

Contents

Preface — VI

Giancarlo Cravotto and Pedro Cintas

1 Microwave chemistry: history, development and legacy — 1

- 1.1 Introduction — 1
- 1.2 How it all began — 1
- 1.3 From cooking to chemistry — 3
- 1.4 The thermal conundrum — 5
 - 1.4.1 The search for specific effects: a long journey — 6
- 1.5 Efficient and fine-tuned heating: the role of outliers — 11
 - 1.5.1 Conveying MW energy: susceptors — 11
 - 1.5.2 A peculiar device: cooling while heating — 12
- 1.6 Efficient by design: tailor-made reactors — 13
- 1.7 Conclusions — 14

Paolo Veronesi

2 An Introduction to dielectric heating — 18

- 2.1 The electromagnetic spectrum and the industrial, scientific, and medical frequencies — 18
- 2.2 Basis of dielectric heating — 19
 - 2.2.1 Selectivity — 24
 - 2.2.2 Self-regulating reactions — 26
 - 2.2.3 Volumetric heating — 26
 - 2.2.4 Inversion of temperature profile — 27
 - 2.2.5 Rapid heating — 28
 - 2.2.6 Thermal runaway — 28

Cristina Leonelli

3 Microwave generators, transmission, and interaction with different materials — 31

- 3.1 Introduction — 31
- 3.2 Microwave generators — 33
 - 3.2.1 Magnetron — 33
 - 3.2.2 Solid-state generators — 34
 - 3.2.3 Other microwave sources — 35
- 3.3 Wave Propagation — 36
 - 3.3.1 Waveguide modes — 36
- 3.4 Antennas — 38

3.5	Microwave chambers —	39
3.5.1	Single-mode cavities —	39
3.5.2	Multimode applicators —	40
3.5.3	Leakage suppression —	42
3.6	Radiant microwave applicators —	43
3.7	Monitoring and control of microwave applicators —	45
3.7.1	Temperature measurement —	45
3.7.2	Pressure measurement —	47
3.7.3	Power control —	48
3.8	Maintenance —	49
3.9	Safety —	49
3.10	Conclusions —	50

György Keglevich and Zoltán Mucsi

4	Interpretation of the rate enhancing effect of microwaves —	53
4.1	Introduction —	53
4.2	Thermal versus nonthermal effects for rate enhancement —	53
4.3	Reaction energetics versus MW assistance —	54
4.4	Modeling the rate-enhancing effect of MWs —	57

Marilena Radoiu

5	Industrial microwave reactors: components and set up —	65
5.1	MW heating and process scale-up —	65
5.2	MW equipment —	66
5.2.1	The MW generator —	67
5.2.2	The MW power transmission line —	73
5.2.3	MW applicators —	75
5.3	Good engineering practice —	76
5.3.1	Quick estimation of theoretical power P_a —	76
5.3.2	Simple calorimetry to asses available MW power of equipment —	78
5.4	Economics and process scale-up —	79
5.4.1	Power requirements for heating a product —	79
5.4.2	Choice of MW frequency —	80
5.5	What can be improved – good engineering practice, good manufacturing practice —	81
5.6	Industrial applications —	81
5.6.1	Food processing —	81
5.6.2	Drying at atmospheric or vacuum pressure —	83
5.6.3	Plasma processing —	84
5.6.4	Chemistry —	85
5.7	Conclusions —	86

5.8	A two-page definition guide to MW energy for beginners —	87
5.8.1	What is MW energy? —	87
5.8.2	How are MWs generated? —	87
5.8.3	What are dielectric properties? —	87
5.8.4	What happens to other materials? —	88
5.8.5	Ionizing and nonionizing radiation —	88

Antonio de la Hoz and Pilar Prieto

6	The impact of microwaves in organic synthesis —	91
6.1	Introduction —	91
6.2	Acceleration effects —	92
6.3	Multistep synthesis —	94
6.4	Natural products —	95
6.5	Homogeneous and heterogeneous catalysis —	97
6.6	Biocatalysis —	101
6.7	Reactions involving radicals —	102
6.8	Selectivity under microwave irradiation —	104
6.9	Computational calculations in MAOS —	106

Yuji Wada, Dai Mochizuki, Taishi Ano, Masato M. Maitani, Shuntaro Tsubaki, and Naoto Haneishi

7	Chemical reactions on the interfaces of solids under microwaves —	113
7.1	Introduction —	113
7.2	In situ observation of selective heating of inorganic particles dispersed in solution —	115
7.3	Accelerated chemical reactions by nonequilibrium local heating of solid interfaces —	120
7.4	Strategic design of zeolite filled with carbon at its core —	122
7.5	Summary —	125

Satoshi Horikoshi and Nick Serpone

8	Some aspects of catalysis with microwaves —	127
8.1	Historical aspects of catalyzed reactions under microwave radiation —	127
8.2	Heterogeneously catalyzed reactions —	129
8.2.1	Advantages of MW-assisted heterogeneous catalytic method —	129
8.2.2	Microwave heterogeneous gas-phase catalytic systems —	131
8.2.3	Microwave heterogeneous liquid-phase catalytic systems —	137
8.3	Problems with the MW catalytic method and possible solutions —	140
8.4	Conclusions —	144

Frédéric Delbecq, Rafael Luque, and Christophe Len

- 9 Microwaves in flow chemistry — 149**
- 9.1 Introduction — 149
- 9.2 Different flow reactors for microwave applications — 152
- 9.2.1 Microfluidic systems for chemistry — 152
- 9.2.2 Mesofluidic system for chemistry — 153
- 9.3 Applications of microwaves in flow chemistry — 155
- 9.3.1 Production of nanoparticles — 155
- 9.3.2 Organic synthesis — 160

Ángel Díaz-Ortiz and José R. Carrillo

- 10 Microwaves in green and sustainable chemistry — 167**
- 10.1 Microwaves and the 12 principles of green chemistry.
 Energy Efficiency — 167
- 10.1.1 Dielectric properties (solvents and polar compounds) — 168
- 10.1.2 Use of susceptors — 169
- 10.1.3 Thermal effects — 170
- 10.2 Reactions in green solvents — 171
- 10.2.1 Solvent-free reactions — 171
- 10.2.2 Reactions in water — 172
- 10.2.3 Reactions in ionic liquids — 173
- 10.2.4 Fluorous chemistry — 174
- 10.3 Reactions with solid supports — 175
- 10.4 Synergy with other sustainable technologies — 176
- 10.4.1 Ultrasound — 176
- 10.4.2 Electrochemistry — 177
- 10.4.3 Photochemistry — 178
- 10.4.4 Flow chemistry — 179
- 10.5 Conclusions — 180

Abhishek Sharma and Erik Van der Eycken

- 11 Synthesis of medium-sized heterocycles under microwave
 irradiation — 184**
- 11.1 Introduction — 184
- 11.2 Microwave-assisted synthesis of seven-membered heterocycles — 185
- 11.2.1 Benzazepine and benzoxazepine derivatives — 185
- 11.2.2 Diazepines and their analogs — 188
- 11.2.3 Thiazepine and thiadiazepine derivatives — 191
- 11.2.4 Oxacycles — 193
- 11.3 Microwave-assisted synthesis of eight-membered heterocycles — 194

- 11.4 Microwave-assisted synthesis of nine-membered heterocycles and beyond — 199
- 11.5 Conclusion — 202

Jacek Wojnarowicz, Tadeusz Chudoba, Andrzej Majcher, and Witold Łojkowski

- 12 **Microwaves applied to hydrothermal synthesis of nanoparticles — 205**
 - 12.1 Introduction — 205
 - 12.2 Benefits of microwave synthesis in a Teflon® reaction chamber — 205
 - 12.3 Reactions initiated by microwaves in a liquid environment — 210
 - 12.4 Obtaining nanometric ZnO in hydrothermal processes — 213
 - 12.5 Obtaining ZnO nanopowders in microwave reactors — 214
 - 12.6 Solvothermal production of ZnO nanopowders in microwave reactors — 217
 - 12.7 Comparison of different methods of obtaining ZnO NPs — 219
 - 12.8 Summary — 220

Rodrigo González-Prieto, Santiago Herrero, Reyes Jiménez-Aparicio, Emilio Morán, Jesús Prado-Gonjal, José Luis Priego, and Rainer Schmidt

- 13 **Microwave-assisted solvothermal synthesis of inorganic compounds (molecular and non molecular) — 225**
 - 13.1 Introduction — 225
 - 13.2 Influence of parameters and reaction conditions — 227
 - 13.2.1 Solvent — 227
 - 13.2.2 Reaction time — 228
 - 13.2.3 Temperature — 229
 - 13.2.4 Reactant ratio — 230
 - 13.2.5 Other variables — 231
 - 13.3 Molecular solids — 231
 - 13.3.1 Discrete species — 231
 - 13.3.2 Polymeric species — 234
 - 13.4 Nonmolecular solids — 236
 - 13.4.1 Binary metallic oxides — 238
 - 13.4.2 Oxides also containing hydrogen — 240
 - 13.4.3 Ternary oxides — 240
 - 13.4.4 Other materials — 242

Satoshi Horikoshi and Nick Serpone

- 14 **Microwave-assisted synthesis of nanoparticles — 248**
 - 14.1 Introduction — 248
 - 14.2 Nanoparticle: definition — 248

- 14.3 Homogeneous and heterogeneous nucleation — **249**
- 14.4 Microwave nanoparticle synthesis — **251**
- 14.5 Advantage(s) of the microwave method — **252**
- 14.5.1 Uniform nucleating particle size — **252**
- 14.5.2 Synthesis of nanoparticles of uniform sizes: mechanism — **254**
- 14.5.3 Efficient synthesis of metal nanoparticles at different microwave frequencies — **257**
- 14.5.4 Advantage(s) of shape control — **259**
- 14.5.5 Microwave local heating effects — **259**
- 14.5.6 Microwave synthesis of core-shell nanoparticles — **260**
- 14.6 Microwave desktop system of nanoparticle synthesis in continuous-flow reactors — **262**
- 14.7 Synthesis of core-shell metal chalcogenide nanoparticles — **266**
- 14.8 Epilog — **267**

Dariusz Bogdal

- 15 Microwaves in polymer chemistry — 270**
- 15.1 Free-radical polymerization — **271**
- 15.2 Controlled radical polymerization — **273**
- 15.2.1 Atom transfer radical polymerization — **273**
- 15.2.2 Nitroxide-mediated polymerization — **275**
- 15.2.3 Reversible addition-fragmentation chain transfer — **276**
- 15.3 Ring-opening polymerization — **276**
- 15.4 Ring-opening metathesis polymerization — **279**
- 15.5 Microwave-assisted acyclic diene metathesis (ADMET) — **281**
- 15.6 Step growth polymerization and preparation of composite/hybrid materials — **282**

Sandrine Perino, Emmanuel Petitcolas, and Farid Chemat

- 16 Microwave extraction of natural products in the teaching laboratory: fundamentals of essential oils green extraction — 293**
- 16.1 Introduction — **293**
- 16.2 Microwave versus conventional heating — **294**
- 16.3 Experimental setup — **294**
- 16.3.1 Portable microwave-assisted extraction — **294**
- 16.3.2 Solvent-free microwave extraction — **295**
- 16.3.3 Microwave hydrodiffusion and gravity — **296**
- 16.4 Advantages — **299**
- 16.4.1 Green production rapidity — **299**
- 16.4.2 Green production efficiency — **299**
- 16.4.3 Green production messages — **300**
- 16.5 Future prospects — **300**

Cláudia P. Passos and Manuel A. Coimbra

- 17 Microwave extraction of bioactive compounds from industrial by-products — 302**
 - 17.1 Industrial waste, byproducts, or coproducts? — 303
 - 17.2 Availability and opportunities for industrial byproduct recycling — 305
 - 17.3 Microwave extraction — 306
 - 17.3.1 Essential oils — 320
 - 17.3.2 Phenolics — 322
 - 17.3.3 Polysaccharides — 324
 - 17.3.4 Other MAE applications — 326
 - 17.4 From laboratory to pilot – perspectives on the industrial scale — 326
 - 17.5 Conclusion — 326

Simona Collina and Serena Della Volpe

- 18 The Use of microwaves in drug discovery — 334**
 - 18.1 Introduction — 334
 - 18.2 MAOS in drug discovery: synthesis of small molecules — 335
 - 18.3 MAOS in drug development: synthesis of radioligands for PET — 343
 - 18.4 MAE: drug discovery based on natural products — 346
 - 18.5 MAOS and biotechnology — 348
 - 18.6 Conclusions — 351

Karin Engen, Jonas Sävmarker, Luke R. Odell, and Mats Larhed

- 19 Microwave heating in medicinal chemistry — 358**
 - 19.1 Introduction — 358
 - 19.2 Lead identification — 360
 - 19.3 Lead optimization — 364
 - 19.4 MW-assisted synthesis of active pharmaceutical ingredients — 366
 - 19.4.1 Imatinib — 366
 - 19.4.2 Sildenafil — 367
 - 19.4.3 Fluoxetine — 368

Silvia Tabasso

- 20 Microwave-assisted biomass conversion — 370**
 - 20.1 Introduction — 370
 - 20.2 Composition of biomass — 371
 - 20.3 Microwave interactions with biomass — 373
 - 20.3.1 Hydrothermal conversion of cellulose — 374
 - 20.3.2 Microwave-assisted pyrolysis of biomass — 376

- 20.4 Case studies — 378**
- 20.4.1 Application of microwave heating in lignocellulosic biomass pretreatment for bioethanol production — 378**
- 20.4.2 MW-assisted valorization of postharvest tomato plant wastes (PHTP) — 379**
- 20.5 Conclusion — 381**

Zhilin Wu and Giancarlo Cravotto

- 21 Microwave technology for environmental remediation — 383**
- 21.1 Microwave-induced plasmas — 383**
- 21.1.1 Dissociation of hydrogen sulfide — 385**
- 21.1.2 Desulfurization and denitrification of flue gas — 386**
- 21.1.3 Abatement of greenhouse gas: PFCs — 386**
- 21.1.4 Destruction of VOCs — 387**
- 21.2 MW-assisted evaporation and desorption — 388**
- 21.2.1 Ammonia evaporation from wastewater — 388**
- 21.2.2 Desorption of organic pollutants on granulated activated carbon — 388**
- 21.2.3 Dehydration of sludge, solid waste and biomass — 389**
- 21.2.4 Desorption of organics from contaminated soil — 390**
- 21.2.5 Stripping of oil from drill cuttings — 391**
- 21.2.6 Regeneration of adsorbents — 391**
- 21.3 Microwave-driven pyrolysis — 394**
- 21.3.1 Organic waste and biomass — 395**
- 21.3.2 Sewage sludge — 397**
- 21.3.3 Municipal solid waste — 401**
- 21.3.4 Polymeric materials — 401**
- 21.3.5 Waste oil — 404**
- 21.4 Microwave-enhanced decomposition — 405**
- 21.4.1 Decomposition of gaseous pollutants — 405**
- 21.4.2 Organic wastewater treatment — 407**
- 21.4.3 Soil remediation — 415**

María M. Delgado-Povedano and María D. Luque de Castro

- 22 Microwaves in the omics field — 429**
- 22.1 Introduction — 429**
- 22.1.1 Steps in the analytical process — 430**
- 22.1.2 Omics definitions — 431**
- 22.1.3 Common aspects of MW-assisted steps in omics — 432**
- 22.2 MW assistance in genomics and transcriptomics — 434**
- 22.2.1 MW assistance in sample preparation in genomics and transcriptomics — 434**

22.2.2	MW-assisted detection in genomics and transcriptomics —	437
22.3	MW assistance in proteomics —	438
22.3.1	MW assistance in sample preparation in proteomics —	438
22.3.2	MW assistance in identification/quantitation in proteomics —	441
22.4	MW assistance in metabolomics —	441
22.4.1	MW-assisted drying in metabolomics —	442
22.4.2	MW-assisted solid–liquid extraction in metabolomics —	442
22.4.3	MW-assisted digestion in metabolomics —	444
22.4.4	MW-assisted liquid–liquid extraction in metabolomics —	445
22.4.5	MW-assisted steam distillation in metabolomics —	445
22.4.6	MW-assisted derivatization in metabolomics —	445
22.5	Trends in MW assistance in omics —	446

Cezar Augusto Bizzi, Erico Marlon de Moraes Flores, and Marcia Foster Mesko

23	Microwaves in sample preparation for elemental determination —	452
23.1	Introduction to microwave-assisted sample preparation —	452
23.2	Microwave-assisted wet digestion/dissolution —	454
23.2.1	Microwave-assisted wet digestion of organic matrices —	454
23.2.2	Microwave-assisted wet decomposition/dissolution of inorganic matrices —	465
23.3	Microwave-assisted extraction —	466
23.3.1	Microwave-assisted extraction for speciation studies —	467
23.4	Microwave-assisted sample combustion —	468
23.4.1	Dry ashing —	469
23.4.2	Microwave-induced combustion —	470
23.5	Safety aspects, quality control, and quality assurance —	474
23.5.1	General aspects of safety —	474
23.5.2	Analytical quality assurance —	477
23.6	Conclusions —	480

Juliano Smanioto Barin, Fábio Andrei Duarte, Paola de Azevedo Mello, and Éder Lisandro de Moraes Flores

24	Microwave-assisted sample preparation for organic analysis —	488
24.1	Introduction —	488
24.2	General aspects of microwave-assisted extraction —	489
24.3	Applications of MAE to the analysis of organic compounds —	497

Richard Morrison

25	Microwave chemistry in the organic instructional laboratory —	505
25.1	Introduction —	505
25.2	Advantages of microwave promotion —	506
25.2.1	Safety —	506

25.2.2	Yields and product purity —	507
25.2.3	Reduced heating times —	507
25.2.4	Reactant and reagent unknowns —	508
25.3	Examples of instructional laboratory experiments that utilize microwave promotion —	508
25.4	Conclusions —	520

A snapshot of more common commercial microwave reactors — 523