

Contents

Contributors to Volume 49	vii
Volumes in the Series	xix
Editors' Preface	xlix
Series Editors' Preface	liii

Part 1 FUNDAMENTALS AND APPLICATIONS

POTENTIOMETRIC SENSORS

Chapter 1. Clinical analysis of blood gases and electrolytes by ion-selective sensors

Andrzej Lewenstam

1.1 Introduction	5
1.2 General characteristics of clinical analysis of electrolytes and gases.	6
1.2.1 Clinical sample, analytical matrix.	6
1.2.2 Types and design of ion-sensors and gas-sensors used in clinical analysis	8
1.3 Electrochemical measurement in clinical analysis	10
1.4 Application of sensors from the producer's point of view.	12
1.5 Sensors used in routine clinical measurements: a brief overview	14
1.5.1 Hydrogen ISSs (pH electrodes).	14
1.5.2 Sodium ISSs.	14
1.5.3 Potassium ISSs	15
1.5.4 Lithium ISSs	15
1.5.5 Calcium ISSs	15
1.5.6 Magnesium ISSs.	16
1.5.7 Chloride ISSs.	16
1.5.8 Carbon dioxide GSSs	17
1.5.9 Bicarbonate ion-selective electrodes	17
1.5.10 Oxygen GSSs	17
1.5.11 Reference electrodes.	18

Contents

3.3	Design of EPME	57
3.3.1	Design of carbon paste based EPMEs	57
3.3.2	Design of PVC-based EPMEs	58
3.3.3	Design of molecularly imprinted polymers based enantioselective sensors	58
3.4	Application of EPMEs in enantioanalysis	59
3.4.1	EPMEs based on cyclodextrins	59
3.4.2	EPMEs based on maltodextrins	63
3.4.3	EPMEs based on antibiotics	65
3.4.4	EPMEs based on crown ethers	67
3.4.5	EPMEs based on fullerenes	68
3.5	Conclusions	68
	References	69

Chapter 4. Ion sensors with conducting polymers as ion-to-electron transducers

Johan Bobacka and Ari Ivaska

4.1	Introduction	73
4.1.1	Principle of ion-to-electron transduction in conventional ISEs	73
4.1.2	Principle of ion-to-electron transduction in conducting polymer-based ISEs	74
4.1.3	Design and fabrication of conducting polymer-based ISEs	74
4.1.4	Conducting polymers used as ion-to-electron transducers	76
4.1.5	Conducting polymers used as ion-selective membranes	76
4.2	Application	77
4.2.1	Analytical performance of solid-contact ISEs	77
4.2.2	Conducting polymer-based pH sensors	78
4.2.3	Polypyrrole-based nitrate sensor	79
4.2.4	Sensors for surfactants	79
4.2.5	Pharmaceutical analysis	79
4.2.6	ISEs for measurements in non-aqueous solvents	80
4.2.7	Solid-state ion sensors with low detection limits	80
4.2.8	Conducting polymer-based reference electrode	80
4.3	Conclusions	81
	Acknowledgments	81
	References	82

Contents

<i>Chapter 5. Light-addressable potentiometric sensors (LAPS): recent trends and applications</i>	
Torsten Wagner and Michael J. Schoning	
5.1	Introduction 87
5.2	Theoretical background. 88
5.3	Applications of LAPS 96
5.3.1	Characterisation of LAPS. 96
5.3.2	Biological applications based on LAPS 101
5.3.3	Alternative applications and materials for LAPS devices 108
5.4	Conclusions. 115
	References 117

VOLTAMMETRIC (BIO)SENSORS

<i>Chapter 6. Stripping-based electrochemical metal sensors for environmental monitoring</i>	
Joseph Wang	
6.1	Introduction 131
6.2	Principles 132
6.2.1	Anodic stripping voltammetry 132
6.2.2	Potentiometric stripping analysis. 134
6.2.3	Adsorptive stripping voltammetry 134
6.3	Working electrodes for stripping analysis: from mercury electrodes to disposable strips. 135
6.4	Bismuth-based metal sensors 136
6.5	In situ metal sensors. 138
6.6	Remote metal sensors. 138
6.7	Conclusions. 139
	Acknowledgments. 140
	References 140
<i>Chapter 7. Graphite-epoxy electrodes for stripping analysis</i>	
Arben Merkoçi and Salvador Alegret	
7.1	Introduction 143
7.1.1	In Situ generation of mercury 144
7.1.2	Mercury-free modified electrodes 144
7.1.3	Bismuth electrodes. 144
7.1.4	Composite electrodes 145
7.2	Construction and surface characterization of composite electrodes 146

Contents

Chapter 10. Peptide-modified electrodes for detecting metal ions

J. Justin Gooding

10.1	Introduction	189
10.1.1	The binding of metals by amino acids and peptides	189
10.1.2	Using peptides to detect metal ions.	192
10.1.3	Peptide-modified electrodes as metal ion selective sensors	193
10.2	Application	195
10.2.1	Interfacial design	195
10.2.2	The detection of copper ions at Gly-Gly-His-modified electrodes	198
10.2.3	Peptide-modified electrodes for other metals: towards multianalyte arrays	203
10.3	Conclusions.	207
	Acknowledgments ,	208
	References	208

Chapter 11. Reproducible electrochemical analysis of phenolic compounds by high-pressure liquid chromatography with oxygen-terminated diamond sensor

Chiaki Terashima and Akira Fujishima

11.1	Introduction	211
11.2	Applications	214
11.2.1	Electrode characterization	214
11.2.2	Electrochemical oxidation of 2,4-dichlorophenol	216
11.2.3	Deactivation of diamond electrodes.	219
11.2.4	Regeneration of diamond electrodes ,	219
11.2.5	Flow injection analysis	221
11.2.6	Hydrodynamic voltammetry	223
11.2.7	Chromatographic separation	224
11.2.8	Column-switching HPLC	225
11.3	Conclusions.	228
	References	229

GAS SENSORS

Chapter 12. Chemical sensors for mercury vapour

Vladimir M. Mirsky and Majlinda Vasjari

12.1	Introduction	235
------	------------------------	-----

Contents

12.2	Mercury–gold interaction	236
12.3	Transducers for mercury sensors based on thin gold layers.	238
12.4	Selectivity improvement	242
12.5	Calibration	245
12.6	Conclusion	248
	Acknowledgment	249
	References	249

ENZYME BASED SENSORS

Chapter 13. Application of electrochemical enzyme biosensors for food quality control

Beatriz Serra, Ángel Julio Reviejo and José Manuel Pingarrón

13.1	Introduction	255
13.2	Food quality control	255
13.3	Process control applications	288
13.4	Conclusions and some remarks from the commercial point of view.	288
	References	289

Chapter 14. Electrochemical biosensors for heavy metals based on enzyme inhibition

Aziz Amine and Hasna Mohammadi

14.1	Introduction	299
14.2	Parameters affecting the enzyme inhibition system.	301
14.3	Analytical characterization of biosensors-based enzyme inhibition	302
14.4	Conclusions.	306
14.5	Future perspectives.	307
	References	307

Chapter 15. Ultra-sensitive determination of pesticides via cholinesterase-based sensors for environmental analysis

Frank Davis. Karen A. Law. Nikos A. Chaniotakis, Didier Fournier. Tim Gibson. Paul Millner, Jean-Louis Marty. Michelle A. Sheehan. Vladimir I. Ogurtsov, Graham Johnson. John Griffiths.

Anthony P.F. Turner and Seamus P.J. Higson

15.1	Introduction	311
15.2	Application	314

Contents

15.2.1	Synthesis of the acetylcholinesterase	314
15.2.2	Immobilisation of the enzymes	314
15.2.3	Use of microelectrodes	317
15.2.4	Multiple pesticide detection	320
15.2.5	Signal processing for pesticide detection	323
15.3	Conclusions	326
	References	327
 Chapter 16. Amperometric enzyme sensors for the detection of cyanobacterial toxins in environmental samples		
M. Campàs and J.-L. Marty		
16.1	Introduction	331
16.1.1	Cyanobacterial toxins: the overview	331
16.1.2	Cyanobacteria growth and blooms–toxin release . . .	336
16.1.3	Analytical methods for microcystin and anatoxin-a(s) detection.	336
16.1.4	Environmental and health effects–guideline values.	337
16.2	Application	338
16.2.1	Protein phosphatase-based biosensor for electrochemical microcystin detection	338
16.2.2	Acetylcholinesterase-based biosensor for electrochemical anatoxin-a(s) detection	344
16.3	Conclusions.	346
	Acknowledgments	347
	References	347
 Chapter 17. Electrochemical biosensors based on vegetable tissues and crude <i>extracts</i> for environmental, food and pharmaceutical analysis		
Orlando Fatibello-Filho, Karina O. Lupetti, Oldair D. Leite and Iolanda C. Vieira		
17.1	Introduction	357
17.1.1	Electrochemical biosensors based on vegetable tissues	358
17.1.2	Electrochemical biosensors based on crude extracts (homogenates)	362
17.2	Application	366
17.2.1	Preparation of a typical electrode based on a slice of plant material.	366
17.2.2	Preparation of typical carbon paste electrode based on tissue powder.	366

Contents

20.2	AFM images of DNA-electrochemical biosensors	414
20.3	DNA-electrochemical biosensors for detection of DNA damage	417
20.4	DNA damage produced by reactive oxygen species (ROS) . .	418
20.4.1	Quercetin	419
20.4.2	Adriamycin	424
20.4.3	Nitric oxide	428
20.5	Conclusion	432
	References	433
 <i>Chapter 21. Electrochemical genosensing of food pathogens based on graphite-epoxy composite</i>		
Maria Isabel Pividori and Salvador Alegret		
21.1	Introduction	439
21.1.1	Contamination of food, food pathogens and food safety	439
21.1.2	Food pathogen detection and culture methods	440
21.1.3	Rapid detection methods to detect food pathogens	442
21.1.4	Biosensing as a novel strategy for the rapid detection of food pathogens	443
21.2	DNA electrochemical biosensors	444
21.2.1	Immobilization of DNA and detection features	444
21.2.2	Transducer materials for electrochemical DNA biosensing	446
21.2.3	Electrochemical genosensing of food pathogens based on DNA dry-adsorption on GEC as electrochemical transducer	448
21.2.4	Electrochemical genosensing of food pathogens based on DNA wet-adsorption on GEC as electrochemical transducer	451
21.2.5	Electrochemical genosensing of food pathogens based on Av-GEB biocomposite as electrochemical transducer	452
21.2.6	Electrochemical genosensing of food pathogens based on magnetic beads and m-GEC electrochemical transducer	454
21.3	Conclusions	459
	Acknowledgments	461
	References	461

Contents

Chapter 22. *Electrochemical immunosensing of food residues by affinity biosensors and magneto sensors*

Maria Isabel Pividori and Salvador Alegret

22.1	Introduction	467
22.1.1	Contamination of food, food residues, and food safety	467
22.1.2	Pesticides and drug residues detection methods	469
22.1.3	Rapid detection methods for the food residues. Immunochemical methods	471
22.1.4	Antibodies as immunological reagents. Immobilization strategies	474
22.1.5	Biosensing as a novel strategy for the rapid detection of food residues.	477
22.2	Electrochemical biosensing of food residues based on universal affinity biocomposite platforms	479
22.2.1	Transducer materials for electrochemical immunoassay and analytical strategies	479
22.3	Electrochemical biosensing of food residues based on magnetic beads and M-GEC electrochemical transducer.	484
22.3.1	Transducer material for electrochemical immunoassay, magnetic beads, and analytical strategies	484
22.4	Conclusions.	487
	Acknowledgments.	489
	References	489

THICK AND THIN FILM BIOSENSORS

Chapter 23. *Screen-printed electrochemical (bio)sensors in biomedical, environmental and industrial applications*

John P. Hart, Adrian Crew, Eric Crouch, Kevin C. Honeychurch and Roy M. Pemberton

23.1	Introduction	497
23.2	Biomedical	499
23.2.1	Glucose.	499
23.2.2	Mediators for H_2O_2	499
23.2.3	Mediators capable of direct electron transfer with GOD.	503
23.2.4	The use of glucose dehydrogenase (GDH)	503
23.2.5	Cholesterol	504
23.2.6	Lactate.	506
23.2.7	Ascorbic acid, steroid and protein hormones	508

Contents

25.2.2	Immunochemical reagents: design of immunogen and enzyme labelled compound	592
25.2.3	Dose–response curves for some PCB mixtures	594
25.2.4	PCB pollution in environment and food samples	596
25.3	Conclusions	599
	Acknowledgment	599
	References	599

Chapter 26. *Thick- and thin-film DNA sensors*

Maria Begoña González-García, Maria Teresa Fernandez-Abedul and Agustín Costa-García

26.1	Introduction	603
26.1.1	Genosensors on thick- and thin-film electrodes	604
26.1.2	Pretreatments followed with real samples	616
26.1.3	Experimental conditions for hybridisation reaction	618
26.2	Applications	620
26.2.1	Enzymatic genosensor on gold thin-films to detect a SARS virus sequence	620
26.2.2	Genosensors on streptavidin-modified thick-film carbon electrodes to detect <i>Streptococcus pneumoniae</i> sequences	626
26.2.3	Genosensor on streptavidin-modified screen-printed carbon electrodes for detection of PCR products	634
26.3	Conclusions	636
	References	637

Chapter 27. *Screen-printed enzyme-free electrochemical sensors for clinical and food analysis*

Khiena Z. Brainina, Alisa N. Kositzina and Alla Ivanova

27.1	Introduction and application	643
27.1.1	Immunosensor	645
27.1.2	Non-enzymatic urea sensor	650
27.1.3	Sensor and method for AOA measurement	655
27.2	Conclusion	662
	Acknowledgment	664
	References	664

Contents

Chapter 28. Analysis of meat, wool and milk for glucose, lactate and organo-phosphates at industrial point-of-need using electrochemical biosensors

A.L. Hart

28.1	Introduction	667
28.1.1	Terms	667
28.1.2	Electrochemical biosensors in an industrial context	668
28.2	Electrochemical biosensors for milk, meat and wool	671
28.2.1	Milk and dairy products	671
28.2.2	Meat	675
28.2.3	Wool	678
28.3	Testing biosensors: brief comments on experimental design and statistics	680
28.4	Conclusion	681
	Disclaimer	682
	References	682

Chapter 29. Rapid detection of organophosphates, Ochratoxin A and Fusarium sp. in durum wheat via screen printed based electrochemical sensors

D. Compagnone, K. van Velzen, M. Del Carlo, Marcello Mascini and A. Visconti

29.1	Introduction	687
29.1.1	Biotic and abiotic contaminants in durum wheat	687
29.1.2	Screen-printed electrochemical sensors for the detection of acetylcholinesterase inhibitors	689
29.1.3	Screen-printed electrochemical DNA sensors for identification of microorganisms	693
29.1.4	Screen-printed electrochemical immunosensors for the detection of toxins	697
29.2	Application	698
29.2.1	Screen-printed electrochemical sensors for the detection of dichlorvos and pirimiphos-methyl	701
29.2.2	Screen-printed electrochemical sensors for the detection of ochratoxin in durum wheat	709
29.2.3	Screen-printed electrochemical sensors for the detection of <i>Fusarium</i> sp. DNA	711
29.3	Conclusions	714
	Acknowledgement	715
	References	715

Contents

Acknowledgments	883
References	883
 Chapter 36. <i>Microfluidic-based electrochemical platform for rapid immunological analysis in small volumes</i>	
Joel S. Rossier and Frédéric Reymond	
36.1 Introduction	885
36.1.1 Basic principle of the standard ELISA technique	886
36.1.2 Specific feature of ELISA in microtitre plates	887
36.1.3 Analysis time in diffusion-controlled assays (Nernst–Einstein diffusion rule)	887
36.1.4 Capillary immunoassays	889
36.2 Polymer microfluidic-based ELISAs with electrochemical detection	890
36.2.1 Immuchip TM : a disposable cartridge with polymer microfluidic electrochemical cells	890
36.2.2 Immuspeed TM : a bench-top instrument for microfluidic assays	891
36.2.3 Principles of microfluidic ELISAs with electrochemical detection	891
36.2.4 Microfluidics control thanks to integrated electrochemical flow sensors	891
36.2.5 Enzymatic detection by means of amperometry	892
36.3 IMMUSOFT TM : a program for computer-driven microfluidic assays	894
36.3.1 Method creator: establishment of assay protocols	895
36.3.2 Analysis menu: computerised assay realisation and control	897
36.3.3 Results menu: measurement display and data processing	900
36.4 Performances exemplified with the immunoassay of alkaline phosphatase	901
36.5 Conclusion and perspectives	904
References	904
 Chapter 37. <i>Scanning electrochemical microscopy in biosensor research</i>	
Gunther Wittstock, Malte Burchardt and Carolina Nunes Kirchner	
37.1 Introduction	907

Contents

<i>Procedure 2. Determination of cesium in natural waters using polymer-based ion-selective electrodes</i>	
Aleksandar Radu, Shane Peper and Dermot Diamond.	e13
<i>Procedure 3. Enantioanalysis of S-Captopril using an enantioselective, potentiometric membrane electrode</i>	
Raluca-Ioana Stefan-van Staden, Jacobus Frederick van Staden and Hassan Y. Aboul-Enein.	e21
<i>Procedure 4. Determination of Ca(II) in wood pulp using a calcium-selective electrode with poly(3,4-ethylenedioxythiophene) as ion-to-electron transducer</i>	
Johan Bobacka, Mercedes Vazquez, Fredrik Sundfors, Konstantin Mikhelson, Andrzej Lewenstam and Ari Ivaska.	e25
<i>Procedure 5. Titration of trimeprazine base with tartaric acid in isopropanol solution using polyaniline as indicator electrode</i>	
Johan Bobacka, Viktor Lax, Tom Lindfors and Ari Ivaska.	e29
<i>Procedure 6. Determination of cadmium concentration and pH value in aqueous solutions by means of a handheld light-addressable potentiometric sensor (LAPS) device</i>	
Torsten Wagner, Joachim P. Kloock and Michael J. Schoning.	e35

VOLTAMMETRIC SENSORS

<i>Procedure 7. Determination of lead and cadmium in tap water and soils by stripping analysis using mercury-free graphite-epoxy composite electrodes</i>	
Arben Merkoçi, Ulku Anik-Kirgoz and Salvador Alegret.	e47
<i>Procedure 8. Direct electrochemical measurement on skin surface using microelectrodes</i>	
Audrey Ruffien-Ciszak, Pierre Gros and Maurice Comtat	e53
<i>Procedure 9. Direct electrochemical measurements in dermo-cosmetic creams</i>	
Coline Guitton, Pierre Gros and Maurice Comtat	e59

Contents

<i>Procedure 10. Biosensor for integral toxicity</i> Luigi Campanella and Tania Gatta	e69
<i>Procedure 11. Photosensor of environmental permanence</i> Luigi Campanella and Tania Gatta	e75
<i>Procedure 12. Biosensors for the determination of radicals</i> Luigi Campanella and Tania Gatta	e79
<i>Procedure 13. The determination of metal ions using peptide-modified electrodes</i> Edith Chow and J. Justin Gooding	e83

CONTINUOUS MONITORING

<i>Procedure 14. Deposition of boron-doped diamond films and their anodic treatment for the oxygen-terminated diamond sensor</i> Chiaki Terashima and Akira Fujishima	e95
--	-----

GAS SENSORS

<i>Procedure 15. Chemoresistor for determination of mercury vapor</i> Majlinda Vasjari and Vladimir M. Mirsky	e105
--	------

ENZYME ELECTRODES

<i>Procedure 16. Determination of gluconic acid in honey samples using an integrated electrochemical biosensor based on self-assembled monolayer modified gold electrodes</i> S. Campuzano, M. Gamella, Beatriz Serra, Ángel Julio Reviejo and Jose Manrrel Pingarrón	e113
<i>Procedure 17. Preparation of Prussian blue modified screen-printed electrodes via a chemical deposition for mass production of stable hydrogen peroxide sensors</i> Francesco Ricci, Danila Moscone and Giuseppe Palleschi	e119
<i>Procedure 18. Electrochemical sensor array for the evaluation of astringency in different tea samples</i> Saverio Mannino and Matteo Scampicchio	e125

Contents

- Procedure 19. Characterization of the PDO Asiago cheese by an electronic nose*
S. Benedetti and Saverio Mannino e131
- Procedure 20. Determination of methyl mercury in fish tissue using electrochemical glucose oxidase biosensors based on invertase inhibition*
Aziz Amine and Hasna Mohammadi e139
- Procedure 21. Protein phosphatase inhibition-based biosensor for amperometric microcystin detection in cyanobacterial cells*
M. Campàs, D. Szydłowska and Jean-Louis Marty. e151
- Procedure 22. Voltammetric determination of paracetamol in pharmaceuticals using a zucchini (Cucurbita pepo) tissue biosensor*
Orlando Fatibello-Filho, Karina Omuro Lupetti, Oldair Donizeti Leite and Iolanda C. Vieira. e157
- Procedure 23. Determination of total phenols in wastewaters using a biosensor based on carbon paste modified with crude extract of jack fruit (Artocarpus integrifolia L.)*
Orlando Fatibello-Filho, Karina O. Lupetti, Oldair D. Leite and Iolanda C. Vieira. e163
- Procedure 24. Construction of an enzyme-containing microelectrode array and use for detection of low levels of pesticides*
Frank Davis, Karen A. Law, Anthony P.F. Turner and Seamus P.J. Higson. e169

AFFINITY SENSORS

- Procedure 25. PCB analysis using immunosensors based on magnetic beads and carbon screen-printed electrodes in marine sediment and soil samples*
S. Centi, G. Marrazza and M. Mascini. e177
- Procedure 26. Construction of amperometric immunosensors for the analysis of cholera antitoxin and comparison of the performances between three different enzyme markers*
Rodica E. Ionescu, Chantal Gondran, Serge Cosnier and Robert S. Marks. e185

Contents

- Procedure 34.** *Electrochemical determination of sulfonamide antibiotics in milk samples using a class-selective antibody*
Emanuela Zacco, Roger Galve, Javier Adrian, Francisco Sanchez Baeza, Maria Pilar Marco, Salvador Alegret and Maria Isabal Pividori e237

THICK AND THIN FILM BIOSENSORS

- Procedure 35.** Preparation of electrochemical screen-printed immunosensors for progesterone and their application in milk analysis
Roy M. Pemberton and John P. Hart e245
- Procedure 36.** Genosensor on gold thin-films with enzymatic electrochemical detection of a *SARS* virus sequence
Patricia Abad-Valle, Maria Teresa Fernandez-Abedul and Agustín Costa-Garcia e251
- Procedure 37.** Genosensor on streptavidin-modified thick-film carbon electrodes for *TNFRSF21* PCR products
David Hernandez-Santos, Maria Begoiia Gonzalez-Garcia and Agustín Costa-Garcia e257
- Procedure 38.** Electrochemical immunosensor for diagnosis of the forest-spring encephalitis
Khiena Z. Brainina, Alisa N. Kositzina, Maya Yu. Rubtsova, Boris M. Sergeev and Svetlana Yu. Saraeva e265
- Procedure 39.** Non-enzymatic urea sensor
Khiena Z. Brainina, Alisa N. Kositzina and Svetlana Yu. Saraeva e271
- Procedure 40.** Potentiometric determination of antioxidant activity of food and herbal extracts
Khiena Z. Brainina, Alla V. Ivanova, Elena N. Sharafutdinova and Svetlana Yu. Saraeva e277
- Procedure 41.** Convenient and rapid detection of cholinesterase inhibition by pesticides extracted from sheep wool
Alan L. Hart. e285