

## Contents

1. <i>Basis for Identification</i>	1
Identification, 1	
The Systematic Approach, 1	
Microscopic and Physical Methods, 3	
Analytical Procedures, 4	
Approach to Student "Unknowns" and Method of Using the Text, 5	
Laboratory Notebook and Reports, 7	
2. <i>Fractionation and Purification Procedures</i>	9
Introduction, 9	
Selection of Fractionation Procedures, 10	
CRYSTALLIZATION, 11	
Selection of Solvents, 11	
Measurement of Solvents and Other Liquids, 14	
Preparation of Solutions for Crystallization, 15	
Filtration of the Hot Solution and Formation of Crystals, 17	
Drying of Crystals, 23	
DISTILLATION, 26	
Apparatus and Procedure for Simple Distillation at Atmospheric Pressure, 27	
Apparatus and Procedure for Fractional Distillation, 30	
Apparatus and Procedure for Distillation under Reduced Pressure, 33	
Apparatus and Procedure for Steam Distillation, 35	
SUBLIMATION, 35	
EXTRACTION, 37	
3. <i>Determination of Physical Constants in Analysis of Organic Substances</i>	41
Melting Points, 41	
Boiling Points, 52	
Refractive Indices, 54	
Density, 58	
Optical Rotation, 61	
Molecular Weights, 62	
4. <i>Preliminary Steps in the Examination of an Unknown Substance</i>	67
ANALYSIS FOR ELEMENTS, 68	
Detection of Carbon, 69	

- ↘ Fusion with Sodium, 69
  - ↘ Detection of Sulfur, 71
  - ↘ Detection of Nitrogen, 72
  - ↘ Detection of Halogens, 72
  - ↘ Detection of Oxygen, 75
  - ↘ Test for Peroxides, 76
5. *Classification by Solubility and by Acid-Base Character* 77
- PART I: CLASSIFICATION BY SOLUBILITY, 78
- Molecular Structure and Interactions, 78
  - ↘ Solubility in Water, 81
  - ↘ Solubility in Ethyl Ether, 84
  - ↘ Solubility in Dilute Hydrochloric Acid, 85
  - ↘ Solubility in Dilute Sodium Hydroxide, 88
  - ↘ Solubility in Dilute Sodium Bicarbonate, 89
  - ↘ Solubility in Concentrated Sulfuric Acid, 91
  - ↘ Determining the Solubility for Classification, 92
  - ↘ Designations for the Solubility Divisions, 93
- PART II: CLASSIFICATION BY THE ACID-BASE CHARACTER, 95
- Mixed Indicators in Nonaqueous Solvents, 98
  - Davidson's Indicator Systems, 99
  - Procedures for Using the Indicators, 101
6. *Tests for the Classification of an Unknown* 105
- PART I: AN INVENTORY AND A FORWARD LOOK, 105
- P-1 Gross Observations, 106
  - ↘ P-2 Tests for Aromatic Structure, 107
  - ↘ P-3 The Ignition Test, 109
  - P-4 Tests for Salts, 109
  - P-5 Tests for Active Unsaturation, 111
  - ↘ P-6 The Iodoform Formation Test, 112
- PART II: TESTS FOR SPECIAL CLASSES, 113
- 6.1 Acids and Anhydrides, 114
  - 6.2 Acid Halides, 117
  - ↘ 6.3 Alcohols, 119
  - 6.4 Alkyl and Aryl Halides, 122
  - 6.5 Unsubstituted Amides, 123
  - 6.6 Substituted Amides, 126
  - 6.7 Amines, 128
  - ↘ 6.8 Carbohydrates, 134
  - ↘ 6.9 Carbonyl Compounds, 136
  - 6.10 Esters, 140
  - 6.11 Ethers, 141

- 6.12 Hydrazines, 142
- 6.13 Hydrocarbons, 142
- 6.14 Nitrates and Nitrites, 143
- 6.15 Nitriles, 144
- 6.16 Nitro Compounds, 144
- 6.17 Nitroso Compounds, 146
- 6.18 Oximes, Hydrazones, and Semicarbazones, 147
- 6.19 Phenols, 147
- 6.20 Sulfides, Disulfides, and Sulfones, 150
- 6.21 Thiols (Mercaptans and Thiophenols), 151

7. *Physical Methods for the Determination of Functional Groups in Organic Compounds*

157

CHROMATOGRAPHIC PROCEDURES, 157

Introduction, 157

Principle of Chromatographic Fractionation, 158

General Procedure for Paper Chromatography, 160

Application of the Sample on Paper, 162

Selection of Solvent Systems for Development of Paper Chromatograms, 163

Elution of Spots, 163

Test Tube Technique for Paper Chromatography, 165

Location of Zones on Paper Chromatograms, 166

Use of Paper Chromatography in Identification Work, 167

Mixed  $R_f$  Values, 168

INFRARED SPECTROGRAPHY, 168

Introduction, 168

Infrared Radiation and Units of Expression, 169

Origin of Infrared Absorption Spectra, 169

Measurement of Infrared Absorption Spectra, 170

Characteristic Infrared Absorption Bands of Functional Groups, 173

INTERPRETATION OF INFRARED SPECTRA, 176

Introduction, 176

Alkanes, Alkenes, Alkynes, and Aromatic Structures, 179

Carbon-Halogen Functions, 180

Carbon-Oxygen Functions—Carbonyl Compounds, 181

Carbon-Oxygen Functions—Hydroxy Compounds: Alcohols, 181

Carbon-Nitrogen Functions, 184

Sulfur Functions, 186

APPLICATION OF INFRARED SPECTRA TO STUDENTS' UNKNOWNNS, 186

Student's Report on Unknown A, 186

Student's Report on Unknown B, 187

8. *Separation of Mixtures*

193

General Principles, 193

Preliminary Tests for a General Mixture, 194

Chemical Tests, 195	
A General Procedure for the Separation of Mixtures, 199	
Suggestions for Separating Intra-class Mixtures, 205	
Alternate Methods for the Separation of Mixtures, 208	
Separation of Mixtures by Chromatography, 209	
The Use of Ion Exchange Resins, 212	
9. <i>Coordination of Data and Tentative Identification of Unknown</i>	215
Correlation and Interpretation of Data and Literature Search, 216	
Use of Library, 216	
10. <i>Preparation of Derivatives: I</i>	225
Introduction, 225	
Selection of Derivatives, 225	
Recommended Derivatives, 226	
Other Derivatives, 227	
Precautions for Beginners in the Preparation of Small Quantities of Derivatives, 227	
ACETALS, 228	
Hydrolysis of Acetals, 228	
ACID ANHYDRIDES AND ACID HALIDES, 229	
ACIDS, 229	
<i>Amino Acids</i> , 229	
<i>N</i> -Acyl and <i>N</i> -Aroyl Derivatives of Amino Acids, 230	
Chromatographic Detection of Amino Acids, 233	
<i>Carboxylic Acids</i> , 236	
Anilides, <i>p</i> -Toluidides, and Other Substituted Amides of Carboxylic Acids, 236	
Solid Esters of Carboxylic Acids, 243	
ALCOHOLS, 247	
3,5-Dinitrobenzoates and <i>p</i> -Nitrobenzoates, 249	
$\alpha$ -Naphthylurethans, 252	
Benzoates of Polyhydroxy Compounds, 254	
ALDEHYDES, 257	
Phenylhydrazones, 258	
2,4-Dinitrophenylhydrazones, 259	
Semicarbazones, 261	
Dimethone Derivatives, 262	
AMIDES, IMIDES, AND UREAS, 267	
Characterization by Hydrolysis, 267	
Xanthyl Derivatives of Amides, 269	
Mercuric Salts and Other Derivatives of Amides, 270	
AMINES, 271	
Benzamides of Amines, 271	
Sulfonamides of Amines, 274	
Substituted Thioureas of Amines, 275	

- Quaternary Ammonium Salts of Amines, 276
- CARBOHYDRATES, 280
- Substituted Phenylhydrazones, Osazones, and Osotriazoles, 281
- Specific Rotation of Carbohydrates and Their Derivatives, 286
- ESTERS, 287
- Derivatization of the Acidic Part of an Ester Without Hydrolysis, 289
- Derivatization of the Acidic and Alcoholic Components After Hydrolysis, 291
- Derivatization of the Alcoholic Component, 292
- Examples of Complete Characterization of Esters, 292
- ETHERS, 293
- Derivatives from Aliphatic Ethers, 294
- Derivatives from Aromatic Ethers, 296

*Preparation of Derivatives: II*

301

- HALOGEN COMPOUNDS, 301
- Alkyl and Cycloalkyl Halides*, 302
- S-Alkyl Isothiuronium Picrates, 302
- Picrates of  $\beta$ -Naphthyl Ethers, 304
- Aryl Halides*, 304
- Nitro Derivatives of Aryl Halides, 305
- Sulfonamides of Aryl Halides, 307
- HYDROCARBONS, 309
- Alkanes, Cycloalkanes, Alkenes, and Alkynes*, 309
- Oxidation of a Cycloalkane to a Dicarboxylic Acid, 311
- Derivatives of Olefins and Terpenes, 312
- Aromatic Hydrocarbons*, 313
- Nitration of Aromatic Hydrocarbons, 313
- Picrates and 2,4,7-Trinitrofluorenone Adducts of Aromatic Hydrocarbons, 315
- Oxidation of Side Chains, 315
- KETONES, 318
- Oximes, 319
- Substituted Hydrazones, Semicarbazones, and Other Derivatives, 319
- NITROGEN FUNCTIONS, 321
- Nitriles*, 321
- Hydrolysis of Nitriles to Carboxylic Acids, 321
- Reduction of Nitriles to Amines and Their Characterization by Preparation of Substituted Thioureas, 323
- Nitro Compounds*, 324
- Derivatization of Nitro Compounds by Reduction to Amines, 325
- Derivatization by Oxidation of Side Chains, 326
- Derivatization of Nitro Compounds by Further Nitration, 327
- PHENOLS, 328
- 3,5-Dinitrobenzoates, 329
- Urethans, 329
- Aryl Oxyacetic Acids, 331

SULFUR FUNCTIONS, 333

Bromo Derivatives, 332

*Sulfonamides and Sulfonchlorides*, 333

*Sulfonic Acids*, 335

*S-Benzylisothiuronium Derivatives of Sulfonic Acids*, 336

Aryl Amine Salts of Sulfonic Acids, 337

*Thioethers*, 338

*Thiols (Mercaptans and Thiophenols)*, 339

Thioethers, 339

Thioesters, 340

*Tables of Organic Compounds with Their Constants and Derivatives*, 343

*Appendix*, 427

*Index of Text*, 439

*Index of Tables*, 451