

Contents

1	Sampling and sampling techniques	1
	(the late) <i>K. Grasshoff</i>	
1.1	Introduction	1
1.2	General principles, error and accuracy	2
1.3	Sampling	5
1.4	Water samplers	11
	References to Chapter 1	19
2	Filtration and storage	21
	(the late) <i>K. Grasshoff</i>	
2.1	Filtration	21
2.1.1	General remarks	21
2.1.2	Characteristics and composition of filters	21
2.1.3	Filtration procedures	23
2.2	Storage	25
2.2.1	General remarks	25
2.2.2	Storage for analysis of the major compounds	26
2.2.3	Storage for the analysis of nutrients	27
2.2.3.1	General remarks	27
2.2.3.2	Storage of samples for analysis of dissolved phosphate	27
2.2.3.3	Storage of samples for analysis of total phosphorus	28
2.2.3.4	Storage of samples for analysis of nitrogen compounds	28
2.2.3.5	Storage of samples for analysis of silicate	29
	References to Chapter 2	30
3	Determination of salinity	31
	(the late) <i>K. Grasshoff</i>	
3.1	Definition of salinity and the salinity-chlorinity relationship	31

VIII *Contents*

3.1.1	History	31
3.1.2	New definition of salinity	33
3.1.3	Standard seawater	37
3.2	The Mohr-Knudsen titration of chlorinity	38
3.2.1	Introduction	38
3.2.2	Principles of the determination	39
3.2.3	Apparatus	40
3.2.4	Reagents	41
3.2.5	Procedure	42
3.2.5.1	Standardization of the silver nitrate solution	42
3.2.5.2	Calculation of the calibration factor	43
3.2.5.3	Titration of the sample	44
3.2.5.4	Calculation of the chlorinity	44
3.2.6	Range and accuracy	45
3.3	Micro-chlorinity determination	45
3.3.1	Introduction	45
3.3.2	Principle of the determination	46
3.3.3	Apparatus	48
3.3.4	Reagents	48
3.3.5	Procedure	49
3.3.5.1	Standardization of the silver nitrate solution	49
3.3.5.2	Titration of the sample	49
3.3.5.3	Calculation of chlorinity	49
3.4	Determination of salinity with the salinometer	49
3.4.1	Introduction	49
3.4.2	Principle of the method	50
3.4.3	Apparatus	53
3.4.4	Procedure	53
3.4.4.1	Subsampling and storage	53
3.4.4.2	Standardization of the salinometer	53
3.4.4.3	Preparation of the substandard	55
3.4.4.4	Measurement of the samples	55
3.4.5	Conversion of relative conductivity into salinity	56
3.4.6	Precision and accuracy	56
	References to Chapter 3	58
4	Determination of oxygen	61
	(the late) <i>K. Grasshoff</i>	
4.1	Introduction	61
4.2	Principle of the determination	63

4.3	Possible sources of systematic errors	64
4.4	Reagents	65
4.5	Instruments	66
4.6	Procedure	68
4.6.1	Standardization of the thiosulphate solution	68
4.6.2	Subsampling and fixation of the dissolved oxygen	68
4.6.3	Storage	69
4.6.4	Titration	69
4.6.5	Determination of the reagent blank	70
4.6.6	Calculation of the result	70
4.6.7	Accuracy	71
	References to Chapter 4	72

5 Determination of hydrogen sulphide 73

S. Fonselius

5.1	Introduction	73
5.2	Analytical methods	74
5.2.1	Colorimetric analysis	74
5.3	Reagents	75
5.4	Special apparatus	76
5.5	Sampling	76
5.6	Procedure	76
5.6.1	Adding reagents	76
5.6.2	Preservation of samples	77
5.6.3	Dilution of samples	77
5.6.4	Analysis	77
5.6.5	Units	78
5.7	Standardization and calibration of the method	78
5.7.1	Thiosulphate solution	78
5.7.2	Standardization of the sulphide working solution	78
5.7.3	Photometric standard samples	79
5.8	Titrimetric method	79
	References to Chapter 5	

X *Contents*

6	Determination of thiosulphate 81 (the late) <i>K. Grasshoff</i>
6.1	Introduction 81
6.2	Principle of the determination 82
6.3	Apparatus 82
6.4	Reagents 82
6.5	Sampling and storage 83
6.6	Procedure 83
6.6.1	Standardization of the thiosulphate solution 83
6.6.2	Titration of the sample 83
6.7	Calculation of the thiosulphate content of the sample 84
6.8	Interference 84
	References to Chapter 6 84
7	Determination of pH 85 (the late) <i>K. Grasshoff</i>
7.1	Introduction 85
7.2	Principles of the measurement of pH 85
7.2.1	Activity of pure water 85
7.2.2	Activity of seawater 86
7.2.3	Principle of the measuring technique 87
7.3	Instruments and reagents 92
7.3.1	Instruments 92
7.3.2	Reagents 93
7.4	Sampling and storage 93
7.5	Determination of pH 93
7.5.1	Calibration of the pH meter 93
7.5.2	Measurement of pH in seawater samples 94
7.6	Accuracy and precision 95
7.7	Calculation of the in situ pH 95

7.7.1	Temperature correction	95
7.7.2	Pressure correction	96
	References to Chapter 7	97
8	Determination of alkalinity and total carbonate	99
	<i>T. Almgren, D. Dyrsen and S. Fonselius</i>	
8.1	Introduction	99
8.2	List of symbols	99
8.3	Approaches to the carbonate system in seawater	100
8.3.1	Definitions	100
8.3.2	Survey of methods	101
8.3.3	Calculation of carbonate species	102
8.4	Methods	103
8.4.1	The back titration method by <i>Gripenberg</i>	103
8.4.1.1	Principle of the method	103
8.4.1.2	Sampling and storage	104
8.4.1.3	Reagents	104
8.4.1.4	Equipment	104
8.4.1.5	Standardization of the solutions	105
8.4.1.6	The analysis of samples	106
8.4.1.7	Modification according to <i>Koroleff</i>	107
8.4.1.8	Other methods	106
8.4.1.9	Precision	107
8.4.2	The pH method	108
8.4.2.1	Theory	108
8.4.2.2	Procedure for obtaining f_{H^+} values	108
8.4.2.3	Analysis of the sample	109
8.4.2.4	Chemicals and special apparatus	109
8.4.2.5	Modifications of the method	109
8.4.2.6	Accuracy	109
8.4.3	The potentiometric titration method	110
8.4.3.1	Theory	110
8.4.3.2	Procedure	114
8.4.3.3	Special apparatus	115
8.4.3.4	Precision of Alk_1 and CO_2 and accuracy of the method	116
8.4.3.5	Future computations	116
8.4.4	The photometric titration method	117
8.4.4.1	Theory	117
8.4.4.2	Titrator	118
8.4.4.3	Reagents	119
8.4.4.4	Procedure	119

8.5	Practical hints on the methods	120
8.5.1	Time required for analysis	120
8.5.2	Comparison of the methods	120
8.5.3	Equipment	121
8.6	Some aspects of sampling	121
8.7	Concluding remarks	122
	References to Chapter 8	122

9 Determination of nutrients 125

9.1	Determination of phosphorus	125
	<i>F. Koroleff</i>	
9.1.1	Chemistry of phosphorus in seawater	125
9.1.2	Determination of dissolved inorganic phosphate	126
9.1.2.1	Outline of the method	126
9.1.2.2	Range of the method	126
9.1.2.3	Precision	126
9.1.2.4	Interferences	127
9.1.2.5	Equipment	128
9.1.2.6	Reagents	128
9.1.2.7	Sampling and storage	129
9.1.2.8	Procedures	129
9.1.3	Determination of dissolved inorganic phosphate in the presence of arsenic	131
9.1.3.1	Introduction	131
9.1.3.2	Outline of the method	131
9.1.3.3	Reagents	131
9.1.3.4	Procedures	131
9.1.4	Determination of dissolved inorganic phosphate by an extraction procedure (high-sensitivity method)	132
9.1.4.1	Introduction	132
9.1.4.2	Outline of the method	132
9.1.4.3	Range of the method	132
9.1.4.4	Interferences	132
9.1.4.5	Equipment	133
9.1.4.6	Reagents	133
9.1.4.7	Sampling and storage	133
9.1.4.8	Calibration	133
9.1.4.9	Determination of blanks	133
9.1.4.10	Analysis of samples	134
9.1.5	Determination of total phosphorus by acid persulphate oxidation	134
9.1.5.1	Introduction	134
9.1.5.2	Outline of the method	134

9.1.5.3	Range and precision	134
9.1.5.4	Interferences	135
9.1.5.5	Equipment	135
9.1.5.6	Reagents	135
9.1.5.7	Sampling and storage	135
9.1.5.8	Calibration	135
9.1.5.9	Determination of blanks	136
9.1.5.10	Analysis of samples	136
9.1.6	Determination of total phosphorus by alkaline persulphate oxidation	136
9.1.6.1	Principle of the method	136
9.1.6.2	Range and precision	137
9.1.6.3	Interferences	137
9.1.6.4	Equipment	137
9.1.6.5	Reagents	137
9.1.6.6	Sampling and storage	137
9.1.6.7	Procedures	138
9.1.7	Determination of polyphosphates	138
9.1.7.1	Procedure	138
9.1.8	Alternative methods	139
9.2	Determination of nitrite	139
	(the late) <i>K. Grasshoff</i>	
9.2.1	Introduction	139
9.2.2	Principle of the method	139
9.2.3	Special equipment	140
9.2.4	Reagents	141
9.2.5	Sampling	141
9.2.6	Procedures	141
9.2.6.1	Calibration	141
9.2.6.2	Determination of nitrite content of the samples	142
9.2.7	Precision and interference	142
9.3	Determination of nitrate	143
	(the late) <i>K. Grasshoff</i>	
9.3.1	Introduction	143
9.3.2	Principle of the determination	144
9.3.3	Special equipment	146
9.3.4	Reagents	147
9.3.5	Preparation of the reductor	147
9.3.6	Sampling and storage	147
9.3.7	Procedures	148
9.3.7.1	Calibration	148
9.3.7.2	Measurement of the samples	148
9.3.8	Checking the efficiency of the reductor	149
9.3.9	Precision and systematic errors	149
9.3.10	Interferences	150

9.4	Determination of ammonia	150
	<i>F. Koroleff</i>	
9.4.1	Abundance and chemistry in seawater	150
9.4.2	Determination of ammonia-nitrogen	151
9.4.2.1	Introduction	151
9.4.2.2	Outline of the method	152
9.4.2.3	Range of the method	152
9.4.2.4	Precision	152
9.4.2.5	Interferences	153
9.4.2.6	Equipment	153
9.4.2.7	Reagents	153
9.4.2.8	Sampling and storage	154
9.4.2.9	Calibration	155
9.4.2.10	Salt effect	155
9.4.2.11	Reagent blank	156
9.4.2.12	Pre-treatment of samples	156
9.4.2.13	Analysis of samples	156
9.4.3	The indophenol procedure with no citrate added	157
9.5	Determination of urea	158
	<i>F. Koroleff</i>	
9.5.1	Abundance and chemistry in seawater	158
9.5.2	Determination of urea-nitrogen	158
9.5.2.1	Introduction	158
9.5.2.2	Outline of the method	159
9.5.2.3	Range of the method	159
9.5.2.4	Precision	159
9.5.2.5	Interferences	160
9.5.2.6	Equipment	160
9.5.2.7	Reagents	160
9.5.2.8	Sampling, storage and pre-treatment	160
9.5.2.9	Calibration	161
9.5.2.10	Optical blanks	161
9.5.2.11	Analysis of samples	162
9.5.3	Automated analysis	162
9.6	Total and organic nitrogen	162
	<i>F. Koroleff</i>	
9.6.1	Occurrence in seawater	162
9.6.2	Determination of total and organic nitrogen	163
9.6.3	Determination of total nitrogen after persulphate oxidation	164
9.6.3.1	Outline of the method	164
9.6.3.2	Range of the method	164
9.6.3.3	Precision	165
9.6.3.4	Interferences	165
9.6.3.5	Equipment	165

9.6.3.6	Reagents	165
9.6.3.7	Sampling and storage	166
9.6.3.8	Calibration	167
9.6.3.9	Determination of blank	167
9.6.3.10	Salt effect	168
9.6.3.11	Analysis of samples	168
9.6.4	Simultaneous oxidation of nitrogen and phosphorus compounds by persulphate	168
9.6.5	Kjeldahl nitrogen	169
9.6.5.1	Outline of the method	169
9.6.5.2	Capabilities	169
9.6.5.3	Precision	170
9.6.5.4	Interferences	170
9.6.5.5	Equipment	170
9.6.5.6	Reagents	170
9.6.5.7	Sampling and storage	171
9.6.5.8	Calibration	171
9.6.5.9	Reagent blank	172
9.6.5.10	Analysis of samples	172
9.6.6	Determination of soluble organic nitrogen by UV light oxidation	173
9.7	Determination of silicon	174
	<i>F. Koroleff</i>	
9.7.1	Abundance and chemistry in seawater	174
9.7.2	Determination of dissolved inorganic silicate	175
9.7.2.1	Introduction	175
9.7.2.2	Outline of the method	175
9.7.2.3	Range of the method	176
9.7.2.4	Precision	176
9.7.2.5	Interferences	176
9.7.2.6	Equipment	177
9.7.2.7	Reagents	177
9.7.2.8	Sampling and storage	178
9.7.2.9	Calibration	178
9.7.2.10	Salt error	179
9.7.2.11	Reagent blank	179
9.7.2.12	Pre-treatment of samples	179
9.7.2.13	Analysis of samples	180
9.7.3	Determination of total silicon	180
9.7.3.1	Introduction	180
9.7.3.2	Principle of the method	180
9.7.3.3	Range, capacity, precision and interferences	181
9.7.3.4	Equipment	181
9.7.3.5	Reagents	181
9.7.3.6	Sampling and storage	181
9.7.3.7	Procedures	181

9.7.4	Determination of particulate silicon	182
9.7.5	Total silicon by carbonate fusion	183
9.7.5.1	Reagents	183
9.7.5.2	Procedure	183
	References to Chapter 9	184
	Section 9.1	184
	Section 9.2	184
	Section 9.3	185
	Section 9.4	185
	Section 9.5	186
	Section 9.6	186
	Section 9.7	187
10	Determination of trace metals	189
	10.1 – 10.6.4 <i>K. Kremling</i>	
	10.6.5 <i>J. Olafsson</i>	
	10.6.6 – 10.6.8 <i>M. O. Andreae</i>	
	10.6.9 – 10.6.11 <i>F. Koroleff</i>	
10.1	Introduction	189
10.2	Materials and cleaning procedures	189
10.3	Purification of reagents	191
10.4	Sample handling	193
10.5	The blank	195
10.6	Analytical methods	196
10.6.1	Cadmium, copper, iron, nickel, cobalt and zinc	197
10.6.1.1	Principle of the method	197
10.6.1.2	Reagents and equipment	199
10.6.1.3	Analysis of the sample	200
10.6.1.4	Calculation of results	202
10.6.1.5	Precision and blank determination	203
10.6.2	Manganese	203
10.6.2.1	Principle of the method	204
10.6.2.2	Reagents and equipment	204
10.6.2.3	Analysis of the sample	204
10.6.2.4	Calculation of results	205
10.6.2.5	Precision and blank determination	205
10.6.3	Chromium	205
10.6.3.1	Principle of the method	206
10.6.3.2	Reagents and equipment	206

10.6.3.3	Analysis of the sample	207
10.6.3.4	Calculation of results	207
10.6.3.5	Precision and blank determination	208
10.6.4	Zinc	208
10.6.4.1	Principle of the method	208
10.6.4.2	Reagents and equipment	210
10.6.4.3	Analysis of the sample	211
10.6.4.4	Sources of error	212
10.6.4.5	Calculation of results	212
10.6.4.6	Precision and blank determination	213
10.6.5	Mercury	213
10.6.5.1	Principle of the method	214
10.6.5.2	Reagents and equipment	214
10.6.5.3	Analysis of the sample	215
10.6.5.4	Test procedures and sources of error	216
10.6.5.5	Calculation of results	216
10.6.5.6	Precision and determination of blank	217
10.6.6	Arsenic	218
10.6.6.1	Principle of the method	218
10.6.6.2	Reagents and equipment	219
10.6.6.3	Analysis of the sample	222
10.6.6.4	Test procedures and sources of error	222
10.6.6.5	Quantitation of the results	223
10.6.6.6	Precision and systematic errors	224
10.6.6.7	Sample collection, treatment and storage	224
10.6.7	Antimony	225
10.6.7.1	Principle of the method	225
10.6.7.2	Reagents and equipment	226
10.6.7.3	Analysis of the sample	228
10.6.7.4	Test procedures and sources of error	229
10.6.7.5	Quantitation of the results	229
10.6.7.6	Precision and systematic errors	229
10.6.7.7	Sample collection, treatment and storage	229
10.6.8	Germanium	230
10.6.8.1	Principle of the method	230
10.6.8.2	Reagents and equipment	230
10.6.8.3	Analysis of the sample	233
10.6.8.4	Test procedures and sources of error	234
10.6.8.5	Quantitation of the results	235
10.6.8.6	Precision and systematic errors	235
10.6.8.7	Sample collection, treatment and storage	235
10.6.9	Iron	236
10.6.9.1	Principle of the method	236
10.6.9.2	Range and precision	237
10.6.9.3	Interferences	237
10.6.9.4	Equipment	237

10.6.9.5	Reagents	237
10.6.9.6	Sampling and storage	238
10.6.9.7	Procedures	238
10.6.10	Manganese	239
10.6.10.1	Principle of the method	239
10.6.10.2	Range and precision	240
10.6.10.3	Interferences	240
10.6.10.4	Equipment	240
10.6.10.5	Reagents	240
10.6.10.6	Sampling and storage	241
10.6.10.7	Procedures	241
10.6.11	Aluminium	242
10.6.11.1	Principle of the method	242
10.6.11.2	Range and precision	242
10.6.11.3	Interferences	242
10.6.11.4	Equipment	243
10.6.11.5	Reagents	243
10.6.11.6	Sampling and storage	243
10.6.11.7	Procedures	244
	References to Chapter 10	

11 Determination of the major constituents 247

K. Kremling

11.1	Introduction	247
11.2	Principal determinations of chlorinity ratios and major chemical species	247
11.2.1	Calcium	247
11.2.2	Strontium	248
11.2.3	Magnesium	248
11.2.4	Sulphate	249
11.2.5	Bromide	249
11.2.6	Boron	249
11.2.7	Fluoride	249
11.3	Analytical methods	250
11.3.1	Calcium	250
11.3.1.1	Principle of the method	250
11.3.1.2	Reagents and equipment	251
11.3.1.3	Standardization of the EGTA solution	251
11.3.1.4	Analysis of the sample	251
11.3.1.5	Calculation of results	252
11.3.1.6	Precision	252
11.3.1.7	Photometric EGTA titration with zincon and Zn-EGTA as indirect indicator	252

11.3.2	Strontium	252
11.3.2.1	Principle of the method	253
11.3.2.2	Reagents and equipment	253
11.3.2.3	Analysis of the sample	254
11.3.2.4	Calibration	254
11.3.2.5	Calculation of results	254
11.3.2.6	Precision	255
11.3.2.7	Ion-exchange separation scheme with Amberlite CG 120	255
11.3.3	Magnesium	255
11.3.3.1	Principle of the method	255
11.3.3.2	Reagents and equipment	256
11.3.3.3	Standardization of EDTA solution	256
11.3.3.4	Analysis of the sample	257
11.3.3.5	Calculation of results	258
11.3.3.6	Precision	258
11.3.3.7	Ion-exchange separation of magnesium	258
11.3.4	Sulphate	259
11.3.4.1	Principle of the method	259
11.3.4.2	Reagents and equipment	259
11.3.4.3	Analysis of the sample	259
11.3.4.4	Calculation of results	260
11.3.4.5	Precision	260
11.3.5	Bromide	260
11.3.5.1	Principle of the method	260
11.3.5.2	Reagents and equipment	261
11.3.5.3	Standardization of the sodium thiosulphate solution	261
11.3.5.4	Analysis of the sample	262
11.3.5.5	Calculation of results	262
11.3.5.6	Precision	262
11.3.6	Boron	262
11.3.6.1	Principle of the method	263
11.3.6.2	Reagents and equipment	263
11.3.6.3	Analysis of the sample	263
11.3.6.4	Calibration	264
11.3.6.5	Calculation of results	264
11.3.6.6	Precision	264
11.3.6.7	Mannitol boric acid method	264
11.3.7	Fluoride	264
11.3.7.1	Principle of the method	265
11.3.7.2	Reagents and equipment	265
11.3.7.3	Analysis of the sample	265
11.3.7.4	Calibration	266
11.3.7.5	Calculation of results	266
11.3.7.6	Precision	266
11.3.7.7	Potentiometric method with ion-specific electrode	266
	References to Chapter 11	267

12	Determination of organic constituents	269
12.1	Determination of particulate organic carbon and nitrogen	269
	<i>M. Ehrhardt</i>	
12.1.1	Introduction	269
12.1.2	Apparatus	271
12.1.3	Analytical grade reagents	271
12.1.4	Sample preparation	272
12.1.4.1	Sampling	272
12.1.4.2	Filtration	272
12.1.4.3	Sample preservation	273
12.1.5	Analysis	273
12.1.6	Calibration	274
12.1.7	Blanks	275
12.2	Preparation of lipophilic organic seawater concentrates	276
	<i>M. Ehrhardt</i>	
12.2.1	Introduction	276
12.2.2	Outline of the method	277
12.2.3	Reagents	277
12.2.4	Apparatus and glassware	278
12.2.5	Cleaning the resin	279
12.2.6	Sample preparation	280
12.2.7	Sample storage	281
12.2.8	Blanks	281
12.3	Determination of petroleum residues dissolved and/or finely dispersed in surface seawater	281
	<i>M. Ehrhardt</i>	
12.3.1	Principle of the method	282
12.3.2	Reagents	283
12.3.3	Apparatus	283
12.3.4	Glassware	284
12.3.5	Cleaning glassware	285
12.3.6	Sampling and sample storage	286
12.3.7	Column chromatographic clean-up	286
12.3.8	Blanks	287
12.3.9	Spectrofluorimetric analysis	287
12.3.10	Calibration and quantification	287
12.3.11	Interferences	289
12.3.12	Sensitivity and range of the method	289
12.4	Determination of selected organochlorines in seawater	290
	<i>J. C. Duinker and M. T. J. Hillebrand</i>	
12.4.1	Introduction	290
12.4.2	Analytical techniques	291

- 12.4.2.1 Gas chromatographic separation and detection 291
 - 12.4.2.1.1 The gas chromatographic column 291
 - 12.4.2.1.2 The electron-capture detector 293
 - 12.4.2.1.3 Sample injection 293
 - 12.4.2.1.4 Operational conditions and procedures 294
 - 12.4.2.1.5 The gas chromatograph 295
- 12.4.2.2 Identification and quantification 295
 - 12.4.2.2.1 Standards 295
 - 12.4.2.2.2 Calibration 296
 - 12.4.2.2.3 Identification 298
 - 12.4.2.2.4 Sensitivity 298
- 12.4.3 Methods for extraction of organochlorine compounds from seawater solution and suspended particles 298
 - 12.4.3.1 Water 298
 - 12.4.3.1.1 Sorption onto adsorbents 298
 - 12.4.3.1.2 Solvent extraction 299
 - 12.4.3.2 Suspended matter 301
 - 12.4.4 Separation of dissolved and particulate suspended forms 301
 - 12.4.5 Treatment of sample extracts prior to GLC-ECD 302
- 12.4.5.1 Introduction 302
- 12.4.5.2 Method for separation of impurities 303
- 12.4.6 Quantification, extraction efficiency, accuracy and sensitivity 304
 - 12.4.6.1 Quantification 304
 - 12.4.6.2 Extraction efficiency 305
 - 12.4.6.3 Accuracy 307
 - 12.4.6.4 Sensitivity 308
 - 12.4.7 Sampling 308
- 12.5 Polyphenolic substances 310
 - 12.5.1 – 12.5.8 *B. Josefsson, 12.5.9 F. Koroleff*
 - 12.5.1 Introduction 310
 - 12.5.1.1 Humic substances 310
 - 12.5.1.2 Soluble lignin products 310
 - 12.5.2 Method 311
 - 12.5.3 Sampling, filtration and storage 311
 - 12.5.4 Apparatus and standards 312
 - 12.5.4.1 Apparatus 312
 - 12.5.4.2 Standards 312
 - 12.5.5 Capabilities of the method 312
 - 12.5.5.1 Analytical range and precision 312
 - 12.5.5.2 Ultimate detection limit 313
 - 12.5.6 Procedure, coastal waters 313
 - 12.5.6.2 Procedure, open sea samples 314
 - 12.5.7 Concluding remarks 315
 - 12.5.8 Alternative methods 315
 - 12.5.9 The Pearl-Benson or nitroso method 316

12.5.9.1	Introduction	316
12.5.9.2	Outline of the method	316
12.5.9.3	Capabilities	316
12.5.9.4	Interferences	317
12.5.9.5	Reagents	317
12.5.9.6	Sampling and storage	317
12.5.9.7	Determination of blanks	318
12.5.9.8	Calibration	318
12.5.9.9	Analysis of samples	318
12.6	Determination of amino acids and carbohydrates	319
12.6.1 – 12.6.4	<i>R. Dawson and G. Liebezeit, 12.6.5 B. Josefsson</i>	
12.6.1	Introduction	319
12.6.2	General remarks	319
12.6.3	Dissolved free amino acids (DFAA)	320
12.6.3.1	Class reaction	320
12.6.3.2	Reagents	321
12.6.3.3	Calibration	321
12.6.3.4	Manual procedure	321
12.6.3.5	Automatic procedure	322
12.6.3.6	Chromatographic separations of amino acids	323
12.6.3.7	Chromatographic separations of o-phthalaldehyde-amino acids	323
12.6.3.8	Detection	325
12.6.3.9	Equipment	325
12.6.3.10	Columns	326
12.6.3.11	Running parameters	326
12.6.3.12	Preparation of mobile phases	326
12.6.3.13	Pre-column derivatisation	327
12.6.3.14	Calibration	328
12.6.3.15	Dissolved combined amino acids	329
12.6.4	Dissolved carbohydrates	330
12.6.4.1	Class reactions	330
12.6.4.2	Calibration	330
12.6.4.3	Reagents	331
12.6.4.4	Procedure	331
12.6.4.5	Analytical range	332
12.6.4.6	Estimation of polysaccharide content (PCHO)	332
12.6.4.7	Mono- and polysaccharides after aqueous extraction of particulate matter	333
12.6.4.8	Chromatographic separations of carbohydrates	333
12.6.4.9	Equipment	334
12.6.4.10	Detection	336
12.6.4.11	Influence of running parameters on separations	336
12.6.4.12	Sample preparation	337
12.6.4.13	Preparation of buffers and reagents	338
12.6.4.14	Column packing	338
12.6.4.15	Calibration	339

12.6.5	Rapid spectrophotometric determination of total carbohydrates	340
12.6.5.1	Apparatus and reagents	340
12.6.5.2	Capabilities of the method	340
12.6.5.3	Experimental	341
12.6.5.4	Concluding remarks	341
12.6.5.5	Alternative methods	342
	References to Chapter 12	342
	Section 12.1	342
	Section 12.2	343
	Section 12.3	343
	Section 12.4	344
	Section 12.5	345
	Section 12.6	345
13	Automated chemical analysis	347
13.1 – 13.4	<i>H. P. Hansen and (the late) K. Grasshoff</i>	
13.5	<i>P. J. Statham and P. J. LeB. Williams</i>	
13.1	Introduction	347
13.2	Principle of automated analysis	348
13.2.1	The sampler	349
13.2.2	The proportioning pump	351
13.2.3	The analytical manifold	353
13.2.4	The flow-through colorimeter	354
13.2.5	The data acquisition system	357
13.2.6	The system calibration	360
13.3	Automated determination of seawater constituents	361
13.3.1	General outline	361
13.4	Procedures for the automated determination of seawater constituents	362
13.4.1	General remarks	362
13.4.2	Automated determination of ammonia	363
13.4.2.1	Reagents	363
13.4.2.2	The manifold	364
13.4.2.3	Standardization	364
13.4.2.4	Precision and interference	365
13.4.3	Automated determination of nitrite	365
13.4.3.1	Reagents	365
13.4.3.2	Manifold for nitrite	365
13.4.3.3	Precision and interferences	366
13.4.4	Automated determination of nitrate	366
13.4.4.1	The reductor	366
13.4.4.2	Reagents	367

13.4.4.3	The manifold	367
13.4.4.4	Reproducibility and interference	368
13.4.5	The automated determination of dissolved inorganic phosphate	368
13.4.5.1	Reagents	368
13.4.5.2	The manifold	369
13.4.5.3	Reproducibility and interference	370
13.4.6	Automatic determination of total phosphorus in seawater	370
13.4.6.1	Special equipment	371
13.4.6.2	Reagents	372
13.4.6.3	Preparation of the samples	372
13.4.6.4	The manifold	373
13.4.6.5	Range, reproducibility and interference	373
13.4.7	Automated determination of reactive silicate in seawater	374
13.4.7.1	Reagents	374
13.4.7.2	The manifold	376
13.4.7.3	Reproducibility and interference	376
13.4.8	Determination of the pH	376
13.4.9	Determination of total CO ₂	378
13.4.9.1	Reagents	378
13.4.9.2	The manifold	378
13.4.9.3	Standards and calibration	379
13.4.10	The continuous flow determination of salinity	379
13.5	The automatic determination of dissolved organic carbon	380
13.5.1	Introduction	380
13.5.1.1	General analytical strategy	380
13.5.1.1.1	Inorganic carbon removal	381
13.5.1.1.2	Oxidation of organic carbon to carbon dioxide	381
13.5.1.1.3	Carbon dioxide detection	382
13.5.2	Sampling, filtration and storage	383
13.5.2.1	Sampling	383
13.5.2.2	Filtration	383
13.5.2.3	Storage	384
13.5.3	Analysis	384
13.5.3.1	Equipment	384
13.5.3.1.1	Overview	384
13.5.3.1.2	Initial removal of inorganic carbon	385
13.5.3.1.3	The irradiator assembly	386
13.5.3.1.4	Removing carbon dioxide from the irradiated sample and drying of the gas stream	387
13.5.3.1.5	The infrared gas analyser	387
13.5.3.1.6	Manifold	388
13.5.3.1.7	Modifications for seaboard and continuous operation	388
13.5.3.1.8	Special considerations	389
13.5.3.2	Standards and reagents	390
13.5.3.2.1	Low organic carbon content (LOCC) water	390

13.5.2.2	Analytical reagents	390
13.5.3.2.3	Standards	390
13.5.3.3	Analytical procedure	391
13.5.3.3.1	Pre-analysis preparation	391
13.5.3.3.2	Analysis	391
13.5.3.3.3	Sampling frequency	391
13.5.3.3.4	Blanks and calibration	392
13.5.3.3.5	Shut-down procedure	392
13.5.3.3.6	Data analysis	392
13.5.4	Performance	392
13.5.5	Trouble shooting	392
	References to Chapter 13	394

Appendix 397

Index 403