

**HANDBOOK
OF ORGANIC REAGENTS
IN INORGANIC ANALYSIS**

**ZÁVIŠ HOLZBECHER
LUDVÍK DIVIŠ
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**HANDBOOK
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CONTENTS

<i>Preface to the English edition</i>	11
<i>List of symbols</i>	13
<i>List of organic reagents (Ligands and solvents)</i>	15
<i>List of abbreviations used in tables</i>	19
Chapter 1 Introduction	23
1.1 Historical development of applications of organic reagents	24
1.2 The reactivity of organic reagents	25
1.2.1 <i>Complex compounds</i>	26
1.2.2 <i>Complexation and the nature of metals and ligands</i>	29
1.2.3 <i>Literature</i>	31
Chapter 2 Structure and properties of organic reagents and their compounds with metals	32
2.1 Introduction	32
2.2 Nature of bonds in complexes	32
2.2.1 <i>Development of concepts of the nature of bonds</i>	32
2.2.2 <i>Electronic structure of atoms</i>	33
2.2.3 <i>The electronic structure of molecules</i>	43
2.2.4 <i>The ligand field theory</i>	44
2.2.5 <i>The molecular orbital theory</i>	51
2.2.6 <i>Symmetry of molecules</i>	54
2.2.7 <i>Literature</i>	55
2.3 Stereochemistry of organic reagents and their metal complexes	56
2.3.1 <i>Introduction</i>	56
2.3.2 <i>Metal ion effect on stereochemistry of complexes</i>	57
2.3.3 <i>The effect of ligands (donor atoms)</i>	59
2.3.4 <i>Literature</i>	59
2.4 Isomerism of organic reagents and their metal complexes	60
2.4.1 <i>Introduction</i>	60
2.4.2 <i>Geometrical isomerism</i>	60
2.4.3 <i>Optical isomerism</i>	62

2.4.4	<i>Other types of isomerism of complexes and organic reagents</i>	63
2.4.5	<i>Tautomerism</i>	65
2.4.6	<i>Literature</i>	65
2.5	Absorption spectra of organic reagents and their complexes	66
2.5.1	<i>Introduction</i>	66
2.5.2	<i>Electronic absorption spectra</i>	68
2.5.3	<i>Optical activity</i>	85
2.5.4	<i>Infrared spectra</i>	87
2.5.5	<i>Literature</i>	91
2.6	Luminescence of organic reagents and their complexes	91
2.6.1	<i>Introduction</i>	91
2.6.2	<i>Theory of photoluminescence</i>	92
2.6.3	<i>Photoluminescence of organic substances and their metal complexes</i>	99
2.6.4	<i>Chemiluminescence</i>	106
2.6.5	<i>Literature</i>	107
2.7	Solubility of organic reagents and their complexes	108
2.7.1	<i>Properties of solvents</i>	108
2.7.2	<i>Solute-solvent interactions</i>	110
2.7.3	<i>Solubility of organic reagents and complexes</i>	111
2.7.4	<i>Literature</i>	112
2.8	Investigation of the structure of metal complexes with organic ligands	113
2.8.1	<i>Spectroscopic methods</i>	113
2.8.2	<i>Methods of magnetochemistry</i>	115
2.8.3	<i>Resonance methods</i>	116
2.8.4	<i>Diffraction methods</i>	118
2.8.5	<i>Chemical methods</i>	118
2.8.6	<i>Example</i>	119
2.8.7	<i>Literature</i>	120
	References	120
Chapter 3 Equilibria of organic reagents in solutions		121
3.1	Introduction	121
3.2	Thermodynamics of complex-formation equilibria in solution	122
3.2.1	<i>Stability constant of the complex</i>	122
3.2.2	<i>Consecutive complexation equilibria</i>	124
3.2.3	<i>Protonation of organic ligands</i>	125
3.2.4	<i>Distribution of consecutive complexes in solution</i>	126
3.2.5	<i>Conditional stability of complexes</i>	130
3.2.6	<i>Comparison of stability of complexes</i>	133
3.2.7	<i>Experimental determination of the composition and stability of complexes in solution</i>	135
3.3	Properties of complex-forming substances and thermodynamic functions of metal complex equilibria	137
3.3.1	<i>Thermodynamic functions</i>	137

3.3.2	<i>The effect of metal ion and ligand on the thermodynamics of complexation equilibria</i>	138
3.3.3	<i>Thermodynamics of consecutive complexation</i>	146
3.3.4	<i>Chelates</i>	148
3.3.5	<i>Medium effect and the stability of complexes</i>	150
3.3.6	<i>Ion-association complexes</i>	151
3.4	<i>Kinetics of complexation reactions in solution</i>	153
3.4.1	<i>Mechanism of ligand replacement</i>	154
3.4.2	<i>Kinetics of oxidation-reduction reactions of metal complexes with organic ligands</i>	157
3.5	<i>Oxidation-reduction reactions of organic reagents and metal complexes</i>	159
3.5.1	<i>Redox potential</i>	159
3.5.2	<i>The equilibrium constant of a redox reaction</i>	159
3.5.3	<i>The effect of complexation on the redox potential</i>	160
3.5.4	<i>The redox potential of complex compounds containing organic ligands</i>	161
3.5.5	<i>Oxidation-reduction reactions of organic reagents</i>	163
3.6	<i>Partition equilibria of organic reagents and their complexes</i>	163
3.6.1	<i>Extraction equilibria</i>	163
3.6.2	<i>Ion-exchange equilibria</i>	169
3.7	<i>Precipitation equilibria of organic reagents with metal ions</i>	172
3.7.1	<i>Solubility of salts and complexes of organic reagents</i>	173
3.7.2	<i>Factors affecting the solubility of salts and complexes of organic reagents</i>	174
3.8	<i>Masking</i>	175
3.8.1	<i>Completeness of masking</i>	176
3.8.2	<i>Metal and ligand buffers</i>	177
3.9	<i>Literature</i>	179
	<i>References</i>	180
Chapter 4 Applications of organic reagents in inorganic analysis		183
4.1	<i>Separation by precipitation</i>	183
4.1.1	<i>Precipitates of known composition</i>	183
4.1.2	<i>Co-precipitation</i>	185
4.1.3	<i>Literature</i>	187
4.2	<i>Distillation</i>	187
4.3	<i>Extraction</i>	188
4.3.1	<i>Introduction</i>	188
4.3.2	<i>Extraction of chelates</i>	190
4.3.3	<i>Extraction of ion-association complexes</i>	203
4.3.4	<i>Solvent extraction in analytical chemistry</i>	213
4.3.5	<i>Extracting agents</i>	221
4.3.6	<i>Literature</i>	232
4.4	<i>Chromatography</i>	232
4.4.1	<i>Partition chromatography</i>	233

4.4.2	<i>Adsorption chromatography</i>	239
4.4.3	<i>Literature</i>	240
4.5	<i>Ion-exchangers</i>	240
4.5.1	<i>Introduction</i>	240
4.5.2	<i>Separation on ion-exchangers without use of complexing agents</i>	244
4.5.3	<i>Ion-exchange separations with the aid of complexing agents</i>	246
4.5.4	<i>Separations on ion-exchangers saturated with complex-forming ions</i>	255
4.5.5	<i>Selective ion-exchangers</i>	256
4.5.6	<i>Literature</i>	258
4.6	<i>Qualitative analysis</i>	258
4.6.1	<i>Reactions used in tests with organic reagents</i>	258
4.6.2	<i>Experimental technique</i>	262
4.6.3	<i>Selectivity of reactions of organic reagents</i>	264
4.6.4	<i>Sensitivity</i>	266
4.6.5	<i>Literature</i>	268
4.7	<i>Gravimetric analysis</i>	268
4.7.1	<i>Factors influencing the solubility of organic reagents and their metal salts in water</i>	268
4.7.2	<i>Organic reagents employed in gravimetric analysis</i>	270
4.7.3	<i>Completeness of formation and subsequent treatment of precipitates</i>	279
4.7.4	<i>Literature</i>	281
4.8	<i>Titrimetric analysis</i>	281
4.8.1	<i>Introduction</i>	281
4.8.2	<i>Chelometric titrations</i>	281
4.8.3	<i>Methods of end-point location in chelometric titrations</i>	299
4.8.4	<i>Indicators for acid-base titrations</i>	325
4.8.5	<i>Indicators for precipitation titrations</i>	335
4.8.6	<i>Oxidation-reduction indicators</i>	336
4.8.7	<i>Literature</i>	341
4.9	<i>Photometric determination</i>	341
4.9.1	<i>Colorimetry, spectrophotometry, turbidimetry</i>	342
4.9.2	<i>Fluorimetry</i>	368
4.9.3	<i>Methods based on chemiluminescence</i>	374
4.9.4	<i>Literature</i>	374
4.10	<i>Kinetic methods of chemical analysis</i>	375
4.10.1	<i>Literature</i>	378
4.11	<i>Ion-selective electrodes</i>	378
4.11.1	<i>The potential of a membrane electrode</i>	380
4.11.2	<i>Liquid membrane electrodes</i>	381
4.11.3	<i>Solid membrane electrodes</i>	383
4.12	<i>References</i>	384

Chapter 5 Analytical applications of organic reagents 391

5.1 Hydrogen	391
5.2 Alkali metals	393
5.3 Copper	397
5.4 Silver	398
5.5 Gold	399
5.6 Beryllium	400
5.7 Magnesium	414
5.8 Calcium, strontium and barium	415
5.9 Zinc	422
5.10 Cadmium	424
5.11 Mercury	424
5.12 Boron	432
5.13 Aluminium	433
5.14 Gallium and indium	439
5.15 Thallium	440
5.16 Rare-earth elements	441
5.17 Actinium, thorium, uranium and other actinides	443
5.17.1 Thorium	445
5.17.2 Uranium	472
5.18 Carbon	474
5.19 Silicon	474
5.20 Germanium	476
5.21 Tin	477
5.22 Lead	477
5.23 Titanium	478
5.24 Zirconium and hafnium	487
5.25 Nitrogen	488
5.26 Phosphorus	489
5.27 Arsenic and antimony	490
5.28 Bismuth	497
5.29 Vanadium	499
5.30 Niobium and tantalum	500
5.31 Oxygen	514
5.32 Sulphur	515
5.33 Selenium and tellurium	520
5.34 Polonium	521
5.35 Chromium	521
5.36 Molybdenum and tungsten	526
5.37 Fluorine	536
5.38 Chlorine, bromine and iodine	545
5.39 Manganese	546
5.40 Technetium	547
5.41 Rhenium	548
5.42 Iron	554
5.43 Cobalt	556
5.44 Nickel	569
5.45 Ruthenium	570

5.46 Rhodium	576
5.47 Palladium	577
5.48 Osmium	579
5.49 Iridium	593
5.50 Platinum	594
Chapter 6 Selection of organic reagents used in analytical chemistry	600
6.1 Literature	600
Index	712

PREFACE TO THE ENGLISH EDITION

The recent rapid advances in analytical chemistry have mainly been made in the field of new analytical methods based on instrumental techniques; however, the chemical reaction of a suitable reagent with the substance to be determined still remains the true basis of numerous methods of detection, separation, and determination. Organic reagents play a predominant role and find wide application in spectrophotometric (colorimetric) methods, titrimetry (as titrants and indicators), spot tests, and last but not least in separational methods (precipitation, masking, and extraction reagents, ion-exchangers), and preconcentration procedures.

Every year there are published hundreds of papers on the reactions and possible applications of new and/or old organic reagents for inorganic analysis. The study of these reagents still attracts many chemists—some of these reagents allow development of highly sensitive, selective, and rapid methods for the analysis of a variety of materials, needing only simple instrumentation. The vast amount of information available in this field brings about problems whenever an adequately comprehensive and sufficiently critical review is attempted. The development of the theory should help to achieve better understanding of basic principles and rules on the reactivity of organic reagents with inorganic ions and the properties of the complexes formed. It should also be useful in preparations of new reagents with desired properties. Nevertheless, the choice of a reagent suited for a particular analytical application may still be a challenging problem.

At present there are available only a few monographs, which cover predominantly either the theory or the applications of the reactions of organic reagents. This book attempts to provide a unified approach both to the theory and practical applications. The modern developments in the theory of the properties of organic reagents and their complexes with metal ions will be discussed. Emphasis will be laid on the correla-

tions between the structure and the properties of the organic reagents for inorganic analysis, the types of chemical reactions and the equilibria involved. In addition to that, concise information will be provided on the analytical properties of the metal ions and the organic reagents used nowadays for their detection, separation, and determination. Besides the modern approaches, some of the older theories will also be used, if convenient, since they are still of practical value for the analyst.

The following authors have contributed to the book: Prof. Z. HOLZBECHER (Chap. 1, Sections 2.6, 4.9, 4.10, 5.12–16, 5.18–30, and Chap. 6), DR. L. DIVIŠ (Sections 4.6, 4.7, 5.1–11), DR. M. KRÁL (Sections 2.1–5, 2.8), DR. L. ŠŮCHA (Chapter 3 and Sections 4.8, 4.11, 5.17, 5.31–36, 5.42–44), and DR. F. VLÁČIL (Sections 2.7, 4.1–5, 5.37–41, 5.45–50).

The selection of material and its treatment cover such a wide field, the bibliography of which would probably require by itself several hundreds of pages, that they are necessarily subjective. Even so, the authors believe that the book will be useful not only to those who need a rapid orientation in the field but also for advanced workers, helping them to choose the proper reagent for the particular application in the analysis of various materials.

The authors would like to express their thanks to all those who have helped in any way and contributed to this book. In particular they are indebted to Dr. R. A. Chalmers for his useful comments and numerous suggestions and corrections which have helped to improve the English edition. Sincere thanks should also be accorded to Dr. S. Kotrlý for his stimulating discussion and careful translation.

Prague, December 1973.

The Authors

LIST OF SYMBOLS

A	singly degenerate state (term); absorbance
a	activity
α	separation factor (extraction)
α_L	side-reaction coefficient of the ligand L
α_M	side-reaction coefficient of the metal M
B	singly degenerate state (term)
β	width of elution peak for $c = c_{\max}/e$
β	overall stability constant of a complex
β'	conditional stability constant of a complex
c	velocity of light; total (analytical) molar concentration
D_M	distribution ratio (extraction); distribution coefficient (ion-exchangers)
d	one-electron orbital for $l = 2$
δ	distribution coefficient for the formation of a complex species
E	per cent extraction; energy; redox potential; twofold degenerate state (term)
E^0	standard redox potential
E^f	formal redox potential
ϵ	molar absorption coefficient; relative permittivity (dielectric constant)
η	luminescence energy yield; cross-contamination factor (ion-exchangers)
F	intensity of fluorescence; FARADAY constant
f	one-electron orbital for $l = 3$
G	GIBBS free energy
H	enthalpy
h	PLANCK'S constant
I	ionic strength
K	equilibrium constant
K_a	dissociation constant of an acid

K_D	distribution constant (extraction)
$K_{ex}, \mathcal{K}_{ex}$	extraction constant
$K_{N/n}^M, K_{nN}^M$	selectivity coefficient
K_s	solubility product
K'_s	conditional solubility product
k	consecutive stability (association) constant of a complex
κ	quantum efficiency of luminescence
L	ligand
L	luminescence centre
λ	wavelength
M	metal; metal ion
M	electron trap; molar concentration (mole $\cdot$ l $^{-1}$)
μ	chemical potential
N	normal concentration (equivalents per litre)
n	principal quantum number
$\bar{n}$	formation function of a complex
ν	frequency of electromagnetic radiation
ν_m	amount of a substance in moles
ν_v	amount of a substance in equivalents
p	one-electron orbital for $l = 1$
pH	$= -\log [H^+]$
pL	$= -\log [L]$
pM	$= -\log [M]$
π_M	capacity of metal buffer
R	recovery (extraction)
R	gas constant
S	solvent
S	singlet electronic state (electronic term)
$S_{A/B}$	enrichment factor
s	one-electron orbital for $l = 0$; spin quantum number of electron; estimated standard deviation
σ	wavenumber; standard deviation
T	threefold degenerate state (term); triplet (metastable) state (cf. luminescence); thermodynamic temperature (in K)
t	time; temperature
V_{max}	volume of the eluting agent corresponding to a particular elution peak
V_0	interstitial volume
v	vibrational quantum number; vibrational level
γ	molar activity coefficient
z	ionic charge

LIST OF ORGANIC REAGENTS (LIGANDS AND SOLVENTS)

ac	acetate
acac	acetylacetone
AcOH	acetic acid
AmOH	amyl alcohol
APANS	Thorin [2-(2-hydroxy-3,6-disulpho-1-naphthylazo)-benzene- arsonic acid, usually a disodium salt]
APDC	1-pyrrolidinecarbodithioic acid, ammonium salt
BAL	2,3-dimercapto-1-propanol
BCMDTC	bis(carboxymethyl)dithiocarbamate
BHEDTC	bis(2-hydroxyethyl)dithiocarbamate
bipy	2,2'-bipyridyl
BMFP	4-benzoyl-3-methyl-1-phenyl-5-pyrazolone
BuOH	butyl alcohol
CHENTA	see DCTA (CyDTA)
CH ₃ ox	8-hydroxy-2-methylquinoline (CH ₃ -oxine)
CyDTA	see DCTA
DBM	dibenzoylmethane
DBPS	di-n-butylphosphoric acid
DCTA	(1,2-cyclohexylenedinitrilo)tetra-acetic acid (DCyTA, CyDTA, CDTA)
DDC	diethyldithiocarbamate
DHG	<i>N,N</i> -dihydroxyethylglycine
dien	diethylenetriamine
DIOX	dioxan
DIPE	di-isopropyl ether
Di-SNADNS	4,5-dihydroxy-3,6-bis(4-sulphonaphthylazo)-2,7-naphtha- lenedisulphonic acid
DMF	dimethylformamide

DMG	dimethylglyoxime (2,3-butanedione dioxime; biacetyl dioxime)
DMPA	2,3-dimercaptopropionic acid
DMSA	dimercaptosuccinic acid
DMSO	dimethyl sulphoxide
DPM	dipivaloylmethane
DTPA	diethylenetriamine- <i>N,N,N',N'',N''</i> -penta-acetic acid (DETAPA)
DVB	divinylbenzene
EDTA	ethylenediaminetetra-acetic acid (the anion)
EGTA	ethylene glycol-bis(2-aminoethylether)- <i>N,N'</i> -tetra-acetic acid
en	ethylenediamine
en-sal	bis-salicylaldehyde ethylenedi-imine
EtOH	ethanol
4-etpy	4-ethylpyridine
ferron	8-hydroxy-7-iodoquinoline-5-sulphonic acid (the anion)
gly	glycine (aminoacetic acid, the anion)
- (glyc)	
HEDTA	<i>N'</i> -(2-hydroxyethyl)ethylenediamine- <i>N,N,N'</i> -triacetic acid
Hox	8-hydroxyquinoline (undissociated)
HTTA	2-thenoyltrifluoroacetone
IBMK	isobutyl methyl ketone
KelF	polytrifluorochloroethylene
MeOH	methanol
MIBK	isobutyl methyl ketone
MPA	3-mercaptopropionic acid
NaDDC	sodium diethyldithiocarbamate
NTA	nitrilotriacetic acid
OAL	anion-exchanger, see p. 675
ox	8-hydroxyquinoline (the anion)
(oxine)	
PADNS	6,7-dihydroxy-5-(2-pyridylazo)-2-naphthalenesulphonic acid, sodium salt
PAN	1-(2-pyridylazo)-2-naphthol (the anion)
PAR	4-(2-pyridylazo)resorcinol (the anion)
penten	pentaethylenehexamine
phen	1,10-phenanthroline
pic	picolinic acid (the anion)
picO	picolinic acid <i>N</i> -oxide
PVC	poly(vinyl chloride)
py	pyridine