

TREATISE
ON
ANALYTICAL
CHEMISTRY

PART II
ANALYTICAL CHEMISTRY
OF THE ELEMENTS
VOLUME 5

54.6.73
K.81
P.2. V.5

TREATISE ON ANALYTICAL CHEMISTRY

Edited by I. M. KOLTHOFF

School of Chemistry, University of Minnesota

and PHILIP J. ELVING

Department of Chemistry, University of Michigan

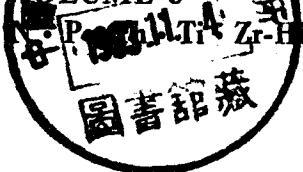
with the assistance of ERNEST B. SANDELL

School of Chemistry, University of Minnesota

PART II

ANALYTICAL CHEMISTRY
OF THE ELEMENTS

VOLUME 5



INTERSCIENCE PUBLISHERS, NEW YORK-LONDON

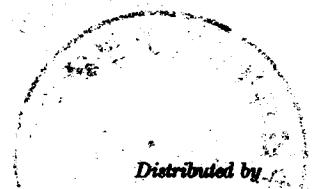
502968

DR 63/5

Copyright © 1961 by
INTERSCIENCE PUBLISHERS, INC.

ALL RIGHTS RESERVED

LIBRARY OF CONGRESS CATALOG CARD NUMBER 59-12439



Distributed by

Interscience Publishers, Inc., 250 Fifth Avenue, New York 1, N. Y.

For Great Britain and Northern Ireland:

Interscience Publishers Ltd., 88/90 Chancery Lane, London, W. C. 2

PRINTED IN U. S. A. BY MACK PRINTING CO., EASTON, PA.

TREATISE ON ANALYTICAL CHEMISTRY

PART II ANALYTICAL CHEMISTRY OF THE ELEMENTS

SECTION A

**Systematic Analytical Chemistry of the
Elements**

VOLUME 5:

**NITROGEN • PHOSPHORUS • THORIUM
TITANIUM • ZIRCONIUM-HAFNIUM**

AUTHORS OF VOLUME 5

JOHN BEUKENKAMP

WILLIAM RIEMAN III

A. J. CLEAR

MILTON ROTH

F. S. GRIMALDI

EDWARD R. SCHEFFER

RICHARD B. HAHN

Authors of Volume 5



John Beukenkamp
*Titanium Division, National Lead Company,
South Amboy, New Jersey*



Arthur J. Clear
*Scientific Services Branch,
Picatinny Arsenal, Dover,
New Jersey*



Frank S. Grimaldi
*Analytical Laboratories
Branch, U. S. Geological
Survey, Washington, D. C.*

AUTHORS OF VOLUME 5

**Richard B. Hahn**

*Department of Chemistry,
Wayne State University,
Detroit, Michigan*

**William Rieman III**

*School of Chemistry, Rutgers,
The State University,
New Brunswick, New
Jersey*

**Milton Roth**

*Chief, Analytical Chemistry
Section, Picatinny Ar-
senal, Dover, New Jersey*

**Edward R. Scheffer**

*Titanium Division, Na-
tional Lead Company,
South Amboy, New Jersey*

PART II. ANALYTICAL CHEMISTRY OF THE ELEMENTS

CONTENTS—VOLUME 5

SECTION A. Systematic Analytical Chemistry of the Elements

Titanium. By <i>Edward R. Scheffer</i>	1
I. Introduction.....	2
A. Occurrence.....	3
B. Industrial Processes Involving Titanium.....	4
1. Titanium Dioxide Pigment.....	4
2. Titanium Metal.....	4
3. Miscellaneous Uses.....	5
C. Toxicology and Industrial Hygiene.....	5
II. Properties.....	5
A. Physical and Physiochemical Properties.....	5
B. Electrochemical Properties.....	7
C. Optical Properties.....	8
1. Absorption.....	8
2. Characteristic and Strongest Emission Spectral Lines.....	8
D. Chemical Properties.....	8
1. Oxides and Hydrous Oxides.....	8
2. Solubility.....	10
3. Reactions.....	10
a. Precipitation.....	10
b. Colorimetric.....	11
c. Ignition.....	12
d. Oxidation and Reduction.....	12
III. Sampling.....	13
A. Titanium Metal and Alloys.....	13
B. Oxides, Ores, Minerals, Slags, Titanates, Metalloids.....	14
C. Halides.....	14
D. Organic Titanium Compounds.....	15
IV. Separation and Isolation.....	15
A. Decomposition, Dissolution, and Other Preliminary Treatment of Inorganic Materials.....	15
1. Acid.....	15
a. Titanium Metal and Alloys.....	15
b. Oxides.....	16
c. Minerals and Ores.....	16
d. Double Salts and Titanates.....	16
e. Halides.....	17
2. Fusion.....	17
B. Decomposition of Organic Compounds.....	17
1. Oxidation.....	17
2. Alkaline Fusion.....	18
3. Hydrolysis.....	18
C. Selective Separation Methods.....	18
1. Precipitation.....	18
a. Hydrolytic.....	19

CONTENTS

b. Alkali.....	19
c. Organic.....	20
d. Miscellaneous.....	22
2. Volatilization.....	22
3. Solvent Extraction.....	23
4. Ion Exchange.....	24
V. Detection and Identification.....	26
A. Colorimetric.....	26
B. Instrumental.....	27
VI. Determination.....	29
A. Gravimetric.....	29
B. Titrimetric.....	30
C. Polarographic.....	34
D. Photometric.....	36
1. Colorimetry.....	36
2. Emission Spectrography.....	38
3. X-Ray Spectrography.....	39
VII. Analysis of Titanium Metal and its Alloys.....	40
VIII. Determination and Analysis of Titanium Compounds.....	42
A. X-Ray Diffraction.....	42
B. Assay and Analysis of Titanium Oxides and Compounds.....	43
1. Titanium.....	43
2. Other Constituents.....	45
a. Halides.....	45
b. Carbon, Nitrogen, and Sulfur.....	45
C. Analysis of Organic Titanium Compounds.....	46
IX. Determination of Titanium in Specific Materials.....	47
A. Ores, Rocks, and Minerals.....	48
B. Ceramic Materials.....	48
C. Metals and Alloys.....	48
D. General.....	49
X. Recommended Laboratory Procedures.....	49
A. Titrimetric.....	49
B. Colorimetric.....	51
C. Valence States.....	52
1. Titanium(III).....	52
2. Titanium(II).....	53
3. Titanium Metal.....	56
4. Titanium(IV).....	56
References.....	56
Zirconium and Hafnium. By Richard B. Hahn.	61
I. Introduction.....	64
A. History.....	64
1. Discovery of Zirconium.....	64
2. Discovery of Hafnium.....	65
B. Occurrence.....	66
1. In Nature.....	66
2. In Industrial Products.....	68
C. Industrial Processes Involving Zirconium.....	69
1. Mining and Concentration of Zircon.....	69
2. Conversion of Zircon to Other Compounds.....	69
3. Separation of Hafnium.....	70
4. Conversion to Metal.....	71
D. Toxicology and Industrial Hygiene.....	71
II. Properties of Zirconium and Hafnium.....	72
A. Physical Properties.....	72
B. Electrochemical Properties.....	72
C. Optical Properties.....	74
1. Absorption Spectra.....	74
2. Emission Spectra.....	74

3. X-Ray Spectra.....	75
D. Chemical Properties.....	76
1. Oxidation States in Aqueous Solution.....	76
2. Reactions of the Free Elements.....	76
3. Simple Compounds.....	77
4. Ionic Species.....	78
5. Chemistry in Aqueous Solution.....	78
6. Complex Ions and Compounds.....	79
III. Sampling of Zirconium-Containing Materials.....	80
A. Rocks, Minerals, and Ceramics.....	80
B. Metals and Alloys.....	80
IV. Separation and Isolation of Zirconium and Hafnium.....	81
A. The General Problem.....	81
B. Separation of Zirconium from Other Elements.....	81
1. Preliminary Treatment and Dissolution.....	81
2. Selected Separation Methods.....	82
a. Electrolysis.....	82
b. Solvent Extraction.....	82
c. Ion Exchange.....	83
(1) Cation Exchangers.....	83
(2) Anion Exchangers.....	83
d. Paper Chromatography.....	84
e. Precipitation.....	84
V. Detection and Identification.....	85
A. Chemical Tests.....	85
B. Spectrographic Methods.....	86
VI. Determination.....	86
A. Gravimetry.....	86
1. Inorganic Precipitants.....	86
a. Precipitation as Zirconium Hydroxide.....	86
b. Precipitation as the Arsenate.....	88
c. Precipitation as the Iodate.....	89
d. Precipitation as the Selenite.....	89
e. Precipitation as the Phosphate.....	89
2. Organic Precipitants.....	90
a. Organic Bases.....	91
b. Organic Acids or Their Salts.....	91
c. Arsonic Acids.....	91
d. Chelate Compounds.....	95
(1) Cupferron.....	95
(2) Mandelic Acid.....	95
e. Phosphonic Acids.....	97
B. Titrimetry.....	97
1. Neutralization Reactions.....	97
2. Precipitation Reactions.....	97
3. Amperometric Titrations.....	98
4. Complexometric Reactions.....	98
C. Polarography.....	99
D. Photometry.....	100
1. Direct Colorimetric Methods.....	100
2. Indirect Colorimetric Methods.....	101
3. Fluorometric Methods.....	102
4. Turbidimetric Methods.....	102
VII. Individual Determination of Zirconium and Hafnium.....	103
A. Introduction.....	103
B. Determination of Zirconium/Hafnium Ratios.....	103
C. Methods That Distinguish between Zirconium and Hafnium.....	104
1. Emission Spectroscopy.....	104
a. Determination of Small Amounts of Zirconium.....	104
b. Determination of Hafnium.....	105
2. X-Ray Methods.....	105

a. X-Ray Absorbance	105
b. X-Ray Fluorescence	106
VIII. Determination of Radioactive Zirconium and Hafnium	106
A. Introduction	106
B. Radioactive Zirconium	108
C. Radioactive Hafnium	108
D. Activation Analysis	108
IX. Analysis of Zirconium Metal and Its Alloys	109
A. Introduction	109
B. Determination of Metallic Elements in Zirconium Metal and Zircaloy	110
1. Dissolution of Zirconium Alloys	110
2. Zirconium	110
3. Aluminum	110
4. Cadmium	110
5. Chromium	110
6. Copper	111
7. Hafnium	111
8. Iron	111
9. Lead	111
10. Magnesium	111
11. Manganese	111
12. Molybdenum	111
13. Nickel	112
14. Tin	112
15. Titanium	112
16. Tungsten	112
17. Vanadium	112
18. Zinc	112
19. Rare Earth Elements	113
C. Determination of Nonmetallic Elements in Zirconium	113
1. Introduction	113
2. Boron	113
3. Carbon	113
4. Chlorine	113
5. Phosphorus	114
6. Silicon	114
7. Nitrogen	114
8. Oxygen	114
9. Hydrogen	115
X. Analysis of Zirconium Compounds	115
A. Zirconia	115
1. Introduction	115
2. Dissolution	115
3. Zirconium	116
4. Hafnium	116
5. Aluminum	116
6. Titanium	116
7. Iron	116
8. Silicon	116
9. Other Elements	117
B. Other Inorganic Zirconium Compounds	117
1. Insoluble Compounds	117
2. Soluble Compounds	117
C. Organic Compounds	117
XI. Determination of Zirconium in Specific Materials	118
A. Ores and Minerals Containing Large or Moderate Amounts of Zirconium	118
B. Ores and Rocks Containing Small or Trace Amounts of Zirconium	118
C. Alloys	118
1. Steels	118
2. Magnesium Alloys	119
3. Other Alloys	120

XII. Selected Laboratory Procedures.	120
A. Decomposition and Dissolution of Zirconium Minerals and Acid-Insoluble Compounds.	120
1. Fusion with Borax.	120
2. Fusion with Sodium Carbonate and Sodium Peroxide.	121
B. Dissolution of Metals and Alloys.	121
1. Zirconium Metal, Zircaloy, and Other Alloys of High Zirconium Content.	121
a. Dissolution in Hydrofluoric Acid.	121
b. Dissolution in Sulfuric Acid or Perchloric Acid.	122
2. Steels and Other Ferrous Alloys Containing Small Amounts of Zirconium.	122
a. Dissolution in Hydrochloric Acid.	122
b. Dissolution in Sulfuric Acid.	122
3. Magnesium Alloys.	123
4. Other Alloys.	123
C. Qualitative Tests for Zirconium.	123
1. Precipitation of Zirconyl Phosphate.	123
2. Spot Test Using <i>p</i> -Dimethylaminoazophenylarsonic Acid.	123
3. Detection with Pyrocatechol Violet.	124
D. Gravimetric Methods.	124
1. Precipitation with Mandelic Acid.	124
2. Precipitation as the Phosphate.	126
3. Determination of Zirconium/Hafnium Ratios by Precipitation as the Selenite.	126
E. Titrimetric Methods.	127
1. Direct Titration with EDTA.	127
2. EDTA Method Involving Back-Titration with Bismuth.	128
F. Colorimetric Methods.	129
1. Alizarin Red S as Reagent.	129
2. Pyrocatechol Violet as Reagent.	130
References.	131
Thorium. By F. S. Grimaldi.	139
I. Introduction.	142
A. Occurrence.	142
1. Thorium Minerals and Ores.	142
2. Industrial Processes and Products.	143
B. Industrial Processes.	144
1. Extraction of Thorium from Monazite.	144
2. Preparation of Thorium Metal.	145
3. Thorium Hydrides.	145
C. Toxicology and Industrial Hygiene.	145
II. Properties of Thorium.	146
A. Physical Properties.	146
1. Thorium Metal.	146
2. Thorium Isotopes.	147
B. Electrochemical Properties.	147
C. Optical Properties.	147
1. Emission Spectra.	147
2. X-Ray Spectra.	150
D. Chemical Properties.	150
1. Chemical Properties of Thorium.	150
2. Properties of Analytically Important Thorium Compounds.	152
a. Thorium Nitrate.	152
b. Thorium Hydroxide.	152
c. Thorium Dioxide.	153
d. Thorium Fluoride.	153
e. Thorium Oxalate.	154
f. Thorium Sulfate.	155
g. Thorium Iodate.	155
h. Thorium Molybdate.	156

CONTENTS

i. Thorium Phosphates.....	156
j. Thorium Carbonate.....	156
k. Thorium Peroxide.....	156
III. Separation and Isolation of Thorium.....	157
A. Preparation of the Solution for Analysis.....	157
1. Rocks.....	157
2. Monazite.....	158
3. Refractory Thorium-Bearing Minerals Containing Nb, Ta, and Ti; Black Sands.....	158
4. Thorianite.....	158
5. Alloys.....	159
6. Worn-Out Gas Mantles.....	159
7. Tungsten Filaments.....	159
B. Methods of Separation.....	159
1. Precipitation Methods.....	159
a. Precipitation with Oxalate.....	159
b. Precipitation with Hydrofluoric Acid.....	160
c. Precipitation with Ammonium Hydroxide.....	160
d. Precipitation with Hexamethylenetetramine (Hexamine).....	161
e. Precipitation with Hydrogen Peroxide.....	161
f. Precipitation with Iodate.....	161
g. Precipitation with Organic Acids.....	162
(1) Benzoic Acid.....	162
(2) Diphenic Acid (2,2'-Biphenyldicarboxylic Acid).....	162
2. Solvent Extraction.....	164
a. Chelate Extraction Systems.....	164
(1) 2-Thienyltrifluoroacetone (4,4,4-Trifluoro-1-(2-thienyl)-1,3-butanedione; TTA).....	165
(2) Cupferron, 8-Quinolinol, and Acetylacetone.....	168
b. Nitrate Extraction Systems.....	168
(1) Tributyl Phosphate (TBP).....	168
(a) Effect of Nitric Acid and TBP Concentration.....	169
(b) Effect of Thorium Concentration.....	171
(c) Effect of Salting-Out Agents.....	171
(d) Effect of Cations.....	172
(e) Effect of Anions that Form Complexes with Thorium.....	175
(f) Equilibration Time.....	176
(2) Mesityl Oxide.....	176
c. Chloride Extraction Systems.....	178
3. Separations by Partition Chromatography.....	179
4. Separations with Cation Exchangers.....	180
5. Separations with Anion Exchangers.....	181
a. Chloride System.....	181
b. Nitrate System.....	181
IV. Detection and Identification.....	182
A. General Scheme of Qualitative Analysis.....	182
B. Paper Chromatography.....	182
C. Emission Spectra.....	182
D. X-Ray Spectrometry.....	182
V. Methods of Determination.....	183
A. Gravimetric Methods.....	183
B. Titrimetric Methods.....	184
1. Complexometric Titrations Based on the Disodium Salt of Ethylenediaminetetraacetic Acid (EDTA).....	184
a. Direct EDTA Titration.....	184
(1) Alizarin Red S.....	184
(2) Pyrocatechol Violet.....	184
(3) SPADNS.....	185
(4) SNADNS Indicators.....	185
b. Indirect Spectrophotometric Titration.....	185
Indirect Visual Titration.....	186

2. Amperometric Titrations.....	186
a. With Ammonium Molybdate.....	186
b. With Fluoride.....	186
3. Miscellaneous Titrimetric Methods.....	186
a. Titration with Fluoride, SPADNS Indicator.....	186
b. Titration with Oxalic Acid.....	187
c. Titration Based on Separation of Thorium with Organic Acids.....	187
(1) <i>m</i> -Nitrobenzoic Acid.....	187
(2) <i>p</i> -Aminosalicylic Acid.....	187
(3) Anthranilic Acid.....	187
(4) Oxalohydroxamic Acid.....	188
C. Polarographic Determination of Thorium.....	188
D. Spectrometric Methods.....	189
1. Spectrophotometric Methods.....	189
a. Thoron.....	189
b. Morin.....	191
c. Dinitrosochromotropic Acid.....	192
d. Other Reagents.....	192
(1) SPADNS.....	192
(2) Di-SNADNS.....	193
(3) Quercetin.....	194
2. Emission Spectroscopy.....	194
3. Mass Spectrometry.....	194
4. X-Ray Fluorescence Spectrometry.....	195
E. Radiochemical Methods.....	195
1. Natural Radioactivity.....	195
2. Nuclear Photographic Emulsions.....	196
3. Neutron Activation.....	196
VI. Analysis of Thorium Metal, Alloys, and Compounds.....	197
A. Thorium Metal.....	197
1. Determination of Aluminum.....	197
2. Determination of Iron.....	198
3. Determination of Rare Earth Elements.....	198
4. Determination of Thorium Oxide.....	198
5. Determination of Uranium.....	198
6. Determination of Zirconium.....	198
7. Miscellaneous.....	198
B. Thorium Alloys.....	199
1. Thorium-Aluminum.....	199
2. Thorium-Cerium.....	199
3. Thorium-Magnesium.....	199
4. Thorium-Uranium.....	199
C. Thorium Compounds.....	199
1. Thorium Nitrate.....	199
a. Determination of Nitric Acid.....	199
b. Determination of Sulfate.....	199
c. Determination of Rare Earths.....	200
2. Thorium Dioxide.....	200
a. Determination of Silicon.....	200
VII. Selected Laboratory Procedures.....	200
A. Decomposition of Monazite and Perchloric Acid.....	201
B. Oxalate Separation.....	201
1. Procedure 1.....	201
2. Procedure 2.....	201
C. Fluoride Separation.....	202
D. Hexamine Separation.....	202
E. Peroxynitrate Separation.....	203
F. Ammonium Hydroxide Separation.....	203
G. Iodate Separation.....	204
1. Iodate Separation from Nitric Acid Medium.....	204
2. Iodate Separation from Oxalic Acid Medium.....	204

3. Iodate Separation from Tartaric Acid-Hydrogen Peroxide Medium.....	205
a. Ores.....	205
b. Silicate Rocks.....	206
H. Separation with Organic Acids.....	206
1. Benzoic Acid.....	206
a. Procedure 1.....	206
b. Procedure 2.....	206
2. Diphenic Acid.....	207
I. Extraction with Mesityl Oxide, Aluminum Nitrate as Salting Agent.....	207
J. Direct EDTA Titration, Alizarin Red S Indicator.....	207
K. Amperometric Titration with Molybdate.....	208
L. Polarography, <i>m</i> -Nitrobenzoic Acid.....	209
M. Spectrophotometry.....	209
1. Thoron- <i>meso</i> -Tartaric Acid Method.....	209
2. Dinitrosochromotropic Acid.....	210
References.....	210
Nitrogen. By A. J. Clear and Milton Roth	217
I. Introduction.....	221
A. Scope.....	221
B. Occurrence.....	221
1. In Nature.....	221
2. In Industrial Products and Processes.....	222
3. As an Impurity.....	223
C. Industrial Processes Involving Nitrogen.....	223
D. Toxicology and Industrial Hygiene.....	224
II. Properties.....	225
A. Physical.....	225
B. Chemical.....	225
III. Sampling.....	226
IV. Detection and Identification.....	228
V. Quantitative Determination.....	229
A. Absorption Methods.....	229
B. Spectrometry.....	230
1. Mass Spectrometry.....	230
2. Optical Spectroscopy.....	231
C. Methods for Nitrogen in Admixture with Other Gases.....	231
1. Electromagnetic Pump.....	231
2. Radio-Frequency Excitation.....	232
D. Metal Analysis.....	232
VI. Determination of Oxides of Nitrogen and Their Salts.....	233
A. Nitrous Oxide.....	234
1. Qualitative Tests.....	234
2. Combustion and Reduction Methods.....	235
a. With Hydrogen.....	235
b. With Carbon Monoxide.....	235
c. With Copper.....	236
d. With Platinum.....	236
3. Fractional Distillation Methods.....	236
4. Microanalytical Methods.....	237
5. Physical Methods.....	237
a. Mass Spectrometry.....	237
b. Infrared Absorption.....	238
c. Acoustic Gas Analyzer.....	239
B. Nitric Oxide.....	239
1. Qualitative Tests.....	239
2. Combustion Method with Carbon Monoxide.....	239
3. Absorption Media.....	240
a. Oxidation Media.....	240
b. Reduction Media.....	242
c. Complexing Media.....	242
4. Colorimetry.....	243

a. Griess Reagent.....	243
b. Phenoldisulfonic Acid Reagent.....	244
5. Titrimetry.....	244
6. Nitrometry.....	245
7. Infrared and Raman Methods.....	246
C. Nitrogen Dioxide and Nitrogen Tetroxide.....	247
1. Qualitative Tests.....	248
2. Colorimetry.....	249
a. Griess Reagent and Its Modifications.....	249
b. Bratton and Marshall Reagent.....	249
c. Saltzman Reagent.....	250
d. Lingenberg Reagent.....	250
3. Titrimetry.....	251
a. Oxidimetry with Permanganate.....	251
b. Oxidimetry with Ceric Salts.....	251
c. Alkalimetry with Sodium Hydroxide.....	251
4. Physical Methods.....	252
a. Ultraviolet Absorption.....	252
b. Infrared Absorption.....	252
c. Mass Spectrometry.....	253
D. Other Oxides of Nitrogen.....	253
1. Nitrogen Sesquioxide.....	253
2. Nitrogen Pentoxide.....	254
3. Nitrosyl Peroxide.....	254
E. Mixtures of Nitrogen Oxides.....	254
1. Sampling.....	255
2. Nitrogen Oxides.....	255
3. Nitrous Oxide and Nitric Oxide.....	256
4. Nitrous Oxide, Nitric Oxide, and Nitrogen.....	257
5. Nitrous Oxide, Nitric Oxide, Nitrogen Dioxide, and Nitrogen.....	257
6. Miscellaneous Mixtures.....	258
a. Mass Spectrometry.....	258
b. Gas Chromatography.....	259
7. Total Oxides of Nitrogen.....	260
F. Salts of Nitrogen Oxides.....	260
VII. Determination of Oxy Acids of Nitrogen.....	261
A. Nitric Acid.....	261
1. Titrimetry.....	262
a. Sampling.....	263
b. Acidimetry.....	263
c. Redox Methods.....	263
2. Fuming Nitric Acids.....	264
3. Mixtures of Nitric and Sulfuric Acids.....	268
4. Nitro Bodies in Sulfuric Acid and Oleum.....	267
B. Nitrous Acid.....	267
VIII. Determination of Nitrates.....	268
A. Colorimetry.....	268
1. Phenoldisulfonic Acid.....	268
2. Brucine.....	268
3. Xylenol.....	269
4. Strychnine-Sulfuric Acid.....	269
5. Chromotropic Acid.....	269
6. Aniline and α -Naphthylamine.....	269
7. Diphenylamine.....	270
8. 4-Hydroxy,1,3-dimethylbenzene.....	270
9. α -Naphthylamine and Sulfanilic Acid.....	270
10. Ferrous Sulfate.....	270
11. Ultraviolet Absorption in Perchloric Acid.....	270
12. Pyrogallolsulfonic Acid.....	271
13. Michler's Ketone.....	271
14. Diphenylamine and Ultraviolet Light.....	271

B.	Titrimetry.....	271
1.	Stannous Chloride.....	271
2.	Ferrous Salts.....	272
3.	Devarda's Method.....	272
4.	Aluminum Reduction.....	272
5.	Gooch and Gruener Iodometric Method.....	272
C.	Gravimetry.....	273
1.	Nitron.....	273
2.	Dicyclohexyl Phthalate.....	273
D.	Nitrometry.....	273
E.	Chromatography and Ion Exchange.....	273
F.	Polarography.....	274
IX.	Determination of Nitrites.....	275
A.	Colorimetry.....	275
1.	α -Naphthylamine with Various Coupling Agents.....	275
2.	Dimethyl- α -Naphthylamine.....	276
3.	Dimethylaniline.....	276
4.	Zinc Iodide and Starch.....	276
5.	Brucine Hydrochloride.....	276
B.	Titrimetry.....	276
1.	Permanganate.....	276
2.	Iodometry.....	277
3.	Potassium Bromate.....	277
4.	Chlorate.....	277
5.	Hydrazine.....	277
6.	Hydroxylamine.....	278
7.	Alkalimetry.....	278
C.	Gravimetry.....	278
D.	Gas Evolution Methods.....	278
1.	Decomposition with Sulfamic Acid.....	278
2.	Nitrometry.....	278
E.	Polarography.....	279
X.	Determination of Hydrogen Compounds.....	279
A.	Ammonia.....	279
1.	Colorimetry.....	279
a.	Nesslerization.....	279
b.	Hypohalides and Phenols.....	279
c.	Silver Nitrate and Tannin.....	280
d.	Chloramine-T.....	280
e.	Rapid Diffusion Method.....	280
f.	Cupric Carbonate.....	281
2.	Titrimetry.....	281
a.	Acidimetry.....	281
b.	Oxidimetry.....	281
c.	Kjeldahl Method.....	281
d.	Formol Titration.....	281
e.	Nonaqueous Titration.....	282
f.	Indirect Method with Alkali.....	282
g.	Permanganate.....	282
h.	Cupric Carbonate.....	282
3.	Gravimetry.....	282
a.	Tetraphenylboron.....	282
b.	Chloroplatinic Acid.....	283
4.	Gas Evolution Methods.....	283
a.	Nitrometry.....	283
b.	Dumas Method.....	283
5.	Chromatography.....	283
6.	Polarography.....	284
a.	Anodic Oxidation of Mercury.....	284
b.	Indirect Method with Nessler's Reagent.....	284
c.	Amperometric Titration.....	284

7. Other Methods.....	284
a. Method Based on pH Change.....	284
b. Ion Exchange.....	285
B. Hydrazine.....	285
1. Colorimetry.....	285
a. Picryl Chloride.....	285
b. <i>p</i> -Dimethylaminobenzaldehyde.....	285
2. Titrimetry.....	285
a. Iodimetry and Iodometry.....	285
b. Iodate, Periodate, and Iodic Acid.....	286
c. Bromine and Bromate.....	286
d. Hypochlorite.....	286
e. Permanganate.....	287
f. Ferricyanide.....	287
g. Sodium Metavanadate.....	287
h. Sodium Nitrite.....	287
i. Phenylhydrazine or Benzaldehydesulfonic Acid.....	288
j. Chloramine.....	288
k. Formol Titration.....	288
C. Hydroxylamine.....	288
1. Colorimetry.....	288
2. Titrimetry.....	289
a. Bromate and Hypobromite.....	289
b. Oxidation with Various Reagents.....	289
c. Reduction with Titanous Chloride.....	290
3. Polarography.....	290
D. Metal Amides and Nitrides.....	290
1. Amides.....	290
2. Nitrides.....	290
E. Azides.....	291
1. Qualitative Methods.....	291
2. Quantitative Methods.....	291
XI. Inorganic Halogen, Sulfur, and Phosphorus Compounds of Nitrogen.....	292
A. Mono- and Dichloramine.....	292
B. Fluorine Nitrate.....	293
C. Tetrasulfur Dinitride.....	293
D. Disulfur Dinitride.....	293
E. Phosphorus-Nitrogen Compounds.....	293
F. Silicon Nitride.....	293
XII. Recommended Laboratory Procedures.....	293
A. Determination of Nitrosylsulfuric Acid and Nitric Acid in a Mixture of Nitric and Sulfuric Acids Used for Nitration Purposes.....	293
B. Spot Test for Nitrates.....	296
C. Formol Titration Procedure for Ammonium Compounds, e.g., Ammonium Nitrate.....	297
D. Gasometric Method for Azides, e.g., Lead Azide.....	297
E. Nitrometer Method for Nitrates (Standardization: Potassium Nitrate Method).....	299
F. Diazotization Method for Nitrates in Water.....	303
References.....	305
Phosphorus. By William Rieman III and John Beukenkamp.....	317
I. Introduction.....	319
A. Occurrence.....	319
1. In Nature.....	319
2. In Industrial Processes and Products.....	320
3. As an Impurity.....	320
B. Industrial Processes Involving Phosphorus.....	320
1. Manufacture of Elemental Phosphorus and Phosphoric Acid.....	320
2. Manufacture of Superphosphate.....	320
C. Toxicology and Industrial Hygiene.....	321
II. Properties.....	321