

Vogel's Qualitative Inorganic Analysis

Seventh Edition

沃氏定性无机分析 第7版

Revised by G. Svehla



Addison Wesley Longman

世界图书出版公司

Vogel's
Qualitative Inorganic Analysis

Seventh Edition

Revised by

G. Svehla PhD, DSC, FRSC

*formerly Professor of Analytical Chemistry,
University College, Cork*

世界图书出版公司

北京 · 广州 · 上海 · 西安

Longman

Longman Group Limited
Longman House, Burnt Mill, Harlow
Essex CM20 2JE, England
and Associated Companies throughout the world

© Longman Group Limited 1979, 1987, 1996

All rights reserved; no part of this publication may be reproduced, stored in a retrieval system, or transmitted in any form or by any means, electronic, mechanical, photocopying, recording, or otherwise without either the prior written permission of the Publishers or a licence permitting restricted copying in the United Kingdom issued by the Copyright Licensing Agency Ltd., 90 Tottenham Court Road, London W1P 9HE.

Trademarks

Throughout this book trademarked names are used. Rather than put a trademark symbol in every occurrence of a trademarked name, we state that we are using the names only in editorial fashion and to the benefit of the trademark owner with no intention of infringement of the trademark.

First published under the title *A Text-book of Qualitative Chemical Analysis* 1937

Second edition 1941

Reissue with Appendix 1943

Third edition under the title *A Text-book of Qualitative Chemical Analysis including Semimicro Qualitative Analysis* 1945

Fourth edition under the title *A Text-book of Macro and Semimicro Qualitative Inorganic Analysis* 1954

Fifth edition 1979

Sixth edition under the title *Vogel's Qualitative Inorganic Analysis* 1987

Seventh edition 1996

British Library Cataloguing in Publication Data

A catalogue entry for this title is available from the British Library.

ISBN 0-582-21866-7

Library of Congress Cataloging-in-Publication Data

A catalog entry for this title is available from the Library of Congress.

This edition of *Vogel's Qualitative Inorganic Analysis*, **Seventh edition** is published by arrangement with Addison Wesley Longman Limited, London

Licensed for sale in the mainland territory of the People's Republic of China only.
Not for sale in Hong Kong

书 名: Vogel's Qualitative Inorganic Analysis 7th ed.
作 者: G. Svehla
中译名: 沃氏定性无机分析 第7版
出版者: 世界图书出版公司北京公司
印刷者: 北京中西印刷厂
发、行: 世界图书出版公司北京公司(北京朝内大街137号 100010)
开 本: 大 32 印张: 11.25
版 次: 1997年9月第1版 1997年9月第1次印刷
书 号: ISBN 7-5062-3397-5/O · 199
版权登记: 图字 01-97-0954
定 价: 52.00 元

世界图书出版公司北京公司已获得 Addison-Wesley Longman Limited
授权在中国境内独家重印、发行。

Preface to the seventh edition

The seventh edition of Vogel's *Qualitative Inorganic Analysis* contains some new material, which has been added in response to readers' comments.

First of all, Chapter 5 was extended to include more on preliminary tests, dissolution and fusion of samples. This will help users who wish to tackle real samples – industrial, agricultural, environmental, etc.

Furthermore, atomic spectrometric tests have been added to the reactions of metal ions, as the necessary instrumentation is nowadays commonly found in laboratories; testing for metals in this way can be carried out quickly and reliably. Only the essential details are given – fuel, wavelength, light source as well as preparation of standards. It was felt necessary to add a short section on the theory and instrumentation of atomic spectrometry.

A number of health and hazard warnings have also been included. Nomenclature (especially that of organic reagents) has been modified so that readers should be able to find such chemicals in modern catalogues. Figures have been updated, though I was reluctant to change them to show only full-glass apparatus (as some have suggested), because this can be quite expensive and beyond the budgets of certain users. Instead, I have given information on commercially available all-glass devices in the text. To save space, preparations of reagents have been removed from the main text; the reader will find them in the Appendix.

I have also added comments in the margins, highlighting the most important facts and points described in the adjoining text. Hopefully, all these additions will enhance the practical value of the book, which first appeared about sixty years ago.

I would like to acknowledge many friends and students for their helpful suggestions. I am especially indebted to Dr Colin Graham (Birmingham) and to Mr Alan Robinson (Belfast) for reading and correcting the manuscript. Two postgraduate students in Cork, Miss Drewan McCaul and Mr Ronan Ennis, have carried out most of the atomic spectrometric tests experimentally; I wish to thank them for their efforts and I hope they will find the experience useful in their professional life.

As in the past, any suggestions for improvement will be welcomed by the revisor.

G. Svehla
Department of Chemistry
University College
Cork
Ireland

From preface to the first edition

Experience of teaching qualitative analysis over a number of years to large numbers of students has provided the nucleus around which this book has been written. The ultimate object was to provide a text-book at moderate cost which can be employed by the student continuously throughout his study of the subject.

It is the author's opinion that the theoretical basis of qualitative analysis, often neglected or very sparsely dealt with in the smaller texts, merits equally detailed treatment with the purely practical side; only in this way can the true spirit of qualitative analysis be acquired. The book accordingly opens with a long Chapter entitled 'The Theoretical Basis of Qualitative Analysis', in which most of the theoretical principles which find application in the science are discussed.

The writer would be glad to hear from teachers and others of any errors which may have escaped his notice: any suggestions whereby the book can be improved will be welcomed.

A. I. Vogel
Woolwich Polytechnic London S.E.18

From preface to the fifth edition

Vogel's *Qualitative Inorganic Analysis* has been in continuous use in universities and polytechnics since its first publication in 1937. The fourth edition has now been in use for more than twenty years, and it was therefore considered appropriate to prepare a new one.

Since Dr Vogel died in 1966, the publishers asked me to prepare this new edition. When undertaking the enormous task, I wanted to preserve all that made this popular book so good: the detailed theoretical introduction, the well illustrated laboratory instructions and the rich selection of reactions. Nevertheless, because of the age of the text and changes in emphasis and style of the teaching of qualitative inorganic analysis, some rather drastic changes have had to be made.

When launching this new edition I would like to repeat what the author said in the first edition: any suggestions whereby the book can be improved will be welcomed.

G. Svehla
*Department of Chemistry
Queen's University
Belfast, N. Ireland*

From preface to the sixth edition

Previous editions of Vogel's *Qualitative Inorganic Analysis* were used mainly as university textbooks.... With the advent of more complex, mainly instrumental techniques, teaching of the reactions of ions and traditional qualitative analysis has moved from the classroom almost entirely into the laboratory. When preparing the sixth edition, this fact had to be taken into consideration.

The new edition is aimed more to be a laboratory manual than a textbook. With this aim in mind, the text has been rearranged and shortened. Furthermore, dangerous experiments and those involving carcinogenic materials have been removed.

G. Svehla
Department of Chemistry
University College
Cork
Ireland

Contents

<i>Preface to seventh edition</i>	ix
<i>From preface to the first edition</i>	x
<i>From preface to the fifth edition</i>	x
<i>From preface to the sixth edition</i>	xi
Chapter 1 Introduction	1
Chapter 2 Experimental techniques	3
2.1 Introduction	3
2.2 Dry tests	4
2.3 Wet reactions; macro apparatus and analytical operations on a macro scale	15
2.4 Semimicro apparatus and semimicro analytical operations	23
2.5 Micro apparatus and microanalytical operations	39
2.6 Spot test analysis	45
2.7 Detection of metals by flame atomic spectrometric methods	54
Chapter 3 Reactions of the cations	59
3.1 Classification of cations (metal ions) in analytical groups	59
3.2 Notes on the study of the reactions of ions	60
3.3 First group of cations: lead(II), mercury(I), and silver(I)	61
3.4 Lead, Pb (A_r : 207.19)	62
3.5 Mercury, Hg (A_r : 200.59) – mercury(I)	67
3.6 Silver, Ag (A_r : 107.868)	71
3.7 Second group of cations: mercury(II), lead(II), bismuth(III), copper(II), cadmium(II), arsenic(III) and (V), antimony(III) and (V), and tin(II) and (IV)	76
3.8 Mercury, Hg (A_r : 200.59) – mercury(II)	77
3.9 Bismuth, Bi (A_r : 208.98)	79
3.10 Copper, Cu (A_r : 63.55)	83
3.11 Cadmium, Cd (A_r : 112.40)	88
3.12 Arsenic, As (A_r : 74.92) -- arsenic(III)	91
3.13 Arsenic, As (A_r : 74.92) – arsenic(V)	93
3.14 Special tests for small amounts of arsenic	95

3.15	Antimony, Sb (A_r : 121.75) – antimony(III)	99
3.16	Antimony, Sb (A_r : 121.75) – antimony(V)	102
3.17	Special tests for small amounts of antimony	104
3.18	Tin, Sn (A_r : 118.69) – tin(II)	104
3.19	Tin, Sn (A_r : 118.69) – tin(IV)	107
3.20	Third group of cations: iron(II) and (III), aluminium(III), chromium(III) and (VI), nickel(II), cobalt(II), manganese(II) and (VII), and zinc(II)	108
3.21	Iron, Fe (A_r : 55.85) – iron(II)	109
3.22	Iron, Fe (A_r : 55.85) – iron(III)	113
3.23	Aluminium, Al (A_r : 26.98)	118
3.24	Chromium, Cr (A_r : 51.996) – chromium(III)	122
3.25	Oxoanions of Group III metals: chromate and permanganate	127
3.26	Cobalt, Co (A_r : 58.93)	127
3.27	Nickel, Ni (A_r : 58.71)	131
3.28	Manganese, Mn (A_r : 54.938) – manganese(II)	135
3.29	Zinc, Zn (A_r : 63.38)	139
3.30	Fourth group of cations: barium(II), strontium(II), and calcium(II)	143
3.31	Barium, Ba (A_r : 137.34)	144
3.32	Strontium, Sr (A_r : 87.62)	147
3.33	Calcium, Ca (A_r : 40.08)	149
3.34	Fifth group of cations: magnesium(II), sodium(I), potassium(I), and ammonium(I)	152
3.35	Magnesium, Mg (A_r : 24.305)	152
3.36	Potassium, K (A_r : 39.098)	156
3.37	Sodium, Na (A_r : 22.99)	159
3.38	Ammonium, NH_4^+ (M_r : 18.038)	160

Chapter 4 Reactions of the anions 163

4.1	Scheme of classification	163
4.2	Carbonates, CO_3^{2-}	164
4.3	Hydrogen carbonates, HCO_3^-	166
4.4	Sulphites, SO_3^{2-}	168
4.5	Thiosulphates, $\text{S}_2\text{O}_3^{2-}$	171
4.6	Sulphides, S^{2-}	174
4.7	Nitrites, NO_2^-	176
4.8	Cyanides, CN^-	179
4.9	Cyanates, OCN^-	181
4.10	Thiocyanates, SCN^-	182
4.11	Hexacyanoferrate(II) ions, $[\text{Fe}(\text{CN})_6]^{4-}$	185
4.12	Hexacyanoferrate(III) ions, $[\text{Fe}(\text{CN})_6]^{3-}$	187
4.13	Hypochlorites, OCl^-	188
4.14	Chlorides, Cl^-	190
4.15	Bromides, Br^-	192
4.16	Iodides, I^-	195
4.17	Fluorides, F^-	198

4.18	Nitrates, NO_3^-	199
4.19	Chlorates, ClO_3^-	202
4.20	Bromates, BrO_3^-	204
4.21	Iodates, IO_3^-	206
4.22	Perchlorates, ClO_4^-	207
4.23	Borates, BO_3^{3-} , $\text{B}_4\text{O}_7^{2-}$, BO_2^-	208
4.24	Sulphates, SO_4^{2-}	211
4.25	Peroxodisulphates, $\text{S}_2\text{O}_8^{2-}$	214
4.26	Silicates, SiO_3^{2-}	215
4.27	Hexafluorosilicates (silicofluorides), $[\text{SiF}_6]^{2-}$	217
4.28	Orthophosphates, PO_4^{3-}	218
4.29	Pyrophosphates, $\text{P}_2\text{O}_7^{4-}$, and metaphosphates, PO_3^-	221
4.30	Phosphites, HPO_3^{2-}	221
4.31	Hypophosphites, H_2PO_2^-	223
4.32	Arsenites, AsO_3^{3-} , and arsenates, AsO_4^{3-}	224
4.33	Chromates, CrO_4^{2-} , and dichromates, $\text{Cr}_2\text{O}_7^{2-}$	224
4.34	Permanganates, MnO_4^-	228
4.35	Acetates, CH_3COO^-	229
4.36	Formates, HCOO^-	232
4.37	Oxalates, $(\text{COO})_2^{2-}$	234
4.38	Tartrates, $\text{C}_4\text{H}_4\text{O}_6^{2-}$	236
4.39	Citrates, $\text{C}_6\text{H}_5\text{O}_7^{3-}$	239
4.40	Salicylates, $\text{C}_6\text{H}_4(\text{OH})\text{COO}^-$ or $\text{C}_7\text{H}_5\text{O}_3^-$	240
4.41	Benzoates, $\text{C}_6\text{H}_5\text{COO}^-$ or $\text{C}_7\text{H}_5\text{O}_2^-$	242
4.42	Succinates, $\text{C}_4\text{H}_4\text{O}_4^{2-}$	243
4.43	Hydrogen peroxide, H_2O_2 (the perhydroxyl ion, OOH^-)	244
4.44	Dithionites, $\text{S}_2\text{O}_4^{2-}$	247
Chapter 5	Selected tests and separations	249
5.1	Introduction	249
5.2	Preliminary tests on liquid samples (samples in solution)	249
5.3	Preliminary tests on non-metallic solid samples	250
5.4	Preliminary tests on metal samples	252
5.5	Dissolution of the sample	253
5.6	Examination of the insoluble residue	254
5.7	Testing for a single cation in solution	256
5.8	Separation and identification of cations in mixtures	258
5.9	Special tests for mixtures of anions	265
Chapter 6	Reactions of some less common ions	274
6.1	Introduction	274
6.2	Thallium, Tl (A_r : 204.34) – thallium(I)	274
6.3	Thallium, Tl (A_r : 204.34) – thallium(III)	276
6.4	Tungsten, W (A_r : 183.85) – tungstate	276

6.5	Separation and identification of Group I cations in the presence of thallium and tungsten	278
6.6	Molybdenum, Mo (A_r : 95.94) – molybdate	278
6.7	Gold, Au (A_r : 196.97) – gold(III)	281
6.8	Platinum, Pt (A_r : 195.09)	283
6.9	Palladium, Pd (A_r : 106.4)	285
6.10	Selenium, Se (A_r : 78.96) – selenites, SeO_3^{2-}	287
6.11	Selenium, Se (A_r : 78.96) – selenates, SeO_4^{2-}	288
6.12	Tellurium, Te (A_r : 127.60) – tellurites, TeO_3^{2-}	289
6.13	Tellurium, Te (A_r : 127.60) – tellurates, TeO_4^{2-}	290
6.14	Separation and identification of Group II cations in the presence of molybdenum, gold, platinum, palladium, selenium, and tellurium	291
6.15	Vanadium, V (A_r : 50.94) – vanadate	293
6.16	Beryllium, Be (A_r : 9.01)	296
6.17	Titanium, Ti (A_r : 47.90) – titanium(IV)	298
6.18	Zirconium, Zr (A_r : 91.22)	300
6.19	Uranium, U (A_r : 238.03)	303
6.20	Thorium, Th (A_r : 232.04)	304
6.21	Cerium, Ce (A_r : 140.12) – cerium(III)	306
6.22	Cerium, Ce (A_r : 140.12) – cerium(IV)	307
6.23	Separation of Group III cations in the presence of titanium, zirconium, thorium, uranium, cerium, vanadium, thallium, and molybdenum	308
6.24	Lithium, Li (A_r : 6.94)	310
	Appendix	313
	Index	334

The purpose of chemical analysis is to establish the composition of naturally occurring or artificially manufactured substances. This is usually done in two distinct steps. First, *qualitative analysis* is used to identify the sample components. This is followed with *quantitative analysis*, by which the relative amounts of these components are determined.

The present book describes the traditional methods of qualitative inorganic analysis. These can be divided broadly into two categories: *dry tests* which are carried out on solid samples, usually at higher temperatures; and, more commonly, *wet reactions* involving dissolved samples and reagent solutions. The chemical change (or its absence) is observed and used for the elucidation of sample composition.

In order to be able to do such analyses it is essential to study these reactions in a systematic way. Chapter 2 describes the laboratory equipment and skills necessary for such tests. Chapter 3 contains the reactions of the most common cations, while in Chapter 4 those of the most common anions are introduced with some explanations. Once the reader is familiar with these, he/she can attempt analyses of unknown samples, as described in Chapter 5. The book is concluded with the reactions of the less common ions (Chapter 6).

It must be emphasized that the study of 'classical' qualitative inorganic analysis is invaluable for any intending chemist, as this is where he/she first comes across and handles materials which are discussed in the traditional courses of inorganic chemistry. After a few weeks spent in the qualitative analytical laboratory the young chemists become familiar with solids, liquids, gases, acids, bases, salts – the bread and butter of every chemist's knowledge and skills.

The intelligent study of qualitative inorganic analysis requires a certain level of theoretical background in general and inorganic chemistry. These, being taught in the introductory courses of chemistry at colleges and universities, will not be described here. Such a background involves chemical symbols, formulae, equations; theory of electrolytes, equilibria in electrolyte solutions; acid-base theory, strength of acids, pH, buffer systems, hydrolysis; morphology and structure of precipitates and colloids, precipitation equilibria; formation, structure and stability of complexes; balancing redox equations, redox potentials; the principles of solvent extraction and the distribution law. These are described to the necessary extent in most introductory chemistry texts and also in the first chapter of the 5th Edition of this book.¹

¹ *Vogel's Textbook of Macro and Semimicro Qualitative Inorganic Analysis* (5th edn) revised by G. Svehla. Longman 1979.

1.1 Introduction

Warning on hazards

Users of this book should be aware of the fact that almost all the reagents involved in qualitative inorganic analysis are **poisonous**, and some of the operations can be **dangerous**. It should be remembered that samples themselves often contain substances which are **environmentally hazardous**. It is important to consult appropriate safety legislation that is extant in your country. This normally relates not only to the use of certain toxic substances but also to their labelling and storage. The disposal of waste solutions must also be given serious consideration. In many countries there are special regulations governing the acquisition and disposal of radioactive materials (among which uranium and thorium are mentioned in this book). When special care is needed (e.g. handling cyanides, compounds of mercury, cadmium and arsenic and working with hydrogen sulphide) a warning is included in the text. Students and experienced chemists alike should always follow good laboratory practice (GLP), work in tidy, clean, well-lit laboratories. If necessary or if in doubt one must use fume cupboards with good ventilation. Safety glasses must be worn at all times and in many cases suitable gloves should be used. A person should never work alone in a laboratory, especially beyond normal working hours.

Students must be supervised during practicals by adequately trained personnel. It is worthwhile to spend some time at the beginning of a practical course on explaining safety measures in the laboratory, including practice with fire extinguishers. It is prudent to keep a written record of such safety courses, with participants acknowledging by their signature that they have attended.

2.1 Introduction

Although it is assumed that the reader is familiar with basic laboratory operations such as dissolution, evaporation, crystallization, distillation, precipitation, filtration, decantation, bending of glass tubes, preparation of ignition tubes, boring of corks, etc., a brief discussion of those laboratory operations which are of special importance in qualitative inorganic analysis, will be given here.

Qualitative analysis may be carried out on various scales. In *macro analysis* the quantity of the substance employed is 0.1 to 0.5 g and the volume taken for analysis is about 20 ml. In what is usually termed *semimicro analysis* these quantities are reduced by a factor of 10–20, i.e. about 0.05 g material and 1 ml solution are employed. For *micro analysis* the factor is of the order of 100–200. The special operations needed for semimicro and micro work will be discussed in somewhat more detail, together with the apparatus needed to perform these.

Advantages of
semimicro scale

It must be said that *the semimicro scale is most appropriate for the study of qualitative inorganic analysis*; some of the special advantages being as follows:

(a) Reduced consumption of chemicals with a considerable saving in the laboratory budget.

(b) The greater speed of analysis, due to working with smaller quantities of materials and the saving of time in carrying out the various standard operations of filtration, washing, evaporation, saturation with hydrogen sulphide, etc.

(c) Increased sharpness of separation, e.g. washing of precipitates, can be carried out rapidly and efficiently when a centrifuge replaces a filter.

(d) The amount of hydrogen sulphide used is considerably reduced.

(e) Much space is saved both on the reagent shelves and more especially in the lockers provided immediately below the bench for the housing of the individual person's apparatus; this latter merit may be turned to good use by reducing the size of the bench lockers considerably and thus effectively increasing the accommodation of the laboratory.

(f) The desirability of securing a training in the manipulation of small amounts of material.

Macro, semimicro and micro procedures will be discussed separately in this book to cater for all requirements. The readers should familiarize themselves first with macro operations, even if they adopt the semimicro

2.2 Experimental techniques

scale throughout. It may be said that when the general technique of semi-micro analysis has been mastered and appreciated, no serious difficulty should be encountered in adapting a macro procedure to the semimicro scale. Among micro scale operations, spot tests are of special importance; for this reason these will be described in a separate section.

Qualitative analysis utilizes two kinds of tests, *dry tests* and *wet reactions*. The former are applicable to solid substances, while the latter apply to solutions. We begin with the discussion of the most important dry tests.

2.2 Dry tests

A number of useful tests can be carried out in the dry, that is before dissolving the sample for wet analysis. The information obtained in a comparatively short time often provides a clue to the presence or absence of certain substances. With this knowledge the course of wet analysis may be modified and shortened. Instructions for some important dry tests are given below.

Heating

1. **Heating** the substance is placed in a small ignition tube (bulb tube), prepared from soft glass tubing, and heated in a Bunsen flame, gently at first and then more strongly. Small test-tubes, 60–70 mm × 7–8 mm, which are readily obtainable and are cheap, may also be employed. Sublimation may take place, or the material may melt or may decompose with an attendant change in colour, or a gas may be evolved which can be recognized by certain characteristic properties.

Sublimation

Sublimation yields a deposit of solid substance in the upper, colder parts of the test-tube. A **white** deposit occurs if ammonium salts, mercury(I) or mercury(II) chloride, or arsenic(III), antimony(III) or selenium(IV) oxides are present. A **yellow** deposit originates from sulphur, arsenic(III) sulphide and mercury(I) or (II) iodide. The deposit can be **black** if mercury(I) or (II) sulphides are present, and a **metallic** deposit may occur as the result of decomposition of other mercury salts, amalgams, arsenic(III) and cadmium compounds.

Colour change

Colour change can occur, usually indicating decomposition. The most common changes are associated with the removal of water of crystallization.

Gases

Gases produced may be colourless or coloured, occasionally with a characteristic smell. They can be identified with appropriate reagents, as described later under the reactions of cations and anions. **Carbon dioxide** can form if certain carbonates or organic materials are present. **Sulphur dioxide** can result when heating sulphites, thiosulphates or sulphides. **Chlorine** occurs if certain chlorides (e.g. magnesium chloride) are heated, while **bromine** or **iodine** can be formed when heating bromides or iodides in the presence of oxidizing agents. Nitrates yield **nitrogen dioxide**; formates and oxalates, **carbon monoxide**. Heating cyanides yields **cyanogen**. When heating ammonium salts mixed with alkalis, **ammonia** can occur. **Oxygen** is obtained if chlorates, perchlorates, bromates or iodates are heated.

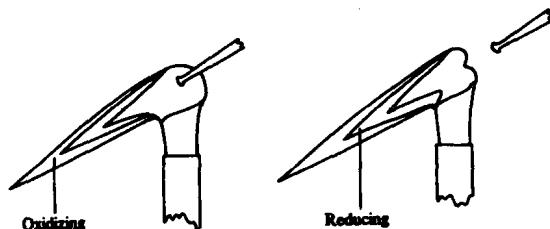


Fig. 2.1

Blowpipe tests

2. Blowpipe tests a luminous Bunsen flame (air holes completely closed), about 5 cm long, is employed for these tests. A **reducing flame** is produced by placing the nozzle of a mouth blowpipe just outside the flame, and blowing gently so as to cause the inner cone to play on the substance under examination. An **oxidizing flame** is obtained by holding the nozzle of the blowpipe about one-third within the flame and blowing somewhat more vigorously in a direction parallel with the burner top; the extreme tip of the flame is allowed to play upon the substance. Figure 2.1 illustrates the oxidizing and reducing flames.

The tests are carried out upon a clean charcoal block in which a small cavity has been made with a penknife or with a small coin. A little of the substance is placed in the cavity and heated in the oxidizing flame. Crystalline salts break into smaller pieces; burning indicates the presence of an oxidizing agent (nitrate, nitrite, chlorate, etc.). More frequently the powdered substance is mixed with twice its bulk of anhydrous sodium carbonate or, preferably, with 'fusion mixture' (an equimolecular mixture of sodium and potassium carbonates; this has a lower melting point than sodium carbonate alone) in a reducing flame. The initial reaction consists of the formation of the carbonates of the cations present and the alkali salts of the anions. The alkali salts are largely adsorbed by the porous charcoal, and the carbonates are, for the most part, decomposed into the oxides and carbon dioxide. The oxides of the metals may further decompose, or be reduced to the metals, or they may remain unchanged. The final products of the reaction are therefore either the metals alone, metals and their oxides, or oxides. The oxides of the noble metals (silver and gold) are decomposed, without the aid of the charcoal, to the metal, which is often obtained as a globule, and oxygen. The oxides of lead, copper, bismuth, antimony, tin, iron, nickel, and cobalt are reduced either to a fused metallic globule (lead, bismuth, tin, and antimony) or to a sintered mass (copper) or to glistening metallic fragments (iron, nickel, and cobalt). The oxides of cadmium, arsenic, and zinc are readily reduced to the metal, but these are so volatile that they vaporize and are carried from the reducing to the oxidizing zone of the flame, where they are converted into sparingly volatile oxides. The oxides thus formed are deposited as an incrustation round the cavity of the charcoal block. Zinc yields an incrustation which is yellow while hot and white when cold; that of cadmium is brown and is moderately volatile; that of arsenic is

2.2 Experimental techniques

Bunsen flame

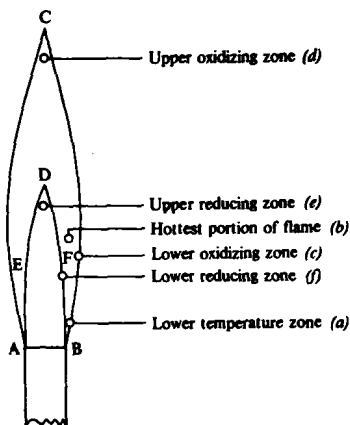


Fig. 2.2

white and is accompanied by a garlic odour due to the volatilization of the arsenic. A characteristic incrustation accompanies the globules of lead, bismuth, and antimony.

The oxides of aluminium, calcium, strontium, barium, and magnesium are not reduced by charcoal; they are infusible and glow brightly when strongly heated. If the white residue or white incrustation left on a charcoal block is treated with a drop of cobalt nitrate solution and again heated, a bright-blue colour, which probably consists of either a compound or a solid solution of cobalt(II) and aluminium oxides (Thenard's blue), indicates the presence of aluminium;¹ a pale-green colour, probably of similar composition (Rinnmann's green), is indicative of zinc oxide; and a pale pink mass is formed when magnesium oxide is present.

Flame tests on dry samples

3. Flame tests in order to understand the operations involved in the flame colour tests and the various bead tests to be described subsequently, it is necessary to have some knowledge of the structure of the non-luminous Bunsen flame (Fig. 2.2).

The non-luminous Bunsen flame consists of three parts: (1) an inner blue cone **ADB** consisting largely of unburnt gas; (2) a luminous tip at **D** (this is only visible when the air holes are slightly closed); and (3) an outer mantle **ACBD** in which complete combustion of the gas occurs. The principal parts of the flame, according to Bunsen, are clearly indicated in Fig. 2.2. The lowest temperature is at the base of the flame (**a**); this is employed for testing volatile substances to determine whether they impart any colour to the flame. The hottest part of the flame is the fusion zone at **b** and lies at about one-third of the height of the flame and approximately equidistant

¹ A blue colour is also given by phosphates, arsenates, silicates, or borates.