

Contents

List of contributing Authors — XVII

Alfred Golloch

- 1 Introduction — 1**
- References — 3

Alfred Golloch

- 2 Analytics of rare earth elements – basics and methods — 5**
- 2.1 Electronic configurations of RE elements and analytical properties — 5
- 2.2 The development of rare earth analytics from 1940 to present — 7
 - 2.2.1 Determination methods applied during the period from 1940–1960 — 8
 - 2.2.2 Separation methods applied during the period 1940–1960 — 9
 - 2.2.3 Rare earths analysis during the period 1960–1980 — 10
 - 2.2.4 Literature review 1978 — 13
 - 2.2.5 Situation of rare earth analytics 1980-present — 13
- References — 14

Part I: Sample preparation

Beibei Chen, Man He, Huashan Zhang, Zucheng Jiang, Bin Hu

- 3 Chromatographic techniques for rare earth elements analysis — 19**
- 3.1 Introduction — 19
- 3.2 Liquid chromatography — 20
 - 3.2.1 Ion exchange chromatography — 20
 - 3.2.1.1 Ion exchanger — 20
 - 3.2.1.2 Basic properties of ion exchange resins — 24
 - 3.2.1.3 Mobile phase — 25
 - 3.2.1.4 Application of IEC in separation of REEs — 29
 - 3.2.2 Ion chromatography — 31
 - 3.2.2.1 Principle of the method — 32
 - 3.2.2.2 Double-column IC — 33
 - 3.2.2.3 Single-column IC — 33
 - 3.2.2.4 Application of IC in separation of REEs — 34
 - 3.2.3 Reversed phase ion pair chromatography (RPIPC) — 37
 - 3.2.3.1 Ion pair reagent — 38
 - 3.2.3.2 Application of RPIPC in the separation of REEs — 39
 - 3.2.4 Extraction chromatography — 42

3.2.4.1	Support material and stationary phase —	43
3.2.4.2	Application of extraction chromatography on the separation of REEs —	43
3.2.4.3	Centrifugal partition chromatography —	44
3.2.5	Thin-layer chromatography (TLC) and paper chromatography (PC) —	48
3.2.5.1	Paper chromatography —	49
3.2.5.2	Thin-layer chromatography —	50
3.3	Gas chromatography —	53
3.4	Capillary electrophoresis —	54
3.4.1	Basic knowledge and principle —	54
3.4.1.1	Zeta potential —	54
3.4.1.2	Electrophoresis —	55
3.4.1.3	Electroosmotic flow —	55
3.4.1.4	Separation efficiency and resolution —	56
3.4.2	Influencing factors on CE separation —	57
3.4.2.1	Voltage —	57
3.4.2.2	Buffer composition —	57
3.4.2.3	Buffer pH —	57
3.4.2.4	Adducts —	57
3.4.2.5	Temperature —	58
3.4.3	Applications in REEs analysis —	58
3.5	Supercritical fluid chromatography —	59
	References —	63

Bin Hu, Man He, Beibei Chen, Zucheng Jiang

4 Separation/Preconcentration techniques for rare earth elements analysis — 75

4.1	Introduction —	75
4.2	Precipitation/coprecipitation —	76
4.2.1	Oxalate precipitation —	76
4.2.2	Co-precipitation —	76
4.3	Liquid liquid extraction (LLE) —	78
4.3.1	Extractants for REEs —	78
4.3.1.1	Neutral phosphorus —	79
4.3.1.2	Acidic phosphorus —	80
4.3.1.3	Oxygen-containing organic extractants —	81
4.3.1.4	Nitrogen-containing compounds —	81
4.3.1.5	Chelate extractant for REEs —	84
4.3.1.6	Supramolecular extractants and others —	86
4.3.2	Extractant concentration and extraction equilibrium constant —	87
4.3.3	Medium pH —	88

4.3.4	Salting-out agent —	89
4.3.5	Extraction systems for REEs and their application —	90
4.3.5.1	Neutral complex extraction system —	90
4.3.5.2	Acidic complex extraction system —	91
4.3.5.3	Ion association complex extraction system —	93
4.3.5.4	Synergistic extraction system —	94
4.4	Liquid phase microextraction —	94
4.4.1	Single drop microextraction —	96
4.4.2	Hollow fiber liquid phase microextraction —	98
4.4.2.1	Two phase HF-LPME —	100
4.4.2.2	Three phase HF-LPME —	101
4.4.3	Dispersive liquid liquid microextraction —	102
4.4.4	Solidified floating organic drop microextraction —	104
4.4.5	Affecting factors —	106
4.5	Cloud point extraction (CPE) —	109
4.5.1	Application of CPE for trace REEs analysis —	110
4.5.2	Affecting factors —	110
4.5.2.1	Surfactants —	110
4.5.2.2	Sample pH and chelating agent —	110
4.5.2.3	Extraction temperature and time & centrifugation time —	112
4.5.2.4	Ionic strength —	113
4.6	Solid phase extraction and solid phase microextraction —	113
4.6.1	Carbon nanotubes and graphene oxide —	114
4.6.2	Silica-based materials —	119
4.6.3	Chelating resin and ionic-exchange resin —	120
4.6.4	Metal oxide nanostructured materials —	121
4.6.5	Ion-imprinted materials —	123
4.6.6	Metal-organic frameworks —	123
4.6.7	Restricted access materials —	124
4.6.8	Capillary microextraction —	125
	References —	128

Part II: Methods for the elemental analysis of rare earths and for the analysis of rare earth containing molecular compounds

Ahmed H. El-Khatib, Lena Telgmann, Uwe Lindner, Jana Lingott,
Norbert Jakubowski

5	Analysis and speciation of lanthanoids by ICP-MS — 141
5.1	Introduction — 142
5.2	Fundamentals of ICP-MS — 142
5.2.1	Sample preparation — 143
5.2.2	Sample introduction — 144
5.2.3	The ion source — 145
5.2.4	Interface — 146
5.2.5	Lens system — 147
5.2.6	Mass analyzers — 147
5.2.6.1	Quadrupole analyzer — 147
5.2.6.2	ICP-QMS combined with collision and reaction cells — 148
5.2.6.3	ICP-sector field mass analyzer — 149
5.2.6.4	Time-of-flight mass analyzer — 150
5.2.7	Detector and computer — 152
5.3	Analytical figures of merit — 153
5.4	Speciation of Gd-based contrast agents — 153
5.5	Analysis of Gd-based contrast agents in medical samples — 158
5.6	Imaging of Gd-based contrast agents in tissues — 160
5.6.1	Brain — 161
5.6.2	Other tissues — 162
5.7	Analysis of Gd-based contrast agents in environmental samples — 164
5.8	Summary and outlook — 166
	References — 166

Man He, Bin Hu, Beibei Chen, Zucheng Jiang

6	Inductively coupled plasma optical emission spectrometry for rare earth elements analysis — 171
6.1	Introduction — 171
6.1.1	Spectral interference — 176
6.1.2	Matrix effect — 180
6.1.3	Acid effect — 184
6.1.4	Sensitivity-enhancing effect of organic solvent — 185
6.1.4.1	Affecting factors — 185

6.1.4.2	Enhanced sensitivity caused by organic solvents in REEs analysis — 186
6.2	Sample introduction for ICP — 192
6.2.1	Pneumatic nebulization and ultrasonic nebulization — 192
6.2.2	Flow injection — 194
6.2.2.1	FIA coupled with ICP-OES for direct determination of trace REEs — 194
6.2.2.2	Standard addition method in FIA — 195
6.2.2.3	On-line separation/preconcentration-ICP-OES for trace REEs analysis — 197
6.2.3	Laser ablation — 199
6.2.4	Electrothermal vaporization — 200
6.2.4.1	Analytical performance — 201
6.2.4.2	ETV devices and operation parameters — 201
6.2.4.3	Limit of conventional ETV system — 203
6.3	ETV-ICP-OES for REE analysis — 204
6.3.1	Fluorination-assisted ETV-ICP-OES for REEs analysis — 205
6.3.1.1	Vaporization mechanism of REEs fluorination — 205
6.3.1.2	Affecting factors for fluorination vaporization — 208
6.3.1.3	Analytical performance — 212
6.3.2	Low temperature ETV-ICP-OES for REEs analysis — 212
6.4	Application of ICP-OES in the quantification of REEs in real samples — 214
6.4.1	High purity REE analysis by ICP-OES — 214
6.4.1.1	Detection limit of REEs in REE matrix — 214
6.4.1.2	Analytical line and internal line — 216
6.4.1.3	Matrix concentration and solid detection limit — 217
6.4.2	REE ores analysis by ICP-OES — 218
6.4.3	Trace REE analysis by ICP-OES in alloys and other samples — 219
	References — 221

Jörg Niederstraßer

7	Application of spark atomic emission spectrometry for the determination of rare earth elements in metals and alloys — 227
7.1	Introduction — 227
7.2	Spark emission spectrometry basics — 228
7.3	Setup of a spark emission spectrometer — 230
7.4	The analysis process — 235
7.5	Quantitative analysis — 236
7.5.1	Calibration and recalibration — 236
7.5.2	Evaluation of calibration and analysis results — 238

7.6	Using spark emission spectrometry —	239
7.7	Analysing rare earths using spark emission spectrometry —	241
7.7.1	Industrial use of rare earths —	241
7.7.2	Spectrometric prerequisites —	243
7.7.3	Calibration samples —	243
7.8	Analysis of aluminium alloys —	246
7.8.1	Calibration (analysis function) and accuracy —	246
7.8.2	Detection limits —	248
7.8.3	Repeatability —	248
7.9	Analysis of magnesium alloys —	249
7.9.1	Calibration (analysis function) and accuracy —	249
7.9.2	Detection limits —	251
7.9.3	Repeatability —	251
7.10	Analysis of iron alloys —	253
7.10.1	Calibration (analysis function) and accuracy —	253
7.10.2	Detection limits —	254
7.10.3	Repeatability —	255
7.10.4	Long-term stability —	255
7.11	Analysis of zinc alloys —	257
7.11.1	Calibration (analysis function) and accuracy —	257
7.11.2	Detection limits —	258
7.11.3	Repeatability —	258
7.12	Conclusion —	260
	Bibliography —	260

Elisabeth Kreidt

8	Photophysical properties and characterisation of lanthanoids —	263
8.1	Introduction —	263
8.2	Photophysical properties of lanthanoids —	264
8.2.1	Electronic structure, energy levels and transitions —	264
8.2.2	Antenna effect —	266
8.2.3	Quenching and strategies for the improvement of lanthanoid luminophores —	267
8.2.4	Definition of parameters —	268
8.2.5	Information available from luminescence data and the special case Eu^{3+} —	269
8.3	Photophysical characterisation —	271
8.3.1	Set up of a spectrometer —	271
8.3.2	Cuvettes and sample preparation —	272
8.3.3	Characterisation of the antenna —	273
8.3.4	Steady state emission spectra —	274
8.3.5	Determination of luminescence lifetimes —	275

- 8.3.5.1 Observable luminescence lifetime τ_{obs} — 275
- 8.3.5.2 Radiative lifetime τ_{rad} — 277
- 8.3.6 Absolute quantum yields ϕ_{Ln}^L — 278
- 8.3.6.1 Relative methods — 278
- 8.3.6.2 Absolute method — 280
- 8.4 Less commonly studied phenomena — 280
- 8.4.1 Circularly polarised luminescence (CPL) — 280
- 8.4.2 Energy transfer processes between lanthanoids and upconversion — 281
- 8.5 Summary and outlook — 284
- References — 284

Rainer Schramm

9 Use of X-ray fluorescence analysis for the determination of rare earth elements — 289

- 9.1 Introduction — 289
- 9.2 Principle of X-ray fluorescence analysis — 290
- 9.3 XRF methods — 292
- 9.3.1 Energy dispersive X-ray fluorescence analysis (EDXRF) — 292
- 9.3.2 Wavelength dispersive X-ray analysis (WDXRF) — 293
- 9.3.3 Comparison of EDXRF – WDXRF — 294
- 9.3.4 Other XRF techniques — 294
- 9.3.4.1 Handheld XRF instruments — 294
- 9.3.4.2 Total reflection XRF — 294
- 9.4 Sample preparation — 295
- 9.4.1 Pressed pellets techniques — 295
- 9.4.2 Fusion technology — 298
- 9.4.3 Additional sample preparation techniques — 299
- 9.5 Practical application of REEs determination — 300
- 9.6 Calibration — 307
- 9.7 Summary — 310
- References — 311

Heinz-Günter Stosch

10 Neutron activation analysis of the rare earth elements — 313

- 10.1 Introduction — 313
- 10.2 Principles of neutron activation: Activation equation, cross sections — 314
- 10.3 Equipment — 318
- 10.3.1 Neutron sources — 318
- 10.3.1.1 The fission reactor — 318
- 10.3.1.2 Accelerators, neutron generators, isotopic neutron sources — 319

10.3.2	The counting system —	320
10.3.2.1	Detectors —	320
10.3.2.2	Interaction of electromagnetic radiation with matter —	323
10.4	Practical considerations —	324
10.4.1	Instrumental versus radiochemical NAA —	324
10.4.2	Samples and standards —	330
10.4.3	Counting strategies —	332
10.4.4	RNAA – a fast separation scheme —	336
10.4.5	Data reduction and sources of error —	338
10.5	Conclusion —	342
	References —	342

Sven Sindern, Meyer F. M., Gronen L. H.

11	Automated quantitative rare earth elements mineralogy by scanning electron microscopy —	347
11.1	Introduction —	348
11.2	Quantitative and automated mineralogy —	349
11.3	Scanning electron microscopy —	351
11.4	SEM-based automated quantitative mineralogy —	352
11.4.1	General characteristics, functions —	352
11.4.2	Analytical systems —	357
11.4.2.1	Semi automated image analysis of SEM data —	357
11.4.2.2	First generations of automated mineralogy systems —	358
11.4.2.3	Current automated mineralogy systems —	358
11.5	Quantitative REE mineralogy —	360
11.6	Concluding remarks —	365
	References —	366

Part III: Application of rare earth elements analysis

Sven Sindern, Tobias Fusswinkel

12	Analysis of rare earth elements in rock and mineral samples by ICP-MS and LA-ICP-MS —	373
12.1	Introduction —	374
12.2	Technical development —	377
12.3	Physical and chemical effects on concentration and isotope ratio determination —	380
12.4	Determination of REE concentrations —	382
12.4.1	Sample preparation —	382
12.4.2	Quantification —	383

- 12.5 Determination of isotope ratios by multi collector (MC) -ICP-MS — **386**
- 12.5.1 Solution MC-ICP-MS — **386**
- 12.5.2 LA-MC-ICP-MS — **388**
- 12.6 Concluding remarks — **389**
- References — **390**

Sarah Theiner, Mario Corte Rodriguez, Heike Traub

13 Novel applications of lanthanoids as analytical or diagnostic tools in the life sciences by ICP-MS based techniques — 399

- 13.1 Introduction — **400**
- 13.2 Bio-conjugation of biomolecules — **401**
- 13.2.1 Bioconjugation by lanthanoid-containing tags — **402**
- 13.3 Principles of mass cytometry and imaging mass cytometry — **407**
- 13.3.1 Single cell ICP-MS/mass cytometry — **407**
- 13.3.2 Imaging mass cytometry (LA-ICPMS) — **411**
- 13.4 Applications — **413**
- 13.4.1 Identification and quantification strategies for proteins, peptides, RNA and DNA using ICP-MS based detection — **413**
- 13.4.2 Application of lanthanoids in single cell ICP-MS / mass cytometry — **419**
- 13.4.3 Protein determination after separation by gel electrophoresis and by immuno-microarrays — **421**
- 13.4.4 Application of lanthanoids in LA-ICPMS/imaging mass cytometry — **424**
- 13.5 Lanthanoid-containing nanoparticles for medical applications — **431**
- 13.6 Summary and outlook — **433**
- References — **433**

Jürgen Meinhardt, Martin Kilo, Ferdinand Somorowsky, Werner Hopp, Markus Firsching

14 Lanthanoides in glass and glass ceramics — 445

- 14.1 Introduction — **445**
- 14.2 Literature survey of rare earth chemical analysis in glass — **447**
- 14.3 Analytical methods for the determination of main components of glass (except lanthanoides) — **447**
- 14.4 Preparation of sample solutions for glass analysis by ICP-OES — **448**
- 14.4.1 Hydrofluoric acid digestion — **448**
- 14.4.1.1 Hydrofluoric acid – sulfuric acid digestion (procedure B) — **448**
- 14.4.1.2 Hydrofluoric acid – perchloric acid digestion (procedure C)] — **449**

- 14.4.1.3 Modified hydrofluoric acid – perchloric acid digestion — **449**
- 14.4.2 Melt digestion — **449**
- 14.4.2.1 Sodium carbonate melt digestion (procedure A) — **449**
- 14.4.2.2 Sodium carbonate / potassium carbonate melt digestion (procedure 10.4) — **449**
- 14.5 ICP-OES analysis of rare earth elements — **450**
- 14.6 Analysis of special optical glass — **450**
- 14.7 Analysis of glass by topochemical analysis — **451**
- 14.8 Analysis of glass by multi-energy x-ray imaging as a quantitative method for materials characterization — **456**
References — **457**

Sandra Pavón, Martin Bertau

- 15 Recycling of rare earth elements — 461**
- 15.1 Recycling of rare earth elements — **461**
- 15.2 Recycling from fluorescent lamp scraps — **463**
- 15.2.1 Starting material — **463**
- 15.2.2 Acid treatment — **467**
- 15.2.3 Liquid membranes — **468**
- 15.2.4 Solid state chlorination — **470**
- 15.2.4.1 Starting material — **471**
- 15.2.4.2 Optimization — **473**
- 15.2.5 Leaching optimisation — **479**
- 15.2.6 Recycling process — **479**
- 15.2.7 Summary — **481**
- 15.3 RE metal recycling from SmCo magnets — **482**
- 15.3.1 Starting material — **482**
- 15.3.2 Solid-state chlorination optimization — **483**
- 15.3.2.1 Attempts of orientation — **483**
- 15.3.2.2 Simultaneous optimization — **483**
- 15.3.3 Recycling process — **490**
- 15.3.4 Summary — **492**
References — **492**

Index — 497