

# Contents

|  |    |
|--|----|
| <b>1 Principles of Identification</b>                        | 1  |
| 1.1 Introduction   | 1  |
| 1.2 The Concept of Identification                            | 2  |
| 1.3 General Principles for Identification                    | 4  |
| 1.4 Components of Identification                             | 7  |
| 1.5 Types and Objects of Identification                      | 8  |
| 1.5.1 Main Classification                                    | 8  |
| 1.5.2 Subtypes of Identification                             | 9  |
| 1.5.3 Identifiers  | 11 |
| 1.5.4 Known Chemical Substances                              | 13 |
| 1.6 Principal Approaches to Identification                   | 16 |
| 1.7 Metrological Issues                                      | 16 |
| References   | 20 |
| <b>2 Techniques and Methods of Identification</b>            | 23 |
| 2.1 General  | 23 |
| 2.2 Elemental Analysis                                       | 24 |
| 2.3 Electrochemistry   | 26 |
| 2.4 X-ray Diffraction  | 26 |
| 2.5 Microanalytical Systems                                  | 26 |
| 2.6 Biological Techniques for Chemical Analysis              | 27 |
| 2.7 Chromatography and Related Techniques                    | 27 |
| 2.8 Molecular Spectrometry                                   | 27 |
| 2.8.1 UV–Vis Spectroscopy                                    | 29 |
| 2.8.2 IR Spectroscopy  | 30 |
| 2.8.3 NMR Spectroscopy                                       | 30 |
| 2.8.4 Mass Spectrometry and Chromatography Mass Spectrometry | 31 |
| 2.9 Methods  | 35 |
| 2.10 Preceding and Related Procedures                        | 36 |

|          |  |           |
|----------|--|-----------|
| 2.10.1   | Sample Treatment .....   | 36        |
| 2.10.2   | Quantitative Analysis .....  | 37        |
|          | References .....   | 38        |
| <b>3</b> | <b>Probability, Statistics, and Related Methods .....</b>            | <b>41</b> |
| 3.1      | General .....  | 41        |
| 3.2      | Binary Responses of Qualitative Analysis .....                       | 42        |
| 3.3      | Distribution of Measured Quantities .....                            | 43        |
| 3.4      | Multivariate Statistics and Chemometrics .....                       | 45        |
| 3.5      | Bayesian Statistics .....  | 45        |
| 3.6      | Intellectual Operations, Making Decisions .....                      | 49        |
| 3.6.1    | General .....  | 49        |
| 3.6.2    | Hypotheses Connected with Detection .....                            | 49        |
| 3.6.3    | Identification Hypotheses .....                                      | 51        |
| 3.6.4    | Experimental Hypotheses .....  | 53        |
| 3.6.5    | Statistical Hypotheses .....   | 56        |
|          | References .....   | 59        |
| <b>4</b> | <b>Reliability and Errors of Identification .....</b>                | <b>63</b> |
| 4.1      | General .....  | 63        |
| 4.2      | Formal Statistics of False and True Results .....                    | 66        |
| 4.2.1    | Statistics of False Results .....                                    | 66        |
| 4.2.2    | Statistics of True Results .....                                     | 70        |
| 4.2.3    | Replication .....  | 71        |
| 4.2.4    | Predictive Values .....  | 72        |
| 4.2.5    | Bayesian Approach .....  | 74        |
| 4.2.6    | Prior Data and Replication .....                                     | 75        |
| 4.2.7    | Screening of Real Samples .....                                      | 77        |
| 4.2.8    | Other Indices .....  | 78        |
| 4.3      | Concentration Dependence of Detection and Identification Results ... | 79        |
| 4.3.1    | Binary Responses .....   | 79        |
| 4.3.2    | Measurands .....   | 81        |
| 4.4      | Similarity of Spectra: Match Factors .....                           | 90        |
| 4.4.1    | General .....  | 90        |
| 4.4.2    | Mass Spectrometry .....  | 90        |
| 4.4.3    | NMR Spectroscopy .....   | 96        |
| 4.4.4    | IR Spectroscopy .....  | 97        |
| 4.4.5    | UV-Vis Spectroscopy .....  | 97        |
| 4.4.6    | Meaning of MF .....  | 97        |
| 4.5      | Probabilistic Interpretation of Analytical Data .....                | 98        |
| 4.5.1    | True and False Rates .....   | 98        |
| 4.5.2    | Type I and II Error .....  | 99        |
| 4.5.3    | Confidence Probability .....   | 99        |
| 4.5.4    | Spectral Matching and Probability of Identification .....            | 100       |
| 4.5.5    | Spectral Interpretation .....  | 104       |

|  |            |
|--|------------|
| 4.6 Non-numerical Estimates of Reliability .....                                       | 105        |
| References .....   | 107        |
| <b>5 Target Identification in Methods .....</b>  | <b>115</b> |
| 5.1 General .....  | 115        |
| 5.2 Screening .....  | 116        |
| 5.3 Confirmation .....   | 119        |
| 5.4 EPA Confirmatory Methods .....   | 119        |
| 5.5 Confirmation: Guidances and Methods of Various<br>Organizations and Agencies ..... | 120        |
| 5.5.1 General .....  | 120        |
| 5.5.2 Chromatography .....   | 122        |
| 5.5.3 Mass Spectrometry .....  | 123        |
| 5.5.4 Other Techniques .....   | 131        |
| 5.6 Testing and Criticism of Guidances .....   | 134        |
| References .....   | 137        |
| <b>6 Prior Data for Non-target Identification .....</b>                                | <b>141</b> |
| 6.1 General .....  | 141        |
| 6.2 A Variety of Prior Data .....  | 142        |
| 6.3 Set of Abundant Compounds .....  | 143        |
| 6.4 Occurrence and Co-Occurrence Rates .....   | 148        |
| 6.4.1 Kinds of rates .....   | 148        |
| 6.4.2 Databases .....  | 148        |
| 6.4.3 The Co-Occurrence Rate .....   | 151        |
| 6.4.4 Methodological Aspect .....  | 153        |
| 6.5 Identification Hypotheses and Occurrence/Co-Occurrence Rates ...                   | 153        |
| 6.5.1 Redundant Hypotheses .....   | 154        |
| 6.5.2 Deficient Hypotheses .....   | 155        |
| 6.6 Prior Data Involved in Analytical Procedures .....                                 | 159        |
| 6.6.1 Searches in Databases .....  | 159        |
| 6.6.2 Penalty for Rare Compounds .....   | 160        |
| 6.6.3 Information About the Sample .....   | 160        |
| 6.6.4 Plausibility of Analytical Results .....   | 161        |
| References .....   | 162        |
| <b>7 Non-target Identification. Chromatography and Spectrometry .....</b>              | <b>165</b> |
| 7.1 General .....  | 165        |
| 7.2 Gas Chromatography Retention Indices .....   | 170        |
| 7.2.1 Index Types .....  | 170        |
| 7.2.2 Reference Data .....   | 171        |
| 7.2.3 Choice of Reference Values .....   | 171        |
| 7.2.4 Identification Criteria .....  | 175        |
| 7.2.5 GC-MS .....  | 176        |

|   |            |
|---|------------|
| 7.3 HPLC and Related Techniques .....                           | 177        |
| 7.3.1 Introductory Note .....                                   | 177        |
| 7.3.2 Libraries of UV–Vis Spectra .....                         | 177        |
| 7.3.3 Retention Parameters and Their Reproducibility .....      | 178        |
| 7.3.4 Retention Parameters of Peptides and Proteins .....       | 179        |
| 7.3.5 Migration Parameters in Electromigration Techniques ..... | 180        |
| 7.4 Mass Spectrometry .....                                     | 181        |
| 7.4.1 Libraries .....   | 181        |
| 7.4.2 HRMS .....  | 200        |
| 7.4.3 Spectral Interpretation .....                             | 207        |
| 7.5 IR Spectroscopy .....                                       | 208        |
| 7.6 NMR Spectroscopy .....                                      | 212        |
| 7.7 “Omics” .....   | 214        |
| 7.7.1 Metabolomics .....  | 216        |
| 7.7.2 Proteomics .....  | 217        |
| 7.8 Comparison of Spectral Techniques .....                     | 220        |
| References .....  | 221        |
| <b>8 Chemical Qualitative Analysis II .....</b>                 | <b>235</b> |
| 8.1 General .....   | 235        |
| 8.1.1 Concepts and Definitions .....                            | 235        |
| 8.1.2 Analytical Approaches, Techniques, and Methods .....      | 237        |
| 8.1.3 Reliability of Results .....                              | 240        |
| 8.1.4 Reference Materials .....                                 | 242        |
| 8.1.5 Reference Data on Sample Composition .....                | 242        |
| 8.2 Objects .....   | 243        |
| 8.2.1 Food .....  | 243        |
| 8.2.2 Oil Spills .....  | 244        |
| 8.2.3 Microorganisms .....                                      | 247        |
| 8.2.4 “Omics” .....   | 248        |
| 8.2.5 Other Objects .....                                       | 248        |
| References .....  | 248        |
| <b>9 Good Identification Practice .....</b>                     | <b>255</b> |
| 9.1 General .....   | 255        |
| 9.2 Standardization of Terminology .....                        | 256        |
| 9.3 Metrology for Chemical Identification .....                 | 257        |
| 9.4 Instrumental Parameters .....                               | 260        |
| 9.5 Laboratory Practice and Quality Assurance .....             | 261        |
| 9.6 Validation of Methods and Approaches .....                  | 264        |
| 9.6.1 Methods .....   | 265        |
| 9.6.2 Approaches .....  | 266        |
| 9.7 Proficiency Tests, Interlaboratory Comparisons .....        | 267        |
| References .....  | 270        |
| <b>Index .....</b>  | <b>277</b> |

<http://www.springer.com/978-3-642-15360-0>

Chemical Identification and its Quality Assurance

Milman, B.L.

2011, XVIII, 281 p., Hardcover

ISBN: 978-3-642-15360-0