

Contents

Foreword to the 20th edition — V

1 Introduction and basic concepts — 1

1.1 Gravimetry and titrimetry — 1

1.2 Classification of titrations — 4

2 Practical basics of volumetric analysis — 6

2.1 Devices for volume measurement — 7

2.1.1 Measuring devices — 7

2.1.1.1 Volumetric flasks — 8

2.1.1.2 Graduated cylinders — 11

2.1.1.3 Pipettes — 13

2.1.1.4 Burettes — 25

2.1.2 Cleaning and drying — 35

2.1.3 Testing of measuring devices — 37

2.2 Solutions for volumetric analysis — 38

2.2.1 Empirical solutions; standard solutions, according to an equivalent;
usual standard solutions — 38

2.2.1.1 Amount of substance — 40

2.2.1.2 Equivalent particle — 41

2.2.1.3 Molar mass — 42

2.2.1.4 Content of solutions — 44

2.2.2 Production of standard solutions — 50

2.3 Statement of the analysis result — 54

2.3.1 Calculation of the analysis result — 54

2.3.2 Uncertainty of a measured value — 56

2.3.2.1 Measurement deviations: accuracy and precision of a
measurement — 57

2.3.2.2 Determination of uncertainties from other sources — 60

2.3.2.3 Propagation of standard uncertainties — 61

2.3.2.4 Extended uncertainty — 62

2.3.3 Outlier test as a statistical test method — 63

2.3.4 Rounding up the final result — 65

3 Volumetric analysis with chemical end point determination — 68

3.1 Acid-base titrations — 68

3.1.1 Theoretical foundations — 68

3.1.1.1 Acids and bases — 68

3.1.1.2 Autoprotolysis of water — 73

3.1.1.3 Hydrogen ion concentration and pH value — 77

3.1.1.4	Strength of acids and bases — 79
3.1.1.5	Calculation of pH values — 83
3.1.1.6	Buffer solutions — 85
3.1.2	Titration curves — 87
3.1.2.1	Titration of strong acids and bases — 87
3.1.2.2	Titration of weak acids and bases — 89
3.1.3	Acid-base indicators — 91
3.1.3.1	Indicator transition — 91
3.1.3.2	Indicator selection — 96
3.1.4	Practical applications — 98
3.1.4.1	Adjustment of acids — 98
3.1.4.2	Adjustment of alkaline solutions — 101
3.1.4.3	Determination of strong and weak bases — 103
3.1.4.4	Determination of the total alkali content of technical sodium hydroxide — 103
3.1.4.5	Determination of carbonates as well as hydroxides and carbonates side by side — 104
3.1.4.6	Determination of carbonate and hydrogen carbonate side by side — 105
3.1.4.7	Determination of borax — 105
3.1.4.8	Determination of nitrogen according to Kjeldahl — 106
3.1.4.9	Determination of the nitrogen content of saltpetre — 107
3.1.4.10	Determination of the nitrogen content of hard coal — 108
3.1.4.11	Determination of the total nitrogen content of a garden fertilizer — 109
3.1.4.12	Anhydrous titrations — 109
3.1.4.13	Determination of nicotinamide — 111
3.1.4.14	Determination of fenbendazole — 111
3.1.4.15	Determination of pantoprazole sodium salt — 111
3.1.4.16	Determination of diltiazem hydrochloride according to Ph. Eur — 112
3.1.4.17	Determination of formaldehyde using the sulfite method — 112
3.1.4.18	Determination of strong and weak acids — 113
3.1.4.19	Determination of sulfuric acid — 113
3.1.4.20	Determination of acetic acid — 114
3.1.4.21	Determination of boric acid — 115
3.1.4.22	Determination of magnesium by back titration — 117
3.1.4.23	Precipitation process with pH change display — 117
3.1.4.24	Determination of magnesium by direct titration — 118
3.1.4.25	Determination of ammonium salts — 118
3.1.4.26	Formol titration (titration according to Sørensen) — 119
3.1.4.27	Determination of glycine — 119
3.1.4.28	Determination of cationic acids by displacement titration — 119
3.1.4.29	Determination of imipramine hydrochloride according to Ph. Eur — 120
3.1.4.30	Titration of weak acids in anhydrous medium — 120

3.1.4.31	Preparation of 0.1 M tetrabutylammonium hydroxide solution —	120
3.1.4.32	Adjustment of 0.1 M tetrabutylammonium hydroxide standard solution —	121
3.1.4.33	Determination of hydrochlorothiazide according to Ph. Eur. 9.0 —	121
3.1.4.34	Determination of rutoside according to Ph. Eur. 11.0 —	121
3.1.4.35	Determination of glycerol according to Ph. Eur. 11.0 —	122
3.1.4.36	Determination of phosphoric acid —	123
3.1.4.37	Determination after ion exchange —	124
3.1.4.38	Acid value, saponification value and ester value in the analysis of fatty pharmaceuticals and foods (characterization of fatty oils) —	127
3.1.4.39	Determination of the acid value (AV) —	128
3.1.4.40	Determination of the saponification value (SV) —	128
3.1.4.41	Determination of NH-acid compounds —	128
3.1.4.42	Determination of ethinylestradiol —	129
3.1.4.43	Determination of salicylic acid —	130
3.1.4.44	Determination of acetylsalicylic acid —	130
3.2	Precipitation titrations —	130
3.2.1	Theoretical foundations —	131
3.2.1.1	Solute equilibrium —	131
3.2.1.2	Solubility product and solubility —	131
3.2.2	Titration curves —	133
3.2.3	Methods of end point determination —	136
3.2.4	Determination of silver and argentometric determinations —	138
3.2.4.1	Preparation of the customized solutions —	138
3.2.4.2	Determination of silver according to Gay-Lussac —	139
3.2.4.3	Determinations according to Volhard —	140
3.2.4.4	Determinations according to Mohr —	143
3.2.4.5	Determinations according to Fajans —	145
3.2.4.6	Determination of cyanide according to Liebig —	146
3.2.4.7	Argentometric titrations of organic ammonium salts —	147
3.2.4.8	Determination according to Budde —	147
3.2.4.9	Argentometric determination of organically bound chlorine or bromine —	148
3.3	Oxidation and reduction titrations —	149
3.3.1	Theoretical foundations —	149
3.3.1.1	Oxidation and reduction —	149
3.3.1.2	Oxidation number —	152
3.3.1.3	Redox potential —	154
3.3.2	Permanganometric determinations —	157
3.3.2.1	Preparation of the potassium permanganate solution —	158
3.3.2.2	Determination of iron in sulfuric acid solution —	161
3.3.2.3	Determination of iron in hydrochloric acid solution —	164

3.3.2.4	Determination of uranium and phosphate —	168
3.3.2.5	Determination of oxalate —	168
3.3.2.6	Determination of calcium —	169
3.3.2.7	Determination of hydrogen peroxide —	169
3.3.2.8	Determination of peroxodisulfate —	170
3.3.2.9	Determination of nitrite —	170
3.3.2.10	Determination of hydroxylamine —	171
3.3.2.11	Determination of manganese(IV) —	171
3.3.2.12	Determination of manganese(II) —	172
3.3.2.13	Determination of chromium in steel —	173
3.3.2.14	Permanganate index (PMI) —	174
3.3.3	Dichromatometric determinations —	175
3.3.3.1	Preparation of the dichromate solution —	177
3.3.3.2	Determination of iron by spot reaction —	177
3.3.3.3	Determination of iron with redox indicators —	178
3.3.4	Cerimetric determinations —	179
3.3.4.1	Preparation of the cerium(IV) sulfate solution —	180
3.3.4.2	Determination of iron —	181
3.3.4.3	Determination of nitrite —	181
3.3.4.4	Determination of hexacyanoferrate(II) —	182
3.3.4.5	Determination of nifedipine —	182
3.3.4.6	Determination of paracetamol —	183
3.3.4.7	Determination of vitamin K ₃ (menadione) according to Ph. Eur —	183
3.3.5	Ferrometric determinations —	184
3.3.5.1	Preparation of the iron(II) sulfate solution —	184
3.3.5.2	Determination of chromate(VI) and chromium(III) —	185
3.3.5.3	Determination of chromium in steel —	186
3.3.5.4	Determination of vanadium —	186
3.3.6	Bromatometric determinations —	187
3.3.6.1	Preparation of the potassium bromate solution —	187
3.3.6.2	Determination of arsenic and antimony —	187
3.3.6.3	Determination of bismuth —	188
3.3.6.4	Determination of hydroxylamine —	188
3.3.6.5	Determination of metal ions as oxinato complexes —	189
3.3.6.6	Determination of aluminum —	189
3.3.6.7	Determination of 8-hydroxyquinoline (oxine) —	190
3.3.6.8	Bromatometric determination of phenols and anilines —	191
3.3.6.9	Determination of salicylic acid —	191
3.3.6.10	Determination of phenol —	192
3.3.6.11	Determination of sulfonamides according to DAB 7 —	192
3.3.6.12	Determination of sulfanilamide —	192
3.3.6.13	Determination of cystine according to Ph. Eur —	193

3.3.7	Iodometric determinations —	193
3.3.7.1	End point detection —	195
3.3.7.2	Preparation of the starch solution —	197
3.3.7.3	Preparation of the sodium thiosulfate solution —	197
3.3.7.4	Adjusting the sodium thiosulfate solution —	198
3.3.7.5	Preparation of the iodine solution —	201
3.3.7.6	Determination of sulfides —	201
3.3.7.7	Determination of sulfites —	202
3.3.7.8	Determination of hydrazine —	202
3.3.7.9	Determination of arsenic and antimony —	202
3.3.7.10	Determination of tin —	203
3.3.7.11	Determination of mercury —	204
3.3.7.12	Determination of ascorbic acid —	205
3.3.7.13	Determination of iodide —	206
3.3.7.14	Determination of hypochlorite —	206
3.3.7.15	Determination of chlorate, bromate, iodate and periodate —	207
3.3.7.16	Determination of hydrogen peroxide —	208
3.3.7.17	Determination of the peroxide value —	208
3.3.7.18	Determination of higher oxides —	209
3.3.7.19	Determination of copper —	212
3.3.7.20	Determination of oxygen according to Winkler —	215
3.3.7.21	Determination of the iodine value —	215
3.3.7.22	Determination of acetylcysteine according to Ph. Eur —	216
3.3.7.23	Determination of cysteine HCl according to Ph. Eur —	217
3.3.7.24	Determination of phenazone —	217
3.3.8	Determination of manganese in steel with arsenite standard solution —	218
3.3.8.1	Preparation of the sodium arsenite solution —	218
3.3.8.2	Determination of manganese in steel —	218
3.3.9	Determinations with formate standard solution —	219
3.3.9.1	Preparation of the sodium formate solution —	220
3.3.9.2	Determination of hypophosphite (phosphinate) —	220
3.3.9.3	Determination of phosphite (phosphonate) —	221
3.3.10	Other possibilities for redox titration —	221
3.4	Complex formation titrations —	222
3.4.1	Basics of complex formation —	223
3.4.1.1	Designations and definitions —	223
3.4.1.2	Structure of the complexes —	223
3.4.1.3	Nomenclature rules —	225
3.4.1.4	Stability constant —	226
3.4.2	Basics of complexation titrations —	226
3.4.3	Indication of the end point —	232
3.4.4	Chelatometric determinations —	234

3.4.4.1	Preparation of the EDTA solution —	234
3.4.4.2	Determination of magnesium —	235
3.4.4.3	Determination of calcium —	236
3.4.4.4	Determination of water hardness —	237
3.4.4.5	Determination of zinc and cadmium —	238
3.4.4.6	Determination of copper —	239
3.4.4.7	Determination of aluminum —	239
3.4.4.8	Determination of bismuth —	240
3.4.4.9	Determination of iron —	240
3.4.4.10	Determination of phosphate —	241
3.4.4.11	Determination of sulfate —	241
3.4.4.12	Carbamatometric titrations —	242
3.4.4.13	Determination of mercury —	243
3.5	Two-phase titrations —	243
3.5.1	Determination of anion and cation surfactants —	243
4	Volumetric analysis with physical end point determination —	247
4.1	Overview of the indication methods —	247
4.2	Photometric titrations —	250
4.2.1	Theoretical foundations —	250
4.2.2	Practical applications —	252
4.2.2.1	Determination of calcium —	252
4.3	Conductometric titrations —	254
4.3.1	Theoretical foundations —	255
4.3.2	The titration device —	258
4.3.3	Conductivity measurement —	260
4.3.3.1	Wheatstone bridge circuit —	260
4.3.3.2	Direct reading methods —	261
4.3.4	Practical applications —	262
4.3.4.1	Acid-base titrations —	262
4.3.4.1.1	Displacement processes —	263
4.3.4.2	Precipitation titrations —	264
4.3.4.3	Conductivity titrations at elevated temperatures —	265
4.3.5	High-frequency titration —	266
4.4	Potentiometric titrations —	268
4.4.1	Theoretical foundations —	269
4.4.2	Indicator electrodes —	274
4.4.2.1	Metal electrodes —	274
4.4.2.2	Ion-selective electrodes (ISEs) —	277
4.4.3	Reference electrodes —	284
4.4.4	Measuring chains —	286
4.4.5	Currentless potential measurement —	288

4.4.6	Practical applications —	292
4.4.6.1	Precipitation and complexation titrations —	292
4.4.6.2	Acid-base titrations —	295
4.4.6.3	Oxidation and reduction titrations —	296
4.4.7	Evaluation —	299
4.5	Titration with polarized electrodes —	304
4.5.1	Polarization of electrodes —	304
4.5.2	Voltametric titrations —	306
4.5.3	Amperometric titrations —	308
4.5.4	Biamperometric or dead-stop titrations —	309
4.5.4.1	Water determination according to Karl Fischer —	310
4.5.4.2	Determination of primary aromatic amines —	313
4.5.4.3	Determination of procaine according to the European Pharmacopoeia —	314
4.6	Coulometric titrations —	314
4.6.1	Theoretical principles —	314
4.6.2	Practical applications —	317
4.6.2.1	Determination of arsenic with dead-stop indication —	317
4.6.2.2	Determination of thiosulfate —	318
4.6.2.3	Alkalimetric titrations —	318
4.6.2.4	Complexometric titrations —	318
4.6.2.5	Argentometric titrations —	319
4.6.2.6	Redox titrations —	319
4.6.2.7	Coulometric water determination according to Karl Fischer —	320
5	Instrumental volumetric analysis —	322
5.1	Apparative development —	322
5.2	Registering titrators —	324
5.3	End point titrators —	326
5.4	Digital titration systems —	327
6	Overview of the history of volumetric analysis —	331
7	Selected didactic approaches —	341
Appendix — 345		
Bibliography — 349		
Subject index — 359		
Persons index — 379		