

HANDBOOK OF PETROLEUM PRODUCT ANALYSIS

2nd Edition

JAMES G. SPEIGHT, PhD, DSc
CD & W Inc.,
Laramie, WY, USA

WILEY

CONTENTS

Preface	xv
1 Petroleum and Petroleum Products	1
1.1 Introduction	1
1.2 Perspectives	2
1.2.1 Historical Perspectives	2
1.2.2 Modern Perspectives	3
1.3 Definitions	4
1.3.1 Petroleum	4
1.3.1.1 Correlation Index	6
1.3.1.2 Characterization Factor	7
1.3.1.3 Character and Behavior	7
1.3.1.4 Bulk Fractions	8
1.3.2 Natural Gas	8
1.3.3 Natural Gas Liquids and Natural Gasoline	10
1.3.4 Opportunity Crudes	10
1.3.5 High-Acid Crudes	10
1.3.6 Foamy Oil	11
1.3.7 Oil from Shale	11
1.3.8 Heavy Oil	12
1.3.9 Extra Heavy Oil	13
1.3.10 Tar Sand Bitumen	13
1.4 Petroleum Refining	14
1.4.1 Visbreaking	14
1.4.2 Coking	15
1.4.3 Hydroprocessing	16
1.5 Petroleum Products	16
1.5.1 Types	16
1.5.1.1 Gases	17
1.5.1.2 Naphtha, Solvents, and Gasoline	17
1.5.1.3 Kerosene and Diesel Fuel	18
1.5.1.4 Fuel Oil	18
1.5.1.5 White Oil, Insulating Oil, Insecticides	19

1.5.1.6 Lubricating Oil	19
1.5.1.7 Grease	20
1.5.1.8 Wax	20
1.5.1.9 Residua and Asphalt	20
1.5.1.10 Coke, Carbon Black, and Graphite	20
1.5.1.11 Fischer–Tropsch Liquids and Bio-Oil	21
1.5.2 Properties	21
References	23
2 Analytical Methods	26
2.1 Introduction	26
2.2 Chemical and Physical Analyses	27
2.2.1 Boiling Point Distribution	27
2.2.2 Density, Specific Gravity, and API Gravity	27
2.2.3 Emulsion Formation	28
2.2.4 Evaporation	28
2.2.5 Fire Point and Flash Point	28
2.2.6 Fractionation	29
2.2.7 Metal Content	29
2.2.8 Pour Point	29
2.2.9 Sulfur Content	29
2.2.10 Surface Tension and Interfacial Tension	30
2.2.11 Viscosity	30
2.2.12 Water Content	30
2.3 Chromatographic Analyses	31
2.3.1 Adsorption Chromatography	31
2.3.2 Gas Chromatography	31
2.3.3 Gas Chromatography–Mass Spectrometry	33
2.3.4 High-Performance Liquid Chromatography	33
2.3.5 Thin Layer Chromatography	33
2.4 Spectroscopic Analyses	34
2.4.1 Infrared Spectroscopy	35
2.4.2 Mass Spectrometry	36
2.4.3 Nuclear Magnetic Resonance	38
2.4.4 Ultraviolet Spectroscopy	41
2.4.5 X-Ray Diffraction	41
2.5 Molecular Weight	41
2.6 Instability and Incompatibility	42
2.7 The Future	43
References	44
3 Sampling and Measurement	48
3.1 Introduction	48
3.2 Sampling	49
3.2.1 Sampling Protocol	49
3.2.2 Representative Sample	50
3.2.3 Sampling Error	51
3.3 Volume Measurement	51
3.4 Method Validation	52
3.4.1 Requirements	52
3.4.2 Detection Limit	53
3.4.3 Accuracy	53
3.4.4 Precision	54

3.5	Quality Control and Quality Assurance	54
3.5.1	Quality Control	54
3.5.2	Quality Assurance	55
3.6	Assay and Specifications	56
3.6.1	Assay	57
3.6.2	Specifications	58
3.6.2.1	Distillation	61
3.6.2.2	Low-Boiling Hydrocarbons	62
3.6.2.3	Metallic Constituents	62
3.6.2.4	Salt Content	62
3.6.2.5	Sulfur Content	63
3.6.2.6	Viscosity and Pour Point	64
3.6.2.7	Water and Sediment	65
3.6.3	Other Tests	65
	References	67

4 Gases 71

4.1	Introduction	71
4.2	Types of Gases	72
4.2.1	Liquefied Petroleum Gas	72
4.2.2	Natural Gas	73
4.2.3	Shale Gas	74
4.2.4	Refinery Gas	75
4.3	Sampling	77
4.4	Storage	77
4.4.1	Depleted Gas Reservoirs	78
4.4.2	Aquifer Reservoirs	78
4.4.3	Salt Formations	78
4.4.4	Gasholders	78
4.5	Test Methods	78
4.5.1	Calorific Value	79
4.5.2	Composition	80
4.5.3	Density	82
4.5.4	Relative Density	82
4.5.5	Sulfur Content	83
4.5.6	Volatility and Vapor Pressure	83
4.5.7	Water	83
	References	83

5 Naphtha and Solvents 88

5.1	Introduction	88
5.2	Production and Properties	89
5.3	Test Methods	91
5.3.1	Aniline Point and Mixed Aniline Point	92
5.3.2	Composition	92
5.3.3	Correlative Methods	95
5.3.4	Density	95
5.3.5	Evaporation Rate	96
5.3.6	Flash Point	96
5.3.7	Kauri-Butanol Value	97
5.3.8	Odor and Color	97
5.3.9	Volatility	97

5.4 Storage 98
References 98

6 Gasoline 104

6.1 Introduction 104
6.2 Production and Properties 104
6.3 Volatility Requirements and Other Properties 106
6.4 Octane Rating 110
6.5 Additives 111
6.6 Test Methods 112
 6.6.1 Combustion Characteristics 112
 6.6.2 Composition 113
 6.6.3 Corrosiveness 115
 6.6.4 Density 116
 6.6.5 Flash Point and Fire Point 116
 6.6.6 Oxygenates 117
 6.6.7 Stability and Instability 117
 6.6.8 Water and Sediment 119
References 120

7 Aviation and Marine Fuels 126

7.1 Introduction 126
7.2 Production and Properties 126
 7.2.1 Aviation Fuels 126
 7.2.2 Marine Fuels 127
7.3 Test Methods 127
 7.3.1 Acidity 127
 7.3.2 Additives 128
 7.3.3 Calorific Value 128
 7.3.4 Composition 129
 7.3.5 Density 131
 7.3.6 Flash Point 132
 7.3.7 Freezing Point 132
 7.3.8 Knock and Antiknock Properties 132
 7.3.9 Pour Point 133
 7.3.10 Storage Stability 133
 7.3.11 Thermal Stability 134
 7.3.12 Viscosity 134
 7.3.13 Volatility 134
 7.3.14 Water 135
References 136

8 Kerosene 141

8.1 Introduction 141
8.2 Production and Properties 141
8.3 Test Methods 143
 8.3.1 Acidity 144
 8.3.2 Burning Characteristics 144
 8.3.3 Calorific Value 144
 8.3.4 Composition 145
 8.3.5 Density 148
 8.3.6 Flash Point 148

8.3.7	Freezing Point	148
8.3.8	Pour Point	148
8.3.9	Smoke Point	149
8.3.10	Viscosity	149
8.3.11	Volatility	149
8.3.12	Water and Sediment	150
	References	150

9 Diesel Fuel **155**

9.1	Introduction	155
9.2	Production and Properties	155
9.3	Test Methods	156
9.3.1	Acidity	157
9.3.2	Appearance and Odor	157
9.3.3	Ash	157
9.3.4	Calorific Value	157
9.3.5	Carbon Residue	158
9.3.6	Cetane Number	158
9.3.7	Cloud Point	159
9.3.8	Composition	159
9.3.9	Density	161
9.3.10	Diesel Index	161
9.3.11	Flash Point	162
9.3.12	Freezing Point	162
9.3.13	Neutralization Number	163
9.3.14	Pour Point	163
9.3.15	Stability	163
9.3.16	Viscosity	164
9.3.17	Volatility	164
9.3.18	Water and Sediment	164
	References	165

10 Distillate Fuel Oil **169**

10.1	Introduction	169
10.2	Production and Properties	171
10.3	Test Methods	172
10.3.1	Acidity	172
10.3.2	Ash	173
10.3.3	Calorific Value	173
10.3.4	Carbon Residue	174
10.3.5	Cloud Point	174
10.3.6	Composition	174
10.3.7	Density	175
10.3.8	Flash Point	175
10.3.9	Metallic Constituents	176
10.3.10	Pour Point	176
10.3.11	Stability	177
10.3.12	Viscosity	178
10.3.13	Volatility	178
10.3.14	Water and Sediment	179
	References	180

11 Residual Fuel Oil	186
11.1 Introduction	186
11.2 Production and Properties	186
11.3 Test Methods	187
11.3.1 Ash	188
11.3.2 Asphaltene Content	188
11.3.3 Calorific Value	189
11.3.4 Carbon Residue	189
11.3.5 Composition	190
11.3.6 Density	193
11.3.7 Elemental Analysis	194
11.3.8 Flash Point	195
11.3.9 Metallic Constituents	195
11.3.10 Molecular Weight	196
11.3.11 Pour Point	196
11.3.12 Refractive Index	197
11.3.13 Stability and Compatibility	197
11.3.14 Viscosity	198
11.3.15 Volatility	199
11.3.16 Water and Sediment	200
References	201
12 White Oil	207
12.1 Introduction	207
12.2 Production and Properties	209
12.3 Test Methods	209
12.3.1 Acidity or Alkalinity	209
12.3.2 Aniline Point	210
12.3.3 Asphaltene Content	211
12.3.4 Carbonizable Substances	211
12.3.5 Carbon Residue	211
12.3.6 Cloud Point	212
12.3.7 Color and Taste	212
12.3.8 Composition	213
12.3.9 Density (Specific Gravity)	214
12.3.10 Electrical Properties	214
12.3.11 Flash Point and Fire Point	214
12.3.12 Interfacial Tension	215
12.3.13 Iodine Value	215
12.3.14 Oxidation Stability	215
12.3.15 Pour Point	216
12.3.16 Refractive Index	216
12.3.17 Smoke Point	216
12.3.18 Ultraviolet Absorption	216
12.3.19 Viscosity	216
12.3.20 Volatility	217
12.3.21 Water	217
12.3.22 Wax Appearance Point	217
References	217
13 Lubricating Oil	222
13.1 Introduction	222
13.2 Production and Properties	222
13.2.1 Production	224

13.2.2	Properties	225	
13.2.3	Types of Lubricating Oil	226	
13.2.3.1	Automotive Engine Oil	226	
13.2.3.2	Diesel Engine Oil	227	
13.2.3.3	Tractor and Other Engine Oils	227	
13.2.3.4	Aviation Oil	227	
13.2.3.5	Turbine Oil	227	
13.2.3.6	Compressor Oil	227	
13.2.3.7	Industrial Oils	228	
13.3	Used Lubricating Oil	228	
13.4	Test Methods	230	
13.4.1	Acidity and Alkalinity	230	
13.4.2	Ash	231	
13.4.3	Asphaltene Content	231	
13.4.4	Carbonizable Substances	232	
13.4.5	Carbon Residue	232	
13.4.6	Cloud Point	233	
13.4.7	Color	233	
13.4.8	Composition	233	
13.4.9	Density	235	
13.4.10	Flash Point and Fire Point	235	
13.4.11	Oxidation Stability	236	
13.4.12	Pour Point	236	
13.4.13	Thermal Stability	236	
13.4.14	Viscosity	236	
13.4.15	Volatility	237	
13.4.16	Water and Sediment	238	
	References	238	
14	Grease		244
14.1	Introduction	244	
14.2	Production and Properties	245	
14.2.1	Production	245	
14.2.2	Properties	246	
14.3	Test Methods	248	
14.3.1	Acidity and Alkalinity	248	
14.3.2	Anticorrosion Properties	248	
14.3.3	Composition	249	
14.3.4	Dropping Point	249	
14.3.5	Flow Properties	249	
14.3.6	Low-Temperature Torque	250	
14.3.7	Mechanical Stability	250	
14.3.8	Oil Separation	250	
14.3.9	Oxidation Stability	251	
14.3.10	Penetration	251	
14.3.11	Thermal Stability	251	
14.3.12	Viscosity	252	
14.3.13	Volatility	252	
14.3.14	Water Resistance	252	
	References	252	
15	Wax		255
15.1	Introduction	255	
15.2	Production and Properties	256	
15.2.1	Production	256	

- 15.2.2 Properties 256
- 15.3 Test Methods 257
 - 15.3.1 Appearance 257
 - 15.3.2 Barrier Properties 258
 - 15.3.3 Carbonizable Substances 258
 - 15.3.4 Color 258
 - 15.3.5 Composition 258
 - 15.3.6 Density 259
 - 15.3.7 Hardness 259
 - 15.3.8 Melting Point 260
 - 15.3.9 Molecular Weight 260
 - 15.3.10 Odor and Taste 261
 - 15.3.11 Oil Content 261
 - 15.3.12 Peroxide Content 261
 - 15.3.13 Slip Properties 261
 - 15.3.14 Storage Stability 262
 - 15.3.15 Strength 262
 - 15.3.16 Ultraviolet Absorptivity 262
 - 15.3.17 Viscosity 262
 - 15.3.18 Volatility 263
- References 263

16 Residua and Asphalt

265

- 16.1 Introduction 265
- 16.2 Production and Properties 267
 - 16.2.1 Residua 267
 - 16.2.2 Asphalt 267
- 16.3 Test Methods 269
 - 16.3.1 Acid Number 270
 - 16.3.2 Asphaltene Content 271
 - 16.3.3 Bond and Adhesion 272
 - 16.3.4 Breaking Point 272
 - 16.3.5 Carbon Disulfide–Insoluble Constituents 272
 - 16.3.6 Carbon Residue 272
 - 16.3.7 Compatibility 274
 - 16.3.8 Composition 274
 - 16.3.9 Density 275
 - 16.3.10 Distillation 276
 - 16.3.11 Ductility 276
 - 16.3.12 Durability 276
 - 16.3.13 Elemental Analysis 276
 - 16.3.14 Emulsified Asphalt 277
 - 16.3.15 Flash Point 277
 - 16.3.16 Float Test 277
 - 16.3.17 Molecular Weight 277
 - 16.3.18 Penetration 278
 - 16.3.19 Rheology 278
 - 16.3.20 Softening Point 278
 - 16.3.21 Stain 279
 - 16.3.22 Temperature–Volume Correction 279
 - 16.3.23 Thin Film Oven Test 279
 - 16.3.24 Viscosity 279
 - 16.3.25 Water Content 279

16.3.26 Weathering	280
References	280
17 Coke, Carbon Black, and Graphite	285
17.1 Introduction	285
17.2 Production and Properties	286
17.2.1 Coke	286
17.2.1.1 Composition	286
17.2.1.2 Properties	288
17.2.2 Carbon Black	288
17.2.2.1 Composition	288
17.2.2.2 Properties	288
17.2.3 Graphite	289
17.2.3.1 Composition	289
17.2.3.2 Properties	290
17.3 Test Methods	290
17.3.1 Ash	290
17.3.2 Calorific Value	290
17.3.3 Composition	291
17.3.4 Density	292
17.3.5 Dust Control	292
17.3.6 Hardness	292
17.3.7 Metals	292
17.3.8 Proximate Analysis	293
17.3.9 Sulfur	293
17.3.10 Volatile Matter	293
17.3.11 Water	294
References	294
18 Use of the Data	296
18.1 Introduction	296
18.2 Feedstock and Product Evaluation	297
18.2.1 Test Methods	298
18.2.2 Specifications	298
18.3 Feedstock and Product Mapping	298
18.4 Structural Group Analyses	300
18.5 Epilogue	302
References	302
Appendix: Tables of ASTM Standard Test Methods for Petroleum and Petroleum Products	304
Table A01: Test Methods for the Terminology of Petroleum and Petroleum Products	304
Table A02: Test Methods for Sampling Petroleum and Petroleum Products	304
Table A03: Test Methods for the Analysis of Petroleum and Petroleum Products by Absorption Spectroscopy	304
Table A04: Test Methods for the Analysis of Petroleum and Petroleum Products by Mass Spectroscopy	305
Table A05: Test Methods for the Analysis of Petroleum and Petroleum Products by Chromatographic Methods	305
Table A06: Test Methods for the Analysis of Petroleum and Petroleum Products by Gas Chromatography	305

Table A07: Test Methods for Analysis of Petroleum and Petroleum Products by Liquid Chromatography	306
Table A08: Test Methods for the Analysis of Additives and Electrical Properties of Petroleum and Petroleum Products	307
Table A09: Test Methods for the Determination of the Contaminants in Fuels	307
Table A10: Test Methods for the Analysis of the Reactivity and Thermal Properties of Petroleum and Petroleum Products	307
Table A11: Test Methods for Analysis by Correlative Methods of Petroleum and Petroleum Products	308
Table A12: Test for the Elemental Analysis of Petroleum and Petroleum Products	308
Table A13: Test Methods for the Analysis of Hydrocarbons and Contaminants in Petroleum and Petroleum Products	310
Table A14: Test Methods for the Determination of the Flow Properties of Petroleum and Petroleum Products	311
Table A15: Test Methods for the Determination of the Chemical and Physical Properties of Petroleum and Petroleum Products	312
Table A16: Test Methods for the Determination of Instability and Contaminants in Liquid Fuels	313
Table A17: Test Methods for the Determination of the Volatility of Petroleum and Petroleum Products	314
Table A18: Test Methods for the Analysis of Gaseous (C ₄) Hydrocarbons	314
Table A19: Test Methods for the Analysis of Liquefied Petroleum Gas	314
Table A20: Test Methods for the Analysis of Gasoline and Gasoline-Oxygenate Blends	315
Table A21: Test Methods for the Analysis of Oxygenated Fuels	315
Table A22: Test Methods for the Analysis of Aviation Fuels	315
Table A23: Test Methods for the Analysis of Jet Fuel	316
Table A24: Test Methods for the Analysis of Diesel, Non-Aviation Gas Turbine, and Marine Fuels	316
Table A25: Test Methods for the Analysis of Lubricants	316
Table A26: Test Methods for the Environmental Analysis of Lubricants	319
Table A27: Test Methods for the Analysis of the Oxidation of Grease and Lubricants	319
Table A28: Test Methods for the Analysis of Petroleum Coke, Carbon, and Graphite	320
Table A29: Test Methods for the Physical Properties of Fuels, Petroleum Coke, and Carbonaceous Materials (Tar and Pitch)	321
Conversion Factors	323
Glossary	324
Index	341