

QUANTITATIVE
ORGANIC
ANALYSIS
VIA
FUNCTIONAL
GROUPS

Third Edition

BY SIDNEY SIGGIA

Quantitative Organic Analysis

via Functional Groups

THIRD EDITION

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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, I have seen that in the past ten years all existing analytical technologies have grown rapidly along with new ones being born.

This revision is extensive as can be seen by the increase in the size of this book over the second edition. The increase in size is due in part to the addition of new methods and also to an increase in the scope of the discussions. For example, methods for determining trace quantities of each functional group were added to this edition. Also added 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; a discussion of 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 more than 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 co-related, 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 my opinion these methods are the most up to date and/or best in the area being described. All methods have been used in my laboratory. 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 my 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 I 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 dimethyl hydrazine 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, and also 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. Such methods are now available which will differentiate between homologs, isomers of a specie, and even between two of the same functional group on the same molecule.

I wish to 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 this edition. I also wish to thank again all the people who helped with the first and second editions plus those who helped with the preparation of this third edition: E. Kuchar, J. G. Hanna, 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.

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Contents

Introduction	1
1 HYDROXYL GROUPS	8
Esterification Procedures, 9	
Acetic Anhydride, 12	
Phthalic Anhydride, 20	
Pyromellitic Dianhydride, 26	
3,5-Dinitrobenzoyl Chloride, 28	
Hydroxyl Groups in Presence of Amino Groups, 38	
Hydroxyl Groups on Adjacent Carbon Atoms (Glycols), 39	
Acidic Hydroxyl Groups (Enols, Phenols, Nitro-Alcohols), 43	
Mixtures of Alcohols, 53	
Phenols only, 54	
Traces of Hydroxy Compounds, 60	
Primary and Secondary Alcohols, 60	
Phenols, 70	
2 CARBONYL GROUPS	73
Oxime Formation, 73	
Bisulfite Addition, 79	
Hydrazone Formation, 85	
Oxidation Methods, 93	
Schiff Base Formation, 114	
Miscellaneous Methods, 118	
Methods for Trace Quantities of Carbonyl Compounds, 124	
Mixtures of Carbonyl Compounds, 129	
3 CARBOXYLIC ACIDS, SALTS, ESTERS, AMIDES, IMIDES, CHLORIDES, AND ANHYDRIDES	130
Carboxylic Acids, 130	
Carboxylic Acid Salts, 133	
Titrimetric Methods, 133	
Combustion Method, 136	

Esters of Carboxylic Acids, 138	
Saponification Methods, 138	
Trace Quantities of Carboxylic Esters, 140	
Carboxylic Acid Amides, 152	
Potentiometric Titrimetric Methods, 153	
Photometric Titration Method, 158	
Reduction Method, 167	
Determination of Primary Amides, 173	
Determination of Trace Quantities of Amides, 174	
Carboxylic Imides, 179	
Carboxylic Acid Chlorides, 179	
Carboxylic Acid Anhydrides, 187	
By Amide Formation, 187	
Traces of Carboxylic Acid Anhydrides, 195	
Determination of Free Acids in Some Anhydrides, 195	
 4 ALKOXYL AND OXYALKYLENE GROUPS	203
Alkoxyl Groups, 203	
Acidimetric Method, 203	
Iodimetric Approach, 209	
Oxyalkylene Groups, 212	
Iodimetric Method, 212	
In Complex Mixtures, 218	
Determination of Traces of Polyoxyalkylene Compounds, 229	
 5 EPOXIDE GROUPS (OXIRANE OXYGEN)	238
Hydrochlorination Methods, 238	
Other Methods, 253	
 6 ORGANIC PEROXIDES	255
Iodometric Methods, 255	
Ferrous Thiocyanate Colorimetric Method, 266	
Ferrous-Titanous Reduction Method, 273	
Leuco Methylene Blue Method, 280	
Determination of Peroxides Using Arsenious Oxide, 286	
Colorimetric Method for Trace Peroxide Using N,N Dimethyl- <i>p</i> -phenylenediamine, 288	
 7 UNSATURATION	296
Bromination, 297	
Free Bromine in a Solvent, 297	

Bromate-Bromide, 301	
Electrically Generated Bromine, 306	
Iodine Number Methods, 313	
Iodine Monochloride, 314	
Iodine Monobromide Method, 316	
Hydrogenation Methods, 318	
Gasometric Methods, 318	
Electrically Generated Hydrogen Method, 333	
Mercuric Acetate Methods, 341	
Determination of Alpha, Beta-Unsaturated Compounds, 350	
Sodium Bisulfite Method, 351	
Morpholine Method, 356	
Acetylenic Unsaturation, 365	
Analysis of Mixtures of Unsaturated Compounds, 371	
 8	
ACTIVE HYDROGEN	372
Grignard Approach, 372	
Lithium Aluminum Hydride Approach, 379	
 9	
ACETYLENIC HYDROGEN	381
Silver Methods, 382	
Cuprous Method, 395	
Mercuric Method, 397	
 10	
ACETALS, KETALS, AND VINYL ETHERS	399
Hydroxylamine Hydrochloride Method, 399	
Bisulfite Method for Acetals and Vinyl Ethers, 400	
Iodimetric Method Specific for Vinyl Ethers, 403	
Mercuric Acetate Method for Vinyl Ethers, 406	
General Method for Traces of Acetals, Ketals, and Vinyl Ethers, 409	
Method for Traces of Acetals of Acetaldehyde and for Traces of Vinyl Ethers, 409	
 11	
AMINO GROUPS	417
Titration Methods, 421	
Acylation Methods, 446	
Diazotization and Nitrosation Methods, 446	
Bromination (Aromatic Amines Only), 450	
Coupling (Aromatic Amines Only), 450	

	Determination of Amines in Mixtures, 450	
	Primary, Secondary, and Tertiary Amine Mixtures, 450	
	Primary Amines in the Presence of Secondary and Tertiary Amines, 470	
	Secondary Amines in the Presence of Primary and Tertiary Amines, 497	
	Tertiary Amines in the Presence of Primary and Secondary Amines, 502	
	General Mixtures, 510	
	Determination of Trace Quantities of Amines, 510	
12	IMINO GROUPS	518
	Nonaqueous Titration Methods, 518	
	Hydrolysis Methods, 522	
13	TITANOUS AND CHROMOUS REDUCTIONS	526
	Titanous Reduction, 526	
	Chromous Reduction, 529	
14	HYDRAZINES AND HYDRAZIDES	536
	Hydrazines, 536	
	Titration Methods, 536	
	Oxidation Methods, 537	
	Trace Quantities, 542	
	Hydrazides, 543	
15	DIAZONIUM SALTS	544
	Nitrogen Evolution Measurement, 545	
	Coupling Method, 548	
	Reduction Method, 549	
	Determination of Traces of Diazonium Compounds, 549	
	Analysis of Mixtures, 551	
16	QUARTERNARY AMMONIUM COMPOUNDS	552
	Hydroxides, 552	
	Salts, 552	
	Trace Quantities of Quaternary Ammonium Salts, 554	

17	ISOCYANATES AND ISOTHIOCYANATES	558
	Primary Amine Method, 558	
	Secondary Amine Methods, 559	
18	MERCAPTANS	563
	Silver Methods, 563	
	Oxidation Methods, 578	
	Mixtures of Mercaptans and Free Sulfur, 582	
	Colorimetric Methods for Trace Quantities, 595	
19	DIALKYL DISULFIDES	600
	Reduction Methods, 600	
	Oxidation Methods, 605	
	Mixtures with Dialkyl Sulfides, 607	
	Mixtures with Mercaptans, 607	
	Determination of Traces, 613	
20	DIALKYL SULFIDES	614
21	SULFOXIDES	621
22	SULFONIC ACIDS, SULFONATE SALTS, AND SULFONAMIDES	631
	Sulfonic Acids, 631	
	Sulfonate Salts, 631	
	Sulfonamides, 638	
23	TECHNIQUES AND REASONING IN DEVELOPING NEW ANALYTICAL METHODS OR MODIFYING EXISTING METHODS	645
24	THE ROLE OF QUANTITATIVE FUNCTIONAL GROUP DETERMINATION IN THE IDENTIFICATION OF ORGANIC COMPOUNDS	651
25	USE OF DIFFERENTIAL REACTION RATES TO ANALYZE MIXTURES CONTAINING THE SAME FUNCTIONAL GROUP	655
	Mixtures of Hydroxy Compounds, 656	
	Mixtures of Carbonyl Compounds, 662	

Mixtures of Amines, 667

Mixtures of Unsaturated Compounds, 670

Mixtures of Diazonium Compounds, 677

Mixtures of Amides and Nitriles, 679

26 WEIGHING OF VOLATILE OR CORROSIVE LIQUIDS 683

INDEX

687

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 of only 8 years ago. 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 which 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

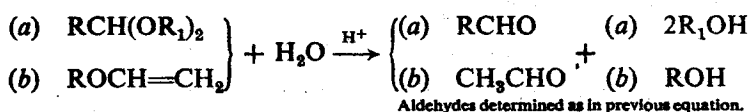
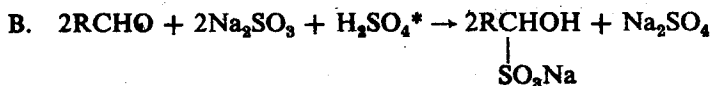
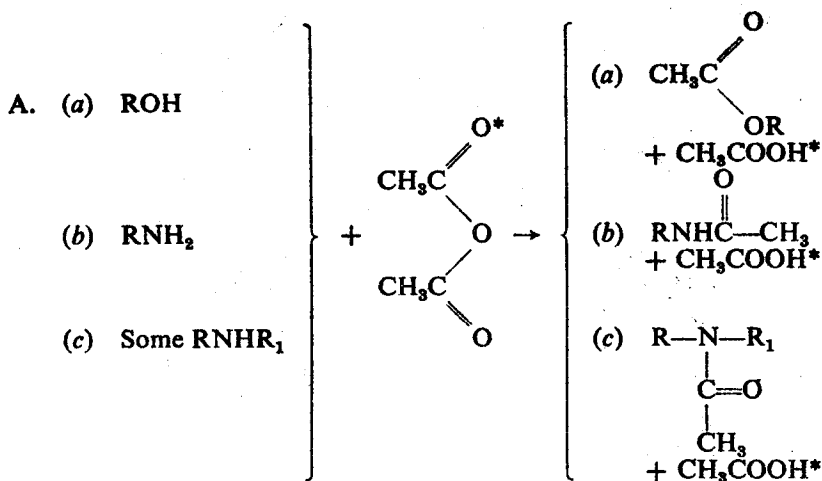
question. The foregoing are broad generalizations; instrumental methods figure to some degree in these types of analysis, and also, these types of analysis are not the only ones where wet methods can be used. This paragraph is meant to indicate that there is a "spectrum" of analytical approaches available 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 go through the calibration of an instrument and 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, burettes, pipettes, beakers, and flasks. This aspect makes analysis possible for individuals and groups of limited means.

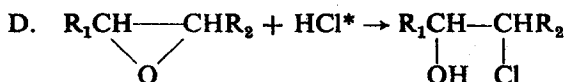
The general principle behind "wet" chemical methods is the use of a characteristic reaction for the group being measured. This reaction must not only be as specific as possible for the functional group, but it must also be rapid, and it must involve a reactant or product which can be easily measured. Hence, fast, specific reactions are used in which the following types of reagents or products 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.

ACID CONSUMED

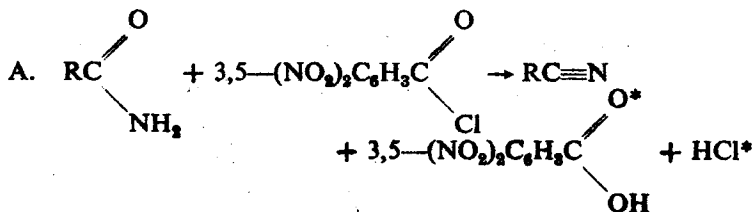


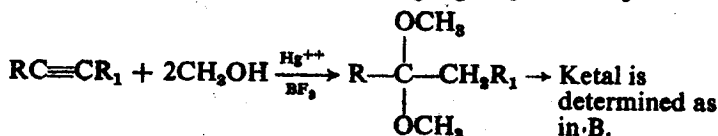
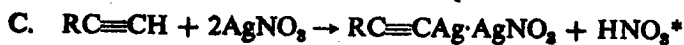
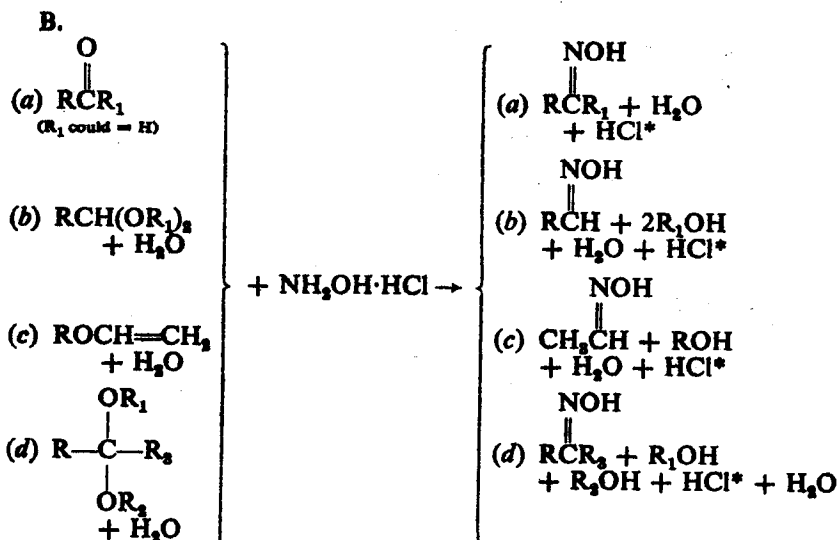
Aldehydes determined as in previous equation.

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



ACID PRODUCED

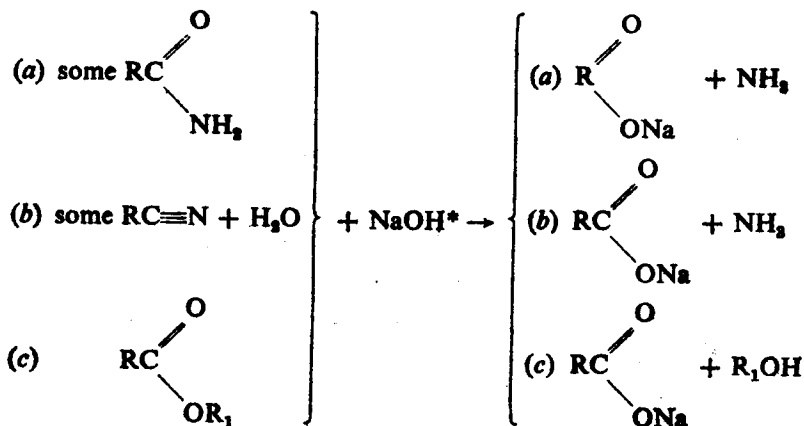


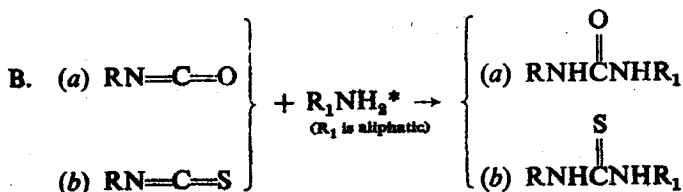


D. Dehydrohalogenation (applicable only to some halogen compounds so that a general equation cannot be written).

BASE CONSUMED

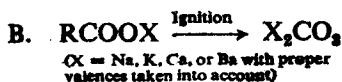
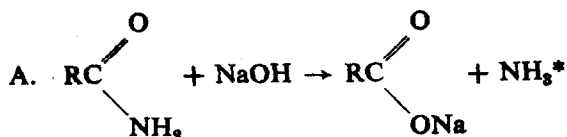
A.



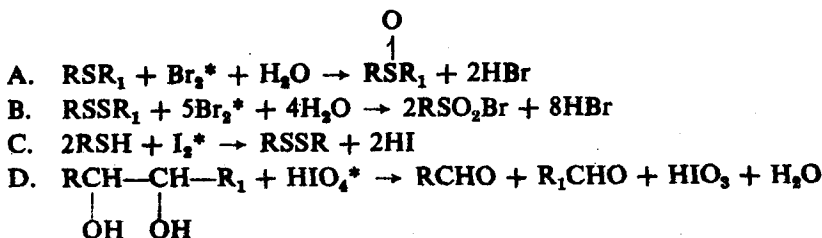


C. Titration of acids with standard alkali.

BASE PRODUCED



OXIDANT CONSUMED



OXIDANT PRODUCED

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

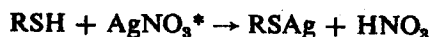
REDUCTANT CONSUMED

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

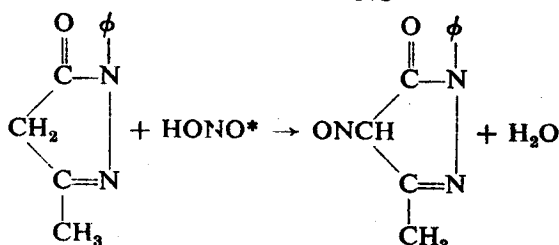
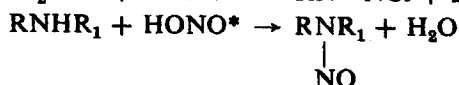
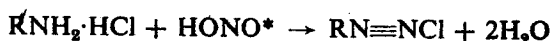
B. As_2O_3 consumed on reaction with peroxides is measured.

Reactions in which easily determinable materials such as water, silver ions, and sodium nitrite are used or produced are also applicable to

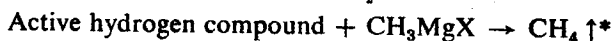
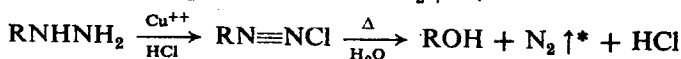
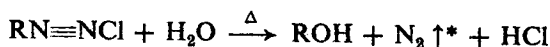
determining functional groups. Water takes part in, or is formed in, the reaction of many functional groups—a system of analysis has sprung up around this basis of measurement and is described in *Aquametry*, by John Mitchell and Donald Smith, Interscience Publishers, New York, 1948. Silver enters into reactions with mercaptans and acetylenic hydrogen compounds, and it is easily determined by standard methods.



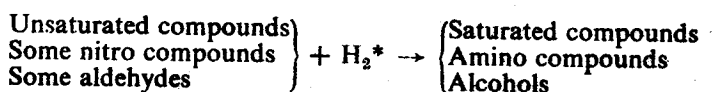
Sodium nitrite takes part in many organic reactions as nitrous acid and can be used to determine primary aromatic amines by diazotization and some secondary aromatic amines and active methylene group compounds by nitrosation.



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