
Introduction to Materials Characterization

R.E. Whan, Materials Characterization Department, Sandia National Laboratories

Scope

Materials Characterization has been developed with the goal of providing the engineer or scientist who has little background in materials analysis with an easily understood reference book on analytical methods. Although there is an abundance of excellent in-depth texts and manuals on specific characterization methods, they frequently are too detailed and/or theoretical to serve as useful guides for the average engineer who is primarily concerned with getting his problem solved rather than becoming an analytical specialist. This Handbook describes modern analytical methods in simplified terms and emphasizes the most common applications and limitations of each method. The intent is to familiarize the reader with the techniques that may be applied to his problem, help him identify the most appropriate technique(s), and give him sufficient knowledge to interact with the appropriate analytical specialists, thereby enabling materials characterization and troubleshooting to be conducted effectively and efficiently. The intent of this Handbook is *not* to make an engineer a materials characterization specialist.

During the planning of this Handbook, it became obvious that the phrase "materials characterization" had to be carefully defined in order to limit the scope of the book to a manageable size. Materials characterization represents many different disciplines depending upon the background of the user. These concepts range from that of the scientist, who thinks of it in atomic terms, to that of the process engineer, who thinks of it in terms of properties, procedures, and quality assurance, to that of the mechanical engineer, who thinks of it in terms of stress distributions and heat transfer. The definition selected for this book is adopted from that developed by the Committee on Characterization of Materials, Materials Advisory Board, National Research Council (Ref 1): "Characterization describes those features of composition and structure (including defects) of a material that are significant for a particular preparation, study of properties, or use, and suffice for reproduction of the material." This definition limits the characterization methods included herein to those that provide information about composition, structure, and defects and excludes those methods that yield information primarily related to materials properties, such as thermal, electrical, and mechanical properties.

Most characterization techniques (as defined above) that are in general use in well-equipped materials analysis laboratories are described in this Handbook. These include methods used to characterize materials such as alloys, glasses, ceramics, organics, gases, inorganics, and so on. Techniques used primarily for biological or medical analysis are not included. Some methods that are not widely used but that give unique or critical information are also described. Techniques that are used primarily for highly specialized fundamental research or that yield information not consistent with our definition of materials characterization have been omitted. Several techniques may be applicable for solving a particular problem, providing the engineer, materials scientist, and/or analyst with a choice or with the possibility of using complementary methods. With the exception of gas chromatography/mass spectroscopy, tandem methods that combine two or more techniques are not discussed, and the reader is encouraged to refer to the descriptions of the individual methods.

Reference

1. *Characterization of Materials*, prepared by The Committee on Characterization of Materials, Materials Advisory Board, MAB-229-M, March 1967

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Organization

The Handbook has been organized for ease of reference by the user. The article "How To Use the Handbook" describes the tables, flow charts, and extensive cross-referenced index that can be used to quickly identify techniques applicable to a given problem. The article "Sampling" alerts the reader to the importance of sampling and describes proper methods for obtaining representative samples.

The largest subdivisions of the Handbook have been designated as Sections, each of which deals with a set of related techniques, for example, "Electron Optical Methods." Within each Section are several articles, each describing a separate analytical technique. For example, in the Section on "Electron Optical Methods" are articles on "Analytical Transmission Electron Microscopy," "Scanning Electron Microscopy," "Electron Probe X-Ray Microanalysis," and "Low-Energy Electron Diffraction." Each article begins with a summary of general uses, applications, limitations, sample requirements, and capabilities of related techniques, which is designed to give the reader a quick overview of the technique, and to help him decide whether the technique might be applicable to his problem. This summary is followed by text that describes in simplified terms how the technique works, how the analyses are performed, what kinds of information can be obtained, and what types of materials problems can be addressed. Included are several brief examples that illustrate how the technique has been used to solve typical problems. A list of references at the end of each article directs the reader to more detailed information on the technique.

Following the last Section is a "Glossary of Terms" and appendices on metric conversion data and abbreviations, acronyms, and symbols used throughout the Volume. The Handbook concludes with a detailed cross-referenced index that classifies the entries by technique names, types of information or analyses desired, and classes of materials. This index, combined with the tables and flow charts in the article "How To Use the Handbook," is designed to enable the user to quickly determine which techniques are most appropriate for his problem.

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How To Use the Handbook

R.E. Whan, K.H. Eckelmeyer, and S.H. Weissman, Sandia National Laboratories

Effective Analytical Approach

The key to the successful solution of most materials problems is close interaction between the appropriate engineers, materials scientists, and analytical specialists. Engineers and other applications-oriented personnel are often the first to encounter material failures or other problems. When this occurs, consultation with a materials specialist is an essential first step in the troubleshooting process. By virtue of his knowledge of materials, the materials specialist can help the engineer define the problem, identify possible causes, and determine what type of information (analytical or otherwise) is needed to verify or refute each possible cause. Once a decision has been made regarding the information needed, they must determine which analytical techniques appear most applicable to the problem.

With the large number of techniques available, it is often difficult to identify the best method or methods for a given problem. The goal of this Handbook is to help engineers and materials scientists identify the most applicable analytical methods and interact effectively with the appropriate analytical specialists, who can help define the analytical test matrix, determine sampling procedures, take the data, and assist in interpreting the data. Together, these workers can solve problems much more effectively than could be done by any one, or even any two, of them.

This collaborative approach to solving a problem has many benefits. When the analyst is fully informed about the nature of the problem and its possible causes, he is much more likely to understand what to look for and how best to look for it. He may be able to suggest complementary or alternative techniques that will yield supplemental and/or more useful

information. He will also be better equipped to detect features or data trends that are unexpected and that can have substantial impact on the problem solution. In short, involving the analyst as a fully informed member of the team is by far the most effective approach to solving problems.

How To Use the Handbook

R.E. Whan, K.H. Eckelmeyer, and S.H. Weissman, Sandia National Laboratories

Tools for Technique Selection

To facilitate the technique identification process, this Handbook contains several reference tools that can be used to screen the analytical methods for applicability. The first of these tools is a set of tables of common methods for designated classes of materials:

- Inorganic solids, including metals, alloys, and semiconductors (Table 1); glasses and ceramics (Table 2); and minerals, ores, and other inorganic compounds (Table 3)
- Inorganic liquids and solutions (Table 4)
- Inorganic gases (Table 5)
- Organic solids (Table 6)
- Organic liquids and solutions (Table 7)
- Organic gases (Table 8)

In these tables, the most common methods (not necessarily all-inclusive) for analyzing a particular class of materials are listed on the left. The kinds of information available are listed as column headings. When a particular technique is applicable, an entry appears in the appropriate column. It should be emphasized that lack of an entry for a given technique does not mean that it cannot be adapted to perform the desired analysis; it means simply that that technique is not usually used and others are generally more suitable. Because there are always situations that require special conditions, the entries are coded according to the legend above each table. For example, a closed circle (•) indicates that the technique is generally usable, whereas an "N" indicates that the technique is usable only for a limited number of elements or groups.

Table 1 Inorganic solids: metals, alloys, semiconductors

Wet analytical chemistry, electrochemistry, ultraviolet/visible absorption spectroscopy, and molecular fluorescence spectroscopy can generally be adapted to perform many of the bulk analyses listed. • = generally usable; N or † = limited number of elements or groups; G = carbon, nitrogen, hydrogen, sulfur, or oxygen; see summary in article for details; S or * = under special conditions; D = after dissolution; Z or ** = semiconductors only

Method	Elem	Alloy ver	Iso/Mass	Qual	Semiquant	Quant	Macro/Bulk	Micro	Surface	Major	Minor	Trace	Phase ID	Structure	Morphology
AAS	D					D	D			D	D	D			
AES	•			•	•			•	•	•	•	S			S
COMB	G	G				G	G				G	G			
EPMA	•	S		•	•	•	•	•		•	•	N	S		•
ESR	N			N	N	N	N				N	N		N	
IA							•	•							•
IC	D,N			D,N	D,N	D,N	D,N			D,N	D,N	D,N			
ICP-AES	D	D		D	D	D	D			D	D	D			
IGF	G	G				G	G				G	G			
IR/FT-IR	Z			Z	Z	Z	Z				Z	Z			
LEISS	•			•	•			S	•	•	•	•			
NAA	•		N	•	•	•	•				•	•			

OES	•	•		•	•	•	•	•	•	•	•	•	•						
OM							•	•		•									•
RBS	•			•	•	•		•		•		•	S	S					
RS	Z			Z	Z	Z	Z	Z				Z	Z	Z					
SEM	•			•	•	S		•		•		•	•	•	S				•
SIMS	•		•	•					•	•	•	•	S						
SSMS	•	•	•	•	•	•	•				•	•	•	•					
TEM	•			•	•	S		•		•	•	•		•	•			•	
XPS	•			•	•				•	•	•	•							
XRD				•	•	S	•			•	•	•		•	•				
XRS	•	•		•	•	•	•						N						

Abbreviations in the column headings are defined in Table 9. The method acronyms are defined in Table 10.

Table 2 Inorganic solids: glasses, ceramics

Wet analytical chemistry, ultraviolet/visible absorption spectroscopy, and molecular fluorescence spectroscopy can generally be adapted to perform many of the bulk analyses listed. • = generally usable; N or † = limited number of elements or groups; S or * = under special conditions; D = after dissolution

Method	Elem	Speciation	Iso/Mass	Qual	Semiquant	Quant	Macro/Bulk	Micro	Surface	Major	Minor	Trace	Phase ID	Structure	Morphology
AAS	D					D	D			D	D	D			
AES	•			•	•			•	•	•	•	S			S
EPMA	•			•	•	•	•	•		•	•	S	S		•
IA							•	•							•
IC	D,N			D,N	D,N	D,N	D,N			D,N	D,N	D,N			
ICP-AES	D			D	D	D	D			D	D	D			
IR/FT-IR	S	S		S	S	S	S			S	S	S	S	S	
LEISS	•			•	•			S	•	•	•	•			
NAA	•		N	•	•	•	•			S	•	•			
OES	•			•	•	•	•			•	•	•			
OM							•	•							•
RBS	•			•	•	•			•	•	S	S			

RS	S	S		S	S	S	S	S	S	S	S	S	S		
SEM	•			•	•			•			•	•	•	S	•
SIMS	•		•	•				•			•	•	S		
SSMS	•		•	•	•	•	•				•	•	•		
TEM	•			•	•	S		•			•	•	•	•	•
XPS	•	N		•	•			•			•	•			
XRD	•			•	•	S		•			•	•		•	
XRS	•			•	•	•		•			•	•	N		

Abbreviations in the column headings are defined in Table 9. The method acronyms are defined in Table 10.

Table 3 Inorganic solids: minerals, ores, slags, pigments, inorganic compounds, effluents, chemical reagents, composites, catalysts

Wet analytical chemistry, electrochemistry, ultraviolet/visible absorption spectroscopy, and molecular fluorescence spectroscopy can generally be adapted to perform many of the bulk analyses listed. • = generally usable; G = carbon, nitrogen, hydrogen, sulfur, or oxygen; see summary in article for details; N or † = limited number of elements or groups; S or * = under special conditions; D = after dissolution

Method	Elem	Speciation	Iso/Mass	Qual	Semiquant	Quant	Macro/Bulk	Micro	Surface	Major	Minor	Trace	Compound/Phase	Structure	Morphology
AAS	D					D	D			D	D	D			
AES	•			•	•			S	•	•	•	S			S
COMB	G				G	G	G			G	G	G			
EPMA	•			•	•	•	•	•		•	•	S	S		•
ESR	N	N		N	N	N	N				N	N		N	
IA							•	•							•
IC	D	S		D	D	D	D			D	D	D			
ICP-AES	D			D	D	D	D			D	D	D			
IGF	G					G	G				G	G			
IR/FT-IR	S, D			S, D	S, D	S, D	S, D		S	S, D	S, D	S, D	S, D	S, D	
ISE	D, N				D, N	D, N	D, N			D, N	D, N	D, N			
LEISS	•			•	•				•	•	•	•			

XRS	•				•	•	•	•	•	•	•	N	
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Abbreviations in the column headings are defined in Table 9. The method acronyms are defined in Table 10.

Table 5 Inorganic gases: air, effluents, process gases

Most of the techniques listed for inorganic solids and inorganic liquids can be used if the gas is sorbed onto a solid or into a liquid. • = generally usable

Method	Elem	Speciation	Compound	Iso/Mass	Qual	Semiquant	Quant	Macro/Bulk	Major	Minor	Trace
GC/MS	•		•	•	•	•	•	•	•	•	•
GMS	•		•	•	•	•	•	•	•	•	•
IR/FT-IR	•	•	•		•	•	•	•	•	•	•
RS	•	•	•		•	•	•	•	•	•	

Abbreviations in the column headings are defined in Table 9. The method acronyms are defined in Table 10.

Table 6 Organic solids: polymers, plastics, epoxies, long-chain hydrocarbons, esters, foams, resins, detergents, dyes, organic composites, coal and coal derivatives, wood products, chemical reagents, organometallics

Most of the techniques for inorganic solids and inorganic liquids can be used on any residue after ashing. • = generally usable; N or † = limited number of elements or groups; S or * = under special conditions; D = after dissolution/extraction; V = volatile solids or components (can also be analyzed by GC/MS), pyrolyzed solids; C = crystalline solids

Method	Elem	Speciation	Compound	Isot/Mass	Qual	Semiquant	Quant	Macro/Bulk	Micro	Surface	Major	Minor	Trace	Structure	Morphology
AES	•				•	•		•	•	•	•	•			
COMB	N						N	N			N	N	N		
EFG	•		•		•	•	•	•			•	•			
EPMA	N				N	N	N		N		N	N	N		N
ESR	N	N			N	N	N	N				N	N	N	
GC/MS	V		V	V	V	V	V	V			V	V	V		•
IA								•	•						•
IC	D,N		D,N		D,N	D,N	D,N	D,N			D,N	D,N	D,N		
IR/FT-IR	D,N	D,•	D,•		D,•	D,•	D,•	D,•		D,S	D,•	D,•	D,•	D,S	
LC			D		D	D	D	D			D	D	D		
LEISS	•				•	•				•	•	•	S		
MFS	D,N	D,N	D,N		D,N	D,N	D,N	D,N	D,N		D,N	D,N	D,N		

Abbreviations in the column headings are defined in Table 9. The method acronyms are defined in Table 10.

Table 8 Organic gases: natural gas, effluents, pyrolysis products, process gas

Most of the techniques listed for organic solids and organic liquids can be used if the gas is sorbed onto a solid or into a liquid. • = generally usable; S = under special conditions; L = after sorption onto a solid or into a liquid

Method	Elem	Speciation	Compound	Iso/ Mass	Qual	Semiquant	Quant	Macro/ Bulk	Major	Minor	Trace	Structure
GC/MS	•		•	•	•	•	•	•	•	•	•	
GMS	•		•	•	•	•	•	•	•	•	•	
IR/FT-IR	•	S	•		•	•	•	•	•	•	•	•
LC			L		L	L	L	L	L	L	L	
RS	•	S	•		•	•	•	•	•	•		•

Abbreviations in the column headings are defined in Table 9. The method acronyms are defined in Table 10.

As a simple example of how to use the tables, suppose that an engineer has a bar of material labeled only "18-8 stainless steel," and he wants to know whether it can be welded. Through consultation with a welding metallurgist he would find that weldable stainless steels contain very small amounts of carbon or alloying elements, such as niobium or titanium, that tie up carbon in order to avoid formation of chromium carbides at the grain boundaries during cooling. In addition, stainless steels that contain selenium or sulfur to improve their machinability are extremely difficult to weld. Therefore, to determine whether the steel is weldable, quantitative analyses for niobium, titanium, selenium, sulfur, and carbon should be performed, as well as for chromium and nickel to document that the material really is an 18-8 type of stainless.

Referring to Table 1, the engineer can look down the list of analytical methods for one having a closed circle (•) under the "Macro/Bulk" column, the "Quant" column, and the "Major" and "Minor" columns. This quickly shows that optical emission spectroscopy, spark source mass spectrometry, and x-ray spectrometry are potentially useful methods. The engineer can then refer to the summaries in the individual articles on these methods to check limitations. For instance, he would find that x-ray spectrometry cannot generally analyze for elements with atomic numbers less than 11, so if this method was selected for analysis of niobium, titanium, selenium, sulfur, chromium, and nickel, another technique, such as high-temperature combustion, inert gas fusion, or vacuum fusion analysis (all having "G"s in the appropriate columns) would have to be employed for carbon determination. The summaries in the articles "Optical Emission Spectroscopy" and "Spark Source Mass Spectrometry," however, indicate that these methods can analyze for all the elements of interest; therefore, one of these would be a logical choice.

Another method for selecting analytical methods is by use of the flow charts in Fig. 1, 2, 3, 4, 5, 6, 7, and 8. Again, a separate chart for each of the different classes of materials has been developed. The charts are based on the type of analyses and/or the type of information desired. The subdivisions separate the analyses into several different categories, depending on the class of materials. For example, the flow chart (Fig. 1) for Inorganic solids: metals, alloys, and semiconductors is divided into bulk/elemental analysis, microanalysis/structure, and surface analysis. Each of these categories is then further subdivided so that the user can follow the flow to exactly the kinds of information or analyses that he needs. Under each category only the most commonly used techniques are listed, in order to keep the flow chart readable. Several other methods may be adapted for use under special conditions or with special attachments or modifications as described in the individual articles.

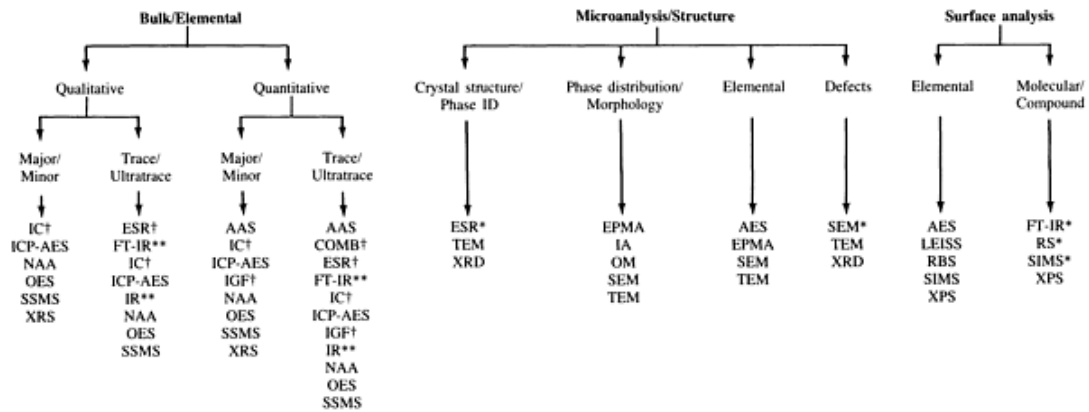


Fig. 1 Flow chart of inorganic solids: metals, alloys, semiconductors. Acronyms are defined in Table 10.

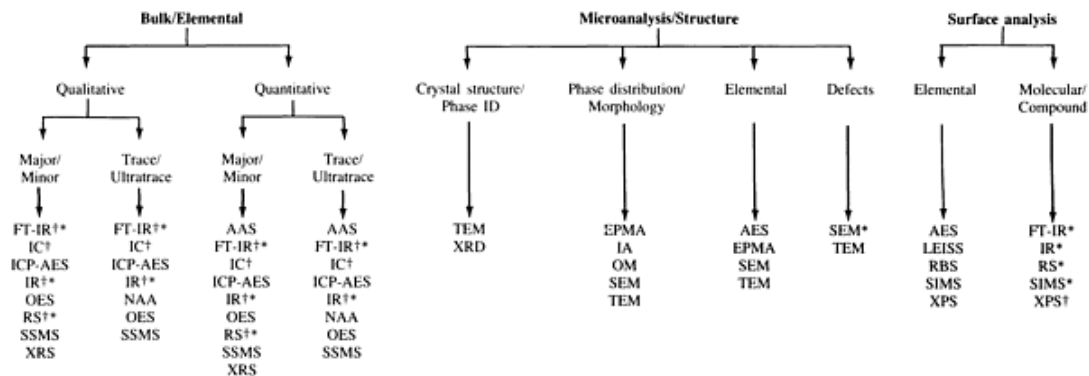


Fig. 2 Flow chart of inorganic solids: glasses, ceramics. Acronyms are defined in Table 10.

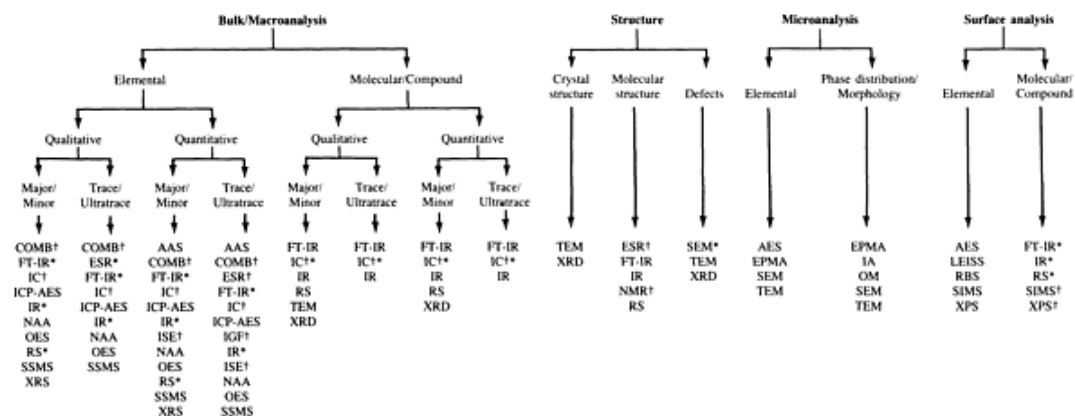


Fig. 3 Flow chart of inorganic solids: minerals, ores, slags, pigments, inorganic compounds, effluents, chemical reagents, composites, catalysts. Acronyms are defined in Table 10.

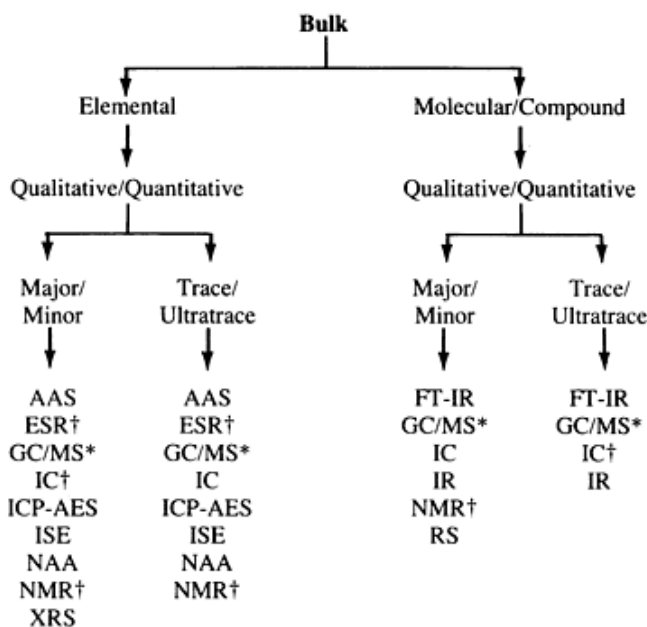


Fig. 4 Flow chart of inorganic liquids and solutions: water, effluents, leachates, acids, bases, chemical reagents. Acronyms are defined in Table 10.

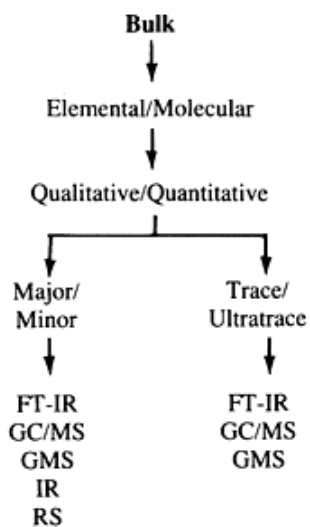


Fig. 5 Flow chart of inorganic gases: air, effluents, process gases. Acronyms are defined in Table 10.

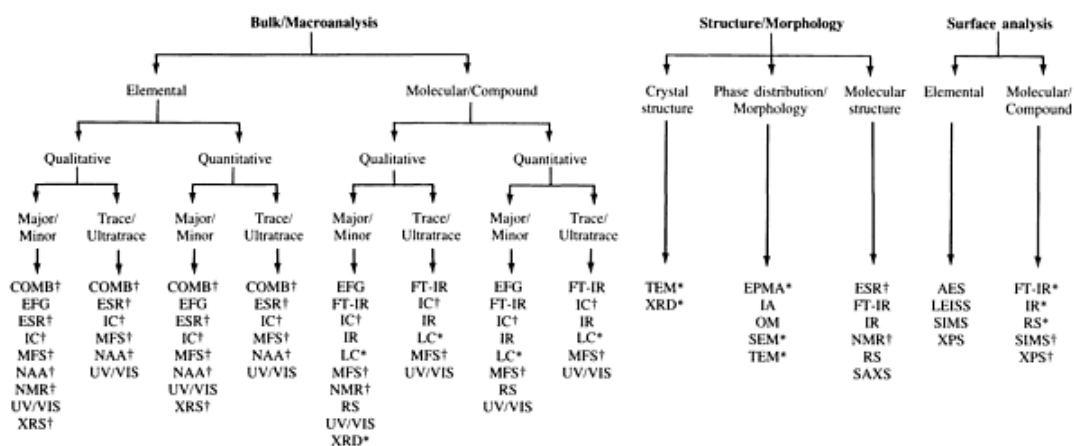


Fig. 6 Flow chart of organic solids: polymers, plastics, epoxies, long-chain hydrocarbons, esters, foams, resins, detergents, dyes, organic composites, coal and coal derivatives, wood products, chemical reagents, organometallics. Acronyms are defined in Table 10.

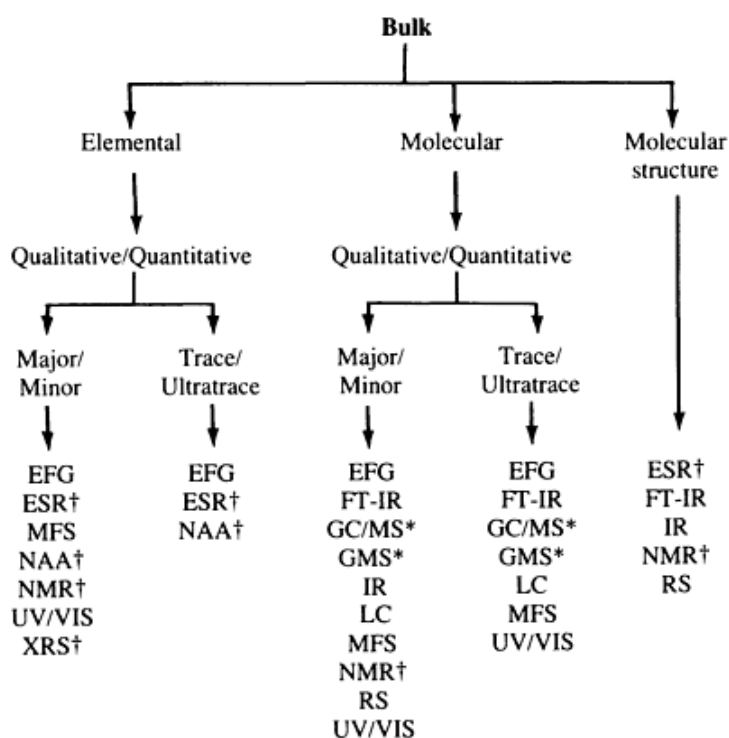


Fig. 7 Flow chart of organic liquids and solutions: hydrocarbons, petroleum and petroleum derivatives, solvents, reagents. Acronyms are defined in Table 10.

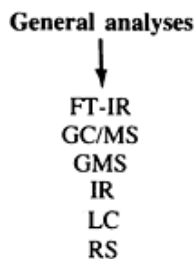


Fig. 8 Flow chart of organic gases: natural gas, effluents, pyrolysis products, process gas. Acronyms are defined in Table 10.

Taking the stainless steel example discussed above, the engineer could examine the flow chart in Fig. 1, follow the flow to "Bulk/Elemental--Quantitative," and look for entries under "Major/Minor." The same techniques identified in the table are cited in the chart, leading the engineer to the appropriate articles in the Handbook.

Finally, the detailed cross-referenced index at the back of the Handbook can be consulted under any or all of the pertinent categories cited above. In this index, techniques are listed not only by categories such as qualitative vs quantitative, macro vs micro, and major vs minor vs trace, but also by typical ways in which they are applied to the solution of materials problems. For example, under the heading "Twinning," the entries listed are metallography, by which twinning can be detected; x-ray diffraction, by which twinning in single crystals can be characterized; and transmission electron microscopy, by which twinning in polycrystalline samples can be characterized. Similarly, under the heading "Inclusions," the entries listed are metallography, by which inclusion morphology can be documented; image analysis, by which inclusion numbers, spacings, and morphologies can be quantified; and scanning electron microscopy, transmission

electron microscopy, electron probe x-ray microanalysis, and Auger electron spectroscopy, by which inclusion chemistries can be determined.

Again, it should be emphasized that this Handbook is meant as a tool to familiarize the nonanalytical specialist with modern analytical techniques and to help him identify techniques that might be applied to his problems. The Handbook is not meant to be an analytical textbook or to replace indispensable consultation with materials and analytical specialists.

How To Use the Handbook

R.E. Whan, K.H. Eckelmeyer, and S.H. Weissman, Sandia National Laboratories

Tables and Flow Charts

The tables and flow charts in this section have been developed as tools to provide information about the most widely used methods of analysis for different classes of materials. These tables and charts are *not* intended to be all-inclusive but to identify the most commonly used techniques for the types of materials to be characterized and the types of information needed. As a result, many techniques that require special modifications or conditions to perform the desired analysis are omitted. The previous section of this article describes how to use these tools. After examining the tables or charts, the reader is encouraged to refer to the appropriate articles in the Handbook for additional information prior to consultation with an analytical specialist.

Abbreviations used in the headings of the tables are defined in Table 9.

Table 9 Abbreviations used in Tables 1 through 8

Elem	Elemental analysis
Alloy ver	Alloy verification
Iso/Mass	Isotopic or mass analysis
Qual	Qualitative analysis (identification of constituents)
Semiquant	Semiquantitative analysis (order of magnitude)
Quant	Quantitative analysis (precision of $\pm 20\%$ relative standard deviation)
Macro/Bulk	Macroanalysis or bulk analysis
Micro	Microanalysis ($\lesssim 10 \mu\text{m}$)
Surface	Surface analysis
Major	Major component ($>10 \text{ wt}\%$)
Minor	Minor component (0.1 to 10 wt%)

Trace	Trace component (1 to 1000 ppm or 0.0001 to 0.1 wt%)
Ultratrace	Ultratrace component (<1 ppm or <0.0001 wt%)

The acronyms listed in Table 10 are used in the tables and charts (for additional acronyms and abbreviations, see the section "Abbreviations and Symbols" in this Volume).

Table 10 Acronyms for materials characterization methods used in Tables 1 through 8

AAS	Atomic absorption spectrometry
AES	Auger electron spectroscopy
COMB	High-temperature combustion
EFG	Elemental and functional group analysis
EPMA	Electron probe x-ray microanalysis
ESR	Electron spin resonance
FT-IR	Fourier transform infrared spectroscopy
GC/MS	Gas chromatography/mass spectrometry
GMS	Gas mass spectrometry
IA	Image analysis
IC	Ion chromatography
ICP-AES	Inductively coupled plasma atomic emission spectroscopy
IGF	Inert gas fusion
IR	Infrared spectroscopy
ISE	Ion selective electrode
LC	Liquid chromatography

LEISS	Low-energy ion-scattering spectroscopy
MFS	Molecular fluorescence spectroscopy
NAA	Neutron activation analysis
NMR	Nuclear magnetic resonance
OES	Optical emission spectroscopy
OM	Optical metallography
RBS	Rutherford backscattering spectrometry
RS	Raman spectroscopy
SAXS	Small-angle x-ray scattering
SEM	Scanning electron microscopy
SIMS	Secondary ion mass spectroscopy
SSMS	Spark source mass spectrometry
TEM	Transmission electron microscopy
UV/VIS	Ultraviolet/visible absorption spectroscopy
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRS	X-ray spectrometry

Sampling

John K. Taylor, Center for Analytical Chemistry, National Bureau of Standards; Byron Kratochvil, Department of Chemistry, University of Alberta

Introduction