Contents

Series Foreword: Developments in Forensic Science *Niamh Nic Daéid* ix

Foreword: *Sean Doyle* xi

List of Figures xiii

List of Tables xix

Introduction: Stable Isotope 'Fingerprinting' or Chemical 'DNA': A New Dawn for Forensic Chemistry? xxi

I How It Works 1

I.1 What are Stable Isotopes? 3
I.2 Natural Abundance Variation of Stable Isotopes 5
I.3 Chemically Identical and Yet Not the Same 8
I.4 Isotope Effects, Mass Discrimination and Isotopic Fractionation 10
I.4.1 Physical Chemistry Background 10
I.4.2 Fractionation Factor α and Enrichment Factor ε 11
I.4.3 Isotopic Fractionation in Rayleigh Processes 13
I.4.4 Isotopic Fractionation Summary 14
I.5 Stable Isotopic Distribution and Isotopic Fractionation of Light Elements in Nature 16
I.5.1 Hydrogen 16
I.5.2 Oxygen 19
I.5.2.1 ^{18}O in Bone Bio-apatite and Source Water 20
I.5.2.2 Bone Remodelling 23
I.5.2.3 Bone Diagenesis 24
I.5.2.3.1 Diagenetic Changes of Bio-apatite 24
I.5.3 Carbon 25
I.5.4 Nitrogen 27
I.5.4.1 Food Chain and Trophic Level Shift 29
I.5.4.2 Diagenetic Changes of Structural Proteins 32
I.5.5 Sulfur 33
I.6 Stable Isotope Forensics in Everyday Life 36
I.6.1 'Food Forensics' 37
I.6.1.1 Authenticity and Provenance of Single-Seed Vegetable Oils 38
I.6.1.2 Authenticity and Provenance of Beverages 39
I.6.1.3 Authenticity and Provenance of other Premium Foods 41

I.6.2 Counterfeit Pharmaceuticals 42
I.6.3 Environmental Forensics 43
I.6.4 Wildlife Forensics 46
I.6.5 Anti-Doping Control 47
I.7 Summary of Part I 49
I.8 Set problems 50
References 51

II Instrumentation and Analytical Techniques 65

II.1 Mass Spectrometry versus Isotope Ratio Mass Spectrometry 67
II.2 Instrumentation and δ Notation 72
II.2.1 Dual-Inlet Isotope Ratio Mass Spectrometry 74
II.2.2 Continuous Flow Isotope Ratio Mass Spectrometry 74
II.2.3 Bulk Material Stable Isotope Analysis 77
II.2.4 Compound-Specific Stable Isotope Analysis 78
II.2.4.1 CSIA and Compound Identification 79
II.2.4.2 Position-Specific Isotope Analysis 81
II.2.4.3 CSIA of Polar, Non-Volatile Organic Compounds 83
II.3 Isotopic Calibration and Quality Control in Continuous Flow Isotope Ratio Mass Spectrometry 85
II.3.1 Two-Point or End-member Scale Correction 86
II.3.1.1 Scale Correction of Measured δ^2H Values 87
II.3.1.2 Scale Correction of Measured δ^{13}C Values 88
II.4 Statistical Analysis of Stable Isotope Data within a Forensic Context 91
II.4.1 Chemometric Analysis 91
II.4.2 Bayesian Analysis 94
II.5 Forensic Stable Isotope Analytical Procedures 100
II.5.1 FIRMS Network 101
II.6 Generic Considerations for Stable Isotope Analysis 102
II.6.1 Generic Considerations for Sample Preparation 102
II.6.2 Generic Considerations for BSIA 104
II.6.2.1 Isobaric Interference 104
II.6.3 Particular Considerations for ^{2}H-BSIA 105
II.6.3.1 Keeping Your Powder Dry 105
II.6.3.2 Total δ^2H versus True δ^2H Values 106
II.6.3.2.1 ^{2}H Isotope Analysis of Human Hair 108
II.6.3.3 Ionization Quench Effect 113
II.6.4 Generic Considerations for CSIA 116
II.6.4.1 Isotopic Calibration during GC/C-IRMS 116
II.6.4.2 Isotope Effects in GC/C-IRMS during Sample Injection 117
II.6.4.3 Chromatographic Isotope Effect in GC/C-IRMS 118
II.7 Summary of Part II 121
II.8 Set Problems 122
II.A How to Set Up a Laboratory for Continuous Flow Isotope Ratio Mass Spectrometry 123
II.A.1 Pre-Installation Requirements 124
II.A.2 Laboratory Location 124
II.A.3 Temperature Control 125
II.A.4 Power Supply 125
II.A.5 Gas Supply 126

II.A.6 Forensic Laboratory Considerations 129
II.A.7 Finishing Touches 130
References 136

III Stable Isotope Forensics: Case Studies and Current Research 143
III.1 Forensic Context 145
III.2 Distinguishing Drugs 149
III.2.1 Natural and Semisynthetic Drugs 149
III.2.1.1 Marijuana 149
III.2.1.2 Morphine and Heroin 150
III.2.1.3 Cocaine 152
III.2.2 Synthetic Drugs 154
III.2.2.1 Amphetamines 154
III.2.2.2 MDMA: Synthesis and Isotopic Signature 157
III.2.2.2.1 Three Different Synthetic Routes – Controlled Conditions 157
III.2.2.2.2 One Synthetic Route – Variable Conditions 164
III.2.2.3 Methamphetamine: Synthesis and Isotopic Signature 164
III.2.3 Conclusions 167
III.3 Elucidating Explosives 169
III.3.1 Bulk Isotope Analysis of Explosives and Precursors 170
III.3.1.1 Ammonium Nitrate 171
III.3.1.2 Hexamine, RDX and Semtex 172
III.3.1.3 Hydrogen Peroxide and Peroxides 176
III.3.2 Isotopic Product/Precursor Relationship 179
III.3.3 Potential Pitfalls 182
III.3.4 Conclusions 183
III.4 Matching Matchsticks 184
III.4.1 ^{13}C-Bulk Isotope Analysis 185
III.4.2 ^{18}O-Bulk Isotope Analysis 186
III.4.3 ^{2}H-Bulk Isotope Analysis 187
III.4.4 Matching Matches from Fire Scenes 188
III.4.5 Conclusions 189
III.5 Provenancing People 190
III.5.1 Stable Isotope Abundance Variation in Human Tissue 191
III.5.2 The Skull from the Sea 194
III.5.3 A Human Life Recorded in Hair 197
III.5.4 Found in Newfoundland 201
III.5.5 The Case of 'The Scissor Sisters' 207
III.5.6 Conclusions 211
III.6 Stable Isotope Forensics of other Physical Evidence 214
III.6.1 Microbial Isotope Forensics 214
III.6.2 Paper, Plastic (Bags) and Parcel Tape 215
III.6.2.1 Paper 215
III.6.2.2 Plastic and Plastic Bags 216
III.6.2.3 Parcel Tape 218
III.6.3 Conclusions 221
III.7 Summary 222

III.A 'Play True?': Stable Isotopes in Anti-doping Control or *Quis custodiet ipsos custodes?* 224
III.A.1 Testosterone Metabolism and ^{13}C Isotopic Composition 226
III.A.2 Analytical Methodology: Gas Chromatography and Peak Identification 230
III.B Sample Preparation Procedures 236
III.B.1 Preparing Silver Phosphate from Bio-apatite for ^{18}O Isotope Analysis 236
III.B.2 Acid Digest of Carbonate from Bio-apatite for ^{13}C and ^{18}O Isotope Analysis 238
III.B.3 Standard Protocol for Preparing Hair Samples for ^{2}H Isotope Analysis 240
References 242

Government Agencies and Institutes with Dedicated Stable Isotope Laboratories **253**

Acknowledgements **255**

Recommended Reading **257**

Author's Biography **261**

Index **263**