

## CONTENTS

<b>INTRODUCTION</b>	<b>v</b>
Definition, Types and Purposes of Titration	v
Aim and Contents of the Book	vi
 <b>SECTION 1: TITRATION PROCEDURE</b> 	
1. Measurement of the Amounts of Reagent and Sample	1
2. Mixing Procedure	4
3. Preliminary Reaction Yielding an Intermediate	5
4. Realization of Reaction	6
5. Speed of Reaction	8
6. Avoidance of Side and Other Unwanted Reactions	10
7. End-Point Determination	11
8. End-Point and Equivalence Point	14
Physical Properties and Measurements in End-Point Determination	16
A. Light Absorption	16
(i) Direct End-Point	16
(a) Coloured or turbidity-producing reactant	16
(b) Use of an added indicator	17
(c) Indicator formed in the course of reaction	18
(d) Cessation of formation of reaction products	19
(ii) Intersection End-Point	21
B. Electrical Properties	24
Potentiometric Titration	25
Conductometric Titration	29
'High Frequency' Titration	29
Amperometric Titration	30
Oscillographic Titration	33
Chronopotentiometric Titration	33
Coulometric Titration at Constant Voltage	34
C. Temperature	34
D. Other Physical Properties	35
Fluorescence	36
Chemiluminescence	37
Flame Emission Spectra	37
Optical Activity	38
Light Refraction	38
Crystal Form	38
Density	38
Viscosity	38
Surface Tension	39
Freezing Point	39

Magnetic Susceptibility	39
Nuclear Magnetic Resonance	39
Dielectric Constant	40
Smell	40
Taste	40
Sound	41
Vapour or Gas Pressure of Reaction Mixture	41
Radioactivity	41
Automatic Titration	43
Reactions Used in the Direct Titration of Organic Compounds	43
(a) Reactions used also in inorganic analysis	44
1. Neutralization	44
2. Displacement	44
3. Oxidation	45
4. Reduction	45
5. Ion Combination	46
6. Complex Formation	47
(b) Reactions used only in organic analysis	47
7. Addition	47
8. Condensation	48
9. Hydrogen Replacement (Substitution)	48
10. Nitrosation	48
11. <b>Physical</b> Titration	49
Examples of Direct Titration of Organic Compounds	50
Material and Literature Covered	50
Classification of Data	52

## SECTION 2: REAGENTS USED IN DIRECT TITRATION OF ORGANIC COMPOUNDS

(Note: this list of reagents does not include all dyes and surface-active compounds used; only those appearing in several references are given, so as to avoid over-burdening the reader with comparatively unimportant titles)

1. Acetamide (Sodium derivative)	54
Acetate Esters (see Esters)	
2. Acetate (Salt)	54
Acetic Acid (see <b>Carboxylic Acids</b> )	
3. Acetic Anhydride	55
4. Acetyl Chloride	56
5. Acids and Bases	56
Acridinium Salts (see Surface-Active Materials)	
6. Alcohols	64

7.	Aldehydes	64
	Alizarin Sulphonate (see Surface-Active Materials)	
8.	Alkali and Alkaline Earth Hydroxides	65
9.	Alkoxides	85
10.	Alkyls and <b>Aryls</b> (Sodium)	104
	Aluminium Bromide and Chloride (see Halides (Inorganic) in Non-Aqueous Solution)	
	Aluminium Chloro-Isopropylate, <b>HCl</b> Complex (see Hydrochloric Acid)	
	Aluminium Ethyl and Phenyl Halides (see Halides (Inorganic) in Non-Aqueous Solution)	
11.	Amines and Heterocyclic Bases	105
	Aminoethoxides (see Alkoxides)	
12.	Ammonia, Ammonium Hydroxide	110
	Amylamine, Secondary (see Amines and Heterocyclic <b>Bases</b> )	
	Aniline (see Amines and Heterocyclic Bases)	
	Anionic Detergents (see Surface-Active Materials)	
	Antimony Trichloride and Tribromide, Pentachloride and <b>Sulphate</b> (see Halides (Inorganic) in Non-Aqueous Solution)	
	Arsenious Sulphide (see Sulphides)	
13.	Ascorbic Acid	111
	Barium Hydroxide (see Alkali and Alkaline Earth Hydroxides)	
14.	Barium ( <b>II</b> )	113
	Benzaldehyde Sulphonic Acid (see Aldehydes)	
	Benzene (see Hydrocarbons)	
	Benzene Diazonium Salts (see Diazonium Salts)	
	Benzenesulphonic Acid (see Sulphonic Acids)	
	Benzidine (see Amines and Heterocyclic Bases)	
15.	Bichromate and Chromic Oxide	114
	Bismihalides (see Halide Complex Anions)	
16.	Bismuth ( <b>III</b> )	117
	Boron Tribromide (see Halides (Inorganic) in <b>Non-Aqueous</b> Solution)	
17.	Bromate	118
18.	Bromine	135
19.	Bromine Chloride	145
	Bromo-Anions of Bi, Cd, Hg (see Halide Complex Anions)	
20.	<b>Bromosuccinimide(N-)</b>	146
	Butyl Acetate (see Esters)	
	Butyl Ether (see Ethers)	
	Butyl Hypochlorite (Tertiary) (see <b>Hypohalites</b> )	
	Butyl Nitrite (see Nitrite)	
	Cadmihalides (see Halide Complex Anions)	

21.	Cadmium (II)	147
22.	Calcium (II)	148
	Calcium Hydroxide (see Alkali and Alkaline Earth Hydroxides)	
	Camphorsulphonic Acid (see Sulphonic Acids)	
23.	Carboxylic Acids	148
	Cationic Detergents (see Surface-Active Materials)	
24.	Cerium (IV)	150
	Cetyl Quaternary Salts (see Surface-Active Materials)	
25.	Chloramine B and T	161
26.	Chlorate	165
27.	Chlorine	166
	Chloro-Anions of Ir, Pt (see Halide Complex Anions)	
	Chloromercuribenzoate( <i>p</i> -) (see Mercury (II))	
28.	Cholesterol	168
	Chromic Oxide (see Bichromate and Chromic Oxide)	
29.	Chromium (II)	168
	Chromium Complex Anions (Reinecke Salt) (see Halide Complex Anions)	
	Cinchonine Sulphate (see Amines and Heterocyclic Bases)	
30.	Cobalt (II)	169
31.	Copper (II)	170
	Copper (III) (see Percuprate)	
	Crystal Scarlet (see Dyes)	
32.	Cyanide	187
	Cyanuric Acid (see Phenols and Heterocyclic Hydroxy-Compounds)	
	Cyclohexane (see Hydrocarbons)	
	Cyclohexylamine (see Amines and Heterocyclic Bases)	
33.	Cyclopentadiene	187
	Cysteine (see Mercaptans)	
	Detergents (see Surface-Active Materials)	
34.	Diazonium Salts	187
	Dibenzylethylenediamine( <i>N,N</i> ) Diacetate (See Amines and Heterocyclic Bases)	
	Dibutylamine( <i>n</i> -) (see Amines and Heterocyclic Bases)	
	Dibutyl Ether (see Ethers)	
	Diethanolamine (see Amines and Heterocyclic Bases)	
	Diethylamine (see Amines and Heterocyclic Bases)	
	Diethyl Ether (see Ethers)	
35.	Digitonin	191
	Dimethylaniline (see Amines and Heterocyclic Bases)	
	Dimethyl $\alpha$ -naphthylamine (see Amines and Heterocyclic Bases)	
	Dinitrophenylhydrazine(2,4-) (see Hydrazines)	

	Diocylsulphosuccinate (see Surface-Active Materials)	
	Diphenylguanidine (see Guanidines)	
	Diphenyl Phosphate (see Phosphate Esters and Salts)	
36.	Diphenylthiocarbazono (Dithizone)	191
37.	Dithionite	192
	<b>Ditolyl(o-)-guanidine</b> (see Guanidines)	
38.	Dyes	194
39.	Electrolytically Generated and Coulometrically Measured Reagents	199
	1. Acid	
	Base	
	2. Others (see under these reagents)	
40.	Electrolytic Reduction	200
41.	Esters	202
	Ethanesulphonic Acid (see Sulphonic Acids)	
	Ethanol (see Alcohols)	
42.	Ethers	202
	Ethoxides (see Alkoxides)	
	Ethoxyresazurin, Ethoxyresorufin (see Quinone-Type Compounds)	
	Ethyl Acetate (see Esters)	
43.	Ethylenediaminetetraacetic Acid	202
	<b>Ethylmaleimide(N-)</b> (see Maleic Anhydride and Related Compounds)	
	Ethyl Nitrite (see Nitrite)	
	<b>Ethylpiperidine(N-)</b> (see Amines and Heterocyclic Bases)	
44.	Ferricyanide	203
45.	Ferrocyanide	209
	Flavianic Acid (see Phenols and Heterocyclic <b>Hydroxy-</b> Compounds)	
46.	Fluoride	209
47.	Fluorine	210
	Fuchsine (see Dyes)	
	Gallium Bromide (see Halides (Inorganic) in Non-Aqueous Solution)	
48.	Gelatine	210
49.	Gold (Trichloride)	210
50.	Guanidines	212
51.	Halides (Inorganic) in Non-Aqueous Solution	212
52.	Halide Complex Anions	217
	<b>Heptaldehyde(n-)</b> (see Aldehydes)	
	<b>Heptylamine(n-)</b> (see Amines and Heterocyclic Bases)	
	Heterocyclic Hydroxy-Compounds (see Phenols and Heterocyclic Hydroxy-Compounds)	

53.	Heteropoly Acids	219
	Hexane (see Hydrocarbons)	
54.	High Molecular Weight Organic Anions and Cations	223
55.	Hydrazines	225
	Hydrobromic Acid (see Inorganic Acids)	
56.	Hydrocarbons	227
57.	Hydrochloric Acid	227
58.	Hydrogen Gas	237
	Hydroxides	
	(see Alkali and Alkaline Earth Hydroxides; Ammonia, Ammonium Hydroxide; Quaternary Ammonium Hydroxides)	
59.	Hydroxylamine (Hydrochloride)	237
	Hydroxymercuribenzoic( <i>o</i> -) Acid and Hydroxy(bis)mercurithymol (see Mercury (II))	
60.	<b>Hypohalites</b>	238
	Indium Bromide (see Halides (Inorganic) in Non-Aqueous Solution)	
61.	Inorganic Acids	242
62.	Iodate	245
	Iodic Acid (see Inorganic Acids)	
63.	Iodide	253
64.	Iodine	254
65.	Iodine Monochloride	269
66.	Iron (II)	273
67.	Iron (III)	277
	Isoquinoline (see Amines and Heterocyclic Bases)	
68.	Karl Fischer Reagent	281
69.	Lanthanum (III)	282
	Lauryl Sulphate (Sodium) (see Surface-Active Materials)	
70.	Lead (II)	282
71.	Lead (IV)	284
72.	Lithium Aluminium Hydride	286
73.	Lithium Aluminium Tetramides	287
	Lithium Hydroxide (see Alkali and Alkaline Earth Hydroxides)	
74.	Magnesium (II)	287
75.	Maleic Anhydride and Related Compounds	288
76.	Manganese (III)	288
77.	Mercaptans	289
	Mercurihalides (see Halide Complex Anions)	
78.	Mercury (I)	290
79.	Mercury (II)	290
	Methanesulphonic Acid (see Sulphonic Acids)	
	Methanol (see Alcohols)	

	Methoxides (see <b>Alkoxides</b> )	
	Methylene Blue (see Dyes)	
	Methyl Violet (see Dyes)	
80.	Molybdate (Ammonium)	302
	Morpholine (see <b>Amines</b> and Heterocyclic Bases)	
	Naphthalene <b><math>\beta</math>-Sulphonic</b> Acid (see Sulphonic Acids)	
	Naphthaquinone ( <b>1,2</b> ) 4-Sulphonate (see Quinone-Type Compounds)	
	Naphthol, <b><math>\beta</math>-</b> (see Phenols and Heterocyclic Hydroxy-Compounds)	
	Naphthol Yellow S (see Dyes)	
81.	Nickel ( <b>II</b> )	302
	Nile Blue (see Dyes)	
	Niobium Penta-bromide and chloride (see Halides (Inorganic) in Non-Aqueous Solution)	
	<b>Nitranilic</b> Acid (see Phenols and Heterocyclic Hydroxy-Compounds)	
	Nitric Acid (see Inorganic Acids)	
82.	Nitrite	303
	Nitron (see <b>Amines</b> and Heterocyclic Bases)	
83.	Nitroprusside (Sodium)	319
	Oxalic Acid (see Carboxylic Acids)	
84.	Oxygen	320
85.	Ozone	320
86.	Perbenzoic Acid	320
87.	Perchloric Acid	321
88.	Percuprate (trivalent copper anion)	364
	<b>Perfluorobutyric</b> Acid (see Carboxylic Acids)	
89.	Periodate	366
	Periodic Acid (see Inorganic Acids)	
90.	<b>Permanganate</b>	368
91.	Persulphate	374
92.	Phenols and Heterocyclic Hydroxy-Compounds	375
	Phenylhydrazine (see Hydrazines)	
	Phenylhydrazine, <b>2,4-dinitro-</b> (see Hydrazines)	
	<b>Phenylmercuric</b> chloride (see Mercury ( <b>II</b> ))	
93.	Phosphates (esters and salts)	377
	Phosphomolybdic Acid (see Heteropoly Acids)	
	Phosphorus Pentachloride (see Halides (Inorganic) in Non-Aqueous Solution)	
	Phosphotungstic Acid (see Heteropoly Acids)	
94.	Physical Titrations	377

<b>95.</b>	Picric Acid	<b>385</b>
	Picolonic Acid (see Phenols and Heterocyclic Hydroxy-Compounds)	
	Piperidine (see Amines and Heterocyclic Bases)	
	Piperidine, N-Ethyl (see Amines and Heterocyclic Bases)	
	Platinum Complex Anions (Chloroplatinic Acid) (see Halide Complex Anions)	
	Polyvinyl Sulphate (Potassium) (see Surface-Active Materials)	
	Potassium Hydroxide (see Alkali and Alkaline Earth Hydroxides)	
	Pyramidone (see Amines and Heterocyclic Bases)	
	Pyrazolone (I-Phenyl-3-Methyl-5-one) (see Phenols and Heterocyclic Hydroxy-Compounds)	
	Pyridines (see Amines and Heterocyclic Bases)	
<b>96.</b>	Quaternary Ammonium Hydroxides	<b>387</b>
<b>97.</b>	Quaternary Salts	<b>394</b>
	Quinoline (see Amines and Heterocyclic Bases)	
<b>98.</b>	Quinone-Type Compounds	<b>395</b>
	Reinecke Salt (see Halide Complex Anions)	
	Safranine (see Dyes)	
	Salicylic Acid (see Carboxylic Acids)	
	Silicotungstic Acid (see Heteropoly Acids)	
<b>99.</b>	Silver (I)	<b>396</b>
<b>100.</b>	Silver (II)	<b>415</b>
<b>101.</b>	Sodium (Metal)	<b>415</b>
	Sodium Hydroxide (see Alkali and Alkaline Earth Hydroxides)	
	Styphnic Acid (see Phenols and Heterocyclic Hydroxy-Compounds)	
	Sulphonamide (see Amines and Heterocyclic Bases)	
	Sulphates and Sulphonates (see Surface-Active Materials)	
<b>102.</b>	Sulphide	<b>415</b>
	Sulphonates (see Surface-Active Materials)	
<b>103.</b>	Sulphonic Acids	<b>416</b>
	Sulphuric Acid (see Inorganic Acids)	
<b>104.</b>	Sulphur Trioxide	<b>419</b>
<b>105.</b>	Surface-Active Materials	<b>420</b>
	Tantalum Pentabromide and Pentachloride (see Halides (Inorganic) in Non-Aqueous Solution)	
	Tellurium Tetrabromide and Tetrachloride (see Halides (Inorganic) in Non-Aqueous Solution)	
	Tetraalkylammonium Hydroxides (see Quaternary Ammonium Hydroxides)	
<b>106.</b>	Tetraphenylborate	<b>428</b>
<b>107.</b>	Thallium (I)	<b>430</b>



CONTENTS

xvii

108.	Thiocyanate	430
	Thioglycollic Acid (see Mercaptans)	
109.	Thiosulphate	430
110.	Thorium (IV)	433
111.	Tillmans' Reagent	434
112.	Tin (II)	440
	Tin Tetrabromide and Tetrachloride (see Halides (Inorganic) in Non-Aqueous Solution)	
113.	Titanium (III)	441
	<b>Toluenesulphonic(p-)</b> Acid (see Sulphonic Acids)	
	<b>Toluidine(o-)</b> (Hydrochloride) (see Amines and Heterocyclic Bases)	
	Trichloroacetic Acid (see Carboxylic Acids)	
	Triethylamine (see Amines and Heterocyclic Bases)	
	Trimercuriacetato-aniline (see Mercury (II))	
	Tripropylamine (see Amines and Heterocyclic Bases)	
	Tungsten Pentabromide (see Halides (Inorganic) in Non-Aqueous Solution)	
114.	<b>Vanadate</b>	446
115.	<b>Vanadium (II)</b>	447
	Vanadium Tetrachloride (see Halides (Inorganic) in Non-Aqueous Solution)	
116.	Water	449
117.	<b>Zinc (II)</b>	450
	Zirconium Tetrachloride (see Halides (Inorganic) in Non-Aqueous Solution)	

SECTION 3: INDEX TO FUNCTIONAL GROUPS  
AND COMPOUND CLASSES

Acetylenes		453
Acids (see under more specific headings, such as Carboxylic Acids, Sulphonic Acids, etc.)		
Acid Chlorides (see Halogen-containing Compounds)		
Alcohols		453
Aldehydes		453
Alkaloids and their Salts		454
Aluminium-containing Compounds		455
<b>Amides</b> and Imides		455
Amines (see Primary Amines; Secondary Amines and Heterocyclic Bases; Tertiary Amines and Heterocyclic Bases; Alkaloids; Synthetic Bases; Purines)		
Amino Acids		456
Ammonium Salts, Substituted		456

Anhydrides	457
<b>Anils</b>	457
Antibiotics and Related Compounds	457
Antimony-containing Compounds	458
Aromatic Hydrocarbons	458
Arsenic-containing Compounds	458
Azidodithiocarbonates	459
Azo-compounds (see also Dyes)	459
Barbituric Acids and Salts	459
Boron-containing Compounds	460
Cadmium-containing Compounds	460
Carbonyl-compounds (see Aldehydes; Ketones)	
Carboxylates	460
Carboxylic Acids	461
Cobalt-containing Compounds	462
<b>Diazoamino</b> Compounds	462
Diazo Compounds	462
Diazonium Salts	462
Disulphides	462
<b>Dithiocarbamic</b> Acids and Salts	462
Dyes	462
Endiols	463
<b>Enols</b> (see also Ketones)	464
<b>Epoxides</b>	464
Esters (see also Nitrate Esters)	464
Ethers	465
Ethylenediaminetetraacetic Acid and Salts	465
Flavones	466
<b>Guanidines</b>	466
Halides (see Ammonium Salts, Substituted or Alkaloids and Salts or Synthetic Bases and Salts for halide salts; and Halogen-contain- ing Compounds for those with Organically Bound Halogen)	
Halogen-containing Compounds	466
Heterocyclic Bases (see Secondary Amines; Tertiary Amines; see also Alkaloids; Dyes; Purines; Synthetic Bases, etc.)	
Heterocyclic Hydroxyl Compounds (see Phenols)	
Hydrazines	467
<b>Hydrazo</b> Compounds	468
Hydrocarbons (see Acetylenes; Aromatic Hydrocarbons; <b>Olefines</b> ; Paraffins; Terpenes)	
Hydroxamates	468
Imides (see <b>Amides</b> )	
Indophenols	468

CONTENTS

xix

Iron-containing Compounds	468
Ketimines	469
Ketones (see also Enols)	469
Lead-containing Compounds	469
Magnesium-containing Compounds	469
Mercaptans	469
Mercury-containing Compounds	470
Methylene Groups, Active	471
Nitrate Esters	471
<b>Nitriles</b>	471
Nitro Compounds	471
<b>Nitroso Compounds</b>	472
<b>Olefines</b>	472
<b>Oximes</b>	473
Paraffins	473
Phenols and Hydroxy-substituted Heterocyclics	473
Phenothiazines	475
<b>Phosphorus-containing Compounds</b>	475
Polysaccharides	476
<b>Porphyrins</b>	476
Primary Amines	476
Proteins and <b>Peptides</b>	477
Purines	477
Pyrazolones	478
Pyrones	479
Quaternary Ammonium Salts (see Ammonium Salts, Substituted)	
Quinones	479
Salts (see note in introduction to Sect. 3)	
<b>Schiff's Bases</b> (see Anils)	
Secondary Amines and Heterocyclic Bases	497
Selenium-containing Compounds	480
Silicon-containing Compounds	480
Sterols	480
Sugars	481
Sulphates	481
Sulphinic Acids and Sulphinates	481
Sulphonamides and Salts	481
Sulphonates	482
Sulphonic Acids	482
Sulphonium Salts	482
Sulphonyl Chlorides (see Halogen-containing Compounds)	
Sulphoxides	483
Synthetic Bases and Salts	483

<b>Tannins (also Synthetic Tannins)</b>	<b>483</b>
<b>Terpenes</b>	<b>484</b>
<b>Tertiary Amines and Heterocyclic Bases</b>	<b>484</b>
<b>Thioacetals</b>	<b>484</b>
<b>Thioethers</b>	<b>484</b>
<b>Thioketones</b>	<b>485</b>
<b>Thiouracils</b>	<b>485</b>
<b>Thioureas</b>	<b>485</b>
<b>Thiuronium Salts</b>	<b>486</b>
<b>Urethanes</b>	<b>486</b>
<b>Vitamins and Related Compounds</b>	<b>486</b>
<b>Xanthates</b>	<b>486</b>
<b>ADDITIONAL INDEX</b>	<b>487</b>
<b>SUPPLEMENTARY INDEX TO INDIVIDUAL COMPOUNDS DETERMINED BY DIRECT TITRATION</b>	<b>489</b>