

Wilson and Wilson's
COMPREHENSIVE ANALYTICAL CHEMISTRY

Edited by
G. SVEHLA, PH.D., D.SC., F.R.S.C.

*Reader in Analytical Chemistry
The Queen's University of Belfast*

VOLUME XVII

Gas and Liquid Analyzers

by Jaroslav Váňa

*Research Institute for Organic Syntheses
Pardubice, Czechoslovakia*



ELSEVIER SCIENTIFIC PUBLISHING COMPANY
AMSTERDAM OXFORD NEW YORK
1982

List of Contents

<i>List of symbols and units</i>	I
<i>Introduction</i>	15
<i>A General</i>	17
1 THE IMPORTANCE OF AUTOMATIC CONTROL OF THE CHEMICAL COMPOSITION OF SUB- STANCES	17
2 BASIC CONCEPTS AND CLASSIFICATION OF ANALYZERS	19
2.1 Instruments	19
2.1.1 The analyzer	19
2.1.2 Automatic analyzers	19
2.1.3 Semi-automatic analyzers	20
2.1.4 The indicator	20
2.2 Classification of automatic analyzers	20
2.2.1 Classification according to the phase analyzed	21
2.2.1.1 Gas analyzers	21
2.2.1.2 Liquid analyzers	21
2.2.1.3 Solid analyzers	21
2.2.2 Classification of analyzers according to their operating principle	22
2.2.2.1 Analyzers based on physical principles	22
2.2.2.2 Analyzers based on physico-chemical principles	23
2.2.2.3 Analyzers based on chemical principles	23

2.2.3	Classification of analyzers according to the performance of the analytical procedure	24
2.2.3.1	Individual analyses	24
2.2.3.2	Periodical analyses	24
2.2.3.3	Continuous analysis	24
2.2.4	Classification of analyzers according to the number of components to be determined	24
2.2.4.1	One-component analyzers	25
2.2.4.2	Multi-component analyzers	25
2.2.4.3	Total analyzers	25
2.2.5	Classification of analyzers according to the location of the analysis	25
2.2.5.1	Laboratory analysis	25
2.2.5.2	Production-line analysis	26
2.2.5.3	Field analysis	26
2.2.6	Classification of analyzers according to their purpose	26
2.2.6.1	Control analyzers	26
2.2.6.2	Analyzers for production monitoring and control	27
2.2.6.3	Concentration-balance analyzers	27
2.2.6.4	Safety precaution analyzers	27
2.2.7	Technical construction of analyzers	28
	References	28
3	GENERAL PROPERTIES OF SUBSTANCES	29
3.1	General properties of gases	29
3.1.1	Solubility of gases	33
3.1.2	Gas adsorption	36
3.2	General properties of liquids	37
3.3	Mixtures of substances	39
3.4	Methods of expressing the composition of substances	40
3.4.1	Mass concentration	40
3.4.2	Volume concentration	41
	References	42
4	REQUIREMENTS PLACED ON ANALYZERS AND SELECTION OF THE ANALYZER TYPE	43
4.1	General requirements	43

4.2	Construction requirements	44
4.3	Selection of analyzer type	45
4.4	Comparison of manual and automatic analyses	45
	References	46
5	BASIC PRINCIPLES OF AUTOMATIC ANALYSIS	47
5.1	Basic rules	47
5.2	Principles of automatic analysis	48
5.3	Analysis of binary mixtures	49
5.4	Analysis of pseudobinary mixtures	51
5.5	Analysis of ternary and multicomponent mixtures	52
5.6	Requirements placed on an ideal analyzer-detector	56
	References	57
6	EVALUATION OF MEASUREMENTS AND THE EFFECTS ON THE PRECISION OF ANALYZER OUTPUT VALUES	58
6.1	Errors of measurement	58
6.1.1	Classification of measuring errors	58
6.1.1.1	Errors arising during evaluation of repeated measurements of a certain quantity	60
6.1.1.2	Errors arising during evaluation of the results of the measurement of a dependence of one quantity on another	61
6.2	Principal characteristic quantities of instruments and analyzers	63
6.3	Effects on the measuring precision of the analyzer	64
6.3.1	The effect of variables of state	64
6.3.2	The effect of the flow-rate	65
	References	66
7	DYNAMIC PROPERTIES OF CONTINUOUS ANALYZERS	67
7.1	Transport delay	67
7.2	Capacity delay	68
	References	74

8	ANALYZER CONSTRUCTION	75
8.1	Analyzer accessories	75
8.1.1	Electrical accessories	75
8.1.1.1	Connection of meters to the analyzer output	76
8.1.1.2	Recorders	77
8.1.2	Sampling devices	78
	References	80
B	<i>Methods and instruments</i>	81
9	DENSITY	81
9.1	Principal relationships	81
9.2	Methods of determining gas densities	83
9.2.1	The instrument described by Pollitzer	83
9.2.2	The Lux gas balance	85
9.2.3	The Pollux densitometer	88
9.3	Instruments for measurement of the density of liquids	89
9.3.1	Float densitometers	90
9.3.1.1	A float densitometer without temperature compensation	91
9.3.1.2	A float densitometer with induction transfer and temperature compensation	91
9.3.1.3	A float densitometer based on the measurement of buoyancy with induction transfer	92
9.3.2	Densitometers based on the measurement of hydrostatic pressure	93
9.3.2.1	A densitometer operating on the principle of hydrostatic pressure measurement without temperature compensation	93
9.3.2.2	Other densitometer types based on measurement of the hydrostatic pressure	95
9.3.3	Densitometers based on a weighing principle	96
9.3.4	Densitometers based on absorption of nuclear radiation	97
9.3.4.1	A simple densitometer based on absorption of nuclear radiation	100

9.3.4.2	A double-beam densitometer based on absorption of nuclear radiation	100
9.3.4.3	The PZhR-2 densitometer	101
9.3.5	Densitometers based on various other principles	102
9.3.5.1	Vibrational densitometers for gases and liquids	102
9.3.5.2	Ultrasonic densitometers	104
9.3.5.2.1	Theoretical principles	104
9.3.5.2.2	Instruments based on the measurement of the velocity of ultrasonic wave propagation	106
9.3.5.2.3	Some constructions of ultrasonic analyzers	107
9.3.5.2.4	Evaluation of ultrasonic analyzers	108
9.4	Use and evaluation of automatic densitometers	108
	References	110
10	THERMAL CONDUCTIVITY	112
10.1	Principal relationships	112
10.2	Measuring methods	115
10.3	Construction of thermal conductivity analyzers	117
10.3.1	Chambers	117
10.3.2	Electrical circuit of a thermal conductivity sensor	118
10.3.3	The effect of temperature	118
10.3.4	The effect of the test gas flow-rate	119
10.3.5	The effect of pressure	119
10.4	Sensitivity of thermal conductivity analyzers	119
10.5	Instruments	121
10.5.1	The TKG-4 thermal conductivity analyzer	121
10.5.2	CALDOS thermal conductivity analyzers	122
10.5.3	The TP 1120 analyzers with two measuring bridges	123
10.5.4	The GACH-239 chlorine analyzer with four measuring bridges	125
10.5.5	An indicator of dangerous concentrations of hydrogen in the atmosphere	126
10.5.5.1	Instrument description	127
10.5.6	Determination of oxygen dissolved in water	130
10.6	Applications of thermal conductivity analyzers	131
10.7	Evaluation of thermal conductivity analyzers	136
	References	137

11	HEAT OF REACTION	139
11.1	Principal relationships	140
11.2	Measuring methods	142
11.3	Instruments	145
11.3.1	Gas analyzers based on the heat of reaction of two gases	145
11.3.1.1	An analyzer of combustible components in flue gases	145
11.3.1.2	A carbon monoxide analyzer	146
11.3.1.3	The TCHG-5 thermochemical gas analyzer	148
11.3.1.4	A simple portable analyzer for the determination of combustible gases	149
11.3.1.5	An indicator of traces of poisonous gases in the air	150
11.3.1.6	A flue gas analyzer based on measurement of the thermal conductivity and of the heat of combustion	151
11.3.1.7	Faults of gas analyzers based on the measurement of the heat of reaction using catalysts	153
11.3.2	Gas analyzers based on the heat of reaction of gases with liquids	154
11.3.2.1	The Thermoflux analyzer	154
11.3.3	Liquid analyzers based on the heat of liquid-liquid reactions	157
11.3.3.1	An analyzer based on the measurement of the heat of neutralization	157
11.3.3.2	An instrument for continuous monitoring of the composition of nitration mixtures	159
11.3.4	Thermometric titrations	161
11.4	Evaluation of analyzers based on the heat of reaction	162
	References	163
12	MAGNETIC SUSCEPTIBILITY	164
12.1	Principal relationships	164
12.2	Use of the magnetic properties of gases	166
12.3	Instruments	166
12.3.1	Analyzers based on the thermomagnetic principle	167
12.3.1.1	Thermomagnetic analyzers using a ring-shaped cell	168
12.3.1.2	The MAGNOS 2 analyzer	172
12.3.1.3	The PERMOLYT oxygen analyzer	173

12.3.1.4	Thermomagnetic analyzers of the MGK type	173
12.3.1.5	The OXYMAT oxygen analyzer	175
12.3.1.6	The MAGNOS 5 analyzer	177
12.3.2	Magnetomechanical instruments	178
12.3.2.1	Beckman oxygen analyzers	180
12.3.2.2	The SERVOMEX oxygen analyzer	182
12.3.3	Special instruments	184
12.3.3.1	An oxygen analyzer described by Kundt	184
12.3.3.2	OXYGOR 1 and OXOR oxygen analyzers	185
12.3.3.3	The OXYMAT 3 oxygen analyzer	187
12.3.4	Use of analyzers measuring magnetic susceptibility for the determination of oxygen dissolved in water	188
12.4	Evaluation of analyzers utilizing the magnetic proper- ties of oxygen	189
	References	190
13	ABSORPTION, REFLECTION AND SCATTER- ING OF ELECTROMAGNETIC RADIATION	192
13.1	Theoretical introduction	192
13.2	Construction elements of analyzers based on absorp- tion of electromagnetic radiation	196
13.3	Analyzers based on absorption of ultraviolet radiation	197
13.3.1	Construction components of ultraviolet analyzers	198
13.3.2	Instruments	199
13.3.2.1	The UF 6201 and UF 6202 chlorine ultraviolet analyzers	199
13.3.2.2	An ultraviolet compensation gas analyzer	200
13.3.2.3	The OKOMETER analyzer	201
13.3.2.4	The UVAMETER analyzer	202
13.3.2.5	LIMAS industrial analyzers	204
13.3.2.6	Mercury vapour analyzers	205
13.3.3	Application of ultraviolet analyzers	206
13.4	Analyzers based on absorption of visible radiation	207
13.4.1	Component parts of colorimetric analyzers	208
13.4.2	Some common types of colorimetric analyzer	209
13.4.2.1	Colorimeters with one radiation detector	209
13.4.2.2	Colorimeters with two radiation detectors	212
13.4.3	Colorimetric gas analyzers without auxiliary reaction	212

13.4.4	Colorimetric gas analyzers with auxiliary reactions	213
13.4.4.1	An oxygen analyzer	215
13.4.4.2	IMCOMETER analyzers	217
13.4.5	Colorimetric liquid analyzers without auxiliary reactions	219
13.4.6	Colorimetric liquid analyzers with auxiliary reactions	219
13.4.6.1	Colorimetric analyzers for monitoring water hardness	219
13.4.6.2	Colorimetric analyzers for monitoring small amounts of silicic acid in water	224
13.4.6.3	The Fuhrmann phosphatometer	226
13.4.6.4	The Fuhrmann analyzer for hydrazine in water	227
13.4.6.5	The Fuhrmann colorimetric analyzer for chlorine in water	228
13.4.6.6	The Fuhrmann dextrometer	229
13.5	Smoke and turbidity monitors	229
13.5.1	Smoke-monitors	231
13.5.1.1	Smoke-monitors placed outside the test gas stream	231
13.5.1.2	Smoke-monitors placed inside the test gas stream	232
13.5.2	Turbidity monitors	233
13.5.2.1	Turbidity monitors based on light absorption	234
13.5.2.2	A submersion turbidity-meter	235
13.5.2.3	Turbidity meters based on scattering of radiation	236
13.5.2.4	Water turbidity meters	237
13.5.2.5	The OLEOTROL analyzer	238
13.5.3	Standardization of turbidity meters	240
13.5.4	Application of turbidity meters	241
13.6	Special instruments	241
13.6.1	Hydrogen sulphide analyzers	241
13.7	Analyzers based on absorption of infrared radiation	243
13.7.1	Principles of infrared analyzers	244
13.7.2	Construction elements of infrared analyzers	246
13.7.3	Types of infrared analyzers	248
13.7.3.1	Infrared dispersionless analyzers with positive filtration	248
13.7.3.2	Infrared analyzers with negative filtration	249
13.7.3.3	Comparison of analyzers with positive and negative filtration	250

13.7.4	Infrared dispersionless analyzers with positive filtration	251
13.7.4.1	Autodetector analyzer	251
13.7.4.2	The URAS infrared analyzer	252
13.7.4.3	INFRALYT infrared analyzers	256
13.7.4.4	Analyzer described by Syromyatkin, Pavlenko and Anisimov	257
13.7.4.5	Infrared analyzers of the GIP series	258
13.7.4.6	Compensation infrared analyzers IREX	259
13.7.4.7	UNOR infrared analyzers	260
13.7.4.8	Infrared monitoring analyzers for two components in a test mixture	262
13.7.5	Infrared dispersionless analyzers with negative filtration	264
13.7.5.1	Infrared analyzer with bolometers	264
13.7.5.2	The INFRAMETER analyzer	266
13.7.5.3	The LIMAS F analyzer	267
13.7.6	Sensitivity and selectivity of infrared analyzers	267
13.7.7	Infrared dispersing analyzers with monochromatic radiation	271
13.7.7.1	Single-beam infrared dispersing analyzers	272
13.7.7.2	Double-beam dispersing analyzers	273
13.7.8	The importance of infrared analyzers	274
	References	276
14	REFRACTIVE INDEX	279
14.1	Basic relationships	279
14.2	Interferometers	284
14.2.1	Riken Keiki portable interferometers	285
14.2.2	Meopta interferometers	289
14.2.3	Automatic interferometers	290
14.3	Refractometers	290
14.3.1	Continuous refractometers based on measurement of the angle of refraction	290
14.3.1.1	Refractometers with a single cuvette	292
14.3.1.2	The Ebbinghaus refractometer	292
14.3.1.3	The Miller, Grawford and Simmons refractometer	293
14.3.1.4	Refractometers with cylindrical refraction planes	294

14.3.2	Refractometers based on measuring the critical angle	295
14.3.2.1	A refractometer based on the measurement of the critical angle with photometric indication	296
14.3.2.2	Refractometers based on measurement of the critical angle with servomechanical indication	297
14.3.3	Special instruments	298
14.3.3.1	The Karrer and Orr refractometer	298
14.3.3.2	OKOMETER refractometers	298
14.4	Application of refractometers in industrial practice	301
14.5	Evaluation of interferometers and refractometers .	302
	References	303
15	POLARIMETRY	305
15.1	Principles	305
15.2	Instruments	306
15.2.1	Polarimeters	307
15.2.1.1	Automatic polarimeters	308
15.2.2	Saccharimeters	309
15.2.2.1	Automatic saccharimeters	309
15.3	Spectropolarimetry	311
15.3.1	The Model 241 polarimeter	312
15.3.2	The Model 241 MC polarimeter	313
15.4	The importance of polarimetry and polarimetric analyzers	313
	References	314
16	MASS SPECTROMETRY	315
16.1	Principal relationship	315
16.2	Principles of the measurement	317
16.2.1	Evaluation of mass spectra	320
16.3	Instruments	324
16.3.1	The M.S. 2 spectrometer from Metropolitan-Vickers Electrical Corp.	324
16.3.2	Some mass spectrometers manufactured in the USSR .	326
16.3.3	The MGA-1100 mass spectrometric gas analyzer .	327
16.3.4	Combination of mass spectrometry with chromatography	328

16.4	Special uses of mass spectrometers	329
16.5	Evaluation of mass spectrometers	329
	References	329
17	CONDUCTOMETRY	331
17.1	Physico-chemical principles	331
17.2	Basic relationships	333
17.3	Measuring methods	334
17.4	Apparatus	340
17.5	Gas analyzers based on measurement of the electrolytic conductance	342
17.5.1	The Ionoflux analyzer	344
17.5.2	The Picoflux analyzer	346
17.5.3	Mikrogas analyzers	348
17.5.4	An analyzer for oxygen dissolved in water based on the measurement of the electrolytic conductance of the nitrous acid	350
17.5.5	Analyzers for oxygen dissolved in water based on the reaction with thallium	351
17.6	Analyzers of liquids based on the measurement of the electrolytic conductance	352
17.6.1	Two-electrode conductometers	353
17.6.1.1	A two-electrode conductometer without temperature compensation	353
17.6.1.2	A two-electrode conductometer with temperature compensation	354
17.6.1.3	A two-electrode conductometer with temperature compensation and a resistance temperature sensor	354
17.6.1.4	A two-electrode conductometer with temperature compensation using a thermistor	355
17.6.1.5	An analyzer for water vapour condensate from the ZPA company	356
17.6.1.6	The ZEPACOND 4 conductometer	358
17.6.1.7	Portable conductometers	359
17.6.2	Four-electrode conductometers	359
17.6.2.1	A four-electrode conductometer with temperature compensation	360

17.6.2.2	A four-electrode conductometer with selsyns and temperature compensation	361
17.7	Electrodeless conductometers	362
17.7.1	Low-frequency conductometers	362
17.7.1.1	Low-frequency conductometers with temperature compensation	364
17.7.1.2	Compensation low-frequency conductometers	364
17.7.1.3	Various types of low-frequency conductometers	365
17.7.2	High-frequency conductometers	366
17.7.2.1	Capacitance sensors	367
17.7.2.1.1	A high-frequency capacitance conductometer	368
17.7.2.2	Inductance sensors	369
17.7.2.2.1	High-frequency conductometers MEOLA	369
17.8	Some applications of conductometers in analyses of liquids	370
17.9	Evaluation of conductometric methods	373
	References	374
 18	 POTENTIOMETRY	376
18.1	Principal relationships	376
18.1.1	Electrode processes	376
18.2	Potentiometric pH measurement	381
18.2.1	pH-measuring electrodes	386
18.2.1.1	Antimony electrodes	387
18.2.1.2	Glass electrodes	388
18.2.2	Reference electrodes	393
18.2.2.1	Calomel electrodes	394
18.2.2.2	The silver chloride electrode	395
18.2.2.3	The thalamide electrode	397
18.2.2.4	The mercury (I) sulphate electrode	397
18.2.3	Combined electrodes	398
18.2.4	Industrial measurements	398
18.2.4.1	Automatic electrode cleaning	399
18.2.5	Industrial pH monitoring	401
18.3	Ion-selective electrodes	405
18.3.1	The physical basis of ion-selective electrodes	406

18.3.2	Construction and functional principles of ion-selective electrodes	408
18.3.2.1	Solid membrane electrodes	409
18.3.2.2	Liquid ion-exchanger electrodes	412
18.3.2.3	Special ion-selective electrodes	414
18.3.3	Some practical hints for the use of ion-selective electrodes	416
18.4	Potentiometric gas analyzers based on solid electrolytes	418
18.4.1	Properties of solid electrolytes	418
18.4.2	The principle of potentiometric analyzers based on solid electrolytes	419
18.4.3	Common oxygen analyzers based on solid electrolytes	420
18.4.4	Application of analyzers based on solid electrolytes	421
18.5	Measurement of redox potentials in automated analysis of redox systems	422
18.5.1	Measurement of redox potentials	424
18.6	Potentiometric titrations	424
18.6.1	Titrator construction	424
18.6.2	The Bran and Lübbe titrometer	427
18.7	Applications of potentiometry	430
18.8	Evaluation of potentiometric methods	430
	References	431
19	AMPEROMETRY	434
19.1	Basic concepts	435
19.2	Electrodes and methods for their activation	437
19.2.1	Indicator electrodes	438
19.2.1.1	Dropping mercury electrodes	438
19.2.1.2	Stationary mercury electrodes	438
19.2.1.3	Noble metal electrodes	438
19.2.1.4	Various electrodes	438
19.2.2	Reference electrodes	439
19.2.2.1	Calomel electrodes	439
19.2.2.2	Metallic reference electrodes	439
19.2.2.3	Carbon reference electrodes	439
19.2.3	Electrode reactivation	439
19.3	Polarography	441

19.3.1	Polarography as an analytical method	442
19.3.2	Applications and advantages of polarography	444
19.4	Amperometric analyzers	444
19.4.1	A polarographic analyzer for zinc ions	445
19.4.2	Analyzers with stationary mercury indicator electrodes	446
19.4.3	An analyzer for SO ₂ in technical gases	449
19.4.4	An analyzer for oxygen in technical gases	450
19.4.5	A nitrogen oxide analyzer	451
19.4.6	An analyzer for chlorine in phosgene	451
19.4.7	An oxygen analyzer described by Tödt	452
19.4.8	The Hersch cell for monitoring traces of oxygen . .	453
19.4.9	The Clark cell	455
19.4.10	The Breuer cell	456
19.4.11	PICOS—an analyzer for traces of various gaseous substances	457
19.4.12	DPG and DPG 5-52 oxygen analyzers	459
19.4.13	Sodium hypochlorite analyzers	460
19.4.14	A hydrogen peroxide analyzer	460
19.4.15	Amperometric analyzers of cyanide and chromate in waste waters	461
19.5	Amperometric titrations	462
19.5.1	Amperometric titrations with a dropping mercury electrode	463
19.5.2	Amperometric titrations with a single polarized electrode	464
19.5.3	Amperometric titrations with two polarized electrodes	464
19.6	Evaluation of amperometric and polarographic analyzers	465
	References	465
20	COULOMETRY	468
20.1	Theoretical	469
20.2	Classification of methods based on electrolysis	470
20.2.1	Constant-potential coulometry	470
20.2.2	Constant-current coulometry	473
20.3	Generation of substances used in coulometry	474
20.4	End-point detection	475

20.5	Coulometric analyzers	476
20.5.1	A coulometric analyzer for gas moisture	476
20.5.2	The Titrilog analyzer	477
20.5.3	The ECHG sulphur dioxide analyzer	478
20.5.4	The Beckman coulometric SO ₂ analyzer	480
20.5.5	The Novák coulometric SO ₂ analyzer	481
20.5.6	Radelkis coulometric analyzers	483
20.5.7	Some coulometric analyzers and their application	485
20.6	Evaluation of coulometric analyzers	486
	References	486
 21	CHROMATOGRAPHY	489
21.1	Classification, concepts and principles of chromatography	490
21.2	Theory of chromatographic separation	493
21.2.1	Chromatographic separation based on the solubility principle	495
21.2.2	Chromatographic separation based on adsorption	498
21.2.3	Chromatographic separation based on ion-exchange	499
21.2.4	Selection of optimum conditions for chromatographic separation	499
21.2.4.1	Effect of temperature on column separation efficiency	499
21.2.4.2	Some requirements for effective chromatographic separation of substances	500
21.3	Construction of gas chromatographs	501
21.3.1	Mobile phase	502
21.3.1.1	Carrier gas	502
21.3.2	Stationary phases	503
21.3.2.1	Supports for gas-liquid chromatography	503
21.3.2.2	Stationary phases	503
21.3.2.3	Adsorbents for gas adsorption chromatography	505
21.3.3	Chromatographic columns	506
21.3.3.1	Capillary columns	508
21.4	Detectors used in chromatography	508
21.4.1	Gas chromatographic detectors	509
21.4.1.1	The thermal conductivity detector	509
21.4.1.2	The Scott detector	513

21.4.1.3	The flame-ionization detector	515
21.4.1.4	Selective flame-ionization detectors	517
21.4.1.5	Ionization detectors using nuclear radiation	519
21.4.1.6	Argon and helium ionization detectors	520
21.4.1.7	The electron capture detector	521
21.4.1.8	The cross-section detector	523
21.4.1.9	The flame-photometric detector	524
21.4.1.10	Detectors based on the measurement of gas density .	526
21.4.2	Liquid chromatography detectors	528
21.4.2.1	Detectors based on the measurement of the refractive index	528
21.4.2.2	Detectors based on the absorption of UV radiation	529
21.4.2.3	Detectors based on measurement of the heat of adsorption	531
21.4.2.4	Fluorescence detectors	533
21.4.2.5	Amperometric detectors	534
21.4.2.6	Transport type detectors	535
21.5	Evaluation of chromatograms	537
21.5.1	Conditions for quantitative evaluation of chromatograms	537
21.5.2	The characteristics of the chromatogram and its parameters	539
21.5.3	Methods of identification of substances	541
21.5.3.1	Identification by comparing elution data	541
21.5.3.2	Identification of substances using chromatographic relationships	541
21.5.3.3	Other identification methods	542
21.5.4	Methods of quantitative determination of substances	543
21.6	Automatic instruments for chromatogram evaluation	546
21.6.1	Mechanical integrators	546
21.6.2	Electronic integrators	548
21.7	Chromatographic methods and construction of chromatographs	548
21.7.1	Gas-solid and gas-liquid chromatography	548
21.7.1.1	Franc's Chromatograph	549
21.7.1.2	Capillary chromatographs	551

21.7.1.3	Some trends in the development of gas chromatographs	552
21.7.2	Liquid chromatography and instrumentation	553
21.7.3	Ion-exchange chromatography	555
21.7.4	Gel chromatography	557
21.7.5	Various chromatographic techniques	561
21.8	Use of computers in chromatography	561
21.9	Evaluation of chromatography	561
	References	563
22	VOLUMETRIC ABSORPTION ANALYSIS OF GASES	567
22.1	Principle of volumetric absorption analyzers	567
22.2	Instruments	569
22.2.1	Single-component absorption analyzers	569
22.2.1.1	The Junkalor absorption analyzer	572
22.2.2	Two-component absorption analyzers	575
22.2.3	An oxygen or hydrogen analyzer	578
22.2.4	A methane gas analyzer	578
22.2.5	Analyzers of organic substances	580
22.3	Special instruments	580
22.3.1	A residual gas analyzer	580
22.4	Evaluation of volumetric absorption analyzers	582
	References	583
C	<i>⁸Special methods and instruments</i>	585
23	MEASUREMENT OF GAS MOISTURE CONTENT	585
23.1	Principal relationships	585
23.2	Instruments	587
23.2.1	Instruments based on the measurement of the dew point temperature	587
23.2.2	Psychrometers	592
23.2.2.1	Instruments	593
23.2.3	Dilatation hygrometers	597
23.2.4	Electrochemical hygrometers	598

23.2.4.1	Instruments based on the measurement of electrolytic conductance	598
23.2.4.2	Instruments measuring the temperature corresponding to an equilibrium moisture content in the hygroscopic substance and the test gas	599
23.2.4.3	Instruments based on an electrolysis principle	600
23.2.5	Capacitance hygrometers based on alumina	601
23.2.5.1	Measurement of gas moisture	602
23.2.5.2	Measurement of liquid moisture	602
23.3	Evaluation of hygrometers	603
	References	603
24	VARIOUS INDICATORS AND DETECTORS	605
24.1	Fire alarms	605
24.1.1	Ionization fire alarms	605
24.1.1.1	An ionization detector of flue gases	607
24.2	Devices for locating leaks in apparatuses	609
24.2.1	Instruments based on emission of positive ions	609
24.2.1.1	An indicator of leaks based on emission of positive ions	610
24.2.2	Instruments based on heat of reaction	611
24.2.2.1	The GA-DET, Type S probe for detection of gas leaks	611
24.2.2.2	The GA-DET, Type P portable device for detection of gas leakage from pipelines in the ground	612
24.2.3	Diverse devices for location of leaks	612
24.3	Semiconductor probes for gas analysis	612
	References	614
25	COLOUR INDICATORS FOR VARIOUS SUBSTANCES IN GASES	616
25.1	Detection tubes	616
25.2	Alcotest tubes for detecting alcohol	617
25.3	Pen detectors of poisonous gases	618
25.4	Portable dust meters	619
25.5	Evaluation of colour indicators	619
	References	620

<i>D</i>	<i>Auxiliary devices for analyzers</i>	621
26	AUXILIARY DEVICES	621
26.1	Auxiliary devices for gas analyzers	622
26.1.1	Sampling devices	622
26.1.2	Filters for removal of mechanical impurities	624
26.1.3	Devices for removal of condensable substances	626
26.1.4	Devices for adjusting constant conditions of state	628
26.1.5	Devices for removal of undesirable components from gas mixtures	631
26.1.6	Gas transport devices	632
26.1.7	Switches for gas sampling sites	634
26.2	Auxiliary devices for liquid analyzers	637
26.2.1	Devices for maintaining constant flow-rates of liquids	637
26.2.2	Devices for removal of mechanical impurities	640
	References	641
27	EXPLOSION-PROOF ANALYZERS	643
27.1	Characteristics and definitions	643
27.2	Types of explosion-proof analyzers	644
27.2.1	Spark-safe analyzers	645
27.2.2	Tightly closed analyzers	645
27.2.3	Analyzers in aerated cases	646
27.3	Various recommendations	648
27.4	Calculation of the lower explosivity limit for various substances	648
	References	649
<i>E</i>	<i>Calibration, installation and maintenance of analyzers</i>	651
28	ANALYZER CALIBRATION	651
28.1	Static methods	652
28.2	Dynamic methods	654
28.2.1	Flow-through diluting systems	655
28.2.1.1	Diluting devices with automatically operated dosing stop-cocks	657

28.2.1.2	Diluting system with electrochemical dosing of the test substance	658
28.2.2	Preparation of gaseous mixtures by saturation with the required substance	660
28.2.3	Preparation of gaseous mixtures by the diffusion method	661
28.3	Evaluation of methods for preparation of calibration mixtures	663
	References	663
29	INSTALLATION AND MAINTENANCE OF ANALYZERS	664
29.1	Analyzer installation	664
29.2	Analyzer maintenance	666
29.2.1	Rules for analyzer maintenance	666
29.3	Specification of analyzer requirements	666
	References	667
F	<i>The use of analyzers</i>	669
30	EXAMPLES OF ANALYZER APPLICATION	669
30.1	Analyzers in the chemical industry	669
30.1.1	Analyzers for monitoring and controlling chemical production lines	669
30.1.1.1	Production of hydrogen chloride	669
30.1.1.2	Production of sulphuric acid	670
30.1.1.3	Production of nitric acid	670
30.1.1.4	Obtaining of sulphur from waste hydrogen sulphide	670
30.1.1.5	Production of acrylonitrile	671
30.1.1.6	Regeneration of the catalyst for fluid cracking	672
30.1.2	Use of analyzers in separation processes	672
30.1.3	Use of analyzers in automatic regulation of the chemical composition of materials	672
30.1.3.1	Regulation of a constant composition of a gaseous mixture	673
30.1.3.2	Regulation of distillate composition	673
30.1.3.3	Regulation of pH	674

30.1.3.4	Regulation of acid and base concentrations	679
30.1.4	Safety analyzers	680
30.1.4.1	Safety of production line operation	680
30.1.4.2	Maintenance of personnel safety on production lines	681
30.2	Analyzers for the control of combustion in power stations	683
30.2.1	Principal facts	684
30.2.2	Determination of the composition of flue gases . . .	688
30.2.3	Sampling devices for flue gas analyzers	691
30.3	Air pollution monitors	695
30.3.1	Air pollution control around industrial centres and cities	695
30.3.1.1	Mobile measuring stations for air pollution monitoring	696
30.3.1.2	Long-range monitoring of atmospheric pollutants . .	698
30.4	Analyzers for monitoring water pollution	700
30.4.1	Automatic stations for water pollution monitoring	701
30.4.2	Chemical treatment of waste waters involving the measurement of the pH and of the redox potential	702
30.4.3	Water analysis for organic substances	704
30.4.3.1	Analyzers for BOD monitoring	705
30.4.3.2	The Aqua Rotor analyzer for COD monitoring . . .	705
30.4.3.3	A carbon analyzer	707
30.5	Analyzers in laboratory practice	708
30.5.1	The Technicon series analyzer	708
30.5.2	The Perkin - Elmer series analyzer	710
30.6	Special uses of analyzers	711
30.6.1	Automatic termination of chemical reactions	711
30.6.2	Measurement of gas flow-rates using analyzers . .	712
	References	714
31	The present and the future of automatic analyzers .	715
Appendices		717
Index		730