Detection and Identification of Organic Compounds

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PLENUM PRESS, NEW YORK • LONDON

SNTL – PUBLISHERS OF TECHNICAL LITERATURE, PRAGUE

Distributed throughout the world with the exception
of the Socialist countries by

PLENUM PRESS
Plenum Publishing Corporation
227 West 17th Street
New York, New York 10011
Distributed in the United Kingdom by
Plenum Publishing Company Limited
Davis House
8 Scrubs Lane, Harlesden,
London NW106SE, England
SBN 306-30476-7
Library of Congress Catalog Card Number 72-110605

Translated by Želimír Procházka
English edition first published in 1971 simultaneously by
Plenum Publishing Corporation and
SNTL — Publishers of Technical Literature, Prague

Printed in Czechoslovakia

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CONTENTS

PREFACE TO THE AMERICAN EDITION

The American edition of our monograph is not a mere translation of the Czech edition, which appeared some five years ago. We have had to respect the fact that even such a short period has sufficed for progress in this field, and that the field of application of methods of organic analysis has widened. We have therefore revised a number of chapters in Part 1, the general part of the monograph – mainly those devoted to chromatographic methods, which have been extended and complemented by methods of thin-layer chromatography and electrophoresis. The chapters on the theory of color reactions and on analytical literature have also been extended; the chapter on spectral methods has been extended by including the use of proton magnetic resonance in organic analysis, and the list of references has been enlarged by adding books of importance for organic analysis.

In Part 2, the part dealing specifically with various elements and chemical groups, we have extended the chapters on solubility and on acids and bases. The methods for the detection and identification of given classes of compounds have also been supplemented by references to recent papers.

The Czech edition was adapted to the working conditions of Czech chemists, mainly with respect to apparatus and equipment. In the American edition we have not included this specific information, since the English-speaking worker has at his disposal a number of commercial publications on new apparatus. Hopefully, the present monograph will be able to serve as a practical handbook of modern chemical analytical methods in organic laboratories in the USA.

PREFACE TO THE CZECH EDITION

The rapid world-wide evolution of industrial organic chemistry requires a continually more intense and deeper study of organic reactions. An essential part of this research is organic analysis, and ever greater demands are being made on it. The increasing number of papers in this field proves that this is so.

A series of specialized monographs on qualitative organic analysis has already been published. The majority of these monographs were written as textbooks for universities and colleges and their extent and structure are given by the requirements and aims of the given school. In addition to this, special monographs appear which treat exhaustively and with much detail specific areas of organic analysis.

In preparing our monograph, we were guided by the knowledge that in practice chemists in organic or biochemical laboratories, both in research institutes and in industrial enterprises, are often faced with problems of the detection and identification of organic compounds which they are not sufficiently trained or experienced to solve. We therefore decided to write a handbook of moderate size and to incorporate in it the experience we have gained in this field, acquired by the performance of practical analyses as well as by the elaboration of original identification methods published in more than 50 papers.

We have endeavored, in contrast to university textbooks, to work up the material primarily from the point of view of practical application, i.e., to show the possibilities of organic analysis and to help laboratory workers in the choice of suitable methods and procedures. Organic analysis has no systematic method analogous to the hydrogen sulfide method of inorganic analysis, and it has, therefore, to combine several methods; a satisfactory result depends on the ability of the analyst to utilize these procedures and to interpret their results correctly.

In the general part of the book the extent and use of various methods are presented; references are made to special publications for methodical details. The main emphasis is laid on the importance of these methods for

the identification of organic compounds and the results obtained by their use, although these methods are usually treated independently and not in connection with classical organic analysis (chromatographic and spectral methods).

In the special part of the book procedures are given for the practical detection and identification of given classes of organic compounds by means of color reactions, the preparation of derivatives, paper chromatography, and gas chromatography, often with reference to other methods as well. We have kept in mind the fact that modern practice requires to an ever-increasing extent work with micro quantities of substances, and we therefore also give instructions for work on a microanalytical scale, using simple procedures which should be possible to carry out in every laboratory. All procedures for the preparation of derivatives have been checked in our laboratories, which has enabled us to give actual yields and melting points found for given single derivatives. We did not wish to rely merely on general procedures, because we know from our own experience that they must often be adapted for given compounds. This is why in this part we give procedures for the identification of specific substances, the yields of which should facilitate the choice of a suitable method for the compounds studied. We have also used the majority of color reactions in our own laboratories, which has enabled us to incorporate our own observations. Moreover, we give certain special color reactions or references to such reactions in order to give the chemist a choice and to save time on literary search. We have devoted great attention to the choice of methods of paper chromatography, because the larger part of our experience is with this method and we cannot imagine the identification of organic compounds without it.

In order to prevent a too schematic approach, we give in typical examples explanations and analyses based on the present state of theoretical chemistry. These examples also demonstrate that complicated problems of organic chemistry cannot be solved by simply following brief directions, but demand deeper thought.

Exhaustive tables of physical constants – for example, melting points of derivatives – should be an integral supplement to a handbook on organic analysis. However, the size of this book does not allow us to insert these tables, and lists of melting points of derivatives are only occasionally given as examples. We plan to publish these tables in a separate volume.

Our aim has been for this book to aid the largest possible number of research chemists in solving problems of organic analyses, and also to be of use to laboratory workers with technical educations in their routine work.

Miroslav Večeřa Jiří Gasparič

PART 1

CHAPTER I

AIMS AND METHODS OF ORGANIC QUALITATIVE ANALYSIS

The basic aims of organic qualitative analysis are the detection and the identification of organic compounds. As other terms for both ideas sometimes appear in the literature, we shall first give their definitions.

By detection we understand a qualitative test based usually on a color or precipitation reaction, on the liberation of a gas, or on behavior during heating, dissolution, etc. This test is usually characteristic of a whole class of compounds; in certain cases it can be specific for individual compounds.

Identification of an organic substance can be carried out by a number of methods used in organic analysis. They differ from detection methods by the fact that measurable data are obtained which can be compared with literature data (concerning the given substance) or with the results of one's own measurements of an authentic sample. Identification can be made, for example, by the comparison of physical constants, by preparing a derivative, or by chromatographic and spectral methods.

The difference between detection and identification will best be explained by the following two examples:

1. If a solution of the tested substance forms a precipitate on the addition of a 2,4-dinitrophenylhydrazine solution in 2 N HCl, this represents a detection of the presence of a carbonyl compound. If the precipitate is isolated and purified by crystallization and its melting point determined, identification has been made, because on comparison with the published data or on measuring the mixture melting point with an authentic sample we can determine the identity of the original substance.

2. The detection of the presence of phenols in a sample can be carried out by coupling them with a diazonium salt in alkaline medium, producing a characteristically colored azo dye. If a diazonium salt without a sulfo or carboxyl group in the molecule is used, the dye formed can be extracted from the reaction mixture with an organic solvent and then identified by paper or thin-layer chromatography.

The identity of two substances can be confirmed even if their structure is not known. The structure determination of an organic substance is

a problem which goes beyond organic analysis, and which has to be solved in combination with organic and physical chemistry. In order to complete the elucidation of the basic ideas and aims of organic analysis, the definition of "determination" should also be given. Under the idea of determination we understand exclusively a quantitative analysis or measurement – for example, the determination of a certain substance, in its crude or pure product or in a mixture, determination of small amounts of impurities, determination of the amount of a functional group in a substance, melting-point determination, molecular-weight determination, etc. As far as methods are concerned, we speak about gravimetric, titrimetric, colorimetric, polarographic, or similar determination. In the chemical literature we often meet such ideas as, for example, qualitative determination, quantitative determination, or qualitative detection. From the point of view of the definitions given above these ideas are unnecessary and sometimes even illogical.

The nature of problems to be solved by an analyst is often such that the basic ideas mentioned are sometimes superposed or appear in various modifications. What is required from organic analysis may vary widely, and if we take into account the enormous variety of organic compounds in general, it will become evident that a true picture of the whole range of problems can only be gained through actual practice.

Let us try to outline at least a few problems with which an analyst may be faced in practice in research institutes or industrial laboratories in the organic chemistry field:

a) A test is to be carried out or the identity of a known compound confirmed. Examples: initial control of the identity of raw materials, determination or confirmation of the identity of a known main or by-product of a known reaction.

b) A substance unknown to the analyst, but described in the literature, is to be identified. Examples: identification of unlabeled raw material in the store room, identification of an isolated unknown by-product from a reaction or from production, identification of some industrial product of a competitive firm, the composition of which is not specified, etc.

c) The structure of an unknown substance, as yet undescribed in the literature, has to be determined. Examples: structure determination of an individual compound isolated from natural material, or of an industrial product the composition of which is not known and is not given even in the patents literature.

d) The presence of one or several known compounds has to be proved in a known mixture. Examples: during the initial control it should be confirmed that all components of the product were really employed; the proof