Table of Contents

Foreword xi

Chapter 1. General Features 1
Bernard MICHAUX

1.1. Definitions 1
1.1.1. Sensors 1
1.1.2. Qualities of measuring sensors 2
1.1.3. Chemical and biochemical sensors. 5
1.2. Classification 6
1.2.1. Mass variation 6
1.2.2. Optics 7
1.2.3. Electrical parameters 8
1.3. Specific problems of chemical sensors. 14
1.3.1. pH measurement: Nernst equation for the glass electrode 14
1.3.2. Ionometry 18
1.3.3. Conclusion concerning chemical sensors 20
1.4. Advantages and drawbacks of chemical microsensors 21
1.5. Perspectives 22
1.6. Bibliography 23

Chapter 2. Chemical Sensors: Development and Industrial Requirements 25
Jacques FOULETIER and Pierre FABRY, based on discussions with Jacques FOMBON

2.1. Introduction. 25
2.1.1. Overview of the various types of chemical sensors 25
2.1.2. General trends 26

2.2. Modern research and development (R&D) management methods applied to sensors 26
2.2.1. Preliminary phases in the industrialization of a new sensor 26
2.2.2. Development and industrialization. 31
2.2.3. Information and establishment of the commercial network 32
2.3. Applications and inventory of the needs. 33
2.3.1. pH sensors 33
2.3.2. Potentiometric selective electrodes 33
2.3.3. Amperometric specific electrodes 36
2.3.4. Conductimetric sensors 36
2.3.5. Biosensors 36
2.3.6. Biomedical applications 37
2.4. New needs and industrial applications 37
2.4.1. Creation of new sensors 38
2.4.2. Reliability and absence of maintenance. 38
2.4.3. Miniaturization and robustness. 38
2.4.4. Lowering the production and use costs 39
2.5. The sensor in the measuring chain 39
2.5.1. General features. 39
2.5.2. Quality and metrology of the standards and of the instruments . . . 40
2.6. Conclusions and prospects 43
2.7. Bibliography 43

Chapter 3. Sensitivity and Selectivity of Electrochemical Sensors 45
Pierre FABRY and Jean-Claude MOUTET, and translated by J.C. POIGNET and Pierre FABRY

3.1. General concepts. 45
3.1.1. Various kinds of electrochemical sensors. 46
3.1.2. Interference and selectivity 49
3.1.3. Nature and shape of materials 50
3.2. Models for the sensitivity and selectivity of potentiometric sensors 51
3.2.1. Basic concepts. 51
3.2.2. Ionic conducting membranes of the first kind 55
3.2.3. Ionic conducting membranes of the second kind 59
3.2.4. Liquid and organic membranes. 63
3.3. Case of amperometric sensors. 64
3.3.1. Principle of sensitivity 64
3.3.2. Selectivity model 65
3.4. Molecular recognition and sensors 68
3.5. Characterization methods 70
3.5.1. Definition and determination of the detection limit. 70

3.5.2. Determination methods of selectivity coefficients 73
3.6. Bibliography 77

Chapter 4. Potentiometric Sensors (Ions and Dissolved Gases) 81
Annie PRADEL and Eric SAINT-AMAN

4.1. Introduction 81
4.1.1. General features 81
4.1.2. Electrode potential 82
4.1.3. Sensitivity of the potentiometric sensors 85
4.1.4. Selectivity of the potentiometric sensors 87
4.2. Membranes 88
4.2.1. General features 88
4.2.2. Glass membranes 89
4.2.3. Crystallized inorganic membranes 95
4.2.4. Polymeric membranes 97
4.3. Current developments in potentiometric sensors 99
4.3.1. All-solid-state sensors 99
4.3.2. All-solid-state microsensors 105
4.4. Bibliography 109

Chapter 5. Amperometric Sensors 115
Alain WALCARIUS, Chantal GONDRAN and Serge COSNIER

5.1. Sensors based upon chemically modified electrodes 115
5.1.1. Introduction 115
5.1.2. Fabrication and characterization 119
5.1.3. Fundamental principles and examples of application 127
5.2. Amperometric biosensors 138
5.2.1. Introduction 138
5.2.2. Immobilization of biomolecules 140
5.2.3. Amperometric biosensors, principle and description 142
5.3. Bibliography 160

Chapter 6. ISFET, BioFET Sensors 173
Nicole JAFFREZIC-RENAULT and Claude MARTELET, translated by
Claude MARTELET

6.1. Structure of ISFET sensors 173
6.1.1. Introduction 173
6.1.2. MOS (metal-oxide semiconductor) structure 174
6.1.3. EOS (electrolyte-oxide semiconductor) structure 177
6.1.4. MOSFET 178
6.1.5. ISFET 179
6.2. Techniques used for ISFET fabrication and operation 180

6.2.1. ISFET fabrication . . . 180
6.2.2. ISFET Measurement set-up . . . 182
6.3. ISFET membranes . . . 183
6.3.1. Detection of H^+ ions . . . 183
6.3.2. Detection of other ions . . . 184
6.4. Detection of molecular species . . . 187
6.4.1. Metabolic biosensors . . . 187
6.4.2. The enzymatic field-effect transistor (ENFET) principle . . . 188
6.4.3. Some ENFET examples . . . 189
6.4.4. ENFET and inhibition mechanisms . . . 192
6.5. BioFETs . . . 193
6.5.1. Systems based on affinity mechanisms . . . 193
6.5.2. BioFET based on cells and living organisms . . . 195
6.6. Commercial devices . . . 197
6.6.1. pH ISFETs . . . 197
6.6.2. Multidetection systems . . . 200
6.7. Conclusion and perspectives . . . 201
6.8. Bibliography . . . 202

Chapter 7. Biosensors and Chemical Sensors Based Upon Guided Optics . . . 209
Jean-Pierre GOURE and Loïc BLUM

7.1. Introduction . . . 209
7.2. Definitions . . . 210
7.2.1. Luminous wave . . . 210
7.2.2. Optical fibers . . . 211
7.2.3. Planar guides . . . 212
7.3. Principles of optical microsensors . . . 213
7.3.1. Definition . . . 213
7.3.2. Modulation of the optical signal . . . 214
7.3.3. Techniques . . . 218
7.3.4. Refractometry . . . 219
7.4. Optical fiber biosensors . . . 220
7.4.1. Configurations of optical fiber biosensors . . . 221
7.4.2. Chemical sensors integrated in optical fiber sensors . . . 221
7.4.3. Optical fiber enzymatic biosensors . . . 223
7.4.4. Biosensors with non-catalytic bioreceptors (affinity biosensors) . . . 225
7.4.5. Chemiluminescence and bioluminescence detection sensors . . . 227
7.5. Perspectives and conclusions . . . 229
7.6. Bibliography . . . 229

Chapter 8. Sensors and Voltammetric Probes for *In Situ* Monitoring of Trace Elements in Aquatic Media 233
Marie-Louise TERCIER-WAEBER and Jacques BUFFLE

8.1. Introduction. 233
8.2. Basic principles of the voltammetric techniques and of their applications to analysis of water. 235
8.2.1. Components and principles 235
8.2.2. Influence of the transport properties of the electroactive species on the voltammetric signal 239
8.2.3. Influence of the speciation of the electroactive compounds on the voltammograms 241
8.3. Voltammetric techniques used for the analysis of trace elements in waters 244
8.3.1. Sensitivity limit of the voltammetric techniques. 244
8.3.2. Various voltammetric techniques 245
8.3.3. Voltammetric determinations of natural samples in the laboratory or on the field 245
8.4. Development of reliable submersible voltammetric probes. 247
8.4.1. Working electrodes. 247
8.4.2. Reference electrodes 252
8.4.3. Voltammetric cells 255
8.4.4. Interference due to the dissolved oxygen 257
8.4.5. Interferences due to the adsorption of organic and inorganic compounds 259
8.4.6. Gel-integrated microsensors 260
8.5. Submersible voltammetric probes reported in the literature 264
8.5.1. Continuous-flow probe based on a microelectrode and a pre-treatment of the sample. 264
8.5.2. Continuous-flow probe based on a macro- or a microelectrode with no sample treatment 264
8.5.3. Probes based on direct immersion of the electrodes. 265
8.5.4. Continuous-flow probe based on a gel-integrated microsensor with no sample pretreatment: the VIP system. 267
8.6. Conclusion 273
8.6.1. Calibration of voltammetric procedures. 274
8.6.2. Development of robust and reliable sensors and probes 275
8.7. Bibliography 275

Chapter 9. Chemometrics 287
Philippe BREUIL

9.1. Introduction. 287
9.1.1. The Problem of multivariate analysis 288

9.1.2. Example: Beer-Lambert law of light absorption . . . 289
9.1.3. General method . . . 290
9.2. A particular case: the linear case . . . 290
9.2.1. Notations and preliminary considerations . . . 290
9.2.2. Simple least square methods . . . 291
9.2.3. Factor analysis . . . 296
9.3. Least squares methods: non-linear case . . . 302
9.3.1. Case when transformations can reduce the problem to linear functions . . . 302
9.3.2. PLS can model non-linear phenomena . . . 303
9.4. Neural networks . . . 303
9.4.1. General structure of the network . . . 304
9.4.2. Learning (i.e. calibration) . . . 304
9.4.3. Prediction . . . 305
9.5. Conclusion . . . 305
9.6. Bibliography . . . 306

Chapter 10. Impedancemetric Sensors . . . 307
Jacques FOULETIER and Pierre FABRY

10.1. Introduction . . . 307
10.2. Fields of application . . . 307
10.3. Conductivity of liquid media . . . 310
10.3.1. Theoretical basis . . . 310
10.3.2. Effect of temperature . . . 312
10.4. Impedance of first kind cell (direct measurement) . . . 313
10.5. Cell configurations and sources of error . . . 317
10.5.1. Types of conductivity cells . . . 317
10.5.2. Characteristics – specifications . . . 321
10.6. Second kind cells . . . 326
10.7. Summary of practical precautions . . . 328
10.8. Bibliography . . . 329

List of Authors . . . 331

Index . . . 335