH)_3$	-	197
15	Yb	Seawater	GFAAS	pH 8, Coprecipitatio on $Fe(OH)_3$ followed by extraction into 2,6-dimethyl-4-heptano ne	-	198
16	Y	River sand	XRF & OES	-	0.005-1%	199
17	Y	River sand	XRF & OES	-	0.01-0.02%	200
18	Y	Coal flyash	Photon activation analysis	-	-	201
19	Y	Air	Oscillopolarography	-	-	202
20	Y	Natural waters	ICPAES	-	0.1-3 ppb	203
21	Ce &Yb	Airborne particulates	NAA	-	-	204
22	Ce & Y	Sea & Pore water	ICPAES	Double coprecipitation with $Mg(OH)_2$ & CaC_2O_4	-	205
23	Pr, Nd & Er	Lake waters	NAA	-	<10 ppb	206
24	Eu & Tb	Waters	Luminescence	Polymethyl methacrylate as sorbent	-	207
25	Dy, Ho, Er & Yb	Waterwater	ICPAES	Sorption resin	-	208
26	REE	Natural waters	NAA	Separation hydrated Sb_2O_5 & precipitation using CaF_2 & $CaCl_2$	-	209
27	REE	Sea water	ICPAES	After coprecipitation with $Fe(OH)_3$	0.1-56 ppt	210

TABLE 3 continued

28	REE	Natural waters	IDMS	-	-	211
29	REE	Ground waters	NAA	Coprecipitation on $Fe(OH)_3$ followed by separation on Dowex AG 1-X8 resin	-	212
30	REE	Waters	ICPAES	-	-	213
31	REE	Hot spring & Lake Waters	NAA	$Al(OH)_3$ as collector	ppb level	214
32	RE	Flyash	ICPMS	HPLC separation	-	215
33	REE	Hot spring water	NAA	$Al(OH)_3$ as collector	ppt levels 197	216
34	REE	Natural waters	ICPMS	-	<0.5 pg/ml	217
35	REE	Seawater	ICPMS	-	-	218
36	REE	Volcanic waters	NAA	-	-	219
37	REE	Catalysts & air born particles	NAA	-	-	220
38	REE	Mineral waters	ICPAES	Ion-exchange separation	-	221
39	REE	Seawater	IC-ICPMS	-	1-10 ng/l	222
40	REE	Spring water	NAA	After preconcentration on hydrated MgO	-	223
41	REE	Dutch drinking water	ICPMS	-	-	224
42	REE	Seawater	ICPMS	Preconcentration on chelex-100	-	225
43	REE	Apple leaves, pine needles	ICPMS	Extraction with bis(2-ethyl hexyl)-orthophosphoric acid	-	226
44	REE	Water	ICPMS	-	0.03-0.4 pg/ml	227

45	REE	Seawater	IC	PAR as post column reagent	Upto 16 ppb	228
46	REE	Geothermal waters	FIAICPMS	-	0.05-0.5 ppb	229
47	REE	Seawater	ICPMS	Preconcentration of oxine complexes on Amberlite X AD-7 resin	0.0015-0.016 pg/ml	230

TABLE 4
Determination of Lanthanides in Geological Samples

Sl.No.	Elements	Matrix	Analysis technique	Reaction condition	Sensitivity/ Limit of detection	Reference
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	La	Rocks &minerals	MAS	Bromophosphonazo	$\varepsilon = 1.6\times10^5$ l $mol^{-1}cm^{-1}$	231
2	La	Fluorozirconate glass	ICPAES	-	-	232
3	La	Phosphate rocks	NAA	-	-	233
4	La	Marble crusts	ICPMS	-	10-500 μg/g	234
5	La	Monazite	MAS	Extraction with Dibenzo[24]-crown-8	-	235
6	Ce	Silicate rocks	NAA	-	-	236
7	Ce	Geological reference materials	AAS	-	-	237
8	Ce	High silica glasses	Spectrography	-	0.033-1%	238
9	Ce	Rocks	MS	-	-	239
10	Ce	RE ores	Fluorescence	-	0.1 μM	240
11	Nd	Glasses	HDMAS	PAN	11 ppb	241
12	Nd	Soils	GFAAS	463.4 nm	0.17 ng	242
13	Nd	Glasses	FIA MAS	PAN, Triton X-100 pH 9.2, 560 nm	27 ppb	243
14	Sm	Apatite minerals	ICPAES	Bis-2-ethylhexyl phosphate extraction, 443.43 nm	0.3 ppm	244
15	Eu	Phosphatic minerals	GFAAS	-	27-157 ppm	245

16	Eu	Silicate matrix	GFAAS	-	0.1 ng	246
17	Eu	Quartz glasses	MAS	Xylenol orange, CPB	$\varepsilon = 1.3 \times 10^{5}$ l $mol^{-1}cm^{-1}$	247
18	Gd	Geological samples	ICPMS	-	0-30 µg/25 ml	248
19	Gd	"	NAA	-	upto 50 ppm	249
20	Dy	Rocks	NAA	-	-	250
21	Dy	Xenotime or Monazite	Fluorimetry	Sulphosalicylic acid & EDTA, pH 11.9, λex = 325 & λem = 576 nm	-	251
22	Er	Silicate rocks	NAA	-	1 µg/g	252
23	Tb	Rocks	Luminescence	λem = 545 nm	-	253
24	Yb	Rocks	GFAAS	-	6 pg	254
25	Yb	Geological samples	MAS	2-(5-bromo-2-pyridylazo)-5-diethyl aminophenol, pH10	0.025-1.363 ppm	255
26	Y	Rocks	XRF	-	2 ppm	256
27	Y	Geological samples	ICPAES	371.03 nm	0.42 ppm	257
28	Y	Rocks	Luminescence	Separation on polyurethane foam	0.001% Y	258
29	Y	Geological samples	AES	-	5 µg/g	259
30	Y	Rocks	luminescence	-	0.001%	260
31	Y	Ores	MAS	5-Br-PADAP	-	261
32	Y	Rocks	XRF	-	-	262
33	Y	Soil	XRF	-	-	263
34	Y	Minerals	MAS	p-nitrochlorophosphanazo, lmax = 730 nm	$\varepsilon = 7.4 \times 10^{4}$ l $mol^{-1}cm^{-1}$	264

TABLE 4 continued

35	Y	Silicate rocks	XRF	-	2 ppm	265
36	Y	"	XRF	LiF crystal	-	266
37	Y	"	EDXRF	-	17.2-60.8 ppm	267
38	Y	Soil	XRF	-	-	268
39	Y	Silicates	EDXRF	-	-	269
40	Y	Zircon	ICPAES	371.03 nm	-	270
41	Y	Coals	XRF	-	-	271
42	Y	Lateritic materials	XRF	-	-	272
43	La, Nd, Pr & Y	Phosphate rocks	ICPAES	-		273
44	La &Eu	Monazite	NAA	-	5 & 0.1 ppm	274
45	La, Ce, Nd	Rocks	NAA	-	-	275
46	Ce, Y & Yb	Geological materials	Spectrography	-	-	276
47	Ce, Sm, Eu & La	Monazite	NAA	-	-	277
48	Ce, La & Y	Rocks	EDXRF	-	-	278
49	Ce &La	Laterite material	XRF	-	-	279
50	Ce, Tb, Eu &Yb	Rocks	NAA	-	-	280
51	Ce, La, Pr, Nd, Sm, Eu, Gd & Y	Graphite powder	Spectrography	-	30 pg - 2 ng	281
52	Ce, Nd, La, Y & Tb	Silicate minerals & rocks	XRF	-	-	282
53	Ce, La & Nd	Dolomites & apatites	XRF	-	1-2 µg	283
54	Ce, La & Nd	Lateritic materials	EDXRF & NAA	-	-	284
55	Ce, Pr & Tb	Geological materials	Luminescence	-	0.001, 0.02 & 0.07 ppm	285
56	Ce & Pr	"	"	-	0.015 &0.06 ppm	286
57	Ce & La	Windshield glass	ICPMS	-	-	287

58	Ce, La, Sm,Eu, Tb, Yb & Lu	Geochemical reference samples	NAA	-	-	288
59	Ce & Eu	Hydrothermal calcites	ICPMS	-	-	289
60	Ce, La & Nd	Geological samples	NAA	-	-	290
61	Ce, Yb, Tb & Lu	Geological samples & Ores	FES	520.139, 398.798, 432.647 & 466.17 nm	0.2-100 ppm	291
62	Ce, Pr, La, Sm, Nd, Yb, Tb, Eu & Lu	Uraniferous rocks	NAA	-	-	292
63	Ce, La, Nd &Sm	"	NAA	-	-	293
64	Ce, La, Pr &Nd	Monazite sand	MAS	PAR, $\lambda max = 490$ nm	-	294
65	Ce, La, Pr & Nd	Apatite	XRF	Anion exchange separation	-	295
66	Ce, Y, & Nd	Ores & minerals	NAA	-	0.5-40% of Ce or 4-13% of Nd	296
67	Nd & Sm	Silicate rocks & minerals	ICPMS	-	0.06 &0.02 μg/g	297
68	Nd &Sm	Geological materials	"	-	-	298
69	Eu &Sm	RE minerals	Fluorimetry	-	0.02 & 2 ppb	299
70	Gd &Ho	Geological samples & ores	NAA	-	-	300
71	Gd, Nd, Pr & Sm	"	FES	$N_2O-C_2H_2$	5-1000 ppm	301
72	Gd &Sm	Geological reference materials	NAA	-	-	302
73	Dy, Ho, Eu, Tm & Yb	Silicate rocks & minerals	ETAAS	-	1.0, 1.0, 0.1, 1.0 & 0.1 ppm	303
74	Dy, Sm, Eu & Tb	Geological samples	Fluorimetry	Pyridine-2,6-dicarboxyllic acid	0.5, 3, 0.015 & 0.009 ng	304

TABLE 4 continued

75	Dy, Eu, Gd, Pr, Sm & La	Rocks	NAA	Coprecipitation on CaF_2	-	305
76	Dy, Ho, Er &Tm	Geological samples	FES	-	0.1-100 ppm	306
77	Tb, Dy, Ho, Er & Yb	Ores	ICPAES	-	-	307
78	REE	Xenotime	EDXRF	Preconcentration on PAN modified naphthalene, pH 8-12	-	308
79	REE	Silicate rocks	ICPAES	Precipitation with oxalic acid	-	309
80	REE	Rocks	SSMS	-	-	310
81	REE	Silicate rocks &Coal	AAS	Coprecipitation with Ca as their oxalates	-	311
82	REE	U ores	NAA	-	-	312
83	REE	Rocks & minerals	XRF	-	-	313
84	REE	Rocks	GFAAS	-	1 pg - 1 ng	314
85	REE	"	ICPAES	-	-	315
86	REE	Allanite	DC arc spectrography	-	-	316
87	REE	Glass	LA-ICPMS	-	10-100 μg/g	317
88	REE	Fe-Mn crusts	ICPAES	-	-	318
89	REE	Deep sea sediments	NAA	-	-	319
90	REE	River sediments	NAA	-	-	320
91	REE	Sediments	ICPAES	-	-	321
92	REE	Geological samples	Spectrography	-	0.1-10,000 ppm	322
93	REE	"	ICPAES	-	-	323

94	REE	Rocks	SSMS	-	-	324
95	REE	Rocks & Minerals	NAA	-	-	325
96	REE	Ores	AAS	-	-	326
97	REE	Rocks	NAA	-	0.1-50 ppm	327
98	REE	Geological materials	ICPAES	-	-	328
99	REE	"	NAA	Preconcentration on $Fe(OH)_3$	-	329
100	REE	Bauxites	NAA	-	-	330
101	REE	Rocks & minerals	NAA	-	1 ppb - 2 ppm	331
102	REE	Monazite &Zircon	SSMS	-	-	332
103	REE	Silicates	ICPAES	Ion exchange separation	-	333
104	REE	Minerals	SIMS	-	>5 to 10 ppm	334
105	REE	Geological samples	SSMS	-	-	335
106	REE	"	HPLC-ICPAES	-	1-10 ppm	336
107	REE	Phosphate minerals	ICPAES	-	10-500 ppm	337
108	REE	Terrestrial materials	NAA	-	-	338
109	REE	Silicate rocks	ETAAS	Coprecipitation with CaC_2O_4 & $Fe(OH)_3$	-	339
110	REE	Rocks	NAA	Precipitated as fluorides	-	340
111	REE	Silicate rocks	AAS	Coprecipitation with CaC_2O_4 & $Fe(OH)_3$	-	341
112	REE	Geological materials	NAA	Ion-exchange separation	-	342
113	REE	Ores	Spectrography	Separation & enrichment by column chromatography	-	343

TABLE 4 continued

114	REE	GEological materials	ICPAES	Cation exchange chromatographic separation	-	344
115	REE	"	NAA	-	-	345
116	REE	Bauxite	Spectrography	Extraction with PMBP polyurethane foam	0.5-387 ppm	346
117	REE	Ores	EDXRF	-	~100 ppm	347
118	REE	Geological materials	ICPMS	-	2-10 ng/g	348
119	REE	"	"	-	-	349
120	REE	"	ICPAES	Ion exchange separation	-	350
121	REE	"	NAA	-	-	351
122	REE	Rocks	DCPAES	-	-	352
123	REE	Rocks & minerals	XRF	-	-	353
124	REE	"	HPLC	PAR as post column reagent	-	354
125	REE	Rocks	XRF	Ion-exchange separation	-	355
126	REE	Rocks	NAA	Recovery as hydroxides, ion-exchange separation followed by precipitation as fluorides	-	356
127	REE	Rocks	ICPAES	-	-	357
128	REE	"	NAA	-	-	358
129	REE	Minerals	NAA	-	-	359
130	REE	Rocks	NAA	-	-	360
131	REE	Geological reference samples	ICPAES	Ion-exchange separation	-	361

132	REE	Meteorites	NAA	Precipitated as oxalates	-	362
133	REE	Minerals	ETAAS & ICPAES	-	-	363
134	REE	"	SIMS	-	-	364
135	REE	Geological samples	SSMS	-	<1 ng	365
136	REE	"	ICPAES	Oxalate coprecipitation & cation exchange separation	-	366
137	REE	Silicate reference materials	ICPAES	-	-	367
138	REE	Rocks & soils	XRF	-	0.026-0.17 ppm	368
139	REE	Rocks & minerals	NAA	-	-	369
140	REE	Rocks	Laser plasma MS	-	0.01-0.1 ppm	370
141	REE	Soil	ICPAES	-	-	371
142	REE	Geological samples	EDXRF	-	-	372
143	REE	Monazites	NAA	-	-	373
144	REE	Rocks	ICPAES	Automated dissolution & separation method was used	-	374
145	REE	"	"	Cyclone spray chamber was used	-	375
146	REE	"	NAA	-	-	376
147	REE	USGS samples	ICPAES	-	-	377
148	REE	-Rocks	GFAAS & XRF	-	-	378
149	REE	Minerals	ICPAES	-	-	379
150	REE	Silicate materials	"	-	-	380

TABLE 4 continued

151	REE	Granites	"	Miniature torch was used	-	381
152	REE	Rocks	NAA	-	0.04-2.2 ppm	382
153	REE	GEological materials	ICPMS	-	-	383
154	REE	Rocks	ICPAES	Ion-exchange separation	-	384
155	REE	"	NAA	"	-	385
156	REE	Geological materials	ICPAES	-	0.01-9.5 ppm	386
157	REE	Rocks	ICPMS	-	-	387
158	REE	Geological samples	ICPAES	Separation medium sized ion exchange column	0.1-1.00 ppm	388
159	REE	Soil	DCPAES	Ion-exchange separation	-	389
160	REE	Rocks	HPLC	Arsenazo III as post column reagent	-	390
161	REE	Monazite	EDXRF	-	-	391
162	REE	Geological samples	ICPMS	Preconcentration by ion exchange	-	392
163	REE	Volcanic rocks	NAA	-	-	393
164	REE	Silicate rocks	ICPMS	-	-	394
165	REE	Rocks	NAA	Preconcentration by extraction chromatography	-	395
166	REE	Soils	ICPAES	"	<1 μg/g	396
167	REE	Graphite	ICPAES & DC arc AES	-	0.01-0.2	397
168	REE	Geological materials	ICPAES	CaC_2O_4 precipitation & ion-exchange separation	-	398
169	REE	"	NAA	-	-	399

170	REE	Rocks	TRXRF	-	0.1 μg/g	400
171	REE	Geological samples	IC	PAR as post column reagent	-	401
172	REE	Marine sediments	ICPAES	-	-	402
173	REE	Rocks	ICPMS	Ion exchange separation	0.3-4.0 pg/ml	403
174	REE	Ores	ICPAES	-	1-100 ppm	404
175	RE	Minerals	NAA	Extraction chromatographic separation	-	405
176	REE	Rocks	ICPAES & NAA	Ion-exchange separation	-	406
177	REE	Rocks	ICPAES	-	40-300 μg/g	407
178	REE	Silicate rocks	ICPAES	-	-	408
179	REE	Rocks	NAA	-	-	409
180	REE	Ores	ICPAES	-	-	410
181	REE	Bauxites	ICPMS, ICPAES	-	-	411
182	REE	Sediments	ICPAES	Ion-exchange separation	-	412
183	REE	Rocks	ICPMS	-	-	413
184	REE	"	ICPAES	Solvent extraction separation	-	414
185	REE	Rocks	NAA	TLC separation	-	415
186	REE	Rocks	IDMS	-	-	416
187	REE	Glass	SSMS	-	-	417
188	REE	Minerals	ICPAES	Separation by extraction chromatography	-	418

TABLE 4 continued

189	REE	Geological materials	ICPAES	Ion-exchange separation and CaC_2O_4 precipitation	-	419
190	REE	Rocks & soils	XRF	-	-	420
191	REE	Geological samples	ICPAES	Ion-exchange separation	0.1-0.2 μg/g	421
192	REE	Rocks	IDMS	-	10-100 μg/g	422
193	REE	Glasses	ICPMS	-	-	423
194	REE	Rocks	SIMS & ICPAES	-	-	424
195	REE	Geochemical reference samples	IDMS & ICPAES	Ion-exchange separation	-	425
196	REE	Ores	ICPAES	Cation exchange separation	-	426
197	REE	Silicate reference samples	SIMS	-	-	427
198	REE	Rocks & minerals	HPLC	Arsenazo III as post column reagent	-	428
199	REE	Silicate rocks	ETAAS	-	-	429
200	REE	Soil & Fertilizers	ICPAES	-	-	430
201	REE	U minerals	NAA	Extractive separation with di(2-ethylhexyl) phosphoric acid	-	431
202	REE	Minerals	ICPMS & ICPAES	-	-	432
203	REE	Monazite	NAA	Separation on Biorad AG1-risin	-	433
204	REE	Ores	ICPAES	-	-	434
205	REE	Ores	XRF	-	0.14-0.96 μg	435

206	REE	Quartz concentrates	ICPMS	-	10-500 ppb	436
207	REE	Geological samples	ICPAES	Preconcentration by L.C.	0.01-100 μg	437
208	REE	"	"	Precocentration by countercurrent chromatography	-	438
209	REE	Rocks	"	-	-	439
210	REE	Silicates	Ion microprobe	-	-	440
211	REE	Rocks	ICPMS	-	4-57 ppb	441
212	REE	"	XRF	-	0.052-0.21 μg/g	442
213	REE	Bauxite	NAA	-	-	443
214	REE	"	XRF & ICPAES	-	0.024-5.4 μg/g	444
215	REE	Marine Fe-Mn crust	ICPMS	-	-	445
216	REE	Geological samples	ICPAES	Preconcentration by countercurrent chromatography	-	446
217	REE	Geological samples	XRF	-	-	447
218	REE	"	NAA	-	-	448
219	REE	Polymetallic modules	ICPAES & ICPMS	-	-	449
220	REE	Rocks	ICPMS	-	2-11 ng/L	450
221	REE	Granites	ICPAES	TLC preconcentration	0.25-5 ppm	451
222	REE	Monazite	NAA	Fluoride/hydroxide precipitation	-	452
223	REE	Bauxite	SEM & EPMA	-	-	453
224	REE	Minerals	ICPMS	Extractive separation	-	454

TABLE 4 continued

225	REE	Flyash or apatite reference material	NAA	Ion-exchange preconcentration	0.01-3.2 µg/g	455
226	REE	Geological samples	FIAICPAES	-	1-10 ppm	456
227	REE	Ores	ICPAES	-	-	457
228	REE	Ores	Isotachophoresis-PIXE		1 ng	458
229	REE	Rocks	ICPMS	-	-	459
230	REE	Silicates	ICPMS	Ion exchange separation	-	460
231	REE	Bauxite	ICPAES	-	-	461
232	REE	Meteorites	ICPMS & NAA	-	0.028-5.9 ng/g & 0.22-0.36 ng/g	462
233	REE	Geological samples	ICPAES	-	0.01-1 µg/g	463
234	REE	Minerals	PIXE & EPMA	-	-	464
235	REE	Monazite	NAA	-	-	465
236	REE	Rocks	ICPMS	-	-	466
237	REE	Silicate materials	ICPAES	Cation exchange isolation	0.01-100 ppb	467
238	RE	Soil	ICPMS	-	0.006-0.024 ppb	468
239	REE	Soil	ICPMS	-	-	469
240	REE	Ores	ICPAES	-	-	470
241	REE	Zircon	ICPMS	Laser ablation sampling	-	471
242	REE	U rich geological materials	ICPAES	Coprecipitation with $Fe(OH)_3$	-	472

TABLE 5
Determination of Lanthanides in Miscellaneous Materials

Sl.No.	Elements	Matrix	Analysis	Reaction conditions	Sensitivity/ Limit of detection	References
(1)	(2)	(3)	(4)	(5)	(6)	(7)
1	Gd & Sm	Aerospace & Nuclear materials	ICPMS	-	0.17 & 0.03 μg/g	473
2	Dy, Eu, Gd & Sm	Nuclear grade Uranium oxide	ICPAES	353.17, 420.5, 364.6 & 442.4 nm	0.1-100 ppm, 3, 2, 6 & 10 ppb	474
3	Dy, Eu & Gd	Nuclear fuels	ICPAES	-	-	475
4	Dy, Gd, Sm &Eu	UF_6 & U_3O_8	ICPAES	Cation exchange separation	0.4-100 ppb	476
5	REE	Nuclear Fuels	HPLC-ICPMS	-	-	477
6	Ce & La	Coal	ICPAES	Preconcentration on poly(dithiocarbamate) resin	-	478
7	Ce, Pr & Nd	Coal & Flyash	NAA	-	-	479
8	Ce	Oils	XRF	-	-	480
9	Metallorganic species	Oils	ICPMS	-	200 pg	481
10	Eu	Archaeological materials	PIXE	-	-	482
11	REE	Brines	ICPMS	-	0.06-0.6 ng/l	483
12	Eu	Blast furnace slag	GFAAS	-	14 pg	484

of RE in bauxite,[346] allanite,[316] graphite powder,[281] quartz and high silica glasses,[238] ores,[343] and geological samples[322] were determined by spectrography.

F. EDXRF

EDXRF is a multielement technique capable of determining individual lanthanides but is not that popular due to its low sensitivity. Two procedures are described for the determination of Sm in Sm-Co alloy[122] and RE metals in cast iron.[79] EDXRF is used for the determination of terbium and dysprosium in Tb-Dy-Fe films[133] and Yttrium in $YBa_2Cu_3O_x$ superconductors.[138,144,149,150,151] The applications of EDXRF to geological samples are few, and these include determination of REE in rocks,[267,269,278] lateritic materials,[284] xenotime,[308] and monazite[391] and in britholite ores.[347]

G. WDXRF

WDXRF allows the determination of individual REE with reasonable sensitivity and still not that popular like NAA, ICP-AES, and ICP-MS techniques for real sample analysis, presumably due to the cumbersome sample preparation. Few WDXRF procedures reported in the literature for metallurgical samples include application to alloys,[40,68,84] steels,[57,92] cast iron,[76] superconductors,[141,143,162,167] ceramics,[101,157] magnetic materials,[123,160] YAG,[114,119] electronic materials,[105,132,179] and river sand samples.[199,200] Traces of REE are determined in geological samples,[372,447] rocks,[256,262,265,266,313,353,355,368,420,442] soils,[263,268,480] coals,[271] lateritic materials,[272,279] minerals,[282,283,295] and ores[435,444] by using WDXRF.

H. NAA

NAA is a multielement analysis technique and has been used extensively for the analysis of geological samples. However, this technique has also been used for the determination of Ce in Al alloys[29,45] and REE in cerium-based magnetic alloys[62] and steels.[82,93,97] It also finds use in determination of Y in $YBa_2Cu_3O_x$ superconductors,[145,148] neodymium in YAG crystals,[110] lanthanum in semiconductors,[100] and REE in high-purity uranium.[175] In environmental analysis REE was determined by NAA in waters,[206,209,212,214,216,219,223] sea water,[184,193,205] airborne particulates,[204,220] and coal dust particulates.[185] NAA finds widespread application in the determination of individual REE in geological reference samples,[249,288,290,300,329,342,345,351,399] rocks,[233,236,250,252,275,280,292,293,305,312,325,327,331,340,356,358,360,369,376,385,393,395,40415,424,448] minerals,[274,330,359,373,382,405,431,433,443,455,465] ores,[277,296] sediments,[319,320,338,452] meteorites,[362] and in coal and fly ash.[479]

I. ICPAES

ICPAES is the most popular and widely used multielement technique, either with or without preconcentration, for the determination of individual REE in metallurgical, environmental, and geological samples. ICPAES procedures were described for the determination of a few REE in Al alloys,[65,71,89,98] cobalt based alloys,[66,90] nickel based alloys,[49,80] Cu alloys,[96] titanium alloys,[56] Mg alloys,[63] steels,[69,72,74,77,81,86,88,94,95] and permanent magnet alloys.[44,64,67,70] Lanthanides present in electronic materials,[102,109,111,112,135,161,165,173,182] superconductors,[137,140,153,164] high purity rare earth oxides,[158,174,178,180] high purity uranium,[168,171] high purity zinc,[181] and high purity titanium[176] were determined by ICPAES. Sensitive ICPAES methods in combination with preconcentration procedures were described for the trace determination of individual lanthanides in natural waters,[187,195,203,221,227] wastewater,[208] seawater,[210] and chemical plant reprocessing solutions.[190] Individual REE either with or without a preconcentration procedures coupled to ICPAES was used for their determination in geological samples,[257,323,328,336,344,350,361,366,377,386,388,398,401,419,421,425,437,438,446,449,456,463,467,472] rocks,[273,309,315,357,374,375,384,406,407,408,414,439] silicate materials,[333,367,380] minerals,[244,270,337,379,381,397,418,451,461] ores,[307,410,426,434,457,469] sediments,[321,412] and soil samples.[371,396,430] Further, ICPAES was employed for the determination of individual REE in nuclear fuels[474,475,476] and coal and other energy-related materials.[478]

J. ICPMS

ICPMS is a multielement technique and is widely used for the determination of individual REE in environmental and geological samples. ICPMS procedures were described for the determination of 14 individual REE in natural waters,[217,224,229] seawater,[218,222,225,230] environmental samples,[226] and fly ash.[215] Individual REE present in geological materials,[248,335,348,349,383,392,460] rocks,[297,298,387,394,403,413,441,450,459,466] minerals,[289 411,432,445,454,471] soils,[468,470] and glass materials[287,317,423,436] were determined by ICPMS. ICPMS also finds use in determining individual REE present in nuclear materials,[473,477] lubricating oil,[481] brines,[483] meteorites,[462] and Greek and Roman marble statues.[234]

K. Miscellaneous Techniques

HPLC procedures with post column detection by arsenazo III were described for the determination in rocks[390,422] and minerals.[354,428] IC procedures were described for the determination of lanthanides in Mg alloys,[99] superconductors,[104] seawater,[228] and geological samples.[401] FES procedures were developed for the determination of lanthanum in RE concentrates[103] and geological samples and ores.[291,301,306] Neodymium in Nd-Fe-B alloys,[39] La and Y in geological samples,[259] and REE in rocks,[352] soils,[389] and ores[404] were determined by DCPAES. SSMS procedures were described for the determination of REE in rocks,[310,324] minerals,[332,365] and glass matrix.[417] SIMS is used for the analysis of La in Fe-Cr-Al alloys[23] and REE in minerals.[334,364,427] Further, IDMS technique is used for the determination of individual REE in natural waters[211] and USGS rock standards.[416] Among the electroanalytical techniques, the following methds were described in the literature. These include:

1. Polarography to determine Eu in Eu-Co-B alloys[43] and Y in $YBa_2Cu_3O_x$.[147]

2. Square wave polarography to determine Eu and Yb in RE materials

3. Amperometric titrimetry to determine yttrium and lanthanum in Y-Ba-Cu-O,[163]

4. Ac oscillopolarographic titration to determine La in $LaNi_4Cu$ alloy,[20,21] $LaNi_{4.5}Sn_{0.5}$ alloy,[22] and yttrium in air.[202] The PIXE technique allows the determination of yttrium in $YBa_2Cu_3O_x$[139] and REE in ores[458] and minerals.[464] TRXRF and SEM and EPMA techniques find applications in determination of individual REE in rocks[400] and Greek bauxites.[453] Atomic fluorescence analysis procedure was described for the determination of Y in $YBa_2Cu_3O_x$ superconductors. Quantitative Auger-electron spectroscopy and photonactivation analysis were used to analyze Co-Sm alloy[120] and coal fly ash[201] for REE.

III. CONCLUSIONS

The determination of individual rare earths is a challenging task for analytical chemists in view of the similar properties of rare earths arising from the lanthanide contraction. MAS and spectrofluorimetric procedures essentially relates to the determination of one particular lanthanide in presence of non-rare earth elements present in alloys and electronic materials. Very few applications are noticed for the determination of REE in environmental and geological samples. Flame AAS is not that sensitive for REE and is essentially employed for the determination of REE in metallurgical samples and electronic materials.

Spectrography and GFAAS techniques were widely used in 1970s and early 1980s for determination of REE in various real samples. The former technique requires elaborate and cumbersome sample preparation, and the latter technique is handicapped by the interference due to matrix. Hence, these techniques are not found to be that popular in 1990s. On the other hand, multielement techniques like NAA, XRF, ICPAES, and ICP-MS were widely used and are being used either directly or with a suitable preconcentration procedure. The future lies in the development of coupled chromatography-atomic spectrometric techniques for the determination of ultratrace amounts of lanthanides and their application to metallurgical, environmental, and geological samples.

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