**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  

*Chemistry and Analysis of Radionuclides.* Jukka Lehto and Xiaolin Hou  
Copyright © 2011 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim  
ISBN: 978-3-527-32658-7
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 – 40K 93
6.5 Cesium – 134Cs, 135Cs, and 137Cs 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 135Cs 96
6.5.3.1 Determination of 135Cs by Neutron Activation Analysis 96
6.5.3.2 Determination of 135Cs 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 10Be 102
7.4 Calcium – 41Ca and 43Ca 102
7.4.1 Nuclear Characteristics and Measurement 102
7.4.2 Determination of 43Ca and 41Ca in Concrete 103
7.5 Strontium – 89Sr and 90Sr 106
7.5.1 Nuclear Characteristics and Sources 106
7.5.2 Measurement of Strontium Isotopes 107
7.5.2.1 Measurement of 90Sr Activity 107
7.5.2.2 Simultaneous Determination of 89Sr and 90Sr 109
7.5.3 Radiochemical Separations of 90Sr and 89Sr 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 Ca(OH)₂ Precipitation Method 113
7.5.3.4 Separation of Radiostrontium by Extraction Chromatography 114
7.6 Radium – ²²⁶⁹Ra and ²²⁸⁹Ra 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 ²²⁶⁹Ra in Rock Samples with Use of Ion Exchange 120
7.6.4.2 Determination of ²²⁶⁹Ra and ²²⁸⁹Ra 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 – ⁵⁵Fe 125
8.3.1 Nuclear Characteristics and Measurement of ⁵⁵Fe 125
8.3.2 Chemistry of Iron 125
8.3.3 Separation of ⁵⁵Fe 128
8.3.3.1 Separation of ⁵⁵Fe by Solvent Extraction 128
8.3.3.2 Separation of ⁵⁵Fe by Extraction Chromatography 129
8.4 Nickel – ⁶⁰⁹⁹Ni and ⁶³⁴⁹Ni 130
8.4.1 Nuclear Characteristics and Measurement of ⁶⁰Ni and ⁶⁴Ni 130
8.4.2 Chemistry of Nickel 131
8.4.3 Separation of ⁶⁰Ni and ⁶⁴Ni 132
8.4.3.1 Separation of Nickel by the DMG Precipitation Method 132
8.4.3.2 Separation of ⁶⁴Ni 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 ⁵⁵Fe and ⁶⁴Ni 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 – ⁹⁹⁰⁹Tc 140
9.3.1 Chemistry of Technetium 141
9.3.2 Nuclear Characteristics and Measurement of ⁹⁹⁰⁹Tc 141
9.3.3 Separation of ⁹⁹⁰⁹Tc 143
9.3.3.1 Yield Determination in ⁹⁹⁰⁹Tc Analyses 143
9.3.3.2 Enrichment of ⁹⁹⁰⁹Tc 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$_2$O$_5$ 158
9.6.3.2 Separation of $^{94}$Nb by Precipitation as Nb$_2$O$_5$ 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 – $^{36}\text{Cl}$ 178
11.3.1 Sources and Nuclear Characteristics of $^{36}\text{Cl}$ 178
11.3.2 Determination of $^{36}\text{Cl}$ 178
11.3.2.1 Determination of $^{36}\text{Cl}$ from Steel, Graphite, and Concrete by Solvent Extraction and Ion Exchange 179
11.4 Iodine – $^{129}\text{I}$ 181
11.4.1 Sources and Nuclear Characteristics of $^{129}\text{I}$ 181
11.4.2 Measurement of $^{129}\text{I}$ 182
11.4.2.1 Determination of $^{129}\text{I}$ by Neutron Activation Analysis 182
11.4.2.2 Determination of $^{129}\text{I}$ by Accelerator Mass Spectrometry 184
11.4.3 Radiochemical Separations of $^{129}\text{I}$ 185
11.4.3.1 Separation of $^{129}\text{I}$ by Solvent Extraction 185
11.4.3.2 Pretreatment of Samples for $^{129}\text{I}$ 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 $^{85}\text{Kr}$ in Air 194
12.4 Determination of $^{85}\text{Kr}$ 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 – $^3\text{H}$ 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 – $^{14}\text{C}$ 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

13.2.5 Separation and Determination of $^{14}$C

13.2.5.1 Removal of Carbon from Samples by Combustion for the Determination of $^{14}$C

13.2.5.2 Determination of $^{14}$C as Calcium Carbonate by Liquid Scintillation Counting

13.2.5.3 Determination of $^{14}$C by Liquid Scintillation Counting with Carbon Bound to Amine

13.2.5.4 $^{14}$C Determination by LSC in Benzene

13.2.5.5 $^{14}$C Determination in Graphite form by AMS

13.2.5.6 Determination of $^{14}$C in Nuclear Waste

### 13.3 Essentials of Tritium and Radiocarbon Radiochemistry

### 14 Radiochemistry of Lead, Polonium, Tin, and Selenium

#### 14.1 Polonium – $^{210}$Po

14.1.1 Nuclear Characteristics of $^{210}$Po

14.1.2 Chemistry of Polonium

14.1.3 Determination of $^{210}$Po

14.2 Lead – $^{210}$Pb

14.2.1 Nuclear Characteristics and Measurement of $^{210}$Pb

14.2.2 Chemistry of Lead

14.2.3 Determination of $^{210}$Pb

14.2.3.1 Determination of $^{210}$Pb from the Ingrowth of $^{210}$Po

14.2.3.2 Separation of $^{210}$Pb by Precipitation

14.2.3.3 Separation of $^{210}$Pb by Extraction Chromatography

14.3 Tin – $^{126}$Sn

14.3.1 Nuclear Characteristics and Measurement of $^{126}$Sn

14.3.2 Chemistry of Tin

14.3.3 Determination of $^{126}$Sn

14.4 Selenium – $^{79}$Se

14.4.1 Nuclear Characteristics and Measurement of $^{79}$Se

14.4.2 Chemistry of Selenium

14.4.3 Determination of $^{79}$Se

14.5 Essentials of Polonium, Lead, Tin, and Selenium Radiochemistry

### 15 Radiochemistry of the Actinides

#### 15.1 Important Actinide Isotopes

15.2 Generation and Origin of the Actinides

15.3 Electronic Structures of the Actinides

15.4 Oxidation States of the Actinides

15.5 Ionic Radii of the Actinides

15.6 Major Chemical Forms of the Actinides

15.7 Disproportionation

15.8 Hydrolysis and Polymerization of the Actinides
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 (137Cs and 134Cs)  375
18.5.3.2  Preconcentration of Pu, Am, Np, and 99Tc  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