

Contents

1	Application of Instrumental Methods in the Analysis of Historical, Artistic, and Archaeological Objects	1
1.1	Archaeology and Conservation of Cultural Heritage	2
1.1.1	Archaeology, Archaeometry, and Archaeological Science	2
1.1.2	Conservation of Cultural Heritage	3
1.1.3	A Brief History of the Scientific Analysis of Cultural Heritage	5
1.2	Role of the Analytical Methods in Archaeometrical and Cultural Heritage Research	9
1.3	Information Provided by the Analytical Research	9
1.3.1	Analytical Information Obtained from the Object	12
1.3.2	Analytical Information Obtained from the Environment	14
1.3.3	Analytical Information Obtained from the Conservation Processes	15
1.4	Analytical Methodologies Applied to Archaeometry and Cultural Heritage Research	16
1.4.1	Requirements of the Analytical Methodologies	16
1.4.2	Sampling Strategy	17
1.4.3	Preparation of Samples	19
1.4.4	Data Measurement and Processing	21
1.5	An Overview of Scientific Methods Applied in Archaeometry and Cultural Heritage Research	21
1.5.1	Analytical Methods	21
1.5.2	Dating Methods	36
	References	44
2	Electrochemical Processes and Techniques	51
2.1	Introduction	51
2.2	Voltammetry of Immobilized Microparticles	53

2.2.1	Voltammetry, General Aspects and Conventions	53
2.2.2	Solid-State Transformations	54
2.2.3	Reductive/Oxidative Dissolution Processes	57
2.2.4	Redox Processes with Phase Changes	58
2.3	Electrochemical Impedance Spectroscopy	60
2.3.1	Impedance Measurements and Impedance Spectroscopy	60
2.3.2	Circuit Elements and Equivalent Circuits	63
2.4	Other Techniques	67
2.4.1	Combination with Non-electrochemical Techniques	67
2.4.2	Scanning Electrochemical Microscopy	67
2.5	A Note on Thermochemical Calculations	68
	References	71
3	Voltammetry: The Essentials	77
3.1	General Aspects	77
3.2	The Electrochemical Reaction	78
3.3	Reversible Solution-Phase Voltammetry Under Diffusion Control	80
3.4	Resistive and Capacitive Effects	83
3.5	Deviations from Reversibility and Coupled Chemical Reactions	86
3.6	Voltammetry of Surface-Confined Species	88
3.7	Voltammetry of Oxidation/Reduction of Ion-Permeable Solids	89
3.8	Voltammetry of Oxidative/Reductive Dissolution Processes	91
3.9	Voltammetry of Solid-to-Solid Redox Transformations	92
3.10	Electrocatalysis	97
	References	99
4	Analytical Issues	103
4.1	Generalities	103
4.2	Identification of Components	104
4.2.1	Voltammetric Parameters	104
4.2.2	Tafel-Type Analysis	108
4.3	Quantification	110
4.3.1	General Aspects	110
4.3.2	Voltammetric and Coulometric Quantification Strategies	110
4.3.3	Standard Addition Methods	113
4.3.4	Quantification in the Presence of Interferents	118
4.4	Speciation	120
4.5	Electrochemical Data Processing	122
4.5.1	Handling Electrochemical Signals	122
4.5.2	Bivariant and Multivariant Techniques	124
	References	124

5	Pigments and Paintings I	129
5.1	Introduction	129
5.2	Identification of Inorganic Pigments	130
5.3	Pigment Mixtures	133
5.4	Identification of Organic Pigments	137
5.5	Pigments and Binding Media	140
5.6	Nanoscale Characterization and Mapping of Pictorial Components	147
	References	153
6	Pigment and Paintings II	157
6.1	Electrochemical Characterization of Workshops	157
6.2	Degradation Processes; Pigment Alteration in Extreme Heritage	163
6.3	Organic–Inorganic Hybrid Pigments: The Maya Blue Problem	168
	References	177
7	Ceramic, Glass, and Glazed Materials I	183
7.1	Ceramic, Glass, and Glazed Heritage	183
7.2	Detection and Characterization of Electroactive Species	184
7.3	Speciation	187
7.4	Characterization of Archaeological Glass Sites	192
7.5	Glass Alteration and Dating	196
	References	202
8	Ceramics, Glasses, and Glazed Materials II	207
8.1	Pottery, an Overview	207
8.2	Electrochemistry of Pottery	207
8.3	Characterization of Archaeological Sites	212
8.4	Information on Manufacturing Techniques	221
8.5	Impedance Analysis	221
8.6	Dating	229
	References	233
9	Organic Materials	237
9.1	Introduction	237
9.2	Vegetal Electrochemistry	237
9.3	Wooden Objects	241
9.4	Paper	245
9.5	Charcoal	248
9.6	Tar Pitch	252
9.7	Dating	255
	References	260

10	Metallic Heritage: Electrochemistry of Corrosion Products	265
10.1	Introduction	265
10.2	Corrosion of Metal Objects	266
10.3	Identification of Metals and Corrosion Products	269
10.4	In-Depth Electrochemistry	272
10.5	Archaeometric Issues	280
10.6	Impedance Analysis	284
10.7	Gold Electrochemistry	289
	References	293
11	Metallic Heritage: Electrochemistry of Metal Objects	299
11.1	Direct Electrochemistry of Metal Artifacts	299
11.2	Diagnosis	300
11.2.1	Polarization Curves	300
11.2.2	Electrochemical Impedance Spectroscopy	303
11.2.3	Open-Circuit Potential	308
11.2.4	Other Techniques	324
11.3	Preservation of Metallic Heritage	324
11.3.1	Selective Removal and Anodization	324
11.3.2	Protective Coatings	325
11.3.3	Electrochemical Treatments, Dechlorination	327
	References	328
12	Electrochemical Metal Dating	335
12.1	Time and Electrochemistry, an Overview	335
12.2	Dating of Corroded Metals	336
12.2.1	Antecedents	336
12.2.2	Lead	337
12.2.3	Copper and Bronze	343
12.2.4	Leaded Bronze	346
12.3	Gold Dating	349
12.4	Prospective on Metal Dating	355
	References	361
	Index	365
	Electrochemical Data Processing	122
	4.3.1 Handling Electrochemical Signals	122
	4.3.2 Bivariate and Multivariate	124
	References	124