

Subject Index

A

Alkylbenzene
 chemical ionization-proton exchange analysis, 42, 44–45
 Kendrick mass analysis, 188–189
 metastable spectra, 107–108
n-Alkylbenzenes
 GC/MS analysis, 108–109
 Arabian Heavy asphaltenes, 108–109
n-Alkylbenzothiophenes, 4, 108, 115
 GC/MS analysis
 background, 94–95
 hydrocarbon and sulfur carbon types, 95, 97–103
 magnified view, 101, 104
 pyrolysis GC/MS and, 95
 homologs, singlet, doublet, and multiplet, 105, 108
 mass spectra, major isomers, 112–115
 metastable spectra, 107–108
 molecular and fragment ions, 108, 111
 Alkylindans, chemical ionization-proton exchange analysis, 42, 44–45
 Alkyltetralins, chemical ionization-proton exchange analysis, 42, 44–45
 Ammonia, oil shale pyrolysis, 133–142
 Ammonia chemical ionization
 geoporphyrin analysis, 92
 metalloporphyrins, 3, 84–85
 mass spectra, 86
 porphyrin mass spectrometry, 88–92
 Arabian heavy asphaltenes
n-alkylbenzenes, 108–109
n-alkylbenzothiophenes, 95–115
 Aromatics, hydrotreatment effect, 156–157
 ASTM Test Methods
 D 2425-83, 25
 D 2786-86, 25, 33–37, 164–166, 168
 Autoscaling, multivariate analysis, 148

B

Benzene, chemical ionization-proton exchange analysis, 40–43
 Biomarker analysis, gas chromatography/mass spectrometry, 3
 Biomarkers, 59–60
 Buddingtonite, pyrolysis of, 141–142

C

¹³C combinations, Kendrick masses, 182, 185–186
 CH³⁴S combinations, Kendrick masses, 182, 185–186
 Chemical ionization (CI) (*see also* Ammonia chemical ionization; Isobutane chemical ionization)
 coal-derived liquids, 145
 metalloporphyrins, 84–92
 reagent gas pressure, 138
 role in SFC-MS, 21
 SFC-MS interfaces and flow restrictors, 9
 sterane analysis, mass spectrometry, 49
 Chemical ionization-proton exchange (CIPE), 3
 jet fuel analysis, 38–45
 peak identification, 45
 CHY software program, 185, 188
 Coal-derived liquids
 chemical ionization-proton exchange analysis, 40–43
 low-voltage mass spectrometry, 144–153
 SFC-MS analyses, 10–21
 Coal extracts
 LVHRMS-direct insertion probe, 116–125
 molten-caustic treatment, 117
 preparation, 117
 raw versus molten-caustic-treated, 126–131
 Coal tar, SFC-MS analyses, 7–8, 10–11
 Collisionally activated dissociation (CAD) metalloporphyrins, 85

- Computer programming (*see* Hardware; Software programs)
- Contamination, tandem mass spectrometry, 56, 58
- Crude oil, sterane traces in, 47–58

D

- Deuterium exchange, chemical ionization-proton exchange analysis, 40–43
- Diesel fuel
 - SFE-MS analysis, 10–21
 - methane CI mass spectra, 10, 13
- Dipyrrole fragments, pyrrole formation, 89–92
- Direct fluid injection (DFI)
 - mass spectrometry, 10, 12–15
 - SFC-MS interfaces and flow restrictors, 9
- Direct-insertion-probe technique, LVHRMS
 - Bevier coal extracts, 123–125
 - coal-derived materials, 116–125
- Direct-probe inlet mass spectrometry, 16–17
- DS-55 software system, 119–120

E

- ECNCl
 - sterane analysis, 49
 - methane-enhanced, 50–51
- Electron impact spectra
 - CIPE analysis and, 39
 - daughter spectra, 62, 64
 - full-scan, 62–63
- Electron ionization (EI)
 - geoporphyrin analysis, 92
 - metalloporphyrin, 3, 84–92
 - mass spectra, 86
 - porphyrin mass spectrometry, 87–88
 - SFC-MS interfaces and flow restrictors, 9
 - sterane analysis,
 - daughter mass spectra, 51–52
 - mass spectra, 49
- Electron ionization mass spectrometry (EIMS), 134
- Expert systems, 159–171
 - comparisons with other analytical methods, 171
 - future research trends, 170–171

- GC/MS fossil fuel analysis
 - evaluation and reliability, 170
 - experimental systems, 162–163
 - future research, 170–171
 - hydrocarbon carbon number assignment, 165
 - main principles of, 163–170
 - molecular ion search, 165–166
 - need for, 160–162
 - n*-paraffin identification, 163–165
 - quantitation and sorting, 167–170
 - structure assignment, 166–167
 - type analysis, 164
- human expert comparisons, 170–171
- schematic, 161

F

- Factor analysis
 - Factor I spectra, 152, 156
 - Factor II spectra, 152, 156
 - hydrotreatment data, 148, 151–153
- Factor spectrum
 - hydrotreatment data, 148, 152–155
 - time/temperature trends, 153, 155
- Fast atom bombardment (FAB), 1
- Field ionization (FI), coal-derived liquids, 145
- Flame ionization detection
 - CIPE analysis and, 38
 - gas chromatography and, 27
 - supercritical fluid chromatography, 5–6
- Fourier transform infrared spectroscopy (FTIR), 134

G

- Gas chromatography (GC)
 - apparatus, 3-m DuraBond system, 26
 - component discrimination, 27–31
 - flame ionization detection, 27
 - fossil fuel analysis, 159–171
 - mass spectrometry (GC/MS) (*see* Gas chromatography/mass spectrometry)
 - sample introduction methods, 27–28
 - sterane analysis, 48–49
- Gas chromatography/mass spectrometry (GC/MS)
 - n*-alkylbenzothiophenes/*n*-alkylbenzenes, 95–115
 - apparatus used, 26–27
 - ASTM comparisons, 33–37
 - biomarkers, 60

CIPE analysis and, 39
 coal-derived liquids, 145
 comparisons with MS/MS, 2
 computer hardware and software, 27
 expert systems, 160–162
 fuel variations, 34–37
 HTA sample introduction methods, 27–31
 hydrocarbon analysis, 3
 injection port temperature versus area ratios, 27–30
 ion summation chromatograms, 27–28
 jet fuel analysis, 24–37
 limits of detection, 31, 33–34
 short column and simulated distillation, 25–27
 software programs for, 159–171
 splitless versus on-column injection, 30–31
 sterane analysis, 52–53
 Geoporphyrins
 defined, 84–85
 EI and ammonia CI analysis, 90

H

Hardware (computer), Hewlett Packard-Interface Buss (HPIB), 135
 Heuristics, expert systems, 161–162
 HFR interface, SFC-MS analysis, 15
 High Resolution Mass Spectral analysis, Kendrick masses and, 172–193
 Hydroaromatics, hydrotreatment effect, 156–157
 Hydrocarbon
 carbon number assignment, 165–166
 homologs, coal extracts, 119–120
 LVHRM-direct-insertion-probe techniques, 124
 Hydrocarbon-type analysis (HTA), 3
 fuel variations, 34–37
 jet fuels, GS/MS, 24–37
 sample introduction methods, 27–28
 versus ASTM test methods, 33–37
 Hydronium ion, ammonia determination, 140
 Hydrotreatment effect, 4
 average mass spectra, 148–150
 coal-derived liquids, 144–153
 sample identification, 145–146
 Hydroxy-polynuclear aromatic hydrocarbons, 20–21

I

IF-THEN-Else rules, 162
 Indans, chemical ionization-proton exchange analysis, 40–43
 Injection techniques
 area ratio accuracies, 31
 gas chromatography, 28–31
 Integrated Two-Stage Liquefaction (ITSL)
 coal-derived liquids, 144–146
 schematic, 145–146
 Ion current instability, direct-insertion-probe techniques, 120–121
 Ionization techniques, 1–3
 Isobutane chemical ionization
 ammonia determination, 137–138
 ammonia from oil shale pyrolysis, 133–142
 ammonia volume versus concentration, 149
 isobutane fragment monitoring, 138–140
 quadruple analyzer transmission, 138
 reagent gas pressure, 138
 secondary electron multiplier (SEM) gain, 138

J

Jet fuel analysis
 CIPE method, 38–45
 coal-derived, 40–43
 GS/MS hydrocarbon-type analysis, 24–37

K

Kendrick masses, 4
 ¹²C mass, 174–175
 defect, 175
 factor, 175
 high-resolution mass spectrometry and, 172–193
 root mean square errors, 189
 Knowledge engineering, 162

L

Laser desorption, 1–2
 Liquid chromatography/mass spectrometry (LC/MS), 145
 LISP language, 162

- Low-voltage high-resolution mass spectrometry (LVHRMS), 4
 - direct-insertion-probe technique
 - formula class distributions, 123
 - summary of compound types, 122–123
- Low-voltage, high-resolution mass spectrometry
 - direct-insertion probe and coal-derived materials, 116–125
- Low-voltage mass spectrometry
 - coal-derived liquids, 144–153
 - multivariate analysis and, 4
 - schematic diagram, 147

M

- MAP, *n*-alkylbenzenes analysis, 95, 97–103
- Marine diesel fuel, SFC-MS analysis, 10, 12
- Mass spectrometry (MS) (*see also* Tandem mass spectrometry (MS/MS))
 - n*-alkylbenzothiophenes and *n*-alkylbenzenes, 95–115
 - apparatus, MAT TSQ45, 26
 - chemical ionization-proton exchange and, 38–45
 - coal-derived liquids, 145
 - gas chromatography (*see* Gas chromatography/mass spectrometry (GC/MS))
 - jet fuel analysis, 24–37
 - low-voltage high-resolution (*see* Low-voltage high-resolution mass spectrometry (LVHRMS))
 - metalloporphyrins, 84–85
 - overview, 1
 - software programs for, 159–171
 - sterane analysis, normal MS, 49–51
 - supercritical fluid chromatography (*see* Supercritical fluid chromatography/mass spectrometry (SFC/MS))
- Medium-resolution SIR, 62, 65
- Metalloporphyrins
 - chemical ionization, 84–92
 - electron ionization, 84–92
- Metastable ions, multiple reaction monitoring, 60–64
- Methane chemical ionization, metalloporphyrins, 84–85
- Methylene, repeating unit concept, 173
- Microbore SFC-MS, 15–21
 - hydroxy-PAC fractions, 20–21
- Molecular ions, 165–166

- Molten-caustic-treated coal extracts, LVHRM-direct-insertion-probe techniques
 - Bevier coal extracts, 123–124
 - mole percent determinations, 126–131
- Monoaromatics, hydrocarbon carbon numbers, 165–166
- Monooxygenated compounds, LVHRM-direct-insertion-probe techniques, 124
- MS/MS (*see* Tandem mass spectrometry)
- Multiple reaction monitoring
 - crude oil extracts used, 60–61, 65
 - sterane responses, 65, 67–70
 - triterpenes, 65, 75–78
- Multivariate analysis, standardization, 148

N

- Nitrogen-containing polycyclic aromatic hydrocarbon (NPAC)
 - LVHRM-direct-insertion-probe techniques, 124–125
 - mass spectra from, 16, 18–19, 21
 - SFC-MS analysis, 16–17
- Nominal mass *Z* series (NMZ)
 - first array combinations, 182, 184
 - rectangular array concept, 174–182
 - unassigned peaks, 175, 180–183
- N-paraffins, expert system identification, 163–165

O

- Octaethylporphyrin, EI and ammonia CI analysis, 86–92
- Oil-oil correlation, multiple reaction monitoring, 65–83
- Oil shale (*see* Shale oil)
- On-column injection, gas chromatography, 30–31
- One-ring aromatic neutrals, Kendrick mass rectangular array, 175–182
- On-line mass spectrometry, ammonia from oil shale pyrolysis, 133–142
- Organosulfur compounds (*see* Sulfur)

P

- PCI, sterane analysis
 - daughter mass spectra, 52–53
 - MS/MS, 49
- Petroleum analysis, high-resolution mass spectrometry and, 172–193
- Plasma desorption ionization, 2

Polar modifiers, supercritical fluid chromatography and, 7–9
 Polynuclear aromatic hydrocarbons (PNAs)
 hydrotreatment effect, 156–157
 MS/MS analysis, 2
 Pressure programming, SFC-MS analysis, 15–16
 PROB software program, 185, 188
 Programming for fuel analysis (*see* Software programs)
 Prophyryns, SFC-MS analyses, 10–21
 Pyridine dialyzate, direct-insertion-probe techniques, 121–123
 Pyrolysis
 Buddingtonite, 141–142
 GC/MS
 n-alkylbenzothiophenes, 95
 Arabian Heavy asphaltenes, 105–106
 metastable spectra, 107–108
 sulfur in, 105
 oil shale, 4, 133–134
 Pyrrole formation, mono and tripyrrolic fragments, 89–92

Q

Quadruple analyzer transmission,
 isobutane chemical ionization,
 138
 Quantitation, hydrocarbon mixtures, 167–170

R

READTAP software program, 182, 185
 Reconstructed ion current (RIC)
 hydrocarbon-type analysis, 31,
 33–34, 167–168
 Rectangular array
 ion formulas, 172–193
 second array combinations, 189–192
 Retort, ammonia determination
 SS retort, 135–136
 steam retort, 140–142
 RETROFIT software program, 118–120

S

Secondary electron multiplier (SEM) gain, 138
 Secondary ion mass spectrometry (SIMS), 1
 Selected ion recording (SIR), 60–62, 65
 Separation techniques, overview, 1–2

Shale oil,
 pyrolysis, 4, 133–134
 sterane traces in, 47–58
 Short column GC/MS, 25–27
 SIGMA software system, 148, 151
 Simulated distillation, GC/MS, 25–27
 Software for fuel analysis
 CHY program, 185, 188
 DS-55 system, 119–120
 HP 3497A thermocouple conditioning
 and digitizing system, 135
 HRMS data analysis, 182, 185
 IBM CAPMC4 Chromatography
 Applications Program, 27
 mass spectrometry data with, 4
 PROB program, 185, 188
 READTAP program, 182, 185
 RETROFIT program, 118–120
 SIGMA system, 148
 SPECTR program, 182, 185
 XFER program, 182, 185
 Solid probe analysis
 confirmation, 56–57
 sterane analysis, 49
 tandem mass spectrometry, 53–57
 Sorting
 carbon numbers and isomers, 169–170
 hydrocarbon mixtures, 167–170
 isomer summing, 169
 Specific Z series (SPZ), 174–182
 one-ring aromatic neutrals, 175–181,
 193
 SPECTR software program, 182, 185
 Splitless injection techniques, 29–31
 SS retort, ammonia determination, 135–136
 Stability index (SI)
 defined, 85
 doubly charged ions in EI, 88–89
 electron ionization and, 3–4
 fragmentation under Ammonia CI, 88–89
 metalloporphyrin reactivity, 85
 pyrrole formation, 89–92
 Steam retort, ammonia determination, 140–142
 Steranes
 biomarkers, 59–60
 carbon number distribution, 58
 marine oil, 65, 67–70
 molecular formulas and standard weights, 48
 multiple reaction monitoring
 peak identifications, 65–66

tandem mass spectrometry
 abundance measurements, 55–56
 crude and shale oils, 47–58
 parent spectra, 53–55
 terrestrial oil, 67, 71–74
 Structure assignments, hydrocarbon mixtures, 166–167
 Sulfur
n-alkylbenzenes and, 95, 97–103
 coal extract removal, 119–125
 LVHRM-direct-insertion-probe techniques, 123–125
 Supercritical fluid chromatography (SFC), 203
 flame ionization detector, 5–6
 Supercritical fluid chromatography/mass spectrometry (SFC/MS), 3, 5–21
 direct fluid injection (DFI) and, 10–15
 experimental procedure, 6–7
 fossil fuel analysis, 10–11
 hydroxy-containing polynuclear aromatic compounds, 20–21
 interfaces and flow restrictors, 9
 microbore techniques, 15–21
 nitrogen-containing polycyclic aromatic hydrocarbon (NPAC), 16–19
 polar fluid and column development, 7–9
 polar sediments from marine diesel fuels, 10, 13
 pressure programming, 15–16
 split injection techniques, 15
 Supercritical fluid extraction (SFE)
 fossil fuels, 10, 13–15
 mass spectrometry and, 6–7

T

Tandem mass spectrometry (MS/MS)
 contamination and chemical interface, 56, 58
 metalloporphyrins, 85
 overview, 2
 solid probe configuration, 56–57
 sterane analysis
 CAD daughter spectra, 51
 EI-CAD daughter spectra, 51–52
 sterane traces, 3, 47–58
 Tetralins, chemical ionization-proton exchange analysis, 40–43
 Thermospray, 2
 Trimethylamine, isobutane chemical ionization, 140
 Triple quadrupole mass spectrometry (TQMS)
 ammonia determination, 134–135
 nitric oxide, 136–137
 Tri-sector geometry, multiple reaction monitoring, 61–62
 Triterpene
 biomarkers, 59–60
 marine oil, 65, 76–78
 multiple reaction monitoring, 65, 67
 terrestrial oil, 79–83

U

Ultraviolet absorption detection, 5–6

V

Variance Diagram Technique,
 hydrotreatment data, 152–154

X

XFER software program, 182, 185