

CONTENTS

| | |
|---|------|
| Introduction | xiii |
| Chapter 1: History, Theory, and Terminology. | 1 |
| 1.1 Historical Development of IR Spectrometry | 1 |
| 1.2 The Origin and Measurement of Infrared Absorption Spectra | 4 |
| 1.2.1 The Electromagnetic Spectrum | 4 |
| 1.2.2 Energy Associated with Spectra | 6 |
| 1.2.3 Origin of Spectra | 7 |
| 1.2.4 Presentation of Spectra | 10 |
| 1.3 Nomenclature and Symbols | 12 |
| Chapter 2: Instrumentation | 17 |
| 2.1 Spectrometers | 17 |
| 2.1.1 Introduction | 17 |
| 2.1.2 Baird-Atomic | 18 |
| 2.1.3 Beckman | 22 |
| 2.1.4 Hilger Watts | 27 |
| 2.1.5 Cary-White | 31 |
| 2.1.6 Unicam | 35 |
| 2.1.7 Perkin-Elmer | 36 |
| 2.1.8 Other Foreign Spectrometers | 40 |
| 2.1.9 Quartz NIR Spectrometers | 41 |
| 2.1.10 Recent Spectrometer Literature | 43 |
| 2.1.11 Design Considerations | 44 |
| 2.1.11.1 Sources | 45 |
| 2.1.11.2 Detectors | 46 |
| 2.1.11.3 Amplifiers and Recorders | 48 |
| 2.1.11.4 Dispersive Systems | 48 |
| 2.2 Wavelength Calibration | 49 |
| 2.3 Spectrometer Performance Evaluation | 57 |
| 2.4 Photometric Calibration | 69 |
| 2.5 The Laboratory | 71 |

| | |
|---|-----|
| <i>Chapter 3: Techniques</i> | 73 |
| 3.1 Gas Sampling | 73 |
| 3.2 Liquid Sampling | 80 |
| 3.2.1 Absorption Cells | 80 |
| 3.2.1.1 General Discussion | 80 |
| 3.2.1.2 Window Materials | 81 |
| 3.2.1.3 Makers or Vendors of Cells and Cell Components. | 84 |
| 3.2.1.4 Some Special Purpose Cells | 85 |
| 3.2.1.5 Variable-Path Cells. | 87 |
| 3.2.1.6 Low-Temperature Cells | 88 |
| 3.2.1.7 Heated Cells. | 89 |
| 3.2.1.8 Cells for Aqueous Solutions. | 90 |
| 3.2.1.9 Construction and Repair of Cells | 92 |
| 3.2.1.9.1 Cleaving Salt | 93 |
| 3.2.1.9.2 Grinding Salt | 94 |
| 3.2.1.9.3 Polishing | 95 |
| 3.2.1.9.4 Drilling Salt Plates. | 98 |
| 3.2.1.9.5 Assembly and Disassembly | 98 |
| 3.2.1.9.6 Measurement of Cell Thickness | 99 |
| 3.2.2 Solvents | 102 |
| 3.2.2.1 Tabulation of Data | 102 |
| 3.2.2.2 Discussion | 108 |
| 3.2.3 Solution Preparation | 111 |
| 3.2.4 Handling Absorption Cells | 113 |
| 3.3 Solid Sampling | 116 |
| 3.3.1 Pressed Discs | 116 |
| 3.3.1.1 General | 116 |
| 3.3.1.2 Some Qualitative Applications | 121 |
| 3.3.1.3 Some Quantitative Applications | 121 |
| 3.3.1.4 Pretreatment of Alkali Halides | 124 |
| 3.3.1.5 Effects of Grinding | 125 |
| 3.3.1.6 Dies | 127 |
| 3.3.1.7 Presses, Pressing Techniques. | 129 |
| 3.3.1.8 Pellet Holders | 130 |
| 3.3.1.9 Micropellets. | 132 |
| 3.3.1.10 Anomalous Spectra. | 135 |
| 3.3.1.11 Matrices Other Than Halides | 138 |
| 3.3.2 Mull Techniques. | 139 |
| 3.3.2.1 Mineral Oil Mulls | 139 |
| 3.3.2.2 Other Mulling Liquids | 141 |
| 3.3.3 Other Solid-Phase Sampling Methods | 141 |
| 3.3.3.1 The Powder Method | 141 |

| | |
|---|-----|
| 3.3.3.2 Suspensions | 142 |
| 3.3.3.3 Fused Salts | 143 |
| 3.3.3.4 Films | 143 |
| 3.3.3.5 Cast Films. | 143 |
| 3.3.3.6 Lamination and Impregnation. | 144 |
| 3.3.3.7 Sublimation | 144 |
| 3.3.3.8 Pyrolysis. | 144 |
| 3.4 Microtechniques | 145 |
| 3.4.1 Introduction. | 145 |
| 3.4.2 Microcells | 146 |
| 3.4.3 Scale Expansion. | 149 |
| 3.4.4 Beam Condensers. | 151 |
| 3.4.5 Sampling Gas Chromatograph Effluents | 151 |
| 3.4.6 Manipulation of Microsamples | 153 |
| 3.5 Reflectance Measurements | 154 |
| 3.5.1 Diffuse and Specular Reflectance. | 154 |
| 3.5.2 Attenuated Total Reflectance | 156 |
| 3.6 Beam Attenuators | 159 |
| 3.7 Matrix Isolation | 160 |
| 3.8 Polarized Radiation. | 161 |
| 3.9 NIR Techniques. | 162 |
| 3.9.1 Sample Preparation | 162 |
| 3.9.2 Absorption Cells | 163 |
| 3.9.3 Solvents for the NIR | 164 |
| 3.9.3.1 Tabular Data | 164 |
| 3.9.3.2 Discussion. | 166 |
| 3.10 Far IR Techniques | 168 |
| 3.11 Derivative Spectroscopy | 170 |
| 3.12 Miscellaneous Accessories | 172 |
| 3.12.1 Chart Paper. | 172 |
| 3.12.2 Recorder Pens and Inks | 172 |
| 3.12.3 Purging the Spectrometer. | 172 |
| 3.12.4 External Source | 173 |
| 3.12.5 External Detector | 173 |
| <i>Chapter 4: Qualitative Analysis</i> | 175 |
| 4.1 Spectra-Structure Correlation. | 175 |
| General Discussion. | 175 |
| Table 4.1.1 C—H Stretching Vibrations | 190 |
| Table 4.1.2 C—H Deformation and Skeletal Vibrations | 192 |
| Table 4.1.3 C—C, C=C, and C≡C Vibrations | 195 |
| Table 4.1.4 N—H Stretching Vibrations | 197 |

| | |
|---|------------|
| Table 4.1.5 N—H Deformation Vibrations | 198 |
| Table 4.1.6 Some Charged Amine Vibrations | 198 |
| Table 4.1.7 Vibrations Involving Nitrogen and Oxygen. . . | 199 |
| Table 4.1.8 Miscellaneous Vibrations Involving Nitrogen. | 201 |
| Table 4.1.9 C—O Stretching and Related Vibrations | 202 |
| Table 4.1.10 C=O Stretching Vibrations | 204 |
| Table 4.1.11 OH Stretching Vibrations | 208 |
| Table 4.1.12 Vibrations Involving Phosphorus | 210 |
| Table 4.1.13 Vibrations Involving Sulfur | 211 |
| Table 4.1.14 Vibrations Involving Silicon | 212 |
| Table 4.1.15 Vibrations Involving Halogens | 213 |
| Table 4.1.16 Some Organic Vibrations of Boron | 213 |
| Table 4.1.17 Some Inorganic Vibrations | 214 |
| Table 4.1.18 Nonstandard Abbreviations Used in Spectra- Structure Correlation Tables | 216 |
| Artifacts | 216 |
| Examples | 221 |
| 4.2 Data Storage and Retrieval | 224 |
| Sadtler Catalog | 224 |
| DMS System | 234 |
| IRDC Cards | 235 |
| Wyandotte-ASTM Punched Card Index | 235 |
| ASTM Infrared Optical Coincidence Index | 236 |
| Chapter 5: Quantitative Analysis | 241 |
| 5.1 One Component | 241 |
| 5.1.1 The Laws of Absorption | 241 |
| 5.1.2 One Component, No Irrelevant Absorption | 245 |
| 5.1.3 One Component, Basing Point Correction | 247 |
| 5.1.4 Baseline Method | 248 |
| 5.2 Multicomponent Analysis | 249 |
| 5.3 Differential Analysis | 255 |
| 5.4 Kinetic Studies | 266 |
| 5.5 Hydrogen Bonding | 267 |
| 5.6 Temperature Effect | 268 |
| 5.7 Finite Slit Width | 269 |
| 5.8 Effect of Stray Light | 272 |
| 5.9 Reproducibility | 273 |
| Chapter 6: Applications | 277 |
| 6.1 Acids (Mineral) | 277 |
| 6.2 Acids (Carboxylic) | 277 |
| 6.3 Adsorbed Phases | 279 |

| | |
|---|-----|
| 6.4 Air Analysis | 279 |
| 6.5 Alcohols | 280 |
| 6.6 Aldehydes | 281 |
| 6.7 Amides | 282 |
| 6.8 Amines | 283 |
| 6.9 Boron Compounds | 285 |
| 6.10 Bromine Compounds | 285 |
| 6.11 Carbohydrates | 286 |
| 6.12 Carbonyl Compounds | 286 |
| 6.13 Chlorine Compounds (Organic) | 287 |
| 6.14 Coatings | 289 |
| 6.15 Cosmetics | 290 |
| 6.16 Detergents | 290 |
| 6.17 Dyes, Dye Intermediates, and Pigments | 291 |
| 6.18 Essential Oils | 293 |
| 6.19 Esters | 295 |
| 6.20 Ethers | 296 |
| 6.21 Fats and Oils | 297 |
| 6.22 Fluoroorganics | 301 |
| 6.23 Foods | 301 |
| 6.24 Gas Analysis | 302 |
| 6.25 Hydrocarbons, Aromatic (Monocyclic) | 304 |
| 6.26 Hydrocarbons, Nonaromatic | 306 |
| 6.27 Hydrocarbons, Polynuclear | 308 |
| 6.28 Hydroxyl | 309 |
| 6.29 Inorganic Compounds | 310 |
| 6.30 Iodine and Iodine Compounds | 314 |
| 6.31 Ketones | 315 |
| 6.32 Lactams and Lactones | 316 |
| 6.33 Metal Organics | 316 |
| 6.34 Miscellaneous | 317 |
| 6.35 Nitrates, Nitro and Nitroso Compounds, and Related Substances | 317 |
| 6.36 Nitriles and Related Compounds | 319 |
| 6.37 Nitrogen | 320 |
| 6.38 Nitrogen Compounds (Polycyclic) | 320 |
| 6.39 Oximes | 321 |
| 6.40 Oxirane Compounds | 321 |
| 6.41 Paper and Wood | 321 |
| 6.42 Peroxides and Hydroperoxides | 322 |
| 6.43 Pesticides | 322 |
| 6.44 Petroleum Products | 326 |

| | | |
|------|---|-----|
| 6.45 | Pharmaceuticals | 327 |
| 6.46 | Phenols | 332 |
| 6.47 | Phosphoro-Organics. | 334 |
| 6.48 | Plastics | 335 |
| 6.49 | Polymorphism. | 339 |
| 6.50 | Polyurethanes | 340 |
| 6.51 | Pyridine, Quinoline, and Related Compounds. | 340 |
| 6.52 | Rubber and Other Elastomers | 341 |
| 6.53 | Quinones | 343 |
| 6.54 | Silicones | 343 |
| 6.55 | Sulfur Compounds | 344 |
| 6.56 | Terpenes | 345 |
| 6.57 | Textiles | 345 |
| 6.58 | Thickness Measurement | 346 |
| 6.59 | Tobacco | 347 |
| 6.60 | Water | 347 |
| | <i>Chapter 7: Literature</i> | 351 |
| 7.1 | Books | 351 |
| 7.2 | Spectrum Atlases | 354 |
| 7.3 | Bibliographies | 356 |
| 7.4 | Review Papers | 357 |
| 7.5 | Journals | 359 |
| | References. | 361 |
| | Appendix I: Table of Reciprocals | 405 |
| | Appendix II: Conversion from Percent Transmittance to Absorbance | 413 |
| | Index. | 421 |