Contents

Preface xiii
Biography xv
Acknowledgements xvii

1 A Practical Approach to Quantitative Metal Analysis of Organic Matrices Using ICP-OES 1
1.1 Introduction and Basic Overview 1
1.2 Schematic Representation of the Energies Generated by Atomic Spectroscopic Methods 4
1.3 Excitation Energy (Quantum Theory and Atomic Spectra) 5
1.4 Ionisation Energy and Number of Excited Atoms 7
1.5 Width of Atomic Lines 9
  1.5.1 Natural Broadening 9
  1.5.2 Doppler Broadening 9
  1.5.3 Lorentzian Broadening or Pressure Broadening 9
  1.5.4 Holtzmark Broadening or Resonance Broadening 11
  1.5.5 Field Broadening or Stark Broadening 11
  1.5.6 Self-Absorption and Self-Reversal Broadening 11
1.6 Brief Summary of Atomic Spectroscopic Techniques Used for Elemental Analysis 12
  1.6.1 The Atomic Absorption Spectrophotometer 12
  1.6.2 Atomic Fluorescence Spectroscopy 13
  1.6.3 Direct Current Plasma Optical Emission Spectrometry (DCP-OES) 13
  1.6.4 Microwave Induced Plasma (MIP) 14
  1.6.5 Glow Discharge Optical Emission Spectrometry (GD-OES) 15
  1.6.6 Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) 15
1.7 Summary: Applications of Atomic Spectroscopy 16
References 18
2 Instrumentations Associated with Atomic Spectroscopy

2.1 Instrumentation
2.2 Types of Plasma Sources
  2.2.1 Direct Current Plasma Atomic Emission Spectrograph
  2.2.2 Microwave Induced Plasma
  2.2.3 Optical Emission Spectroscopy
2.3 Sample Introduction Systems
  2.3.1 Mechanical Transfer of Sample/Standards Using Peristaltic Pump, Pressure Valves, Motorised Syringes, etc.
  2.3.2 Nebulisers
  2.3.3 Brief Outline of Atomic Spectroscopy Hyphenated Systems
2.4 Spray Chambers
2.5 ICP-OES Torches
2.6 Optics
  2.6.1 Grating Orders
2.7 Signal Detectors
  2.7.1 Photomultiplier Tubes
  2.7.2 Charge Coupled Devices
References

3 Methodologies of Metal Analysis of Organic Matrices Using ICP-OES

3.1 Sample Preparation Techniques and Methods of Analysis
3.2 Defining Goals
3.3 Steps in Chemical Analytical Protocol
3.4 Sampling and its Importance
3.5 Sample Preparation Methods
  3.5.1 Direct Analysis of Organic Solutions
  3.5.2 Sample Dissolution
  3.5.3 Chemical Extraction of Metals from Organic Matrices
  3.5.4 Dry Ashing without Retaining Aids
  3.5.5 Dry Ashing with Retaining Aids
  3.5.6 Acid Digestion Using Microwave Oven
  3.5.7 Oxygen Bomb Flask Combustion (Low Pressure)
  3.5.8 High Pressure Oxygen Combustion
  3.5.9 Sample Preparation Using Fusion Methods
  3.5.10 Analysis Using Slurry Solution Method
  3.5.11 Sample Preparation Using Leaching Method
  3.5.12 Sample Preparation Using a UV Digester
3.6 Non-Spectral Corrections Using ICP-OES
  3.6.1 Effect of Solvents on ICP-OES
  3.6.2 Effect of Viscosity on Signal Response
  3.6.3 Comparison of Nebulisation Efficiency of Solvents Using ICP-OES
  3.6.4 Choice of Carrier Liquid
3.7 Methodology of Measurement
  3.7.1 Choice of Standard Materials
### Contents

3.7.2 Quantitative Analysis Using Calibration Graph Method 82
3.7.3 Quantitative Analysis Using Standard Addition Method 85
3.7.4 Quantitative Analysis Using Internal Standard Method 87
3.7.5 Quantitative Analysis Using Matrix Matching Method 88
3.7.6 Quantitative Analysis Using Flow Injection Technique 89
3.8 Validation of an Analytical Method 90
3.8.1 Method Validation of Analysis of Organic Matrices 91
3.9 Control and Range Charts 99
3.10 Brief Outline of Measurement Uncertainty 101
References 105

4 Analysis of Plastics, Fibres and Textiles for Metals Content Using ICP-OES 107
4.1 A Brief History of Natural and Synthetic Plastic Materials 107
4.2 A Brief History of Chemistry of Plastics 109
4.3 Chemical Structure of Plastics 110
4.4 Polymerization Process of Plastics 111
4.4.1 Polymerisation by Addition Reactions 112
4.4.2 Polymerisation by Condensation Reactions 112
4.5 Additives in Plastics 113
4.6 Methods of Sample Preparation for Metal Content of Plastics, Fibres and Textiles 115
4.6.1 Sample Preparation Using Dissolution Method 115
4.6.2 Sample Preparation Using Dry Ashing Methods 117
4.6.3 Sample Preparation Using Microwave Acid Digestion Method 119
4.6.4 Sample Preparation Using Oxygen Bomb Combustion Method 121
4.7 Comparative Study of Methods of Analysis of Plastic Samples for Metals Content 121
4.8 Study of Leaching of Metals from Plastics 123
4.8.1 Study of Leaching of Metals from Children’s Toys 124
4.9 Analysis for Toxic Metals in Plastics and Non-Electrical Additives Used in Electrical and Electronic Components as Required by RoHS 125
4.9.1 Method for Metal Analysis of Plastics and Non-Electrical Additives Used in Electrical and Electronic Products 127
4.10 Conclusion 131
References 132

5 Metal Analysis of Virgin and Crude Petroleum Products 133
5.1 Introduction 133
5.2 Brief Introduction to Refining Process in the Petroleum Industry 134
5.3 Metals in Crude Oils and Petroleum Products 135
5.4 Requirements for the Determination of Metal Content in Virgin and Crude Oils 136
5.5 Wear Metals and Metal Contaminants in Lubricating Oils 138
5.6 Brief Outline of the Determination of Metals in Organic Materials Using Atomic Spectroscopy Methods 139
5.7 Application of Atomic Spectroscopic Techniques in the Analysis of Virgin and Wear Oils for Metals Content 140
5.7.1 Choice of Solvents Suitable for Metal Analysis of Crude and Lubricating Oils Using ICP-OES 141
5.7.2 Selection of Representative Samples in the Study of Metal Analysis of High Viscosity and Low Viscosity Oil Blends 141
5.7.3 Physical Properties of Selected Solvents for Dissolving High Viscosity and Low Viscosity Oils for Metal Analysis 142
5.7.4 Methods of Sample Preparation for Metal Analysis of High Viscosity and Low Viscosity Oil Blends 142
5.7.5 Long-Term Study of Metal Analysis Using Kerosene, Teralin and Decalin Solvents Using ICP-OES 143
5.7.6 Comparative Study of Non-Destructive Methods of Analysis of Metals ‘Spiked’ in High Viscosity and Low Viscosity Oil Blends Using ICP-OES 144
5.8 Analysis of Type C and D Fractions for Metal Content Using Dry Ashing Method 149
5.9 Analysis of ‘Metal Spiked’ Oil Blends Using Microwave Acid Digestion for Metals Content 150
5.10 Analysis of ‘Metal Spiked’ Oil Blends Using High Pressure Oxygen Combustion for Metals Content 152
5.11 Comparative Study of Analysis of Trace Levels of Toxic Metals Using Microwave Acid Digestion and Oxygen Bomb Combustion 153
5.11.1 Conclusion to Trace Analysis of Toxic Metals in Oil Products 155
5.12 Extraction Method for the Determination of Metals of High Viscosity and Low Viscosity Oil Blends 155
5.13 Analysis of Old Lubricating Oil for Total Metal Content Using a Slurry Method with Internal Standard 156
5.14 Conclusion 158
References 160

6 Metal Analysis of Structural Adhesives 161
6.1 Introduction 161
6.2 Setting and Curing of Adhesives 162
6.3 Introduction to Modern Synthetic Adhesives 162
6.3.1 Cyanoacrylate Adhesives 162
6.3.2 Anaerobic and Acrylic Adhesives 163
6.3.3 Epoxy Structural Adhesives 165
6.3.4 Phenolic Adhesives 167
6.3.5 Polyurethane Adhesives 167
6.4 Metal Salts and Concomitant Metals in Adhesives 168
6.5 Metals Associated with Cyanoacrylate Adhesives 169
6.6 Non-Destructive Methods of Analysis for Metals Content in Cyanoacrylate Adhesives
    6.6.1 General Method 170
    6.6.2 Standard Addition Method 171
    6.6.3 Internal Standard Method 171

6.7 Destructive Methods of Analysis for Metals Content in Cyanoacrylate Adhesives
    6.7.1 Sample Preparation Using Ashing Method 173
    6.7.2 Sample Preparation Using Microwave Acid Digestion 174
    6.7.3 Sample Preparation Using Oxygen Bomb Combustion 174

6.8 Conclusion to Analysis of Cyanoacrylate Products 175

6.9 Metals Associated with Anaerobic Adhesives 176

6.10 Destructive Methods of Sample Preparation for Metals Content in Anaerobic Adhesives
    6.10.1 Ashing Method of Type A and Type B Anaerobic Adhesives 177
    6.10.2 Sample Preparation of Anaerobic Adhesives Using Microwave Acid Digestion 178
    6.10.3 Sample Preparation of Anaerobic Adhesive Using Oxygen Bomb Combustion 180
    6.10.4 Conclusion to Analysis of Anaerobic Adhesives 180

6.11 Metal Analysis of Chemical Raw Materials Used to Manufacture Anaerobic Adhesives
    6.11.1 Column Extraction of Metal from Liquid Monomers 181

6.12 Analysis of Metal Salt Content Dissolved in Aerosol Solvent(s) 182

6.13 A Study of the Effects of Anaerobic Adhesives on Metallic Substrates 183

6.14 Metals Associated with Epoxy Adhesives 186
    6.14.1 Composition of Epoxy Adhesives 187
    6.14.2 Preparation of Epoxy Adhesive ‘Spiked’ with Ge(AcAc)BF₄ 187
    6.14.3 Determination of the Concentration of Ge(AcAc)BF₄ in Epoxy Adhesives Using Non-Destructive Methods 188
    6.14.4 Determination of the Concentration of Ge(AcAc)BF₄ in Epoxy Adhesives Using Destructive Methods 190
    6.14.5 Conclusion of Metal Analysis of Epoxy Adhesives 192

6.15 Metals Associated with Phenolic Adhesives 193
    6.15.1 Preparation of Typical Phenolic Adhesives Containing Calcium and Copper Sulphonate Salts 193
    6.15.2 Non-Destructive Methods of Analysis of Phenolic Adhesives 194

6.16 Metals Associated with Polyurethane Adhesives 194
    6.16.1 Preparation and Analysis of Polyurethane Adhesives Containing Organometallic Catalysts 195

6.17 Conclusion to Metal Analysis of Phenolic and Polyurethane Adhesives 197

References 198
7 Hyphenated and Miscellaneous Techniques Used with ICP-OES 199

7.1 Introduction 199

7.2 Coupling of Flow Injection Analysis with ICP-OES 200

7.2.1 Theory of Flow Injection 201

7.2.2 Configuration of ICP-OES/FIA System 202

7.2.3 Signal Acquisition and Data Management 203

7.2.4 Reproducibility of Measurements Using ICP-OES/FIA 204

7.2.5 Dispersion and Diffusion of ‘Sample Plug’ in a Carrier Stream 205

7.2.6 Metal Analysis of Organic Compounds Using ICP-OES-FIA 206

7.2.7 Effect of Loop Size on Signal Response 207

7.2.8 Comparative Measurements of Peak Height and Peak Area 208

7.2.9 Effect of Viscosity Using ICP-OES/FIA 209

7.2.10 A Study of Solvent Effects Using ICP-OES/FIA 210

7.2.11 Determination of Limit of Detection and Quantification 210

7.2.12 Conclusions of Analysis Using ICP-OES-FIA 211

7.3 Use of Internal Standard(s) with ICP-OES 213

7.3.1 Conclusion to Internal Standard(s) Study 217

7.4 Coupling of Ion Chromatography with ICP-OES 218

7.4.1 Preconcentration of Metals Using Ion Chromatography 220

7.4.2 Analysis of Lanthanide and Transition Metals with ICP-OES/IC 221

7.5 Coupling of Gas Chromatography with ICP-OES or Atomic Emission Detector 222

7.6 Metal Analysis Using ICP-OES Coupled with Electro-Thermal Vaporisation 224

7.7 Surface Analysis Using Laser Ablation with ICP-OES 226

7.8 Determination of Thickener Content of Paints, Pharmaceutical Products and Adhesives Using ICP-OES 227

7.9 Metal Analysis of Metallo-Pharmaceutical Products 230

7.9.1 Metallic Type Antibiotic Drugs 233

7.9.2 Platinum and Palladium Drugs for Cancer Treatments 234

7.10 Metal Analysis of Infusion and Dialysis and Bio-Monitoring Solutions 235

7.11 Organometallic Compounds 236

7.12 Metals and Metalloid Analysis in Support of Forensic Science 237

7.13 Non-Prescription Nutritional Dietary Supplements 239

7.14 Trace Metal Analysis of Foods 244

7.14.1 General Methods of Metal Analysis of Foods 244

7.14.2 Conclusion to Food Analysis 246

References 246

Index 249