

## CONTENTS

|   |    |
|---|----|
| INTRODUCTION  | 1  |
| THE BALANCE   | 6  |
| Required precision  | 6  |
| The microanalytical balance   | 7  |
| Description, 7. Installation, 7. Cleaning, 9.   |    |
| The ordinary analytical balance   | 11 |
| Remarks   | 12 |
| Literature  | 12 |
| WEIGHING  | 15 |
| Microanalytical balance   | 15 |
| Zero reading, 16. Sensitivity, 17. Precision, 17. Sensitivity cor-<br>rection table, 21. Adjustment of sensitivity, 21.   |    |
| Ordinary analytical balance   | 22 |
| Zero reading, 23. Sensitivity, 23. Precision, 23.   |    |
| Actual weighing, 26. Microanalytical balance, 27. Ordinary analytical<br>balance, 28. Calibration of weights, 28. Preparation of counter-<br>poises, 30.  |    |
| Literature  | 31 |
| WEIGHING EQUIPMENT  | 33 |
| Forceps, 33. Spatula, 33. Probing wire, 33. Camel's-hair brush,<br>33. Desiccator, 34. Platinum wire, 34. Metal tares, 34. Tare<br>bottles, 34. Rack, 34. Chamois, flannel, cotton, 35. Brushes,<br>35.   |    |
| Literature  | 35 |
| LABORATORY UTENSILS   | 36 |
| Microburners, 36. Gas burners, 36. Drying blocks, 36. Hand<br>centrifuge, 37. Pellet press, 37. Glass-cutting devices, 38. Cap-<br>illary pipets, 38. Precision pipets, 38. Centrifuge cones, 39.<br>Wash bottles, 39. Miscellaneous, 40.   |    |
| Literature  | 40 |
| PREPARATION AND WEIGHING OF A SAMPLE FOR ANALYSIS   | 42 |
| General directions, 42. Sampling, 42. Weighing of the sample, 42.<br>Weighing boats, 42. Weighing tube, 44. Weighing cups and<br>bottles, 45. Capillaries for various wet combustion methods,<br>45. Capillaries for the vaporimetric molecular-weight determi-<br>nation, 46. Weighing pipets, 46. |    |

|   |           |
|---|-----------|
| Hygroscopic material  | 48        |
| Literature  | 49        |
| <b>STANDARD SOLUTIONS</b>   | <b>51</b> |
| Principle   | 51        |
| Apparatus, 51. Microburet, 51. Buret stand, 52. Dropping bottles, 53. Titration flask, 53. Steaming apparatus, 53.            |           |
| Reagents, 53. Potassium biiodate, 53. Sodium carbonate, 54.   |           |
| Indicator solutions, 54. Phenolphthalein, 54. Methyl red, 54. Starch solution, 54.  |           |
| 0.01 <i>N</i> Potassium biiodate solution   | 54        |
| 0.01 <i>N</i> Hydrochloric acid solution  | 55        |
| 0.01 <i>N</i> Sodium hydroxide solution   | 56        |
| 0.01 <i>N</i> Sodium thiosulfate solution   | 56        |
| Remarks, 57. Standard solutions, 57. Indicators, 57. Microburets, 58.   |           |
| Literature  | 59        |
| <b>ELEMENTARY ANALYSIS</b>  | <b>62</b> |
| <b>I. DETERMINATION OF METALS</b>   | <b>62</b> |
| Principle   | 62        |
| Apparatus, 62. Micromuffle, 62. Platinum cylinder, 63.  |           |
| Reagents, 63. Sulfuric acid, 63. Nitric acid, 63.   |           |
| Procedure, 63. Calculation, 64.   |           |
| Remarks   | 64        |
| Literature  | 65        |
| <b>II. DETERMINATION OF NEUTRALIZATION EQUIVALENT</b>   | <b>66</b> |
| Principle   | 66        |
| Apparatus   | 66        |
| Reagents, 66. Neutral alcohol solution, 66.   |           |
| Procedure, 67. Calculation, 67.   |           |
| Remarks   | 68        |
| Literature  | 68        |
| <b>III. VOLUMETRIC DETERMINATION OF AMINOID NITROGEN</b>  | <b>69</b> |
| Principle   | 69        |
| Apparatus, 69. Distillation apparatus, 69. Digestion oven, 70. Digestion flask, 71. Titration equipment, 71.                  |           |
| Reagents, 71. Perhydrol, 71. Catalyzers, 71.  |           |
| Procedure, 72. Digestion, 72. Distillation, 73. Titration, 74. Calculation, 74.   |           |
| Remarks   | 75        |
| Literature  | 77        |
| <b>IV. GASOMETRIC DETERMINATION OF NITROGEN</b>   | <b>79</b> |
| Principle   | 79        |
| Apparatus, 79. Kipp generators, 79. Preparation of Kipp generators, 81. Microbubbles, 82. Gasometer, 82. Combustion tube, 83. |           |

# CONTENTS

ix

|  |            |
|--|------------|
| Heating unit, 84. Nitrometer, 85. Calibration table, 87. Introduction funnel, 88.  |            |
| Reagents, 88. Marble, 88. Copper oxide, 88.  |            |
| Procedure, 89. Introduction of temporary filling and sample, 89. Preparation for the combustion, 91. First combustion, 92. Second combustion and sweeping out, 92. Determination of volume of nitrogen, 93. Determination of the air and adsorption error, 94. Calculation, 95.  |            |
| Remarks, 95. Dry ice carbon dioxide generator, 97.   |            |
| Literature   | 99         |
| <b>V. CARBON AND HYDROGEN DETERMINATION</b>  | <b>101</b> |
| Principle  | 101        |
| Apparatus, 101. Oxygen tank, 101. Pressure regulator, 101. Pre-heater, 103. Bubble counter and U-tube, 104. Heating unit, 106. Heating mortar, 106. Combustion tube, 107. Combustion-tube fillings, 107. Simple filling, 107. Simple band filling, 107. Combination filling, 107. Combination band filling, 107. Filling the combustion tube, 108. Conditioning the combustion tube, 110. Absorption tubes, 111. Water absorption tube, 112. Carbon dioxide absorption tube, 113. Counterpoising the absorption tubes, 113. Drying tube and safety tube, 114. Mariotte flask, 114. Aspirator, 115. Miscellaneous, 116. |            |
| Assembling the combustion train  | 118        |
| Reagents, 121. Anhydrous, 121. Ascarite, 121. Copper oxide, 122. Lead peroxide, 122.   |            |
| Testing the apparatus, 123. Wiping and weighing the absorption tubes, 123. Blank test on the aspirator, 125. Blank combustion tests, 126.  |            |
| Actual analysis, 128. Preparation of the sample, 129. Combustion, 129. Attaching the absorption tubes, 129. Combustion of sample, 129. Removal of absorption tubes, 131. Calculation, 132.   |            |
| Remarks, 132. Dry combustion method, 132. Wet combustion methods, 139. Gas volumetric and manometric methods, 140. Semi-micro dry combustion methods, 145.   |            |
| Literature   | 146        |
| <b>VI. DETERMINATION OF HALOGENS</b>   | <b>151</b> |
| Gravimetric Methods  | 151        |
| Wet Combustion (Carius) Method   | 151        |
| Principle  | 151        |
| Apparatus, 151. Furnace, 151. Pressure tubes, 151. Filter tubes, 152. Filtration apparatus, 154.   |            |
| Reagents, 154. Concentrated nitric acid, 154. Silver nitrate, 154.   |            |
| Procedure, 154. Preparation and weighing of the sample, 154. Filling the pressure tube, 155. Sealing the pressure tube, 155. Digestion, 156. Opening the pressure tube, 156. Filtering the precipitate, 157. Dissolving the precipitate, 158. Calculation, 160.  |            |
| Dry Combustion Method  | 160        |
| Principle  | 160        |

|  |     |
|--|-----|
| Apparatus, 160. Oxygen tank and gas wash bottle, 160. Combustion-spiral tube, 160. Combustion stand, 160. Platinum contacts, 160. Precipitation tubes, 160. Filter tubes, filtration apparatus, wash bottles, 161.   |     |
| Reagents, 161. Sodium bisulfite solution, 161.   |     |
| Procedure, 162. Preparation and filling of the combustion tube, 162. Combustion, 162. Precipitation and filtration, 163. Iodine, 164. Calculation, 164.  |     |
| Fusion Method . . . . .  | 165 |
| Principle . . . . .  | 165 |
| Apparatus, 165. Bomb, 165. Precipitation tubes, filter tubes, filtration apparatus, 165.   |     |
| Reagents, 166. Sodium peroxide, 166.   |     |
| Procedure, 166. Mixing, 166. Fusion, 166. Precipitation and filtration, 166. Chlorine, 167. Bromine and iodine, 167. Calculation, 167.   |     |
| Titrimetric Methods . . . . .  | 168 |
| Chlorine and Bromine . . . . .   | 168 |
| Principle . . . . .  | 168 |
| Apparatus, 168. Oxygen tank and gas wash bottle, 168. Combustion apparatus, 168. Heating block, 169. Titration equipment, 169.   |     |
| Reagents, 169. Potassium dichromate, 169. Silver dichromate, 169.  |     |
| Procedure, 170. Preparation and filling of the apparatus, 170. Heating and titration, 171. Calculation, 172.   |     |
| Iodine . . . . .   | 172 |
| Principle . . . . .  | 172 |
| Apparatus, 172. Oxygen tank and gas wash bottle, 172. Combustion tube, 172. Combustion stand, 172. Platinum contacts, 172. Precipitation tubes, 172. Titration equipment, 172.   |     |
| Reagents, 173. Sodium acetate solutions, 173. Bromine, 173.  |     |
| Procedure, 173. Combustion, 173. Transfer and titration, 174. Calculation, 175.  |     |
| Remarks, 175. Reviews and reports, 175. Wet combustion methods, 175. Dry combustion methods, 177. Hydrogenation method, 177. Fusion method, 177. Calcination method, 177. Ionizable halogen, 178. Simultaneous determination of chlorine and bromine, 178. Special iodine methods, 178. Filter tube improvements and substitutions, 178. |     |
| Literature . . . . .   | 179 |
| VII. DETERMINATION OF SULFUR . . . . .   | 182 |
| Gravimetric Wet Combustion (Carius) Method . . . . .   | 182 |
| Principle . . . . .  | 182 |
| Apparatus, 182. Furnace, pressure tubes, 182. Filter funnel, 182. Evaporation apparatus, 182. Porcelain crucible and immersion filter, 183. Suction flask, 184.  |     |
| Reagents, 185. Barium chloride, 185.   |     |
| Procedure, 185. Preparation and weighing of the sample, 185. Filling of the pressure tube, 185. Sealing the pressure tube, 185. Di-  |     |

|   |     |
|---|-----|
| gestion process, 185. Opening the pressure tube, 185. Transfer of the reaction product, 185. Evaporation of the sulfate solution, 186. Transfer of the sulfate, 186. Precipitation, 186. Filtration, 186. Drying and ignition, 187. Calculation, 188. |     |
| Titrimetric Dry Combustion Method . . . . .   | 188 |
| Principle . . . . .   | 188 |
| Apparatus, 188. Oxygen tank, gas wash bottle, combustion-spiral tube, combustion stand, and platinum contacts, 188. Titration equipment, 188.   |     |
| Reagents, 188. Hydrogen peroxide solution, 188.   |     |
| Procedure, 188. Combustion, 188. Titration, 189. Calculation, 190.  |     |
| Remarks, 190. Wet combustion methods, 190. Dry combustion methods, 191. Fusion, 193. Filtration, 193. Titration, 195.   |     |
| Literature . . . . .  | 197 |
| VIII. DETERMINATION OF PHOSPHORUS . . . . .   | 199 |
| Principle . . . . .   | 199 |
| Apparatus . . . . .   | 199 |
| Reagents, 200. Molybdate solution, 200. Nitric-sulfuric acid mixture, 200.  |     |
| Procedure, 200. Wet combustion, 200. Fusions, 201. Precipitation, 201. Filtration, 202. Calculation, 202.   |     |
| Remarks . . . . .   | 202 |
| Literature . . . . .  | 204 |
| IX. OTHER ELEMENTS . . . . .  | 205 |
| Arsenic, 205. Boron, 206. Copper, 206. Mercury, 206. Oxygen, 207. Selenium, 208. Silver, 208.   |     |
| Literature . . . . .  | 208 |
| DETERMINATION OF THE MOLECULAR WEIGHT . . . . .   | 210 |
| I. EBULLIOSCOPIC METHODS . . . . .  | 210 |
| Principle . . . . .   | 210 |
| Apparatus, 210. Pregl's apparatus, 210. Rieche's apparatus, 211. Sucharda-Bobranski-Schmitt apparatus, 212. Precision pipets, 213.  |     |
| Solvents . . . . .  | 213 |
| Procedure, 213. Preparation of the sample, 213. Preparation of the apparatus, 214. Pregl and Rieche apparatus, 214. Sucharda-Bobranski-Schmitt apparatus, 214. Calculation, 215.  |     |
| Remarks . . . . .   | 215 |
| Literature . . . . .  | 216 |
| II. CRYOSCOPIC METHOD . . . . .   | 217 |
| Principle . . . . .   | 217 |
| Apparatus . . . . .   | 217 |
| Solvents, 217. Camphor, 217.  |     |
| Procedure, 218. Calculation, 219.   |     |
| Remarks . . . . .   | 219 |
| Literature . . . . .  | 220 |

|   |     |
|---|-----|
| III. VAPORIMETRIC METHOD . . . . .  | 221 |
| Principle . . . . .   | 221 |
| Apparatus, 221. For low-boiling substances, 221. For high-boiling substances, 221.  |     |
| Procedure, 223. Low-temperature apparatus, 223. Preparation of the sample, 223. Heating, 224. High-temperature apparatus, 224. Preparation of the sample, 224. Filling the apparatus, 225. Heating, 226. Cleaning the apparatus, 226. Correction for heat expansion, 226. Calculation, 227. |     |
| Remarks . . . . .   | 227 |
| Literature . . . . .  | 228 |
| IV. ISOTHERMIC METHOD . . . . .   | 230 |
| Principle . . . . .   | 230 |
| Apparatus, 230. Microscope, 230. Glass plate, 230. Capillaries, 231. Colored glass thread, 231. Desiccator tubes, 231. Glass wool, 231. Adhesive tape, 231. Volumetric flasks, 231. Pipets, 231. Hand centrifuge, 231. Vacuum pump, 231.  |     |
| Reagents, 231. Standard solutions, 231.   |     |
| Procedure, 232. Preparation of the sample solution, 232. Preparation of the capillaries, 233. Filling the desiccator tube, 233. Mounting the desiccator tubes, 233. Method of reading, 234. Interpretation of readings, 236. Calculation, 236.  |     |
| Remarks . . . . .   | 237 |
| Literature . . . . .  | 238 |
| STRUCTURE ANALYSIS . . . . .  | 239 |
| I. DETERMINATION OF ALKOXYL AND ALKIMIDE GROUPS . . . . .   | 239 |
| Alkoxy Groups . . . . .   | 239 |
| Principle . . . . .   | 239 |
| Apparatus, 239. Alkoxy apparatus, 239. Kipp generator, 241. Flasks, 241. Buret, 241.  |     |
| Reagents, 241. Hydriodic acid, 241. Washer solution, 241.   |     |
| Procedure, 242. Preparation of the sample, 242. Introduction of the sample and solubility tests, 242. Preparation of the apparatus and heating, 242. Titration, 243. Calculation, 244.  |     |
| Alkimide Groups . . . . .   | 244 |
| Principle . . . . .   | 244 |
| Apparatus . . . . .   | 244 |
| Reagents, 245. Gold chloride, 245. Ammonium iodide, 245.  |     |
| Procedure, 246. Preparation of the sample and apparatus, 246. Heating, 246. Titration, 246. Calculation, 246.   |     |
| Remarks, 247. <i>O</i> -Alkyl, 247. Iodometric methods, 247. Gravimetric methods, 248. <i>S</i> -Alkyl, 249. <i>N</i> -Alkyl, 249. Hydriodic acid, 249. Other methods, 250.   |     |
| Literature . . . . .  | 250 |
| II. DETERMINATION OF ACYL GROUPS . . . . .  | 252 |
| Alkalimetric Method . . . . .   | 252 |

# CONTENTS

xiii

|  |            |
|--|------------|
| Principle  | 252        |
| Apparatus, 252. Bubble counter and U-tube, 252. Hydrolysis apparatus, 252. Water bath, 253. Pipets, 253. Titration equipment, 253.   |            |
| Reagents, 254. <i>p</i> -Toluene sulfonic acid, 254.   |            |
| Procedure, 254. Solubility tests, 254. Preparation of the sample, 254. Preparation of the apparatus, 255. Hydrolysis, 255. Distillation, 255. Titration, 256. Calculation, 256.                              |            |
| Iodometric Method  | 257        |
| Principle  | 257        |
| Apparatus, 257. Acetyl apparatus, 257. Titration equipment, 257.   |            |
| Reagents, 257. 0.01 <i>N</i> iodine solution, 257.   |            |
| Procedure, 258. Preparation of the apparatus, 258. Charging of the distilling flask, 259. Heating, 259. Transfer of the distillate and titration, 260. Correction for sulfur dioxide, 260. Calculation, 261. |            |
| Remarks  | 261        |
| Literature   | 262        |
| <b>III. DETERMINATION OF GROUPS REACTIVE TO GRIGNARD REAGENT</b>   | <b>263</b> |
| Principle  | 263        |
| Apparatus, 264. Methane generator, 264. Methanometer, 264.   |            |
| Reagents, 265. Nitrogen, 265. Solvents, 266. Grignard reagent, 266.  |            |
| Filling the apparatus, 267. Determination of the blank, 267.   |            |
| Procedure, 269. Preparation of the apparatus, 269. Introduction of the sample, 269. Generation of methane, 269. Addition of aniline, 270. Calculation, 270.  |            |
| Remarks  | 270        |
| Literature   | 271        |
| <b>IV. OTHER METHODS</b>   | <b>273</b> |
| Amines, 273. Electrometric and photoelectric methods, 273. Hydrogenation methods, 273. Isopropylidene groups, 273. <i>C</i> -Methyl groups, 274. Optical rotation, 274.                                      |            |
| Literature   | 274        |
| <b>APPENDIX</b>  | <b>277</b> |
| THE TEACHING OF QUANTITATIVE ORGANIC MICROANALYSIS   | 277        |
| INSTALLATION OF A LABORATORY FOR QUANTITATIVE ORGANIC MICROANALYSIS  | 283        |
| QUALITATIVE ORGANIC MICROANALYSIS  | 290        |
| CALCULATIONS   | 296        |
| NITROGEN REDUCTION TABLES  | 301        |
| LOG TABLES   | 312        |
| <b>AUTHOR INDEX</b>  | <b>331</b> |
| <b>SUBJECT INDEX</b>   | <b>341</b> |