

A Laboratory Manual of Qualitative Organic Analysis

T H I R D E D I T I O N

H. T. OPENSHAW

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A LABORATORY MANUAL OF QUALITATIVE ORGANIC ANALYSIS

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BY

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A LABORATORY MANUAL OF
QUALITATIVE ORGANIC
ANALYSIS

PREFACE

This short manual was originally compiled for the use of students attending classes in practical organic chemistry in the University of Manchester. It has been used for several years, first in type-written form, and later in a privately printed edition. It is now published in the hope that others may find it useful.

In writing this book, the author's principal aim has been to present a logical method for the identification of the commoner types of organic compound. The procedure put forward is, in principle, similar to that of Mulliken, in that it consists of a series of tests for functional groups, which are to be applied in a definite order, and it has proved reliable in dealing with substances and mixtures such as are likely to be encountered by the student.

The final step in the identification of an organic compound normally involves the preparation of several crystalline derivatives of characteristic melting-point. In selecting the derivatives to be included in the tables of melting-points, three main considerations have been borne in mind. First, the derivatives should be easy to prepare; secondly, the melting-points of a large number of such derivatives should be known; and thirdly, the necessary reagents should be readily available, and should be suitable for use by students. Where a reaction of a general type, such as nitration, is employed for the preparation of a derivative, different conditions are required according to the particular substance involved. An attempt has been made to group together the numerous variations of method found in the literature into a relatively small number of standard procedures, and to indicate which procedure is to be used for each specific substance.

Discordant values for the melting-points of many substances are recorded in the literature; in compiling the tables contained in this book, the author has tried to select those values which appear to be the most reliable but such selection is inevitably open to error.

It is possible that, in some cases, the discrepancies are due to thermometric errors; where a choice between 'corrected' and 'uncorrected' melting-points is available, the latter have been employed, since the majority of melting-points recorded in the literature are 'uncorrected'. Although experience in the use of these tables has enabled the author to correct a number of mistakes which were originally present, he realizes that other errors may have escaped detection, and he will be glad to be informed of any such errors, either of data or of method, which may be encountered by users of the manual.

Although the information contained in this book is sufficient for the identification of the majority of common substances, the student should be encouraged to seek further information, whenever necessary, in the larger text-books or the original literature.

Whilst it is impossible to make specific acknowledgement of all sources of information to which reference has been made during the compilation of this manual, the author wishes to express a general indebtedness to the authors of other works on the subject, in particular those mentioned on p. 21. He also wishes to express his very sincere thanks to Professor A. R. Todd, F.R.S., for his continued interest and encouragement, and to his colleagues at Manchester, especially Dr F. S. Spring and Dr C. Horrex, for much valuable advice and constructive criticism.

H.T.O.

UNIVERSITY OF MANCHESTER

November 1945

PREFACE TO THE SECOND EDITION

Experience gained in the use of this book since its original publication has brought to light a few errors, omissions and obscurities, and has suggested some improvements. As the need for reprinting has arisen, opportunity has been taken of making suitable alterations and corrections. At the first reprinting, the principal change was the introduction of the hydroxamic test for esters (p. 9). In the present revision, the most important changes are the deletion of the unsatisfactory stannous chloride test for nitro-compounds on p. 14, and the simplification of the alternative and reliable titanous test. Fuller details are included for the recognition of azo-compounds (p. 15), and for the hydrolysis of anilides (p. 75). Few corrections have been found necessary in the tables, but the table of ketones (p. 51) has been considerably altered; elimination of some of the rarer substances has made room for the inclusion of several ketones which have recently become readily available commercially. A number of minor alterations have also been made throughout the book.

The author wishes to thank those who, either by private communication or in reviews, have made suggestions for the improvement of this manual.

H. T. O.

UNIVERSITY OF ST ANDREWS

July 1950

PREFACE TO THE THIRD EDITION

In preparing the third edition of this book, the text has been extensively revised, and partly rewritten, without altering the general character of the book. The most important change involves the treatment of polyfunctional compounds. Instead of concentrating almost entirely on the functional group first detected, the student is now directed to search for other functional groups by applying those further specified tests which are not invalidated by the presence of the principal function.

Other important changes include modified and expanded directions for the detection of constituent elements, and various improvements of procedure in the conduct of the classifying tests (especially the use of potassium bicarbonate instead of sodium bicarbonate in testing for acids). The section dealing with nitrogenous bases (p. 13) has been completely revised to give a more rational treatment. A new section on the investigation of metallic salts has been introduced. New, simplified or improved methods have been given for the preparation of a number of derivatives, and a reliable procedure for the iodoform test has been included.

The tables have also been thoroughly checked and revised, and in some cases considerably expanded. The aim has been to widen the scope of the *Manual*, as far as is practicable, to include all substances available commercially in a reasonably pure condition at a retail price not exceeding £3 per kilogram.

Contrary to the practice in the earlier editions, 'corrected' melting-points have been used in the tables in preference to 'uncorrected', whenever a choice was available. It has been found in practice that, if thermometers calibrated for 3 in. immersion are used in the usual melting-point apparatus, even though they may be immersed to a depth of only 1 in., the stem correction is insignificant and the readings obtained correspond to 'corrected melting-points'.

In order to accommodate the various additions to the text and tables, without appreciably increasing the size of the book, a number of minor deletions have been made from the text, and some less common substances have been omitted from the tables.

H.T.O.

UNIVERSITY OF ST ANDREWS

May 1954

CONTENTS

PREFACES	<i>page vii</i>
INTRODUCTION	i
SUGGESTED PROCEDURE	i
Preliminary Investigation	i
Detection of Constituent Elements	3
Detection of Characteristic Groupings	5
Section A. Compounds containing carbon, hydrogen and oxygen only	6
Section B. Compounds containing nitrogen	12
Section C. Compounds containing sulphur	15
Section D. Compounds containing halogen	16
Section E. Compounds containing a metal	17
Separation of Mixtures by Chemical Means	18
Preparation of Derivatives	19
STANDARD REFERENCE WORKS	21
EXPLANATION OF TABLES	21
Special Conventions and Abbreviations	23
PREPARATION OF DERIVATIVES (GENERAL)	23
AROMATIC HYDROCARBONS, ETHERS AND HALIDES	27
ALIPHATIC AND ALICYCLIC HYDROCARBONS	28
ALKYL HALIDES	32
ALIPHATIC ETHERS	35
ALCOHOLS	36
PHENOLS	40
ALDEHYDES AND KETONES; QUINONES	46

CARBOHYDRATES AND GLUCOSIDES	<i>page</i> 53
CARBOXYLIC ACIDS	56
ESTERS	58
HYDROXY-ACIDS	66
CARBONIC ACID DERIVATIVES	71
AMINES AND AMINO-ACIDS; ANILIDES	73
AROMATIC NITRO-COMPOUNDS	81
SULPHONIC ACIDS AND RELATED COMPOUNDS	85
AMINOSULPHONIC ACIDS	88
INDEX	90

THE QUALITATIVE ANALYSIS OF ORGANIC SUBSTANCES

INTRODUCTION

A FUNDAMENTAL difference exists between the qualitative analysis of inorganic materials and the identification of organic substances. Inorganic compounds are, for the most part, ionic, and since the number of different ionic species which may be encountered is relatively limited, it is possible to develop a set scheme, by adherence to which a complete analysis may be achieved. Organic compounds, on the other hand, are essentially covalent, and in consequence each one of the enormous number of known compounds is a separate entity, and no rigid scheme can be developed which is applicable to all cases. The method outlined here should therefore be taken only as a guide, since substances may be encountered which show exceptional behaviour. The student requires to have a sound knowledge of the properties of organic compounds, and must use this knowledge to the fullest extent in order to arrive at the correct interpretation of the experimental results.

SUGGESTED PROCEDURE

The method of investigation may be divided roughly into four parts:

- (1) Preliminary investigation of the physical properties, and the physical separation of mixtures where applicable.
- (2) Detection of the elements present.
- (3) Detection of characteristic groupings, and the chemical separation of mixtures.
- (4) Preparation of derivatives for complete characterization.

PRELIMINARY INVESTIGATION

An examination of the physical properties will often indicate whether the material is a single substance or a mixture. In the

case of a solid, a small specimen is heated on a spatula; if it is seen to melt, a melting-point determination is carried out in the usual way. A sharp melting-point usually indicates a single substance. A specimen of the material should be recrystallized, a suitable solvent being found by trial. If the melting-point of the recrystallized material is not more than $3-4^{\circ}$ higher than the original melting-point, it is unlikely that a mixture is present. If a large change in melting-point is observed, a mixture is probable, although such a change could also be caused by solvation of crystals or by reaction between the substance and the solvent; for example, recrystallization of an acid anhydride from water will yield the acid.

In the case of a liquid, a specimen should be distilled. If decomposition occurs at ordinary pressure (preliminary test), the pressure should be reduced. If the whole, or almost the whole, of the substance distils at a sensibly constant temperature (not more than 5° range), then it may be a single substance, although a mixture is not excluded. Distillation over a considerable range of temperature indicates a mixture; in many cases it may be possible to separate the material into two clearly defined fractions. In such a case, the whole sample should be carefully fractionated, and each fraction redistilled; the use of a short column is advantageous, provided that the boiling-point is not very high.

A liquid mixture which cannot be separated readily by fractionation may be separable by chemical means. Such separations involve a knowledge of the functional groups present and must therefore be deferred to a later stage in the investigation (see p. 18). Solid mixtures, also, are usually most satisfactorily separated by chemical means; if no such method can be found, recourse must be made to physical methods, such as utilization of differences of solubility of the components in different solvents, or the sublimation or steam distillation of one component.

If the equipment is available, preparative vapour-phase chromatography may provide an excellent means of separation, particularly for liquid mixtures. Adsorption and partition chromatography can also be applied, but are time-consuming. Paper or thin-layer chromatography may be useful in following the course of a separation. It should be remembered, however, that these sensitive methods will show the presence of impurities in most commercial chemicals.

DETECTION OF CONSTITUENT ELEMENTS

It is not usual to test for **carbon** and **hydrogen** in a substance which is known to be organic.

A little of the substance should be ignited on a crucible lid until all the carbon has burnt away. In difficult cases, cooling, moistening the black residue with ammonium nitrate solution and re-igniting may assist. If a white or coloured residue remains, the presence of a **metal** is indicated. Its nature should be determined by applying the methods of inorganic analysis to the residue.

The presence of **nitrogen**, **sulphur** and the **halogens** is detected by the **Lassaigne test**. A small piece of clean sodium, about the size of a rice-grain, is placed in a $3 \times \frac{3}{8}$ in. test-tube, which is held in a pair of tongs. About 2 drops of the substance, if a liquid, or 0.1 g. if a solid, is added, and the tube is gently warmed. Any vigorous reaction is allowed to subside, and the tube is then heated more and more strongly, until finally a red heat is attained. After maintaining this temperature for 1–2 min., the tube is plunged into 15 c.c. of distilled water contained in a small beaker; the tube crumbles and the remaining sodium dissolves with a flash. This process should always be carried out in the fume cupboard, with the front drawn down to protect the operator. If the substance under investigation refuses to react under these conditions, the procedure may be slightly modified. The substance is introduced into the tube, and mixed with an excess (about 0.3 g.) of pure, anhydrous sodium carbonate. The mixture is covered with a layer of sodium carbonate, and the piece of sodium is placed on top of this. The tube is now heated at the level of the sodium, until the latter melts and begins to vaporize. The heating is gradually extended downwards, so that the substance is slowly volatilized over the hot sodium. Finally, the whole mass is brought to red heat. The further procedure is the same as before.

The fusion converts any nitrogen to sodium cyanide, sulphur to sodium sulphide and halogens to sodium halides; these dissolve when the tube is plunged into water. After stirring and gentle warming, the aqueous solution is filtered. It should be quite colourless; if it is coloured, the heating with sodium was not strong

enough and the test must be repeated. A coloured solution cannot be relied on to give the correct result. The solution is divided into portions and tested as follows:

Sulphur. To a portion of the alkaline solution, 1 drop of a freshly prepared aqueous solution of sodium nitroprusside is added. If any sulphur is present, a deep red-violet colour will be produced. Alternatively, the presence of sulphide ion may be determined by adding lead acetate solution to a portion of the solution which has been acidified with acetic acid.

Nitrogen. To a portion of the solution are added a few drops of a freshly prepared solution of ferrous sulphate; a dark green precipitate of ferrous hydroxide is formed. (If sulphur is present, the precipitate will be black; rather more ferrous solution should be added in this case.) The mixture is heated to boiling, with shaking, cooled and acidified with dilute sulphuric acid. If nitrogen is present, a blue or green colour (Prussian blue) appears immediately, or on the addition of a *trace* of ferric chloride solution. If any doubt exists about the presence of Prussian blue the solution should be filtered. The Prussian blue precipitate, if present, is then retained by the filter and is clearly visible against the white background. In the absence of nitrogen, a pale yellow solution is obtained.

Halogens. The remainder of the solution is acidified with dilute sulphuric acid, and, if nitrogen or sulphur has been found, it is boiled for 2 min. to expel HCN and H₂S. Silver nitrate solution is then added to a portion; a precipitate indicates halogen. A blank test should be carried out on the reagents used. To distinguish the individual halogens, a drop of carbon tetrachloride is added to a fresh portion of the solution, and *very dilute* sodium hypochlorite is added slowly with shaking. Iodine gives a violet colour in the carbon tetrachloride, discharged by excess hypochlorite; bromine gives a yellow colour, stable to excess reagent. Chlorine is detected in the presence of bromine or iodine by boiling a portion of the original solution with an equal volume of concentrated nitric acid for 5 min., then adding silver nitrate.

Beilstein's test is useful as a confirmation. A copper wire is heated in a Bunsen flame until it no longer imparts a green

coloration to the flame. It is then allowed to cool, and a little of the substance is placed on it. On again heating in the flame, if halogen is present a transient green or blue coloration will be produced. As this test is very sensitive, and is also given by some compounds containing no halogen, it should be used only to confirm the *absence* of halogen; contact of the heated wire with anything except the substance under test must be avoided.

Other elements. It is not usual to test for other elements (e.g. P, As) unless there is some reason to suspect their presence.

The most general procedure consists in heating a small quantity of the material with a considerable excess of concentrated sulphuric acid until strong fuming occurs. If the solution remains coloured, it is cooled somewhat, and a few drops of concentrated nitric acid are carefully added. Heating is then continued until the mixture is colourless. The cooled solution is poured into water, and tested for the presence of phosphate, arsenate, or other inorganic ions.

DETECTION OF CHARACTERISTIC GROUPINGS

A variety of reactions may be used for determining to what class of compound an organic material belongs. Those given here have been chosen for simplicity of application and reasonable reliability.

The tests should be applied in the order given. In the case of mixtures, once a functional group has been detected, use should be made of it to separate the components of the mixture (see p. 18), before the further tests are carried out. After the separation, the Lassaigne test should be applied to each pure component, unless a completely negative test was obtained in the first place. Once a functional group has been detected, regard must be taken of its possible influence on the applicability of subsequent tests. In the following sections, the further tests which may be usefully applied are listed at the end of each subsection. When the general nature of the substance has been ascertained, confirmatory tests should be applied whenever possible.

Infra-red spectroscopy is a valuable method for detecting or confirming the presence of certain functional groups and structural features.

SECTION A. COMPOUNDS CONTAINING CARBON,
HYDROGEN AND OXYGEN ONLY**(i) Observe the solubility of the substance in water and in ether**

Solubility is, of course, a relative term, but there is little to be gained by specifying a particular figure above which a substance is said to be 'soluble'. The student should note the approximate degree of solubility of the material in the two solvents, and his conclusions must be governed by his observations. Care must be taken not to confuse a slow rate of solution with insolubility; the material, if solid, should be powdered as finely as possible. If the substance is insoluble in cold water, test its solubility in hot water.

In dealing with a mixture, it is not always easy to detect by simple observation whether or not one of the components is soluble. Hence, with a liquid mixture, a definite volume should be taken, and any diminution in this volume carefully observed. With a solid mixture, filtration, followed by evaporation of the filtrate, will serve to indicate whether any of the material has dissolved; a change in melting-point of the undissolved portion (after thorough drying) may also indicate that some of the material has dissolved.

Substances which are very **soluble in both solvents** are normally of low molecular weight, and are of a fairly polar nature; e.g. the lower aliphatic alcohols, amines, aldehydes and ketones, acids, nitriles and esters, and also a few phenols. The aqueous solution should be tested with litmus paper.

Substances which are **soluble in water and insoluble in ether** are of a highly polar character. They include salts of acids and bases, polyhydroxy compounds (e.g. carbohydrates), sulphonic acids, some hydroxy-acids and poly-carboxylic acids, aliphatic amino-acids, etc. To compounds of this type containing C, H and O only, apply tests (ii) and (iii*b*), and if negative results are obtained, test for carbohydrates (see p. 53).

A very large number of substances are **insoluble in cold water and soluble in ether**. These compounds are either non-polar (hydrocarbons, halides), or have a high proportion of 'non-polar' to 'polar' groupings (higher aliphatic compounds, most aromatic compounds). Some of the latter type are soluble in hot water.