Determination of Organic Compounds: Methods and Procedures

FREDERICK T. WEISS

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Shell Development Company
Emeryville, California

WILEY-INTERSCIENCE

a Division of John Wiley & Sons, New York · London · Sydney · Toronto

Library of Congress Catalog Card Number: 76-114010

ISBN 0-471-92705-8

Printed in the United States of America

10 9 8 7 6 5 4 3 2 1

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PREFACE

Although there is certainly no deficiency of books on the analysis of organic materials, they have generally been written from the standpoint of a specialty, usually setting forth in detail the techniques and accomplishments of that specialty without regard to the application or utilization of other techniques. Since there seemed to be no currently available text that compares the many methods for the analysis of organic compounds, I have striven to put together such a volume. My aim has been, first, to present detailed methods for many of the principal determinations and, second, to give specific data obtained by these methods to indicate accurately their comparative scopes, applications, and limitations. The analyst, faced as he is with an ever-increasing literature, should have available to him a volume of methods in which critical comparisons based on extensive data have been made to allow him to make precise decisions on the design of his determinations. Within the limitations of time and scope, I have endeavored to collect information that will provide guidance for the necessary judgments without involving any but a minimum of theory. My goal in all the writing has been to be of service to the busy analyst, and it is my hope that this book will be useful at the laboratory bench.

Over the last thirty years there have been three major areas of activity in the development of methods for the analysis of organic compounds: (1) functional analysis with chemical reagents, (2) spectroscopic measurements, and (3) separation techniques, among which gas chromatography is now paramount. Each of these areas in turn has generated its own subspecialties. The knowledge of the proper place for each type of analytical equipment or technique and of their interrelationships is generally obtained only by long experience and often by a costly process of comparisons. The attempt has been made in this book to provide some guidance in the utility and choice of methods and techniques in the important types of determination commonly encountered in the analysis of organic compounds.

This volume contains a description of the functional analysis of organic compounds by chemical, spectroscopic, and chromatographic techniques. The recommended methods, given in full detail, are in most cases of wide and general applicability and allow the determination of many of the compounds in a functional series. Laboratory data are given on the application of these methods to pure organic compounds and commercial materials. Critical evaluations, with tabulated results, are included to enable the analyst to choose methods and conditions and to understand their limitations and sensitivities. In addition to describing the determination of the common

functional groups, it has been possible to discuss the analysis of a number of organic materials in detail, including hydrocarbons, organic solvents, heterocyclic materials, surface-active agents, and industrial chemicals, to pick a few examples. Since many of the methods recommended for the determination of functional groups can be applied to polymers, coverage is made, whenever possible, of the analysis of resins and polymers.

A glance at the table of contents will indicate the organization of information. The heart of the text is the series of chapters in which the determination of the organic functional compounds is described. In each of these the methods have been derived from consideration of chemical, spectroscopic, and chromatographic techniques. The recommended methods are set out in detail, except that the sections describing the preparation of the common analytical reagents and some frequently used equipment are given separately in Part Three. Examples of the application of the methods to a series of important types of materials are given in Part Two to illustrate the way in which the techniques can be employed in practical systems of some complexity. The use of chromatography is so basic to the analysis of organic materials that a review of the principal chromatographic methods is included in Part Three to make it possible for the analyst to choose appropriate techniques and conditions.

Several important areas of organic analysis are not discussed. The determination of the elements or physical properties, including molecular weight, is not covered. These measurements are, of course, fundamental in importance but occupy too large an area to be included in one book. In the discussion of functional analysis no effort has been made to provide a complete bibliography of the literature or the historical or theoretical background of the methods, since it is my opinion that this is better done in the many monographs already available to which references are made.

A great deal of the information has been taken from published work of my colleagues and myself. This bias I trust will not offend but was indulged in because I felt that personal knowledge of the validity and limitations of the methods was of great importance. The work described and much of the data provided, unless otherwise indicated, were obtained in the laboratories of the Shell Development Company. It is my responsibility and my pleasure to acknowledge the assistance of my associates, principally from the Analytical Department of the Shell Development Company, Emeryville, California, and the generosity of Shell's management for approval to publish. In particular I should like to express my appreciation to A. E. O'Donnell, G. A. Stenmark, R. N. McCoy, and E. D. Peters for information and advice on functional organic analysis; to D. H. Morman and G. A. Harlow for acid–base reactions and titrations in nonaqueous media; to E. M. Fredericks, H. S. Knight, M. A. Muhs, and F. M. Nelsen for gas chromatography; to

H. Siegel for ion-exchange separations; to J. Boor, Jr., M. Dimbat, and F. T. Eggertsen for advice on polymer analysis; to A. G. Polgar for hydrocarbon analysis; to D. B. Bruss for information on organic electrochemistry; and to J. M. Gordon, J. L. Jungnickel, R. W. Kearney, and P. A. Wadsworth, Jr., for information on organic spectroscopy. On the subject of chromatography it was my good fortune to have the valuable comments of E. R. Adlard of the Shell Thornton Research Center, who was on temporary assignment at Emeryville. Mrs. Dee Murray was always competent and conscientious in putting the manuscript carefully into its final typed form.

Emeryville, California
April, 1970

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PART ONE

Determination of Organic Compounds

CHAPTER

1

DETERMINATION OF SATURATED HYDROCARBONS

Saturated hydrocarbons do not contain functional groups and consequently the saturates behave as inert substances in chemical methods of analysis. The electronic spectra of the saturates is weak and therefore ultraviolet absorption is not important for their determination. The vibrational and rotational infrared spectra and proton magnetic resonance spectra are significant for this class of hydrocarbons and can provide some structural information. However, the two most important tools for the determination and characterization of the saturates are gas chromatography and mass spectroscopy. Gas chromatography alone is useful for identification of specific compounds through C_8, but it is with the combined use of these two techniques that a really powerful and detailed compositional or type analysis can be made of gasoline, kerosine, and heavier materials.

The complexity of many practical samples, such as the saturates fraction from gasoline, stems from the large number of isomers possible in this series, especially above C_9. In the paraffin series the number of isomers calculated to exist by Henze and Blair (1) is listed in Table 1.1, from which it can be seen that very large numbers can be expected at even moderate carbon numbers. The number of possible C_{20} paraffin isomers is calculated to be over 300,000 and for the C_{25} isomers the number is of the order of 30,000,000. Thus a completely detailed analysis cannot be made of wide-range mixtures of hydrocarbons of appreciable molecular weight.

DETERMINATION OF SATURATES BY GAS CHROMATOGRAPHY

The use of gas chromatography for the analysis of complex hydrocarbon samples has been widely described. Golay (2) showed some years ago that high resolution could be obtained using capillary columns and a hydrogen flame detector. Polgár, Holst, and Groennings (3) successfully separated complex mixtures of alkanes and cycloalkanes up to C_8 on silicone-coated glass capillary columns. Schwartz and Brasseaux (4) used a mixture of fluorocarbons and hydrocarbon oils to coat a stainless steel capillary for the

Table 1.1. Number of Possible Isomers for the Paraffinic Hydrocarbons[a]

Paraffin carbon number	Number of isomers
1 (methane)	1
2	1
3	1
4	2
5	3
6	5
7	9
8	18
9	35
10	75
11	159
12	355
13	802
14	1858
15	4347

[a] From Henze and Blair (1).

highly effective separation of saturated hydrocarbon mixtures. They prepared a 39-component blend of the composition given in Table 1.2. This was completely separated into individual components when analyzed on a capillary column coated with a mixture of hexadecane and Kel-F 10157, as is shown in Figure 1.1. The application of this chromatographic separation to that portion of a crude oil distilling below 114°C allowed for the detailed analysis of Figure 1.2, where the peaks are identified by retention times. Sanders and Maynard (5) described the application of a capillary column method for the determination of the individual C_3–C_{12} hydrocarbons in full-range motor gasolines. The analysis, using a 200-ft squalane column programmed for both temperature and inlet pressure, resolved some 240 peaks in application to a typical gasoline. As many as 180 peaks were identified, representing over 98% of the gasoline sample. For assistance in the identification of some of the peaks, a time-of-flight mass spectrometer (Bendix Model 14–101) was coupled to the gas chromatograph, which allowed effective identification of a component on as little as 10^{-8} g eluted from the column.

USE OF INFRARED AND NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY FOR THE DETERMINATION OF SATURATES

Although the saturates do not contain groups reactive to organic reagents, functional analysis in a broader sense still does apply to these molecules.

Table 1.2. Hydrocarbons in the 39-Component Blend Listed in Order of Elution on Hexadecane + Hexadecene + Fluorocarbon Capillary Column[a]

Compound	Symbol	Boiling point, °C
Isopentane	$1C_5$	27.9
Normal pentane	NC_5	36.1
2,2-Dimethylbutane	22 DMB	49.7
Cyclopentane	CP	49.3
2,3-Dimethylbutane	23 DMB	58.0
2-Methylpentane	2 MP	60.3
3-Methylpentane	3 MP	63.3
Normal hexane	NC_6	68.7
Methylcyclopentane	MCP	71.8
2,2-Dimethylpentane	22 DMP	79.2
Benzene	Benzene	80.1
2,4-Dimethylpentane	24 DMP	80.5
2,2,3-Trimethylbutane	223 TMB	80.9
Cyclohexane	CH	80.7
3,3-Dimethylpentane	33 DMP	86.1
1,1-Dimethylcyclopentane	11 DMCP	87.9
2-Methylhexane	2 MH	90.1
2,3-Dimethylpentane	23 DMP	89.8
1,*cis*-3-Dimethylcyclopentane	$1C_3$ DMCP	90.8
3-Methylhexane	3 MH	91.9
1,*trans*-3-Dimethylcyclopentane	$1T_3$ DMCP	91.7
1,*trans*-2-Dimethylcyclopentane	$1T_2$ DMCP	91.9
3-Ethylpentane	3 EP	93.5
2,2,4-Trimethylpentane	224 TMP	99.2
Normal heptane	NC_7	98.4
1,*cis*-2-Dimethylcyclopentane	$1C_2$ DMCP	99.5
Methylcyclohexane	MCH	100.9
1,1,3-Trimethylcyclopentane	113 TMCP	104.9
2,2-Dimethylhexane	22 DMH	106.8
Ethylcyclopentane	ECP	103.5
2,5-Dimethylhexane	25 DMH	109.1
2,4-Dimethylhexane	24 DMH	109.4
2,2,3-Trimethylpentane	223 TMP	109.8
1,*trans*-2,*cis*-4-Trimethylcyclopentane	$1T_2C_4$ TMCP	109.3
Toluene	Toluene	110.6
1,*trans*-2,*cis*-3-Trimethylcyclopentane	$1T_2C_3$ TMCP	110.2
3,3-Dimethylhexane	33 DMH	112.0
2,3,4-Trimethylpentane	234 TMP	113.5
1,1,2-Trimethylcyclopentane	112 TMCP	113.7

[a] From Schwartz and Brasseaux (4).

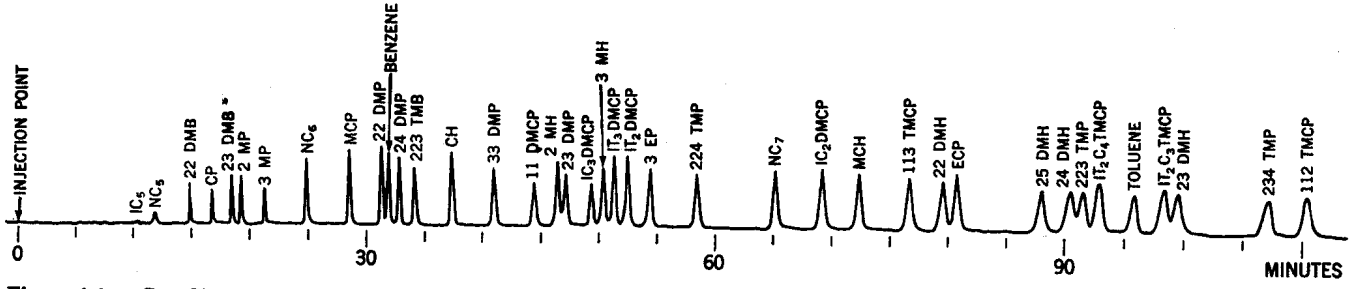

Figure 1.1. Gas Chromatogram of 39-component hydrocarbon blend, Substrate: hexadecane + KEL-F. From Schwartz and Brasseaux (4). Copyright 1963 by the American Chemical Society. Reprinted by permission of the copyright owner.

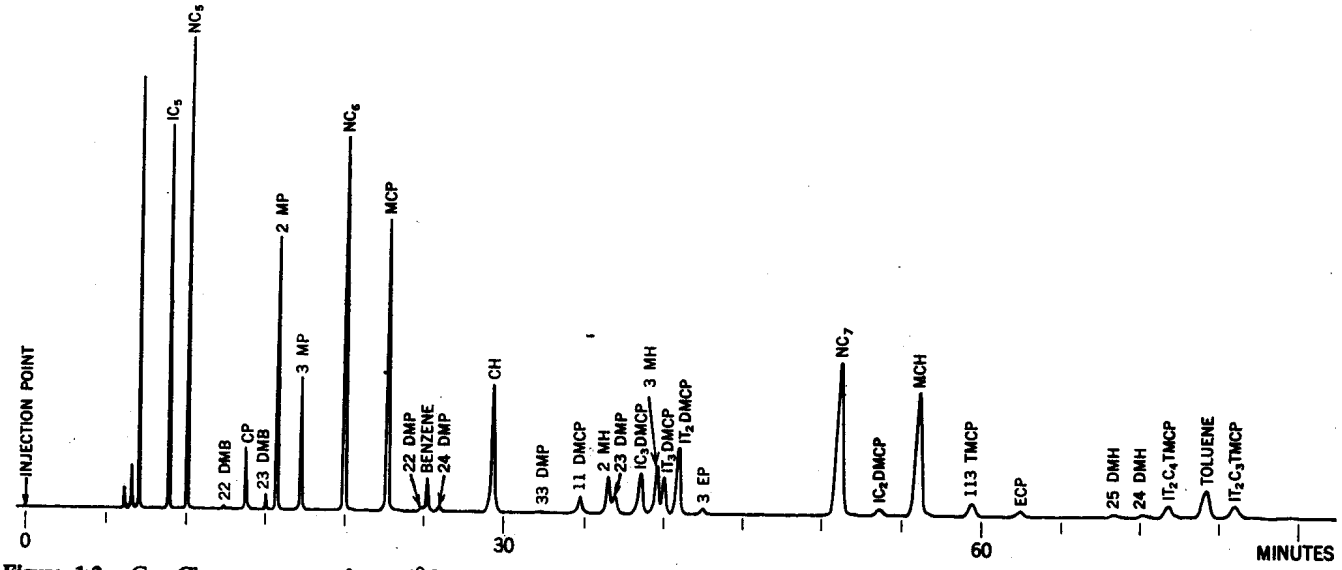

Figure 1.2. Gas Chromatogram of <114°C portion of Ponca City crude oil (4). From Schwartz and Brasseaux (4). Copyright 1963 by the American Chemical Society. Reprinted by the permission of the copyright owner.