

Quantitative Organic Analysis via Functional Groups

FOURTH EDITION

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THE CONNECTICUT AGRICULTURAL EXPERIMENT STATION

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Preface

The field of organic functional group determination by chemical means is still developing very rapidly. This is readily reflected by the number of new methods that appear in this edition. This may seem surprising with the advent and growth of the instrumental methods of analysis. However, we have seen that in the past 10 years all existing analytical technologies have grown quickly, along with new ones being born.

This revision is extensive, as can be judged by the increase in the size of this book over the third edition. This is due in part to the addition of new methods and to an increase in the scope of the discussions. Included is a discussion of the chemistry involved in each system; the historical development that led to the method in the form in which it is presented; the merits and limitations of each approach; and a description of how the spectrum of analytical situations for each functional group is covered by the series of methods presented. The text is also completely cross-referenced, showing the interrelationships between the methods for the different functional groups.

Thus this edition is meant to be a convenient handbook of methods of analysis. It is meant also to present a coordinated picture of the chemical methods of analysis of each functional group and of the field of chemical organic functional group analysis as a whole. The chemical analytical approaches for each group are correlated, and a thread is drawn through each item discussed to tie the pieces together into a whole.

The format of each chapter is as follows. The chemical methods for each functional group are subdivided into the various reactions used to determine that group. The chemical and historical backgrounds are given for the application of each reaction; then a method or series of working methods is presented using the particular reaction. The working procedures are presented in full detail and can be used directly without reference to the original sources. In our opinion these methods are the most up to date and/or best in the area being described. The methods were chosen to meet the following standards: general applicability for the purpose intended, simplicity, accuracy, and precision. For the analysis of some functional groups there were so few methods available that there was little choice. There may be better procedures for the determination of certain groups, but those described are, in our opinion, the best and the simplest. In some procedures, slight changes have been made from the description in the original source. These changes—in the nature of sample

sizes, simpler equipment, reaction time, and solvent—are included because, in the use of these procedures, they were found to improve the method slightly in simplicity, time, general applicability, accuracy, or precision. Thus the term “adopted from” is often used. In the case of reprinted material where we have made some changes, the variation from the original material is specifically noted.

For the interest of the reader and the education of the student, the historical evolution of each approach is described to show how the present methods were derived. For example, in the section on carbonyl group analysis, the evolution of the sulfite-sulfuric acid reagent from the original sodium sulfite or bisulfite is discussed. Also, the use of unsymmetrical dimethylhydrazine rather than the hydrazines originally used for carbonyl groups is discussed.

The discussions of instrumental methods and methods of separations are not included in this edition. These areas are now so large that to include them as they should be included would be impossible in a book of this type; moreover, they are discussed thoroughly elsewhere.*

In addition to the newer methods is a chapter on the use of reaction rates to chemically analyze mixtures of compounds containing the same functional groups. Methods are now available that will differentiate between homologs and between isomers of a species, and even between two of the same functional group on the same molecule.

I thank the management of General Aniline and Film for their encouragement in the writing of the earlier editions of this book and the management of Olin Mathieson Chemical Corporation for their encouragement in writing the third edition. I also thank again all the people who helped with the first and second editions as well as those who helped with the preparation of the third edition: E. Kuchar, A. Gray, H. Nadeau, P. Thomas, R. Stoessel, F. Reidinger, R. Rittner, H. Agahigian, A. Krivis, B. Starrs, Thomas Palmer, and H. Ackermann.

Special thanks go to Sylvia Maraskauskas and Mary Anne Kusmit who handled the typing, correspondence, and related activities in the earlier editions.

In the case of this fourth edition, we thank Alan Carpenter, Satish Mehta, and Thomas Mourey who read the manuscript and proofs and Charlotte Peet who did the secretarial work.

April 1978
Amherst, Massachusetts
New Haven, Connecticut

SIDNEY SIGGIA
J. GORDON HANNA

* *Instrumental Methods of Organic Functional Group Analysis*, edited by Sidney Siggia, Wiley-Interscience, New York, 1972.

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Introduction

This book deals with the chemical analysis of organic compounds based on reactions of the functional groups on these compounds. Thus the method of measurement is based on the determination of the moieties characteristic of the organic compounds being examined.

With the advent of instrumental approaches such as infrared absorption, gas chromatography, and nuclear magnetic resonance, it may seem to some that the wet chemical methods are outmoded. One practicing in the field of analysis, however, knows that this is not the case. In fact in the analytical laboratories of most manufacturers of organic chemicals, the wet chemical analysts usually outnumber the gas chromatographers and the spectroscopists. It is true that the instrumental approaches make possible a great many things that could not be accomplished previously. They also make possible, in some cases, faster analysis than was possible with the wet methods. The chemical field has grown so fast, however, that even with these new, powerful approaches, the chemical methods not only still persist but have continued to flourish; witness the number of new methods in this text over the previous edition. One need only look at elemental analysis (carbon, hydrogen, etc.), which is one of the first quantitative organic analytical approaches to be developed. This approach is still very much used and is continually being developed beyond its present scope with the new, automated furnaces and the new methods for simultaneous determination of multiple elements. Thus the new analytical instruments serve to enlarge the analytical tool kit but do not displace the older analytical approaches. Just as in carpentry, power tools have enlarged the carpenter's tool kit, but the older, hand tools still have a distinct indispensability.

The reason for the persistence of the chemical types of analysis can be summarized as follows:

1. There are many chemical situations that are better handled by chemical, rather than instrumental methods. The broad spectrum of reactions available gives the wet analyst quite a versatility. Hence, for example, we find that the analysis of complex systems relies heavily on wet

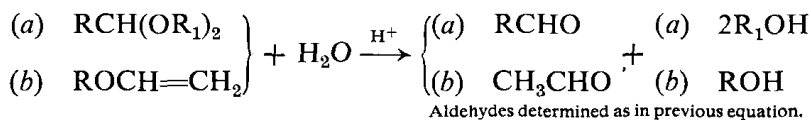
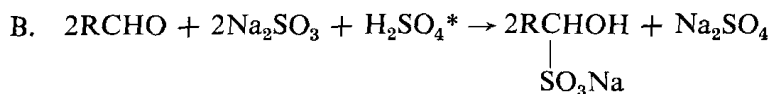
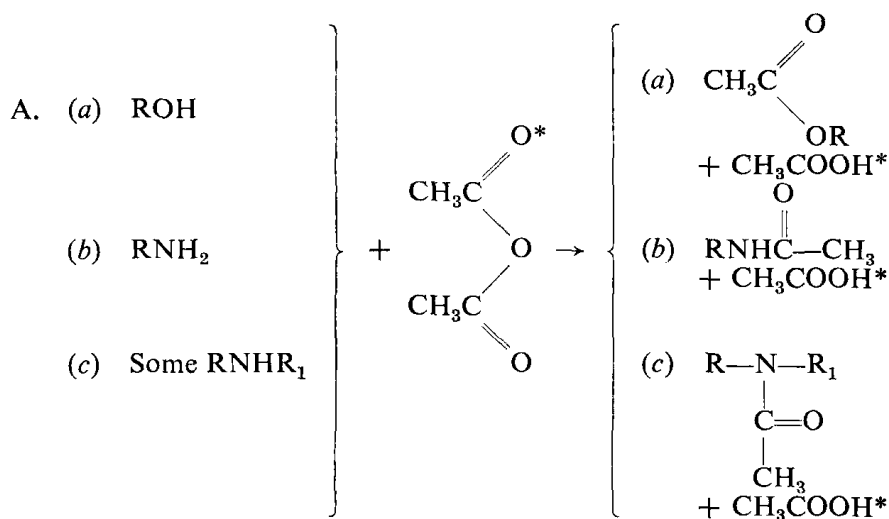
analysis, since specific reactions are generally available for classes of organic compounds. In addition, the area of trace analysis relies heavily on chemical methods to develop specific colors for the materials in question. The foregoing are broad generalizations; instrumental methods figure to some degree in these types of analysis, and also, these types of analysis are not the only ones where wet methods can be used. This paragraph is meant to indicate that there is a "spectrum" of analytical approaches available to the analyst to help solve his diverse problems, and the wet chemical methods occupy a very definite portion of this spectrum.

2. Another advantage to "wet" chemical analysis can be stated as follows. Most instrumental analyses are dependent on calibration curves or calibration data. To obtain the necessary calibrations, pure samples of the compounds in question must be available or preparable. The "wet" chemical methods generally do not require such calibrations. Hence when an analytical laboratory is faced with a rather short series of samples for analyses, it is generally more practical to use the wet methods than to go through the calibration of an instrument and the attendant preparation of standards. In most organic research laboratories and in some plant laboratories, an analyst sees many single samples or small groups of samples that do not recur. It is in these cases that "wet" chemical analyses are the most practical. If a long series of samples is expected, it pays to set up calibrations for an instrument.

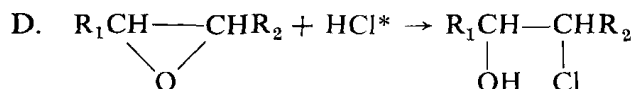
3. The cost of equipment for chemical analysis is generally quite low, since such standard laboratory equipment is used as balances, burets, pipets, beakers, and flasks. This aspect makes analysis possible for individuals and groups of limited means.

The general principle behind "wet" chemical methods is the use of a characteristic reaction for the group being measured. This reaction must not only be as specific as possible for the functional group, but it must also be rapid, and it must involve a reactant or product that can be easily measured. Hence fast, specific reactions are used in which the following types of reagent or product are used or produced: acids, bases, oxidants, reductants, gases, water, metallic ions, precipitates, or colored compounds or complexes. The following reactions are typical of those used for functional group analysis. The material being measured is marked by an asterisk, and the group being determined is on the first compound shown in the equation.

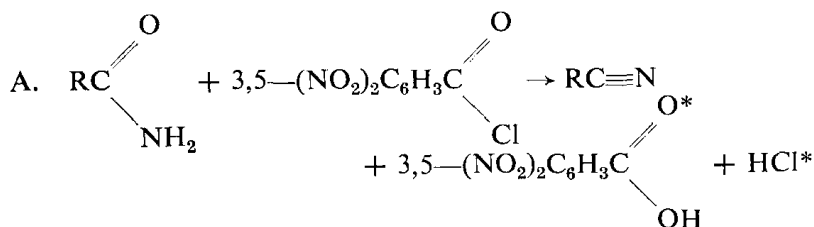
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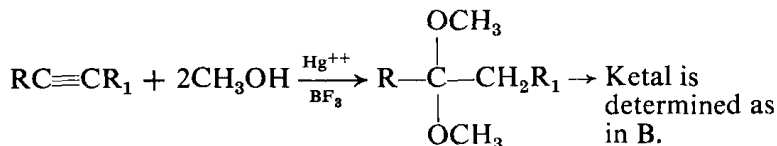
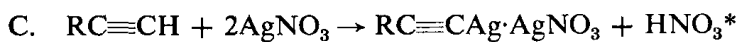
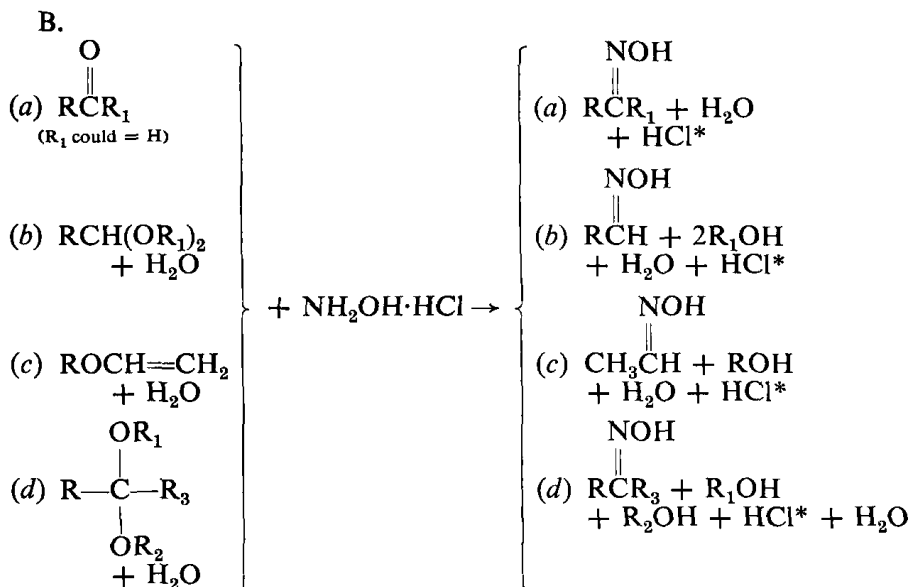


C. Titration of basic materials such as amines (primary, secondary, tertiary), pyridine, quinoline, and carboxylic acids salts with standard acid solutions.



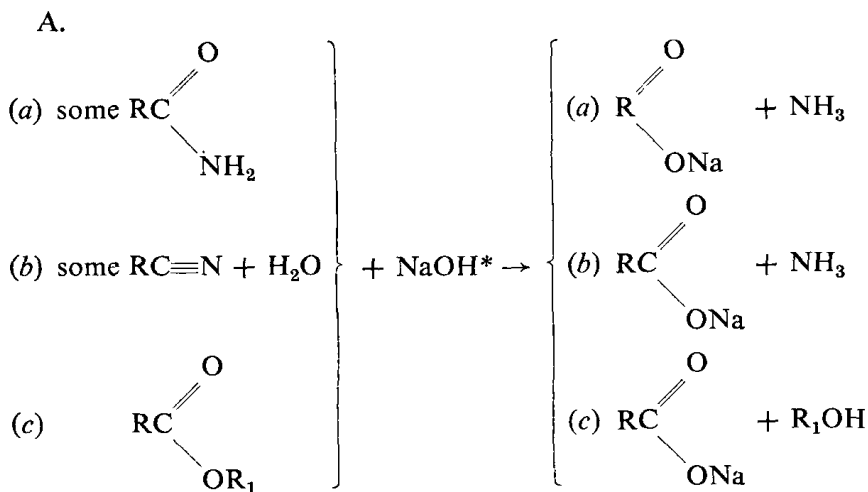
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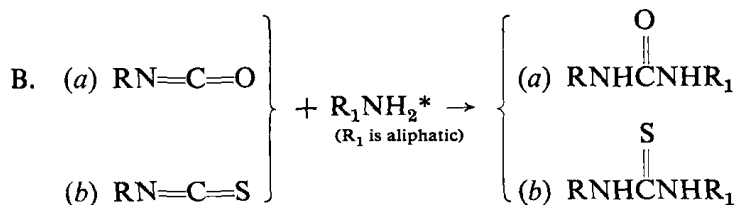




D. Dehydrohalogenation (applicable only to some halogen compounds so that a general equation cannot be written).

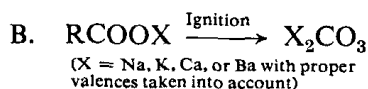
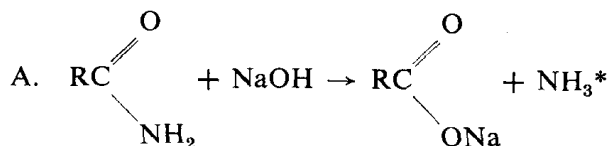
BASE CONSUMED



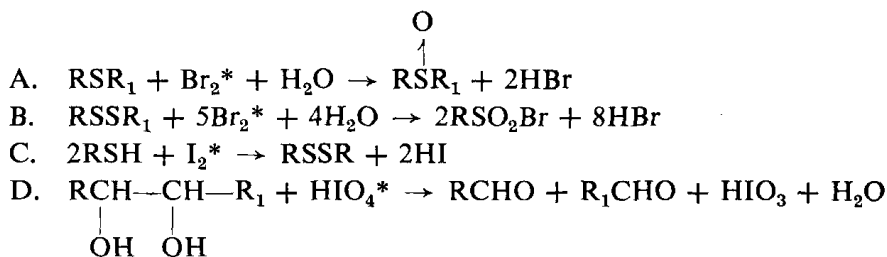


C. Titration of acids with standard alkali.

BASE PRODUCED



OXIDANT CONSUMED



OXIDANT PRODUCED

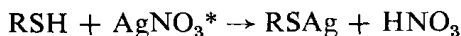
Iodine liberated from iodides by peroxides is measured (not applicable to all organic peroxides).

REDUCTANT CONSUMED

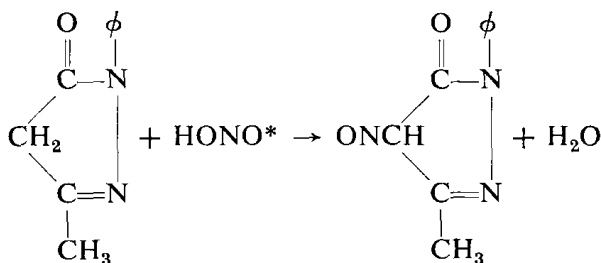
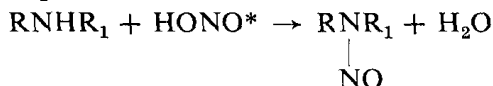
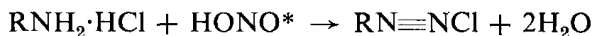
A. TiCl_3 reductions of $-\text{NO}_2$; $-\text{NHNH}-$; $-\text{N}=\text{N}-$; diazonium salts. (TiCl_3^* is measured.)

B. As_2O_3 consumed on reaction with peroxides is measured.

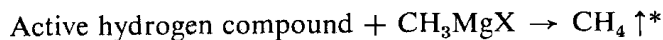
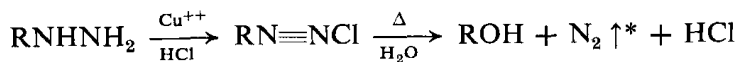
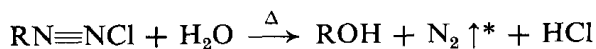
Reactions in which easily determinable materials such as water, silver ions, and sodium nitrite are used or produced are also applicable to determining functional groups. Water takes part in, or is formed in, the reaction of many functional groups—a system of analysis has sprung up around this basis of measurement and is described in *Aquametry* 2nd ed., by John Mitchell (Wiley-Interscience, New York, 1977). Silver enters into reactions with mercaptans and acetylenic hydrogen compounds and it is easily determined by standard methods.



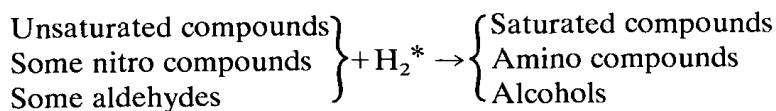
Sodium nitrite takes part in many organic reactions as nitrous acid and can be used to determine primary aromatic amines by diazotization and some secondary aromatic amines and active methylene group compounds by nitrosation.



GAS PRODUCED



GAS CONSUMED



Although there are methods described in this book for determining trace quantities of the various functional groups, practically all the methods in this text can be very simply reduced to a micro scale if such becomes necessary when small amounts of sample are involved. In his textbook *Introduction to the Microtechnique of Inorganic Analysis* (Wiley, New York, 1942), A. A. Benedetti-Pichler describes techniques for micro volumetric and gravimetric analysis. He describes these for inorganic systems, but the techniques are just as applicable to organic systems. Dr. Benedetti-Pichler's approach is to keep the analytical method intact, including concentrations, time of reaction, and so on, but to reduce the scale of the apparatus to permit handling of the small quantities. He uses micro reaction vessels, microburets, and micro gravimetric devices for handling micro samples.