

Jukka Lehto and Xiaolin Hou

 WILEY-VCH

Chemistry and Analysis of Radionuclides

Laboratory Techniques and Methodology



Jukka Lehto and Xiaolin Hou

**Chemistry and Analysis of
Radionuclides**

Related Titles

Lambert, J. D. B. (ed.)

Nuclear Materials

2011

ISBN: 978-3-527-32352-4

Atwood, D. (ed.)

Radionuclides in the Environment

2010

ISBN: 978-0-470-71434-8

Prussin, S. G.

Nuclear Physics for Applications

2007

ISBN: 978-3-527-40700-2

Lieser, K. H.

Nuclear and Radiochemistry

Fundamentals and Applications

2001

ISBN: 978-3-527-30317-5

Jukka Lehto and Xiaolin Hou

Chemistry and Analysis of Radionuclides

Laboratory Techniques and Methodology



WILEY-VCH Verlag GmbH & Co. KGaA

The Authors

Prof. Jukka Lehto

University of Helsinki
Laboratory of Radiochemistry
A.I. Virtasen aukio 1
00014 Helsinki
Finland

Dr. Xiaolin Hou

Technical University of Denmark
Risø National Laboratory for Sustainable Energy
Radiation Research Division
Fredriksborgvej 399
4000 Roskilde
Danmark

All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

© 2011 WILEY-VCH Verlag & Co. KGaA,
Boschstr. 12, 69469 Weinheim, Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Composition Thomson Digital, Noida
Printing and Binding Strauss GmbH, Mörlenbach
Cover Design Adam Design, Weinheim

Printed in the Federal Republic of Germany
Printed on acid-free paper

ISBN: 978-3-527-32658-7

Contents

Preface *XVII*

Acknowledgments *XIX*

1	Radionuclides and their Radiometric Measurement	1
1.1	Radionuclides	1
1.1.1	Natural Radionuclides	1
1.1.2	Artificial Radionuclides	4
1.2	Modes of Radioactive Decay	6
1.2.1	Fission	6
1.2.2	Alpha Decay	8
1.2.3	Beta Decay	10
1.2.4	Internal Transition	12
1.3	Detection and Measurement of Radiation	14
1.3.1	Gas Ionization Detectors	14
1.3.2	Liquid Scintillation Counting	16
1.3.3	Solid Scintillation Detectors	20
1.3.4	Semiconductor Detectors	20
1.3.5	Summary of Radiometric Methods	22
2	Special Features of the Chemistry of Radionuclides and their Separation	25
2.1	Small Quantities	25
2.2	Adsorption	26
2.3	Use of Carriers	28
2.4	Utilization of Radiation in the Determination of Radionuclides	31
2.5	Consideration of Elapsed Time	31
2.6	Changes in the System Caused by Radiation and Decay	31
2.7	The Need for Radiochemical Separations	32

3	Factors Affecting Chemical Forms of Radionuclides in Aqueous Solutions	35
3.1	Solution pH	35
3.2	Redox Potential	38
3.3	Dissolved Gases	42
3.3.1	Oxygen	42
3.3.2	Carbon Dioxide	43
3.4	Ligands Forming Complexes with Metals	46
3.5	Humic Substances	48
3.6	Colloidal Particles	51
3.7	Source and Generation of Radionuclides	52
3.8	Appendix: Reagents Used to Adjust Oxidation States of Radionuclides	54
3.8.1	Oxidants	54
3.8.2	Reductants	55
4	Separation Methods	57
4.1	Precipitation	57
4.2	Solubility Product	58
4.2.1	Coprecipitation	59
4.2.2	Objectives of Precipitation	60
4.2.2.1	Precipitations Specific for the Investigated Radionuclide	60
4.2.2.2	Group Precipitations for the Preconcentration of the Target Radionuclide	61
4.2.2.3	Group Precipitations for the Removal of Interfering Radionuclides and Stable Elements	61
4.3	Ion Exchange	64
4.3.1	Ion Exchange Resins	64
4.3.2	Distribution Coefficient and Selectivity	65
4.3.3	Cation Exchange or Anion Exchange?	66
4.3.4	Ion Exchange Chromatography	67
4.3.5	Ion Exchange in Actinide Separations	68
4.4	Solvent Extraction	70
4.4.1	Extractable Complexes	71
4.4.2	Distribution Constant and Distribution Ratio	72
4.4.3	Examples of the Use of Solvent Extraction in Radiochemical Separations	73
4.5	Extraction Chromatography	74
4.5.1	Principles of Extraction Chromatography	74
4.5.2	Extraction Chromatography Resins	74
4.5.3	Pb and Sr Resins	75
4.5.4	Use of Extraction Chromatography in Actinide Separations	76

5	Yield Determinations and Counting Source Preparation	81
5.1	The Determination of Chemical Yield in Radiochemical Analyses	81
5.1.1	Use of Stable Isotopic Carriers in Yield Determinations	81
5.1.2	Use of Radioactive Tracers in Yield Determinations	82
5.2	Preparation of Sources for Activity Counting	85
5.2.1	Preparation of Source for Gamma Emitters	85
5.2.2	Sample Preparation for LSC	86
5.2.3	Source Preparation for Alpha Spectrometry with Semiconductor Detectors and for Beta Counting with Proportional Counters	87
5.2.3.1	Electrodeposition	88
5.2.3.2	Micro-coprecipitation	88
5.2.3.3	Spontaneous Deposition	89
5.3	Essentials in Chemical Yield Determination and in Counting Source Preparation	89
5.3.1	Yield Determination	89
5.3.2	Counting Source Preparation	90
6	Radiochemistry of the Alkali Metals	91
6.1	Most Important Radionuclides of the Alkali Metals	91
6.2	Chemical Properties of the Alkali Metals	91
6.3	Separation Needs of Alkali Metal Radionuclides	92
6.4	Potassium – ^{40}K	93
6.5	Cesium – ^{134}Cs , ^{135}Cs , and ^{137}Cs	94
6.5.1	Sources and Nuclear Characteristics	94
6.5.2	Preconcentration of Cesium Nuclides from Natural Waters	95
6.5.3	Determination of ^{135}Cs	96
6.5.3.1	Determination of ^{135}Cs by Neutron Activation Analysis	96
6.5.3.2	Determination of ^{135}Cs by Mass Spectrometry	97
6.6	Essentials in the Radiochemistry of the Alkali Metals	98
7	Radiochemistry of the Alkaline Earth Metals	99
7.1	Most Important Radionuclides of the Alkaline Earth Metals	99
7.2	Chemical Properties of the Alkaline Earth Metals	99
7.3	Beryllium – ^7Be and ^{10}Be	102
7.4	Calcium – ^{41}Ca and ^{45}Ca	102
7.4.1	Nuclear Characteristics and Measurement	102
7.4.2	Determination of ^{45}Ca and ^{41}Ca in Concrete	103
7.5	Strontium – ^{89}Sr and ^{90}Sr	106
7.5.1	Nuclear Characteristics and Sources	106
7.5.2	Measurement of Strontium Isotopes	107
7.5.2.1	Measurement of ^{90}Sr Activity	107
7.5.2.2	Simultaneous Determination of ^{89}Sr and ^{90}Sr	109
7.5.3	Radiochemical Separations of ^{90}Sr and ^{89}Sr	109
7.5.3.1	Determination of Chemical Yield in Radiostrontium Separations	110

7.5.3.2	Separation of Radiostrontium by the Nitrate Precipitation Method	110
7.5.3.3	Separation of Radiostrontium by a $\text{Ca}(\text{OH})_2$ Precipitation Method	113
7.5.3.4	Separation of Radiostrontium by Extraction Chromatography	114
7.6	Radium – ^{226}Ra and ^{228}Ra	117
7.6.1	Nuclear Characteristics of Radium Isotopes	117
7.6.2	Measurement of the Activity of Radium Isotopes	117
7.6.3	Need for Determining the Activity of Radium Isotopes	119
7.6.4	Radiochemical Separations of Radium	119
7.6.4.1	Separation of ^{226}Ra in Rock Samples with Use of Ion Exchange	120
7.6.4.2	Determination of ^{226}Ra and ^{228}Ra in Water by Extraction Chromatography	121
7.7	Essentials in the Radiochemistry of the Alkaline Earth Metals	122
8	Radiochemistry of the 3d-Transition Metals	123
8.1	The Most Important Radionuclides of the 3d-Transition Metals	123
8.2	Chemical Properties of the 3d-Transition Metals	124
8.3	Iron – ^{55}Fe	125
8.3.1	Nuclear Characteristics and Measurement of ^{55}Fe	125
8.3.2	Chemistry of Iron	125
8.3.3	Separation of ^{55}Fe	128
8.3.3.1	Separation of ^{55}Fe by Solvent Extraction	128
8.3.3.2	Separation of ^{55}Fe by Extraction Chromatography	129
8.4	Nickel – ^{59}Ni and ^{63}Ni	130
8.4.1	Nuclear Characteristics and Measurement of ^{59}Ni and ^{63}Ni	130
8.4.2	Chemistry of Nickel	131
8.4.3	Separation of ^{59}Ni and ^{63}Ni	132
8.4.3.1	Separation of Nickel by the DMG Precipitation Method	132
8.4.3.2	Separation of ^{63}Ni by Ni Resin	134
8.4.3.3	Separation of Nickel for the Measurement of Nickel Isotopes with AMS	135
8.4.3.4	Simultaneous Determination of ^{55}Fe and ^{63}Ni	135
8.5	Essentials in 3-d Transition Metals Radiochemistry	137
9	Radiochemistry of the 4d-Transition Metals	139
9.1	Important Radionuclides of the 4d-Transition Metals	139
9.2	Chemistry of the 4d-Transition Metals	140
9.3	Technetium – ^{99}Tc	140
9.3.1	Chemistry of Technetium	141
9.3.2	Nuclear Characteristics and Measurement of ^{99}Tc	141
9.3.3	Separation of ^{99}Tc	143
9.3.3.1	Yield Determination in ^{99}Tc Analyses	143
9.3.3.2	Enrichment of ^{99}Tc for Water Analyzes	144

9.3.3.3	Separation of ^{99}Tc from Water by Precipitation and Solvent Extraction	144
9.3.3.4	Separation of ^{99}Tc by Extraction Chromatography	145
9.3.3.5	Separation of ^{99}Tc by Distillation	146
9.4	Zirconium – ^{93}Zr	146
9.4.1	Chemistry of Zirconium	147
9.4.2	Nuclear Characteristics and Measurement of ^{93}Zr	148
9.4.3	Separation of ^{93}Zr	148
9.4.3.1	Determination of ^{93}Zr by TTA Extraction and Measurement by LSC	149
9.4.3.2	Separation of ^{93}Zr by Coprecipitation and Solvent Extraction for the Zr Measurement by ICP-MS	149
9.5	Molybdenum – ^{93}Mo	151
9.5.1	Chemistry of Molybdenum	151
9.5.2	Nuclear Characteristics and Measurement of ^{93}Mo	153
9.5.3	Separation of ^{93}Mo	154
9.5.3.1	Separation of Radioactive Molybdenum by Aluminum Oxide	154
9.5.3.2	Separation of ^{93}Mo by Solvent Extraction	154
9.6	Niobium – ^{94}Nb	156
9.6.1	Chemistry of Niobium	156
9.6.2	Nuclear Characteristics and Measurement of Niobium Radionuclides	157
9.6.3	Separation of ^{94}Nb	157
9.6.3.1	Separation of ^{94}Nb by Precipitation as Nb_2O_5	158
9.6.3.2	Separation of ^{94}Nb by Precipitation as Nb_2O_5 and by Anion Exchange	158
9.6.3.3	Separation of ^{94}Nb by Solvent Extraction	159
9.7	Essentials in the Radiochemistry of 4-d Transition Metals	159
10	Radiochemistry of the Lanthanides	163
10.1	Important Lanthanide Radionuclides	163
10.2	Chemical Properties of the Lanthanides	163
10.3	Separation of Lanthanides from Actinides	165
10.4	Lanthanides as Actinide Analogs	165
10.5	^{147}Pm and ^{151}Sm	167
10.5.1	Nuclear Characteristics and Measurement of ^{147}Pm and ^{151}Sm	167
10.5.2	Separation of ^{147}Pm and ^{151}Sm	168
10.5.2.1	Separation with Ln Resin	168
10.5.2.2	Determination of ^{147}Pm from Urine Using Ion Exchange Chromatography	170
10.5.2.3	Separation of ^{147}Pm from Irradiated Fuel by Ion Exchange Chromatography	170
10.5.2.4	Determination of ^{147}Pm and ^{151}Sm in Rocks	171
10.6	Essentials of Lanthanide Radiochemistry	173

11	Radiochemistry of the Halogens	175
11.1	Important Halogen Radionuclides	175
11.2	Physical and Chemical Properties of the Halogens	176
11.3	Chlorine – ^{36}Cl	178
11.3.1	Sources and Nuclear Characteristics of ^{36}Cl	178
11.3.2	Determination of ^{36}Cl	178
11.3.2.1	Determination of ^{36}Cl from Steel, Graphite, and Concrete by Solvent Extraction and Ion Exchange	179
11.4	Iodine – ^{129}I	181
11.4.1	Sources and Nuclear Characteristics of ^{129}I	181
11.4.2	Measurement of ^{129}I	182
11.4.2.1	Determination of ^{129}I by Neutron Activation Analysis	182
11.4.2.2	Determination of ^{129}I by Accelerator Mass Spectrometry	184
11.4.3	Radiochemical Separations of ^{129}I	185
11.4.3.1	Separation of ^{129}I by Solvent Extraction	185
11.4.3.2	Pretreatment of Samples for ^{129}I Analyses	188
11.4.3.3	Speciation of Iodine Species in Water	188
11.5	Essentials of Halogen Radiochemistry	190
12	Radiochemistry of the Noble Gases	193
12.1	Important Radionuclides of the Noble Gases	193
12.2	Physical and Chemical Characteristics of the Noble Gases	193
12.3	Measurement of Xe Isotopes in Air	194
12.4	Determination of ^{85}Kr in Air	194
12.5	Radon and its Determination	196
12.5.1	Determination of Radon in Outdoor Air and Soil Pore Spaces	197
12.5.2	Determination of Radon in Indoor Air	197
12.5.3	Determination of Radon in Water	197
12.6	Essentials of Noble Gas Radiochemistry	198
13	Radiochemistry of Tritium and Radiocarbon	201
13.1	Tritium – ^3H	201
13.1.1	Nuclear Properties of Tritium	201
13.1.2	Environmental Sources of Tritium	202
13.1.3	Determination of Tritium in Water	203
13.1.4	Electrolytic Enrichment of Tritium	203
13.1.5	Determination of Tritium in Organic Material	204
13.1.6	Determination of Tritium from Urine	204
13.1.7	Determination of Tritium after Conversion into Benzene	205
13.1.8	Determination of Tritium using Mass Spectrometry	205
13.1.9	Determination of Tritium in Nuclear Waste Samples	206
13.2	Radiocarbon – ^{14}C	207
13.2.1	Nuclear Properties of Radiocarbon	207
13.2.2	Sources of Radiocarbon	207
13.2.3	Chemistry of Inorganic Carbon	209

13.2.4	Carbon Dating of Carbonaceous Samples	209
13.2.5	Separation and Determination of ^{14}C	210
13.2.5.1	Removal of Carbon from Samples by Combustion for the Determination of ^{14}C	211
13.2.5.2	Determination of ^{14}C as Calcium Carbonate by Liquid Scintillation Counting	211
13.2.5.3	Determination of ^{14}C by Liquid Scintillation Counting with Carbon Bound to Amine	213
13.2.5.4	^{14}C Determination by LSC in Benzene	213
13.2.5.5	^{14}C Determination in Graphite form by AMS	213
13.2.5.6	Determination of ^{14}C in Nuclear Waste	214
13.3	Essentials of Tritium and Radiocarbon Radiochemistry	215
14	Radiochemistry of Lead, Polonium, Tin, and Selenium	217
14.1	Polonium – ^{210}Po	218
14.1.1	Nuclear Characteristics of ^{210}Po	218
14.1.2	Chemistry of Polonium	219
14.1.3	Determination of ^{210}Po	220
14.2	Lead – ^{210}Pb	221
14.2.1	Nuclear Characteristics and Measurement of ^{210}Pb	221
14.2.2	Chemistry of Lead	223
14.2.3	Determination of ^{210}Pb	224
14.2.3.1	Determination of ^{210}Pb from the Ingrowth of ^{210}Po	225
14.2.3.2	Separation of ^{210}Pb by Precipitation	226
14.2.3.3	Separation of ^{210}Pb by Extraction Chromatography	226
14.3	Tin – ^{126}Sn	228
14.3.1	Nuclear Characteristics and Measurement of ^{126}Sn	228
14.3.2	Chemistry of Tin	229
14.3.3	Determination of ^{126}Sn	230
14.4	Selenium – ^{79}Se	233
14.4.1	Nuclear Characteristics and Measurement of ^{79}Se	233
14.4.2	Chemistry of Selenium	233
14.4.3	Determination of ^{79}Se	235
14.5	Essentials of Polonium, Lead, Tin, and Selenium Radiochemistry	236
15	Radiochemistry of the Actinides	239
15.1	Important Actinide Isotopes	239
15.2	Generation and Origin of the Actinides	239
15.3	Electronic Structures of the Actinides	244
15.4	Oxidation States of the Actinides	245
15.5	Ionic Radii of the Actinides	246
15.6	Major Chemical Forms of the Actinides	247
15.7	Disproportionation	247
15.8	Hydrolysis and Polymerization of the Actinides	249

15.9	Complex Formation of the Actinides	250
15.10	Oxides of the Actinides	250
15.11	Actinium	251
15.11.1	Isotopes of Actinium	251
15.11.2	Chemistry of Actinium	252
15.11.3	Separation of Actinium	253
15.11.4	Essentials of Actinium Radiochemistry	254
15.12	Thorium	255
15.12.1	Occurrence of Thorium	255
15.12.2	Thorium Isotopes and their Measurement	255
15.12.3	Chemistry of Thorium	256
15.12.4	Separation of Thorium	258
15.12.4.1	Separation of Thorium by Precipitation	258
15.12.4.2	Separation of Thorium by Anion Exchange	258
15.12.4.3	Separation of Thorium by Solvent Extraction	259
15.12.4.4	Separation of Thorium by Extraction Chromatography	259
15.12.5	Essentials of Thorium Radiochemistry	259
15.13	Protactinium	260
15.13.1	Isotopes of Protactinium	260
15.13.2	Chemistry of Protactinium	261
15.13.3	Separation of Protactinium	262
15.13.4	Essentials of Protactinium Radiochemistry	263
15.14	Uranium	264
15.14.1	The Most Important Uranium Isotopes	264
15.14.2	Occurrence of Uranium	266
15.14.3	Chemistry of Uranium	267
15.14.4	Hydrolysis of Uranium	269
15.14.5	Formation of Uranium Complexes	269
15.14.6	Uranium Oxides	271
15.14.7	From Ore to Uranium Fuel	271
15.14.8	Measurement of Uranium	272
15.14.9	Reasons for Determining Uranium Isotopes	273
15.14.10	Separation of Uranium	274
15.14.10.1	Separation of Uranium from Other Naturally Occurring Alpha-Emitting Radionuclides	274
15.14.10.2	Determination of Chemical forms of Uranium in Groundwater	274
15.14.10.3	Separation of Uranium from Transuranium Elements by Anion Exchange or by Extraction Chromatography	275
15.14.10.4	Separation of Uranium by Solvent Extraction with Tributylphosphate (TBP)	275
15.14.11	Essentials of Uranium Radiochemistry	275
15.15	Neptunium	277
15.15.1	Sources of Neptunium	277
15.15.2	Nuclear Characteristics and Measurement of ^{237}Np	278
15.15.3	Chemistry of Neptunium	278

15.15.4	Separation of ^{237}Np	280
15.15.4.1	Neptunium Tracers for Yield Determinations	280
15.15.4.2	Preconcentration of Neptunium from Large Water Volumes	282
15.15.4.3	Separation of ^{237}Np by Extraction Chromatography	282
15.15.4.4	Separation of ^{237}Np by Anion Exchange Chromatography	283
15.15.4.5	Separation of ^{237}Np by Solvent Extraction	283
15.15.5	Essentials of Neptunium Radiochemistry	283
15.16	Plutonium	284
15.16.1	Isotopes of Plutonium	284
15.16.2	Sources of Plutonium	286
15.16.3	Measurement of Plutonium Isotopes	287
15.16.4	The Chemistry of Plutonium	289
15.16.4.1	Oxidation States and Plutonium	289
15.16.4.2	Disproportionation	290
15.16.4.3	Hydrolysis	291
15.16.4.4	Redox Behavior	291
15.16.4.5	Complex Formation	293
15.16.5	Separation of Plutonium	293
15.16.6	Tracers Used in the Determination of Pu Isotopes	294
15.16.7	Separation by Solvent Extraction	295
15.16.8	Separation of Pu by Anion Exchange Chromatography	296
15.16.9	Separation of Pu by Extraction Chromatography	297
15.16.10	Separation of Pu from Large Volumes of Water	298
15.16.11	Automated and Rapid Separation Methods for Pu Determination	300
15.16.12	Essentials of Plutonium Radiochemistry	301
15.17	Americium and Curium	302
15.17.1	Sources of Americium and Curium	302
15.17.2	Nuclear Characteristics and Measurement of ^{241}Am , ^{242}Cm , ^{243}Cm , and ^{244}Cm	303
15.17.3	Chemistry of Americium and Curium	304
15.17.4	Separation of Americium and Curium	306
15.17.4.1	Separation of Am and Cm by Ion Exchange	307
15.17.4.2	Separation of Am and Cm by Extraction Chromatography	307
15.17.4.3	Separation of Am and Cm by Solvent Extraction	307
15.17.4.4	Separation of Lanthanides from Am and Cm	308
15.17.5	Essentials of Americium and Curium Radiochemistry	309
16	Speciation Analysis	311
16.1	Considerations Relevant to Speciation	311
16.2	Significance of Speciation	312
16.3	Categorization of Speciation Analyzes	313
16.4	Fractionation Techniques for Environmental Samples	314
16.4.1	Particle Fractionation in Water	314
16.4.2	Fractionation of Aerosol Particles	316
16.4.3	Fractionation of Soil and Sediments	317

16.5	Analysis of Radionuclide and Isotope Compositions	317
16.6	Spectroscopic Speciation Methods	318
16.7	Wet Chemical Methods	321
16.7.1	Coprecipitation	321
16.7.2	Solvent Extraction	322
16.7.3	Ion Exchange Chromatography	323
16.8	Sequential Extractions	324
16.9	Computational Speciation Methods	326
16.10	Characterization of Radioactive Particles	329
16.10.1	Identification and Isolation of the Particles	330
16.10.2	Scanning Electron Microscopic Analysis of the Particles	330
16.10.3	Gamma and X-ray Analysis of the Particles	331
16.10.4	Secondary Ion Mass Spectrometry Analysis of Radioactive Particles	332
16.10.5	Synchrotron-Based X-ray Microanalyses	332
16.10.6	Post-Dissolution Analysis of Particles	334
	Further Reading	335
17	Measurement of Radionuclides by Mass Spectrometry	337
17.1	Introduction	337
17.2	Inductively Coupled Plasma Mass Spectrometry (ICP-MS)	338
17.2.1	Components and Operation Principles of ICP-MS Systems	339
17.2.2	Resolution and Abundance Sensitivity	342
17.2.3	Dynamic Collision/Reaction Cells	343
17.2.4	Detectors	344
17.2.5	Detection Limits	345
17.2.6	^{90}Sr Measurement by ICP-MS	346
17.2.7	^{99}Tc Measurement by ICP-MS	348
17.2.8	Measurement of Uranium and Thorium Isotopes by ICP-MS	348
17.2.9	^{237}Np Measurement by ICP-MS	349
17.2.10	Measurement of Plutonium Isotopes by ICP-MS	349
17.3	Accelerator Mass Spectrometry (AMS)	350
17.3.1	Components and Operation of AMS	350
17.3.2	^{14}C Measurement by AMS	352
17.3.3	^{36}Cl Measurement by AMS	353
17.3.4	^{41}Ca Measurement by AMS	353
17.3.5	^{63}Ni and ^{59}Ni Measurement by AMS	353
17.3.6	^{99}Tc Measurement by AMS	354
17.3.7	^{129}I Measurement by AMS	355
17.3.8	Measurement of Plutonium Isotopes by AMS	355
17.4	Thermal Ionization Mass Spectrometry (TIMS)	356
17.5	Resonance Ionization Mass Spectrometry (RIMS)	358
17.6	Essentials of the Measurement of Radionuclides by Mass Spectrometry	359
	Further Reading	360

18	Sampling and Sample Pretreatment for the Determination of Radionuclides	361
18.1	Introduction	361
18.2	Air Sampling and Pretreatment	362
18.2.1	Sampling Aerosol Particles	362
18.2.1.1	Radioactive Aerosol Particles	363
18.2.1.2	Integral Aerosol Particle Sampling	363
18.2.1.3	Size-Selective Aerosol Particle Sampling	365
18.2.1.4	Passive Aerosol Particle Sampling	366
18.3	Sampling Gaseous Components	366
18.4	Atmospheric Deposition Sampling	369
18.4.1	Dry/Wet Deposition Sampling	369
18.4.2	Ion Exchange Collector	370
18.5	Water Sampling	371
18.5.1	Surface Water Sampling	371
18.5.2	Water Core (Depth Profile)	372
18.5.3	Preconcentration of Radionuclides from Natural Waters	375
18.5.3.1	Preconcentration of Radiocesium (^{137}Cs and ^{134}Cs)	375
18.5.3.2	Preconcentration of Pu, Am, Np, and ^{99}Tc	376
18.6	Sediment Sampling and Pretreatment	377
18.6.1	Surface Sediment Sampling	377
18.6.2	Sediment Core Sampling	379
18.6.3	Sediment Pore Water Sampling	381
18.6.4	Pretreatment of Sediments – Storage, Drying, Homogenizing	383
18.7	Soil Sampling and Pretreatment	384
18.7.1	Planning the Sampling	384
18.7.2	Soil Core Sampling	385
18.7.3	Template Method	387
18.7.4	Trench Method	387
18.7.5	Pretreatment of Soil Samples	388
18.8	Essentials in Sampling and Sample Pretreatment for Radionuclides	388
19	Chemical Changes Induced by Radioactive Decay	391
19.1	Autoradiolysis	391
19.1.1	Dissolved Gases	392
19.1.2	Water Solutions	392
19.1.3	Organic Compounds Labeled with Radionuclides	392
19.1.4	Solid Compounds	393
19.2	Transmutation and Subsequent Chemical Changes	393
19.3	Recoil – Hot Atom Chemistry	394

Index	397
--------------	------------

Preface

I started to give a lecture course on radionuclide analysis to students of radiochemistry in 2001. Two problems quickly became apparent. The first was that I could not properly lecture on this subject if the basic chemistry underlying the behavior of radionuclides in separation procedures was not understood. There seemed to be no sense in talking about precipitation of hydrolyzable metals with ferric hydroxide, for example, if the hydrolysis of metals was not understood. I had to go back to basics and teach the chemistry of the elements. This was a good choice – not least for myself – since I had to refresh my understanding of basic chemical phenomena. The second problem was that there was no adequate textbook on the chemistry of radionuclides. I had a handout from my predecessor to give to the students, but it had been written in the 1970s: it was good but outdated and short. Most books on radiochemistry available at that time, though comprehensive enough, contained little actual chemistry of the radionuclides and concentrated on their radioactive decay processes and the detection and measurement of radiation. In 2005 I began to write a text of my own, in Finnish. Then, seeing a broader need for such a text, I decided to write in English.

After working on the book for three years, I realized that analytical methods cannot be properly described if one has not done the analysis oneself, as was true in my case. I therefore asked Dr. Xiaolin Hou, of Risø National Laboratory, Denmark, to join me in the project. I knew him as a most experienced analytical radiochemist who had personally analyzed a great number of radionuclides in environmental and nuclear waste samples and developed new separation methods. During the past two years we have collaborated in writing this book, and I have learned a host of new things, not just from reading papers but also from extensive discussions with Dr. Hou.

Our book describes the basic chemistry needed to understand the behavior and analysis of radionuclides of most groups of elements, and the analytical methods required to separate the most important alpha- and beta- decaying radionuclides from environmental and nuclear waste samples (e.g., ^{90}Sr and plutonium isotopes). Many new radionuclides have become important in radiochemistry in the past ten to fifteen years. Most of these are very long-lived, appearing in spent nuclear fuel and

nuclear reactor structures and are relevant to safety analysis of the final disposal of the nuclear fuel and decommissioning waste. Mass spectrometric techniques are well suited for the measurement of these radionuclides (^{135}Cs , ^{129}I , etc.) because of their low specific activities. Traditionally, radiometric methods have been used to measure radionuclides, but the development of mass spectrometric techniques has opened up new avenues for the analysis of radionuclides, in particular for their analysis in much lower concentrations. Mass spectrometric measurements also create new requirements for radionuclide analyses, because the interfering radionuclides and other elements which need to be separated before measurement are mostly not the same ones that affect radiometric measurements.

My first intention was to write a book for undergraduate and post-graduate students, but now that the book is finished I see that it could also serve as a handbook for more experienced radiochemists – at least I hope so.

November 1, 2010

Jukka Lehto
Professor in Radiochemistry
University of Helsinki
Department of Chemistry
Finland

Acknowledgments

The authors thank Dr. Kathleen Ahonen for translating part of the book from Finnish and Dr. Shannon Kuismanen, Mr. Howard McKee, and Mr. Stewart Makkonen-Craig for language revision. The comments of Professor Markku Leskelä and Mr. Martti Hakanen from the University of Helsinki, Dr. Sven P. Nielsen and Dr. Jussi Jernstöm from Risø-DTU, Denmark, and Dr. Iisa Outola from STUK, Finland, have led to many improvements in the text, and we warmly thank them for their help. We are grateful to Mr. Lalli Jokelainen for careful preparation of figures and also to Dr. Steffen Happel from Triskem International, France, for providing some of the figures. Finally, we thank Wiley-VCH and Dr. Eva-Stina Riihimäki for publishing the book.

1

Radionuclides and their Radiometric Measurement

1.1

Radionuclides

The first radioactive elements – radium and polonium – were discovered by Marie Curie at the end of the nineteenth century. During the first decades of the twentieth century, tens of natural radioactive elements and their various isotopes in the uranium and thorium decay chains were identified. The first artificial radionuclide, ^{30}P , was produced by Frédéric and Irène Joliot-Curie in an accelerator by bombarding aluminum with protons. Today, more than two thousand artificial radionuclides have been produced and identified, especially after the discovery and use of nuclear fission of uranium and plutonium. This book focuses on radionuclides found in the environment and in nuclear waste. This chapter presents an overview of radionuclides, radioactive decay processes, and the radiometric measurement of radionuclides, which are categorized according to their sources and ways of formation; in later chapters they are classified based on their chemical nature and are discussed in more detail. Radionuclides can be primarily categorized into natural and artificial radionuclides.

1.1.1

Natural Radionuclides

In nature there are three types of radionuclides: those belonging to the decay chains of uranium and thorium, single very long-lived radionuclides, and cosmogenic radionuclides.

The decay chains of uranium and thorium start with two isotopes of uranium and one of thorium, ^{235}U , ^{238}U , and ^{232}Th , which were formed at the birth of the Universe some 13.7 billion years ago, and, since they are so long-lived, they have survived in the earth since its birth 4.5 billion years ago. These three primordial radionuclides each initiate a decay chain leading to the stable lead isotopes ^{207}Pb , ^{206}Pb , and ^{208}Pb , respectively. In between, there are altogether 42 radionuclides of 13 elements, of which nine elements, those heavier than bismuth, have no stable isotopes at all. The three decay chains are depicted in Tables 1.1–1.3. The determination of radionuclides

Table 1.1 Uranium decay chain.

Nuclide	Decay mode	Half-life	Decay energy (MeV)	Decay product
^{238}U	α	4.4×10^9 y	4.270	^{234}Th
^{234}Th	β^-	24 d	0.273	^{234}Pa
^{234}Pa	β^-	6.7 h	2.197	^{234}U
^{234}U	α	245 500 y	4.859	^{230}Th
^{230}Th	α	75 380 y	4.770	^{226}Ra
^{226}Ra	α	1602 y	4.871	^{222}Rn
^{222}Rn	α	3.8 d	5.590	^{218}Po
^{218}Po	α 99.98%	3.1 min	6.874	^{214}Pb
	β^- 0.02%		2.883	^{218}At
^{218}At	α 99.90%	1.5 s	6.874	^{214}Bi
	β^- 0.10%		2.883	^{218}Rn
^{218}Rn	α	35 ms	7.263	^{214}Po
^{214}Pb	β^-	27 min	1.024	^{214}Bi
^{214}Bi	β^- 99.98%	20 min	3.272	^{214}Po
	α 0.02%		5.617	^{210}Tl
^{214}Po	α	0.16 ms	7.883	^{210}Pb
^{210}Tl	β^-	1.3 min	5.484	^{210}Pb
^{210}Pb	β^-	22.3 y	0.064	^{210}Bi
^{210}Bi	β^- 99.99987%	5.0 d	1.426	^{210}Po
	α 0.00013%		5.982	^{206}Tl
^{210}Po	α	138 d	5.407	^{206}Pb
^{206}Tl	β^-	4.2 min	1.533	^{206}Pb
^{206}Pb		stable		

Table 1.2 Actinium decay chain.

Nuclide	Decay mode	Half-life	Decay energy (MeV)	Decay product
^{235}U	α	7.1×10^8 y	4.678	^{231}Th
^{231}Th	β^-	26 h	0.391	^{231}Pa
^{231}Pa	α	32,760 y	5.150	^{227}Ac
^{227}Ac	β^- 98.62%	22 y	0.045	^{227}Th
	α 1.38%		5.042	^{223}Fr
^{227}Th	α	19 d	6.147	^{223}Ra
^{223}Fr	β^-	22 min	1.149	^{223}Ra
^{223}Ra	α	11 d	5.979	^{219}Rn
^{219}Rn	α	4.0 s	6.946	^{215}Po
^{215}Po	α 99.99977%	1.8 ms	7.527	^{211}Pb
	β^- 0.00023%		0.715	^{215}At
^{215}At	α	0.1 ms	8.178	^{211}Bi
^{211}Pb	β^-	36 min	1.367	^{211}Bi
^{211}Bi	α 99.724%	2.1 min	6.751	^{207}Tl
	β^- 0.276%		0.575	^{211}Po
^{211}Po	α	516 ms	7.595	^{207}Pb
^{207}Tl	β^-	4.8 min	1.418	^{207}Pb
^{207}Pb		stable		

Table 1.3 Thorium decay chain.

Nuclide	Decay mode	Half-life	Decay energy (MeV)	Decay product
^{232}Th	α	1.41×10^{10} y	4.081	^{228}Ra
^{228}Ra	β^-	5.8 y	0.046	^{228}Ac
^{228}Ac	β^-	6.3 h	2.124	^{228}Th
^{228}Th	α	1.9 y	5.520	^{224}Ra
^{224}Ra	α	3.6 d	5.789	^{220}Rn
^{220}Rn	α	56 s	6.404	^{216}Po
^{216}Po	α	0.15 s	6.906	^{212}Pb
^{212}Pb	β^-	10.6 h	0.570	^{212}Bi
^{212}Bi	β^- 64.06%	61 min	2.252	^{212}Po
	α 35.94%		6.208	^{208}Tl
^{212}Po	α	299 ns	8.955	^{208}Pb
^{208}Tl	β^-	3.1 min	4.999	^{208}Pb
^{208}Pb		stable		

in the decay chains has been, and still is, a major topic in analytical radiochemistry. They are alpha and beta emitters, most of which do not emit detectable gamma rays, and thus their determination requires radiochemical separations. This book examines the separations of the following radionuclides: U isotopes, ^{231}Pa , Th isotopes, ^{227}Ac , $^{226,228}\text{Ra}$, ^{222}Rn , ^{210}Po , and ^{210}Pb .

In addition to ^{235}U , ^{238}U , and ^{232}Th , there are several single very long-lived primordial radionuclides (Table 1.4) which were formed in the same cosmic processes as those that formed uranium and thorium. The most important of these, with respect to the radiation dose to humans, is ^{40}K . However, as this emits readily detectable gamma rays and does not require radiochemical separations, neither this nor the others are discussed further in this book.

The third class of natural radionuclides comprises cosmogenic radionuclides, which are formed in the atmosphere in nuclear reactions due to cosmic radiation (Table 1.5). These radionuclides are isotopes of lighter elements, and their half-lives vary greatly. The primary components of cosmic radiation are high-energy alpha particles and protons, which induce nuclear reactions when they impact on the nuclei of the atmospheric atoms. Most of the cosmogenic radionuclides are attached to aerosol particles and are deposited on the ground. Some, however, are gaseous, such as ^{14}C (as carbon dioxide) and ^{39}Ar (a noble gas), and thus stay in the atmosphere. In

Table 1.4 Some single primordial radionuclides.

Nuclide	Isotopic abundance (%)	Decay mode	Half-life (y)
^{40}K	0.0117	β^-	1.26×10^9
^{87}Rb	27.83	β^-	4.88×10^{10}
^{123}Te	0.905	EC	1.3×10^{13}
^{144}Nd	23.80	α	2.1×10^{15}
^{174}Hf	0.162	α	2×10^{15}

Table 1.5 Some important cosmogenic radionuclides.

Nuclide	Half-life (y)	Decay mode	Nuclide	Half-life (y)	Decay mode
^3H	12.3	beta	^7Be	0.15	EC
^{10}Be	2.5×10^6	beta	^{14}C	5730	beta
^{22}Na	2.62	EC	^{26}Al	7.4×10^5	EC
^{32}Si	710	beta	^{32}P	0.038	beta
^{33}P	0.067	beta	^{35}S	0.24	beta
^{36}Cl	3.1×10^5	beta/EC	^{39}Ar	269	beta
^{41}Ca	3.8×10^6	EC	^{129}I	1.57×10^7	beta

primary nuclear reactions, neutrons are also produced, and these induce further nuclear reactions. Two important radionuclides are produced in these neutron-induced reactions: ^3H and ^{14}C (reactions 1.1 and 1.2), whose chemistry and radiochemical separations are described in Chapter 13. These radionuclides – tritium and radiocarbon – are generated not only by cosmic radiation but also in other neutron activation processes in nuclear explosions and in matter surrounding nuclear reactors.



1.1.2

Artificial Radionuclides

Artificial radionuclides form the largest group of radionuclides, comprising more than two thousand nuclides produced since the 1930s. The sources of artificial radionuclides are:

- nuclear weapons production and explosions;
- nuclear energy production;
- radionuclide production by reactors and accelerators.

A wide range of radionuclides are produced in nuclear weapons production, where plutonium is produced by the irradiation of uranium in reactors and in nuclear power reactors. Most are *fission products*, and are generated by the neutron-induced fission of ^{235}U and ^{239}Pu . In nuclear power reactors, they are practically all retained in the nuclear fuel; however, in nuclear explosions they end up in the environment – on the ground in atmospheric explosions or in the geosphere in underground explosions. The spent nuclear fuel from power reactors is stored in disposal repositories deep underground. The radionuclide composition of nuclear explosions and the spent fuel from nuclear power reactors differ somewhat for several reasons. Firstly, the fissions in a reactor are mostly caused by thermal neutrons, while in a bomb fast neutrons are

mostly responsible for the fission events, and this results in differences in the radionuclide composition. Secondly, fission is instantaneous in a bomb, while in a reactor the fuel is irradiated for some years. This allows the ingrowth of some activation products, such as ^{134}Cs , that do not exist in weapons fallout. ^{90}Sr and ^{137}Cs are the most important fission products because of their relatively long half-lives and high fission yields. In addition to these, there is range of long-lived fission products, such as ^{79}Se , ^{99}Tc , ^{126}Sn , ^{129}I , ^{135}Cs , and ^{151}Sm , the radiochemistry of which is discussed in this book.

Along with fission products, activation products are also formed in side reactions accompanying the neutron irradiation. The intensive neutron flux generated in the fission induces activation reactions both in the fuel or weapons material and in the surrounding material. These can be divided into two categories, the first comprising the transuranium elements – a very important class of radionuclides in radiochemistry. These are created by successive neutron activation and beta decay processes starting from ^{238}U or ^{239}Pu (Figure 1.1). Of these, the most important and the most radiotoxic nuclides are ^{237}Np , $^{238,239,240,241}\text{Pu}$, $^{241,243}\text{Am}$, and $^{243,244,245}\text{Cm}$, which are discussed further in this book. In addition to transuranium elements, a new uranium isotope ^{236}U is also formed in neutron activation reactions.

Another activation product group comprises radioisotopes of various lighter elements. In addition to tritium and radiocarbon, a wide range of these activation products are formed in nuclear explosions and especially in nuclear reactors. Elements of the reactor's construction materials, especially the cladding and other metal parts surrounding the nuclear fuel, the steel of the pressure vessel and the shielding concrete structures are activated in the neutron flux from the fuel. Part of these activation products, such as elements released from the steel by corrosion, end up in the nuclear waste disposed of during the use of the reactor. A larger part,

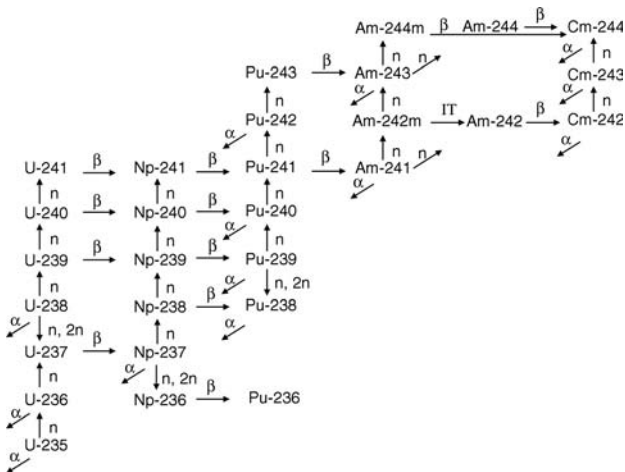


Figure 1.1 Formation of transuranium elements in nuclear fuel and nuclear weapons material (Holm, E., Rioseco, J., and Petterson, H. (1992) Fallout of transuranium elements following the Chernobyl accident. *J. Radioanal. Nucl. Chem. Articles*, **156**, 183).

however, remains in the steel and concrete and ends up in the waste when the reactor is decommissioned. This category has many important radionuclides, such as ^{14}C , ^{36}Cl , ^{41}Ca , ^{55}Fe , ^{59}Ni , and ^{63}Ni , which are discussed later in the book. These are all purely beta-decaying radionuclides that require radiochemical separations. In addition to these, there is a range of activation products, such as ^{60}Co , ^{54}Mn , ^{65}Zn , which emit gamma rays and are thus readily detectable and measurable. In addition to the reactor steel and shielding concrete, the spent fuel, its metal cladding, and other metal parts surrounding the fuel and ending up in the final disposal, contain large amounts of the long-lived beta decaying activation products ^{93}Zr , ^{94}Nb , and ^{93}Mo (together with ^{14}C , ^{36}Cl , ^{59}Ni , ^{63}Ni), which are also discussed in this book.

There are also a number of *radionuclides produced by neutron and proton irradiations in reactors and in cyclotrons*. Their properties are later described only if they are used as tracers in radionuclide analysis. An example is a fairly short-lived gamma-emitting strontium isotope, ^{85}Sr , which is used as a tracer in model experiments for studying the behavior of the beta-emitting fission product ^{90}Sr or as a yield-determinant in ^{90}Sr determinations.

1.2

Modes of Radioactive Decay

This book describes the chemistry and analysis of radionuclides – nuclei which are unstable, that is, radioactive. The instability comes from the fact that the mass of the nucleus is either too high or its neutron to proton ratio is inappropriate for stability. By radioactive decay, the nucleus disposes of the mass excess or adjusts the neutron to proton ratio more closely to what is required for stability. The four main radioactive decay modes – fission, alpha decay, beta decay and internal transition – are briefly described below.

1.2.1

Fission

Spontaneous fission is a characteristic radioactive decay mode only for the heaviest elements. In fission, the heavy nucleus divides into two nuclei of lighter elements which are called fission products. Of the naturally occurring isotopes, only ^{238}U decays by spontaneous fission. Only a very minor fraction, 0.005%, of ^{238}U decays by this mode, the rest decaying by alpha mode. Spontaneous fission becomes more prevailing with the heaviest elements, and for some, such as ^{260}No , it is the only way of decay. Considering the production and amounts of fission products, a more important process than spontaneous fission is induced fission: a heavy nucleus absorbs a particle, most usually a neutron, which results in the excitation and further fission of the nucleus (Figure 1.2). There are several fissionable isotopes, of which ^{235}U and ^{239}Pu are the most important from the point of view of the amounts of fission products generated. These two nuclides are not only fissionable but also fissile, that is, they undergo fission in the presence of thermal neutrons, which enables their use as

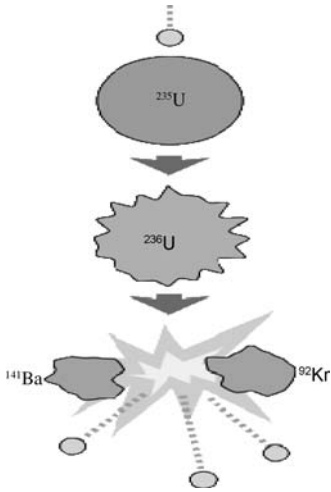


Figure 1.2 An example of a neutron-induced fission of ^{235}U . The reaction is $^{235}\text{U} + n \rightarrow ^{236}\text{U} \rightarrow ^{141}\text{Ba} + ^{92}\text{Kr} + 3n$ (http://en.wikipedia.org/wiki/Nuclear_fission).

nuclear fuel in nuclear reactors. ^{235}U is obtained by isotopic enrichment from natural uranium and ^{239}Pu by the irradiation of ^{238}U in a nuclear reactor and subsequent chemical separation of plutonium from the irradiated uranium.

A large number of fission products are generated in fission processes. Figure 1.3 gives, as an example, the distribution of fission products for ^{235}U from thermal

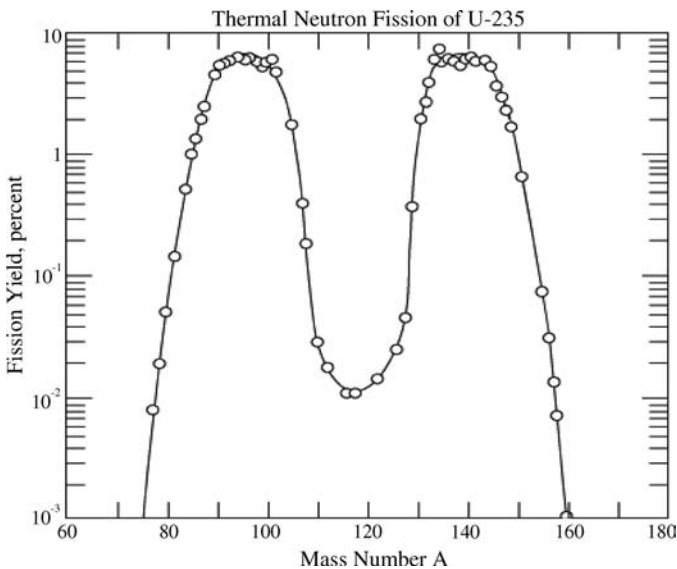
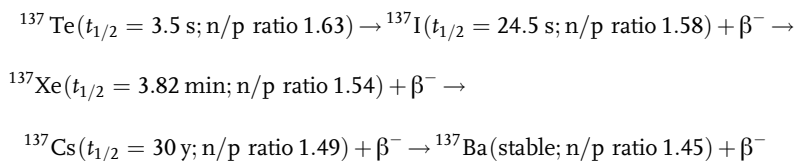


Figure 1.3 Fission yield distribution of ^{235}U as a function of the mass number of the fission product.

neutron-induced fission. As can be seen, the fission is extremely seldom symmetric, that is, the two fission products of one fission event are not of the same mass. Instead, the maxima of fission products are found at the mass numbers 90–100 and at 135–145. At these ranges, the fission yields are between 5% and 7%. This applies to thermal neutron-induced fission; fissions induced by high energy particles become more symmetric with the energy of the bombarding particle.

Most fission products are radioactive since they have an excess of neutrons. In both ^{235}U and ^{239}Pu , the neutron to proton ratio is around 1.6, which is too high for the lighter elements to be stable. For example, for the stable elements in the upper maximum of the fission yield at the mass numbers 135–145, the highest neutron-to-proton ratio is around 1.4, and, through the radioactive decay, by beta minus decay in this case, the nucleus transforms the ratio into an appropriate one. An example of such a decay chain of neutron-rich fission products leading to stable ^{137}Ba is as follows:



1.2.2

Alpha Decay

Alpha decay is also a typical decay mode for the heavier radionuclides. Most actinide isotopes and radionuclides in the uranium and thorium decay chains decay by this mode. A few exceptions among the radionuclides discussed in this book are ^{210}Pb , ^{228}Ra , and ^{241}Pu , which decay solely by beta emission. ^{227}Ac also decays mostly (98.8%) by beta decay. As can be seen from Tables 1.1–1.3, beta decay is a decay mode competing with alpha decay for many radionuclides in the decay chains. In an alpha decay, the heavy nucleus gets rid of excess mass by emitting a helium nucleus, which is called an alpha particle (α). An example is



where ^{226}Ra turns into ^{222}Rn by emitting an alpha particle. Thus, in an alpha decay, the atomic number decreases by two units and the mass number by four. The energies of the emitted alpha particles are always high, typically between 4 and 7 MeV. Since the mass of the alpha particle is relatively high, the daughter nuclide receives considerable kinetic energy due to recoil. For example, when ^{238}U decays to ^{234}Th by alpha emission, the daughter nuclide ^{234}Th gets 0.074 MeV of the 4.274 MeV decay energy and the alpha particle the rest, 4.202 MeV. Even though the fraction of the recoil energy is only 1.7%, this energy is some ten thousand times higher than that of a chemical bond, and thus recoil results in the breaking of the chemical bond by which the daughter nuclide is bound to the matrix. The transformations from parent nuclides to daughter nuclides take place between defined energy levels corresponding to defined