

# ASM HANDBOOK®

## VOLUME 10

### Materials Characterization



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## Foreword

When the Volume 10 Organizing Committee first met in 1983 to begin planning a brand-new *Metals Handbook* on materials characterization, much of the discussion centered on the needs of the intended audience and how to most effectively meet those needs. In a subsequent report sent to Volume 10 authors, committee chairman Dr. Ruth E. Whan summarized the consensus:

"The committee feels strongly that the target audience should be individuals who are involved in materials work and need characterization support, but who are not themselves materials characterization specialists. . . . In general, these people will not be required to personally carry out the required materials characterization tasks, but they will have to interact with organizations and individuals who specialize in various aspects of materials characterization. The goal of the Handbook, then, will be to facilitate these interactions between materials engineers and characterization specialists, i.e., to help the materials engineer use characterization specialists effectively in the solution of his problems. . . .

"The Handbook should be assembled . . . in a way that will enable the materials engineer to make a fairly quick decision about what type of characterization specialist to see, and will also enable him to gain an elementary-level knowledge of how this technique works, how it might provide the information he needs, what types of specimens are needed, etc. The committee feels that if we provide a Handbook that can be easily used by the target audience to help them interact effectively with the appropriate materials specialists, the Handbook will be widely used and we will have performed a worthwhile service."

The tireless efforts by Dr. Whan and her committee, the authors and reviewers, the ASM Handbook Committee, and the ASM Handbook staff have indeed been worthwhile. This volume is one of the few basic reference sources on the subject of materials characterization; it cuts through the confusing and at times intimidating array of analytical acronyms and jargon. We believe that readers will find the format convenient and easy to use.

Dr. Whan and the Volume 10 section chairmen (listed in the Table of Contents) are to be congratulated for recruiting the top analytical specialists from this country and others to contribute to this Handbook. One of our authors, Jerome Karle of the Naval Research Laboratory, was the co-winner of the 1985 Nobel Prize for Chemistry. Karle and Herbert Hauptman of the Medical Foundation of Buffalo shared the award for their revolutionary development of direct determination methods for the crystal structure of chemicals, drugs, hormones, and antibiotics.

The American Society for Metals is honored by the opportunity to work with individuals of such caliber. We thank all of them for making this Handbook possible.

John W. Pridgeon

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ASM International staff who contributed to the conversion of the Volume included Sally Fahrenholz-Mann, Bonnie Sanders, Marlene Seuffert, Gayle Kalman, Scott Henry, Robert Braddock, Alexandra Hoskins, and Erika Baxter. The electronic version was prepared under the direction of William W. Scott, Jr., Technical Director, and Michael J. DeHaemer, Managing Director.

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## Introduction to Materials Characterization

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### 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.

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### 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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## Introduction to Materials Characterization

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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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## Introduction to Materials Characterization

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## Reference

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## How To Use the Handbook

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## 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 information 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.

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## How To Use the Handbook

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## 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 |   |   |   |
| 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 |   |   |
| SEM        | • |   |   | • | • |   |   | • |   | • | • |   | S |   | • |
| SIMS       | • |   | • | • |   |   |   |   | • | • | • | S |   |   |   |
| SSMS       | • |   | • | • | • | • | • |   |   | • | • | • |   |   |   |
| TEM        | • |   |   | • | • | S |   | • |   | • | • |   | • | • | • |
| XPS        | • | N |   | • | • |   |   |   | • | • | • |   |   |   |   |
| XRD        | • |   |   | • | • | S | • |   |   | • | • |   | • | • |   |
| <b>XRS</b> | • |   |   | • | • | • | • |   |   | • | • | 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    | •    |            |          | •    | •         |       |            |       | •       | •     | •     | •     |                |           |            |

|      |      |   |   |      |      |      |      |   |   |      |      |      |      |      |   |
|------|------|---|---|------|------|------|------|---|---|------|------|------|------|------|---|
| NAA  | •    |   | N | •    | •    | •    | •    |   |   | •    | •    | •    |      |      |   |
| OES  | •    |   |   | •    | •    | •    | •    |   |   | •    | •    | •    |      |      |   |
| OM   |      |   |   |      |      |      | •    | • |   |      |      |      |      |      | • |
| RBS  | •    |   |   | •    | •    | •    | •    |   | • | •    | S    | S    |      |      |   |
| RS   | S, D |   |   | S, D | S, D | S, D | S, D |   | S | S, D | S, D | S, D | S, D | S, D |   |
| SEM  | •    |   |   | •    | •    |      |      | • |   | •    | •    |      | S    |      | • |
| SIMS | •    |   | • | •    |      |      |      |   | • | •    | •    | S    | S    |      |   |
| SSMS | •    |   |   | •    | •    | •    | •    | • |   |      | •    | •    | •    |      |   |
| TEM  | •    |   |   | •    | •    | S    |      | • |   | •    | •    |      | •    | •    | • |
| XPS  | •    | • |   | •    | •    |      |      |   | • | •    | •    |      | S    |      |   |
| XRD  |      |   |   | •    | •    | S    | •    |   |   | •    | •    |      | •    | •    |   |
| XRS  | •    |   |   | •    | •    | •    | •    |   |   | •    | •    | N    |      |      |   |

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

**Table 4 Inorganic liquids and solutions: water, effluents, leachates, acids, bases, chemical reagents**

Wet analytical chemistry, electrochemistry, ultraviolet/visible absorption spectroscopy, and molecular fluorescence spectroscopy can generally be adapted to perform the bulk analyses listed. Most of techniques listed for inorganic solids can be used on the residue after the solution is evaporated to dryness. • = generally usable; N or † = limited number of elements or groups; S = under special conditions; V or \* = volatile liquids or components

| Method   | Elem | Speciation | Compound | Iso/Mass | Qual | Semiquant | Quant | Macro/Bulk | Major | Minor | Trace | Structure |
|----------|------|------------|----------|----------|------|-----------|-------|------------|-------|-------|-------|-----------|
| AAS      | •    |            |          |          |      |           | •     | •          | •     | •     | •     |           |
| EFG      | N    | N          | N        |          |      | N         | N     | N          | N     | N     | N     |           |
| ESR      | N    | N          |          |          | N    | N         | N     | N          |       | N     | N     | N         |
| GC/MS    | V, N |            | V        | V        | V    | V         | V     | V          |       | V     | V     |           |
| GMS      | V, N |            | V        | V        | V    | V         | V     | V          | V     | V     | V     |           |
| IC       | •    | •          | S        |          | •    | •         | •     | •          | •     | •     | •     |           |
| ICP-AES  | •    |            |          |          | •    | •         | •     | •          | •     | •     | •     |           |
| IR/FT-IR | •    | •          | •        |          | •    | •         | •     | •          | •     | •     | •     |           |
| ISE      | •    | S          |          |          |      | •         | •     | •          | •     | •     | •     |           |
| NAA      | •    |            |          | N        | •    | •         | •     | •          | •     | •     | •     |           |
| NMR      | N    |            | N        |          | N    | N         |       | N          |       | N     |       | N         |
| RS       | •    |            | •        |          | •    | •         | •     | •          | •     | •     | S     |           |

|     |   |  |  |  |   |   |   |   |   |   |   |  |
|-----|---|--|--|--|---|---|---|---|---|---|---|--|
| XRS | . |  |  |  | . | . | . | . | . | . | N |  |
|-----|---|--|--|--|---|---|---|---|---|---|---|--|

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 | Iso/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  |           |            |

|        |      |      |      |   |      |      |      |      |   |   |      |      |      |     |   |
|--------|------|------|------|---|------|------|------|------|---|---|------|------|------|-----|---|
| NAA    | N    |      |      | N | N    | N    | N    | N    |   |   | N    | N    | N    |     |   |
| NMR    | N    |      | N    |   | N    | N    |      | N    |   |   | N    | N    |      | N   |   |
| OM     |      |      |      |   |      |      |      | •    | • |   |      |      |      |     | • |
| RS     | D, N | D, • | D, • |   | D, • | D, • | D, • | D, • |   | S | D, • | D, • |      | D,S |   |
| SAXS   | •    |      | •    |   | •    |      |      | •    |   |   |      |      | •    |     |   |
| SEM    | N    |      |      |   | N    | N    |      |      | • |   | N    | N    |      |     | • |
| SIMS   | •    |      | S    | • | •    |      |      |      | • | • | •    | •    | •    |     |   |
| TEM    | S    |      | C    |   | N    | N    |      |      | • |   | N    | N    |      | C   | • |
| UV/VIS | D, • | D, • | D, • |   | D, • | D, • | D, • | D, • |   |   | D, • | D, • | D, • |     |   |
| XPS    | •    | N    | S    |   | •    | •    |      |      |   | • | •    | •    |      |     |   |
| XRD    |      |      | C    |   | C    | C    | C, S | C    |   |   | C    | C    |      | C   |   |
| XRS    | N    |      |      |   | N    | N    | N    | N    |   |   | N    | N    | N    |     |   |

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

**Table 7 Organic liquids and solutions: hydrocarbons, petroleum and petroleum derivatives, solvents, reagents**

Most of the techniques listed for inorganic solids and inorganic liquids can be used on any residue after ashing. Many wet chemical techniques can be adapted to perform the analyses listed.

• = generally usable; N or † = limited number of elements or groups; S = under special conditions; V or \* = volatile liquids

| Method   | Elem | Speciation | Compound | Iso/Mass | Qual | Semiquant | Quant | Macro/Bulk | Major | Minor | Trace | Structure |
|----------|------|------------|----------|----------|------|-----------|-------|------------|-------|-------|-------|-----------|
| EFG      | •    |            | •        |          | •    | •         | •     | •          | •     | •     | •     |           |
| ESR      | N    | N          |          |          | N    | N         | N     | N          |       | N     | N     | N         |
| GC/MS    |      |            | V        | V        | V    | V         | V     | V          | V     | V     | V     |           |
| GMS      |      |            | V        | V        | V    | V         | V     | V          | V     | V     | V     |           |
| IR/PT-IR | S    | S          | •        |          | •    | •         | •     | •          | •     | •     | •     | •         |
| LC       |      |            | •        |          | •    | •         | •     | •          | •     | •     | •     |           |
| MFS      | N    |            | N        |          | N    | N         | N     | N          | N     | N     | N     |           |
| NAA      | N    |            |          | N        | N    | N         | N     | N          | N     | N     | N     |           |
| NMR      | N    |            | N        |          | N    | N         | N     | N          | N     | N     |       | N         |
| RS       | S    | S          | •        |          | •    | •         | •     | •          | •     | •     |       | •         |
| UV/VIS   |      |            | •        |          | •    | •         | •     | •          | •     | •     | •     |           |
| XRS      | N    |            |          |          | N    | N         | N     | N          | N     | N     | 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/<br>Mass | Qual | Semiquant | Quant | Macro/<br>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.

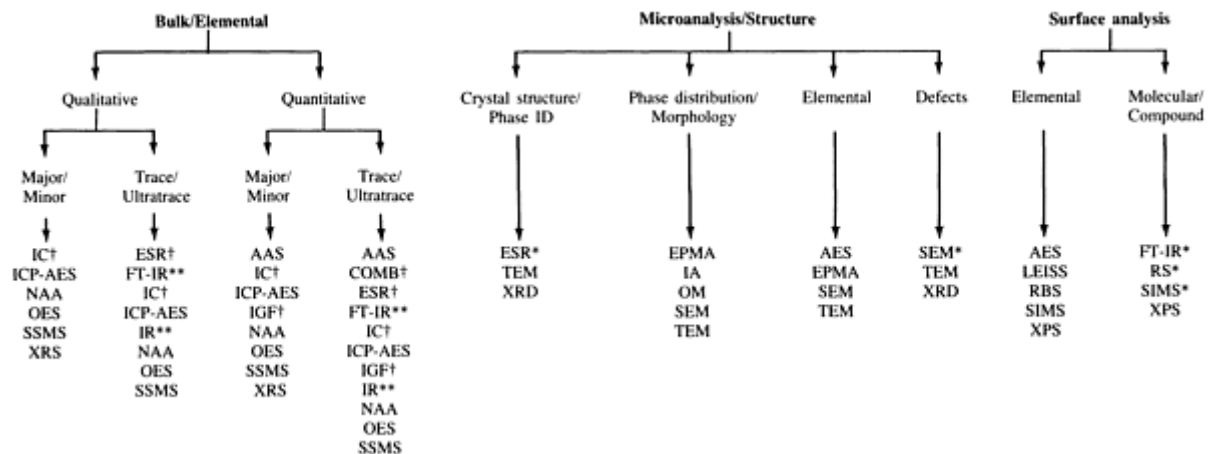


Fig. 1 Flow chart of inorganic solids: metals, alloys, semiconductors. Acronyms are defined in Table 10.

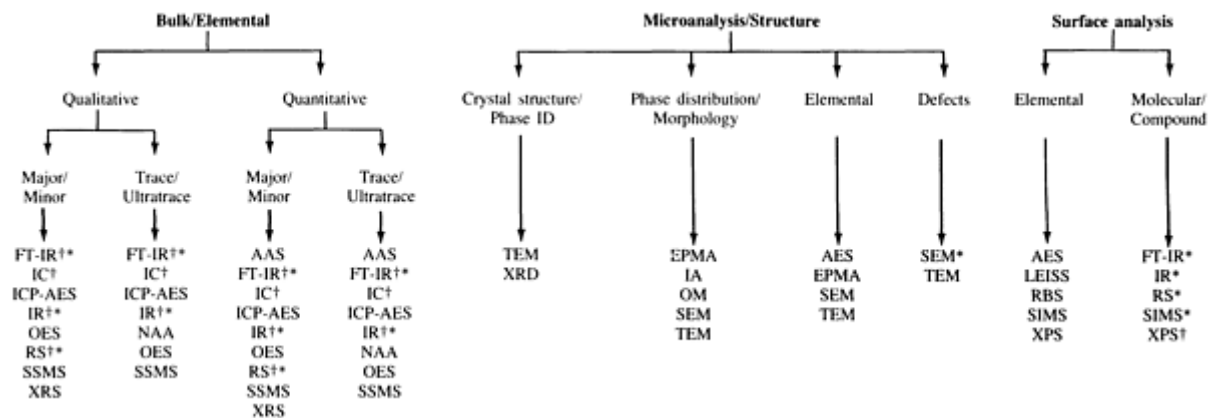


Fig. 2 Flow chart of inorganic solids: glasses, ceramics. Acronyms are defined in Table 10.

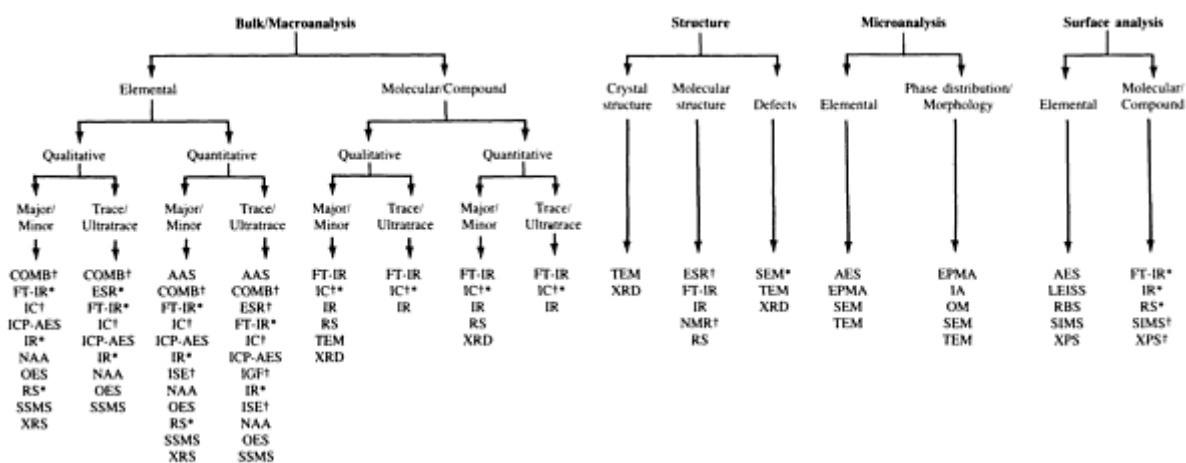


Fig. 3 Flow chart of inorganic solids: minerals, ores, slags, pigments, inorganic compounds, effluents, chemical reagents, composites, catalysts. Acronyms are defined in Table 10.

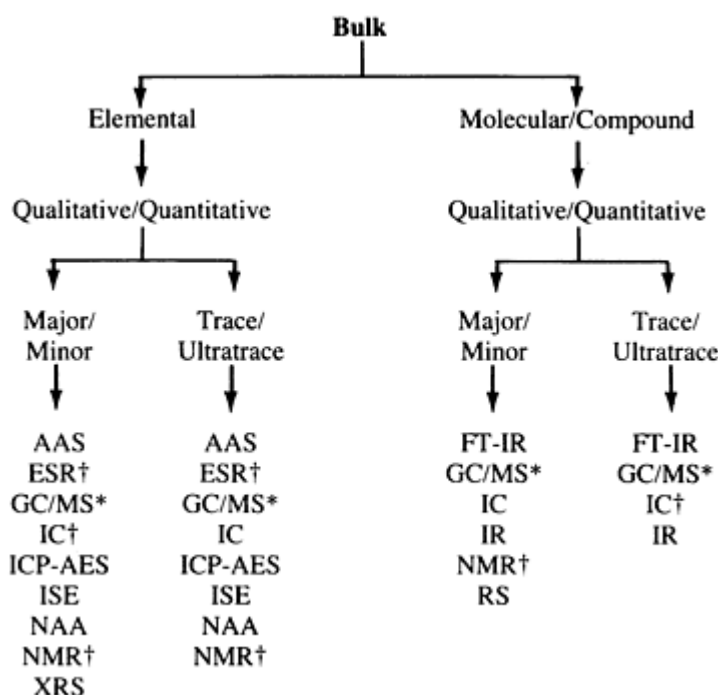


Fig. 4 Flow chart of inorganic liquids and solutions: water, effluents, leachates, acids, bases, chemical reagents. Acronyms are defined in Table 10.

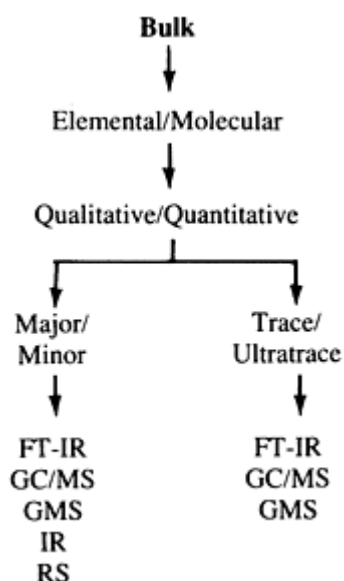


Fig. 5 Flow chart of inorganic gases: air, effluents, process gases. Acronyms are defined in Table 10.

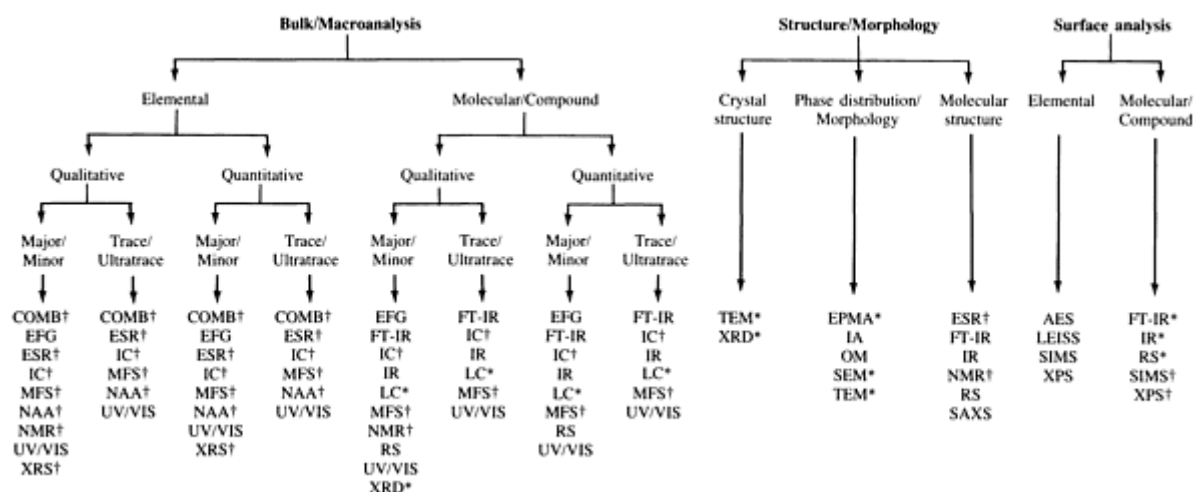


Fig. 6 Flow chart of organic solids: polymers, plastics, epoxies, long-chain hydrocarbons, esters, foams, resins, detergents, dyes, organic composites, coal and coal derivatives, wood products, chemical reagents, organometallics. Acronyms are defined in Table 10.

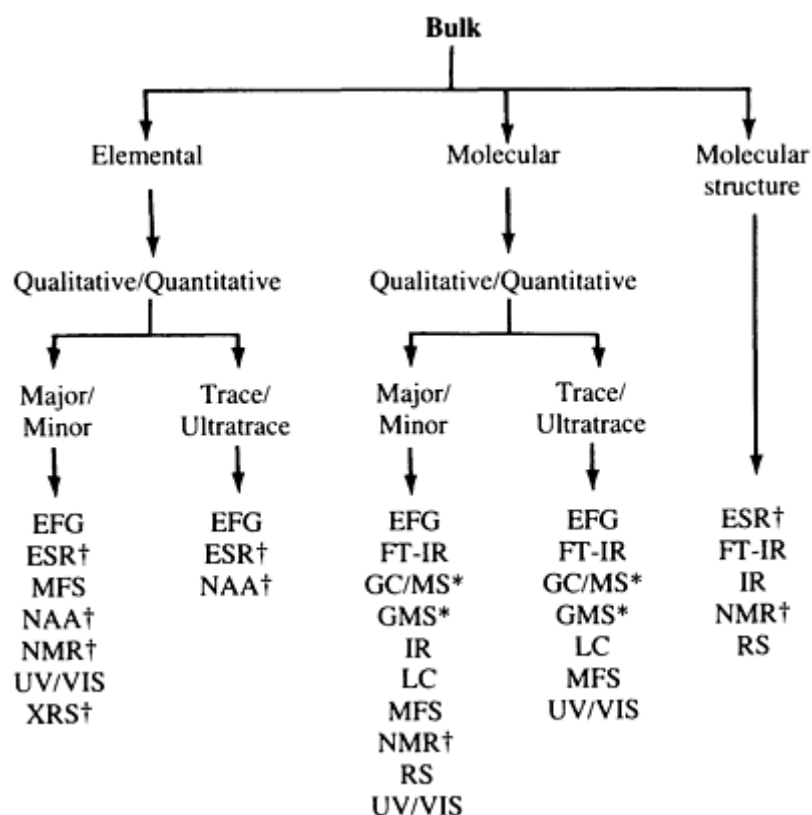


**Fig. 7 Flow chart of organic liquids and solutions: hydrocarbons, petroleum and petroleum derivatives, solvents, reagents. Acronyms are defined in Table 10.**

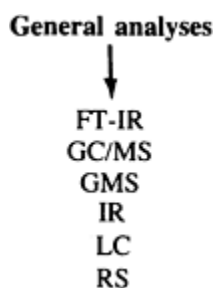


**Fig. 8 Flow chart of organic gases: natural gas, effluents, pyrolysis products, process gas. Acronyms are defined in Table 10.**

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.

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## How To Use the Handbook

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## 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 ( $0.1\ \text{to}\ 10\ \text{wt}\%$ )                       |

|            |                                                      |
|------------|------------------------------------------------------|
| 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                          |

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## Sampling

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## Introduction

Sampling is the selection for testing of a portion of a population. Portions are used for economic and technical reasons for the chemical and physical measurement of raw materials, plant process streams, and the final products and wastes produced by industry. Many industrial decisions relating to quality control of raw materials and end products and to environmental monitoring are based on such measurements.

The reliability of any measurement depends on sample quality. A poorly devised sampling plan or uncertainties in the sampling process, in sample storage, preservation, or pretreatment may obscure results or prevent their interpretation. This article will primarily consider the problem of sampling bulk materials, including minerals, metals, environmentally important substances, and industrial raw materials and waste products.

The design of bulk sampling programs involves:

- Identifying the population from which the sample is to be obtained
- Selecting and withdrawing valid gross samples of this population
- Reducing each gross sample to a laboratory sample suitable for the analytical techniques to be used

Inherent in the design should be an effort to maintain sampling conditions that yield accurate results rapidly and economically. Commonly used terminology is defined in the section "Glossary of Terms" in this Volume.

## Acknowledgement

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## Sampling

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## Preliminary Considerations in Sampling

Many sources of error, such as contaminated apparatus or reagents, biased methods, or operator errors, can be controlled by proper use of blanks (a measurement involving addition of all the reagents, but not the sample), standards, and reference materials. However, controls and blanks will not be useful if the sample is invalid. Accordingly, sampling uncertainty is often treated separately from other uncertainties. For random errors, the overall standard deviation,  $s_o$ , is related to the standard deviation for the sampling operations,  $s_s$ , and to that for the remaining analytical operations,  $s_a$ , by:  $S_o^2 = S_a^2 + S_s^2$ . Whenever possible, measurements should be conducted so that sample variability and measurement variability can be separately evaluated. For a measurement process in statistical control where  $s_a$  is known,  $s_s$  can be evaluated from  $s_o$ , which is determined by analysis of the samples. Alternatively, an appropriate series of replicate measurements or samples can be devised to evaluate both standard deviations.

Further reduction in measurement uncertainty is unimportant once it is one third or less of the sampling uncertainty (Ref 1). Therefore, if the sampling uncertainty is large and cannot be reduced, a rapid, approximate analytical method may be sufficient, and further refinements in measurement may not significantly improve the overall results. In such cases, a rapid method of low precision that permits more samples to be examined may reduce the uncertainty in the average value.

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## Reference cited in this section

1. W.J. Youden, The Roles of Statistics in Regulatory Work, *J. Assoc. Off. Anal. Chem.*, Vol 50, 1967, p 1007

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## Sampling

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## Types of Samples

**Random Samples.** Sampling is occasionally directed at obtaining an extreme value, such as the best or worst case. However, a sample usually is collected to determine the distribution of some characteristic among the population. To obtain the best estimate of this distribution, random sampling may be performed. In random sampling, every part of the population has an equal chance of being included in the sample, regardless of the location or nature of that part.

The distinction between the target population to which conclusions should apply and the parent population from which these samples are actually drawn is important. In practice, these are rarely identical, although the difference may be small. This difference may be minimized by random selection of portions for examination, in which each part of the population has an equal chance of selection. Generalizations based on mathematical probability can be made from such random samples.

A random sample is obtained by basing sample collection on a table of random numbers; it is not selected haphazardly. However, samples selected using a defined protocol tend to reflect biases brought about by decisions of the sampler and the equipment used. In addition, individuals who obtain samples must understand that the apparently unsystematic collection pattern must be followed closely to be valid.

In random sampling of an entire lot of bulk material, the material is divided into a number of real or imaginary segments. For example, a bin of raw material can be conceptually subdivided horizontally and vertically into cells. Each segment is then assigned a number. Segments from which sample increments will come are selected by starting in an arbitrary place in a random number table (Ref 2) and choosing numbers according to a preset pattern, such as adjacent, alternate, or  $n$ th entries, then sampling those segments for the determined number of samples. Because of its simplicity, sampling at evenly spaced intervals over the bulk is often used instead of random sampling, although results must be closely monitored to prevent errors from periodicity in the material.

**Systematic Samples.** Each sample collected systematically and analyzed to reflect or test some systematic hypothesis, such as changes in composition with time, temperature, or spatial locations, should be considered representative of a separate, discrete population under the existing conditions. However, the results may still be statistically tested for the significance of any apparent differences.

A carefully designed sampling plan includes the possibility of unanticipated events or phenomena that could prejudice the analyses. For example, measurements at timed intervals are sometimes made with random start or other superimposed random time element. The less known about a given process, the more randomness is merited. Conversely, the more fully a process is understood, the more efficient is a systematic approach to data acquisition.

**Representative sample** frequently connotes a single sample of a universe or population expected to exhibit average properties of the population. It is not possible to select such a sample by a random process, or to verify if it is representative. A truly representative sample seems valid only if the sample is defined *a priori* as representing a specific purpose, such as the Hazardous Waste Management System, which prescribes seven protocols for obtaining samples that "will be considered by the agency [Environmental Protection Agency] to be representative of the waste" (Ref 3), or if truly homogeneous materials are sampled.

Although it may reduce costs, measurement of samples defined as representative yields information not equaling that from valid random samples of the population, except when the population is homogenized before sampling to produce a

number of similar subsamples. A properly designed and executed random sampling plan provides sample mean and variation between members, neither of which can be obtained by analysis of one "representative sample."

**A composite sample** may be considered a special type of representative sample. Many sampling procedures assume that only average composition is desired, such as bulk, time-weighted, or flow-proportional averages, and specify collection or preparation of a suitable composite. Elaborate crushing, grinding, mixing, and blending procedures have been developed and standardized for preparing solid composites (see the articles "Milling of Brittle and Ductile Materials" and "Blending and Premixing of Metal Powders and Binders" in *Powder Metal Technologies and Applications*, Volume 7 of the *ASM Handbook*). Sampling systems have been developed to obtain liquid (especially water) composites (Ref 4, 5).

Analysis of individual samples permits determination of the average (at the expense of additional analytical effort), of the distribution of samples within the population (between-sample variability), and of within-sample variability (if replicate analyses are conducted). Composite samples provide limited information, and the consequences should be carefully considered before deciding between this approach and the analysis of individual samples.

**Subsampling** is necessary, because the sample received by the analytical laboratory is usually larger than that required for a single measurement. Test portions taken for replicate measurements or for measurement of different constituents by several techniques must be sufficiently alike so that results are compatible. The effort necessary to reduce particle size, mix, or otherwise process the laboratory sample before withdrawing portions (subsamples) for analysis depends on the homogeneity of the original sample.

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## References cited in this section

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3. Hazardous Waste Monitoring System, General, *Fed. Regist.*, Vol 45 (No. 98), 1980, p 33075-33127
4. "Standard Practices for Sampling Water," ASTM D 3370, Vol 11.01, *Annual Book of ASTM Standards*, ASTM, Philadelphia, 1984, p 85-94
5. "Standard Practice for Manual Sampling of Petroleum and Petroleum Products," ASTM D 4057, Vol 05.03, *Annual Book of ASTM Standards*, ASTM, Philadelphia, 1984, p 663-686

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## Sampling

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## The Sampling Plan

Before sampling begins, a model of the overall operation should be established (Fig. 1). The model should define the objectives of the study, although multiple objectives may compete for limited resources. Typical objectives include estimation or evaluation of the average of characteristics in a population and their variability or distribution and determination of whether characteristics of interest in the population meet specified standards or pre-established criteria (Ref 6).

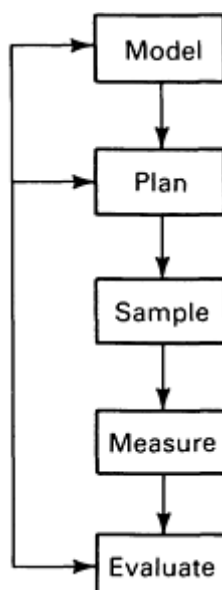


**Fig. 1 Sequence for an overall operation to estimate a property of a system.**

The model should also define the population studied, substance(s) to be measured, extent of speciation and distribution within the population, and precision required as well as identify all assumptions about the population. Once the model is complete, a sampling plan can be established.

The plan should specify the size, number, and location of the sample increments, the extent of compositing, if applicable, and procedures for reducing the gross sample to a laboratory sample and to test portions. Before work begins, this should be written as a detailed protocol that includes procedures for all steps, from sampling to sample treatment, measurement, and data evaluation. It should be revised as necessary for new information.

The protocol dictates when, where, and how to take the sample increments and will establish on-site criteria for collection of a valid sample. Decisions about whether a component is foreign (not part of the population) often must be made at the time of sampling. If possible, criteria for such decisions should be established logically and systematically before sampling begins. The type of container, cleaning procedure, protection from contamination before and after sampling, storage conditions and possible addition of preservatives should be specified.

The analyst should perform or supervise the sampling operation or should provide a written protocol to well-trained individuals aware of the importance of minimizing bias and contamination. Also important are careful labeling and recording of samples. A chain of custody to ensure the integrity of the samples from source to measurement is essential. Details such as temperature position of the collecting probe in the sample stream and flow velocity of the stream should be recorded when the sample is taken. Omission or loss of such information may greatly decrease the value of a sample or render it worthless.

**Sampling Bulk Materials.** Once the substances to be determined and the precision desired have been specified, a sampling plan can be designed that considers:

- Quantity of samples to be taken
- Their sizes
- Location in the bulk material (population) from which they should be taken
- Whether individual samples should be analyzed or a composite prepared

The relative homogeneity of the system affects sample size. Gross samples should be unbiased with respect to the different sizes and types of particles present in the bulk material. The size of the gross sample is often a compromise between the heterogeneity of the bulk material and the cost.

When the properties of a material to be sampled are unknown, a useful approach is to collect a small number of samples, using experience and intuition as a guide to make them as representative of the population as possible, then to analyze for the component of interest. From these preliminary analyses, the standard deviation  $s_s$  of the individual samples can be calculated, and confidence limits for the average composition established using:

$$m = \bar{x} \pm \frac{tS_s}{\sqrt{n}} \quad (\text{Eq 1})$$

where  $\mu$  is the true mean value of the population,  $\bar{x}$  is the average of the analytical measurements, and  $t$  is obtained from statistical tables for  $n$  measurements (often given as  $n - 1$  degrees of freedom) at the desired level of confidence, usually 95%. Tables of  $t$  values are provided in Ref 2 and 11.

On the basis of this preliminary information, a more refined sampling plan can be devised. After one or two cycles, the parameters should be known with sufficient confidence to estimate the optimum size and number of the samples with a high level of confidence. Considerable savings in time and cost result from optimizing the sample program.

**Minimum Size of Individual Increments.** There are several methods for estimating the amount of sample required in a given increment so as not to exceed determined sampling uncertainty. One method uses Ingamells' sampling constant (Ref 7, 8, 9). Because the between-sample standard deviation,  $s_s$ , decreases with increasing sample size, the following relation is often valid:

$$wR^2 = K_s \quad (\text{Eq 2})$$

where  $w$  is the weight of sample analyzed,  $R$  is the relative standard deviation (in percent) of sample composition, and  $K_s$  is the sampling constant, corresponding to the weight of a single sample required to limit the sampling uncertainty to 1% with 68% confidence;  $K_s$  may be determined by estimating  $s_s$  from a series of measurements of samples of weight  $w$ . Once  $K_s$  is evaluated for a given sample, the minimum weight  $w$  required for a predetermined maximum relative standard deviation of  $R$  percent can be readily calculated. This method applies only to subsampling of well-mixed samples and cannot be used if segregation is present.

**Minimum Number of Individual Increments.** Unless the population is known to be homogeneous, or unless an analytical problem necessitates a representative sample, sufficient replicate samples (increments) must be analyzed for the component under study. The minimum number of sample increments necessary to achieve a given level of confidence can be estimated from:

$$n = \frac{t^2 S_s^2}{E^2} \quad (\text{Eq 3})$$

where  $t$  is the Student's  $t$ -table value for the level of confidence desired (Ref 2, 11),  $S_s^2$  is estimated from preliminary compositional measurements on, or from previous knowledge of, the bulk material, and  $E$  is the standard deviation acceptable in the average. Initially,  $t$  can be set at 1.96 for 95% confidence limits, and a preliminary value of  $n$  calculated. The  $t$  value for this  $n$  can then be substituted and the system iterated to constant  $n$ . The expression applies if the sought-for component is distributed in the population in a positive binomial, or Gaussian, distribution, which is characterized by an average,  $\mu$ , larger than the variance of the mean,  $s_s^2$ .

Values of  $\sigma_s$  (and  $s_s$ ) may depend greatly on the size of the individual samples. The value of  $\sigma_s$  may also depend on concentration. If the relative standard deviation is constant with respect to concentration, relative standard deviation and relative error may be substituted for  $s_s$  and  $E$ .

**Sampling a Segregated (Stratified) Material.** Special care must be taken when assessing the average amount of a substance distributed nonrandomly throughout a bulk material. Such segregation may be found, for example, in ore bodies, in different production batches in a plant, or in samples in which settling produces variable composition. To obtain a valid sample of a stratified material:

- Divide the material into real or imaginary segments (strata) based on the known or suspected pattern of segregation
- Further divide the major strata into real or imaginary subsections and select the required number of samples randomly (preferably with the aid of a table of random numbers)
- Take samples proportional in number to the size of each stratum if the major strata are not equal in size

In general, stratified random sampling is preferred to unrestricted random sampling if the number of strata is kept sufficiently small that several samples can be taken from each. In this way, possible variations within the parent population can be detected and assessed without increasing the standard deviation of the sampling step.

**Minimum Number of Individual Increments in Segregated Material.** When a bulk material is highly segregated, many samples must be taken from different segments. A useful guide to estimating the number of samples needed is cited in Ref 10. The variance in sample composition depends on the degree of homogeneity within a given sample increment and the degree of segregation between sample increments (Ref 10):

$$S_s^2 = \frac{A}{wn} + \frac{B}{n} \quad (\text{Eq 4})$$

where  $S_s^2$  is the variance of the average of  $n$  samples using a sample increment weight  $w$ , and  $A$  and  $B$  are constants for a given bulk material;  $A$  is a homogeneity constant, and  $B$  a segregation constant.

Values for  $A$  and  $B$  can be obtained experimentally for a bulk population in two ways. In the first, two sets of increments are collected, one with  $w$  as small and the other as large as feasible. The component of interest is measured and a sampling variance calculated for each set. Values for  $A$  and  $B$  can be calculated from  $A = w_L w_S (S_s^2 - S_L^2) / w_L - w_S$  and  $B = S_L^2 - (A/w_L)$ . A second approach, applicable only to material for which the reciprocal of the average particle mass  $m$  can be estimated, is to collect a series of pairs of increments, each member of a pair being of weight  $w$  and collected from near its partner. The increments are then analyzed or tested, and an intraclass correlation coefficient  $r$  is calculated (Ref 11). Values for  $A$  and  $B$  are then calculated using Eq 4 and the relationship  $r = B/Am$ .

**Sampling Materials in Discrete Units.** If the lot of material under study occurs in discrete units, such as truckloads, drums, bottles, or tank cars, the variance of the analytical result is the sum of the variance between units in the lot, the average variance of sets of samples taken from within one unit, and the variance of the analytical operations. The contribution from each depends on the number of units in the lot and the number of samples taken (Ref 6):

$$s_x^2 = \frac{s_b^2}{n_b} \frac{(N - n_b)}{N} + \frac{s_w^2}{n_b n_w} + \frac{s_t^2}{n_t} \quad (\text{Eq 5})$$

where  $s_x^2$  is variance of the mean,  $s_b^2$  is variance of the units in the lot,  $s_w^2$  is average variance of the samples taken from a segment,  $s_t^2$  is variance of the analytical operations,  $N$  is number of units in the lot,  $n_b$  is number of randomly selected units sampled,  $n_w$  is number of randomly drawn samples from each unit selected for sampling, and  $n_t$  is total number of analyses, including replicates, run on all samples.

If stratification is known to be absent, preparing a composite sample saves measurement time and effort. Equation 5 also applies to this situation. If the units vary significantly in weight or volume, results should be weighted accordingly.

For homogeneous materials, including many liquids and gases,  $s_w^2$  is zero, and the second term on the right side of Eq 5 drops out. If all units are sampled,  $n_b = N$ , and the first term on the right of Eq 5 also drops out.

2. M.G. Natrella, *Experimental Statistics*, National Bureau of Standards Handbook 91, U.S. Government Printing Office, Washington, Aug 1963, p 2-13
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11. G.W. Snedecor and W.G. Cochran, *Statistical Methods*, 7th ed., Iowa State University Press, 1980, p 243

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## Sampling

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## Optimizing Sampling Resources

Sampling plans must include minimizing the cost of determining an estimation of the population mean to within a specified variance or minimizing the variance for a given allocation of funds. For a stratified sampling plan, assuming the strata to be equal in size and in variance within strata, the total cost  $c$  is:

$$c = c_0 + n_1 c_1 + \frac{n_1 n_2 c_2}{n_1 n_2 n_3} \quad (\text{Eq 6})$$

where  $c_0$  is the overhead cost,  $c_1$  is the cost of selecting each of the  $n_1$  strata,  $c_2$  is the cost per sample of collecting  $n_2$  samples within each strata, and  $c_3$  is the cost per analysis for  $n_3$  analyses per sample (Ref 12). For example, if an analysis of variance has provided estimates of  $s_1^2$ ,  $s_2^2$  and  $s_3^2$  for the selection of strata, the sampling within each strata, and the measurement, each contributes to the overall variance by:

$$s^2 = \frac{s_1^2}{n_1} + \frac{s_2^2}{n_1 n_2} + \frac{s_3^2}{n_1 n_2 n_3} \quad (\text{Eq 7})$$

The minimum cost  $c$  for a fixed value of  $\sigma^2$  is obtained (Ref 13):

$$n_1 = \frac{\sqrt{\sigma_1^2/c_1}}{\sigma^2} (\sqrt{\sigma_1^2 c_1} + \quad (\text{Eq 8})$$

$$n_2 = \frac{\sqrt{\sigma_2^2 c_2} + \sqrt{\sigma_3^2 c_3}}{\sqrt{\frac{\sigma_2^2 c_1}{\sigma_1^2 c_2}}} \quad (\text{Eq 9})$$

and

$$n_3 = \sqrt{\frac{\sigma_3^2 c_2}{\sigma_2^2 c_3}} \quad (\text{Eq 10})$$

Because  $n_2$  and  $n_3$  are not affected by the value selected for  $\sigma^2$ , if  $\sigma^2$  is to be reduced, the number of strata  $n_1$  sampled should be reduced while holding  $n_2$  and  $n_3$  constant.

For a fixed total cost  $c$ , the optimum values of  $n_1$ ,  $n_2$ , and  $n_3$  are:

$$n_1 = \frac{c\sqrt{\sigma_1^2/c_1}}{\sqrt{\sigma_1^2 c_1} + \sqrt{\sigma_2^2 c_2} + \sqrt{\sigma_3^2 c_3}} \quad (\text{Eq 11})$$

$$n_2 = \sqrt{\frac{\sigma_2^2 c_1}{\sigma_1^2 c_2}} \quad (\text{Eq 12})$$

$$n_3 = \sqrt{\frac{\sigma_3^2 c_2}{\sigma_2^2 c_3}} \quad (\text{Eq 13})$$

For this system, the optimum allocation beyond the first stage of sampling is the same for fixed total cost as for fixed total variance.

**Example 1.** In sampling a trainload of metal pipe for the percentage of an alloying element, the standard deviation is 0.25 between cars, 0.15 within a car, and 0.08 for a determination. The relative costs of the operation are 5:4:1. The overall standard deviation  $\sigma_o$  in the result is not to exceed 0.10.

The optimum sampling scheme is:

$$n_1 = \left[ \frac{\sqrt{0.25^2/5}}{0.10^2} \right] \left[ \sqrt{(0.25^2)(5)} + \sqrt{(0.15^2)(4)} + \sqrt{(0.08^2)(1)} \right] = 10.5 \quad (\text{Eq 14})$$

$$n_2 = \sqrt{\frac{(0.15^2)(5)}{(0.25^2)(4)}} = 0.67 \quad (\text{Eq 15})$$

$$n_3 = \sqrt{\frac{(0.08^2)(4)}{(0.15^2)(1)}} = 1.07 \quad (\text{Eq 16})$$

Taking  $n_1 = 11$ ,  $n_2 = 1$ , and  $n_3 = 1$ ,  $s_o^2 = 0.25^2/11 + 0.15^2/11(1) + 0.08^2/11(1) = 0.008$ , and  $\sigma_o = 0.09$ . The cost =  $(11 \times 5) + (1 \times 4) + (1 \times 1) = 60$  on the relative scale.

If the costs were fixed at, for example, 40 times that of a single determination on the relative scale, the minimum standard deviation that could be obtained would be:

$$n_1 = 40 \sqrt{\frac{0.25^2}{5}} \div [ \sqrt{(0.25^2)(5)} \quad \quad \quad \text{(Eq 17)}$$

$$+ \sqrt{(0.15^2)(4)} + \sqrt{(0.08^2)(1)} ] = 4.8$$

$$n_2 = \sqrt{\frac{(0.15^2)(5)}{(0.25^2)(4)}} = 0.67 \quad \quad \quad \text{(Eq 18)}$$

$$n_3 = \sqrt{\frac{(0.08^2)(4)}{(0.15^2)(1)}} = 1.07 \quad \quad \quad \text{(Eq 19)}$$

Taking  $n_1 = 5$ ,  $n_2 = 1$ , and  $n_3 = 1$ ,  $c = (5)(5) + (5)(1)(4) + (5)(1)(1)(1) = 50$  and  $s_o^2 = 0.25^2/5 + 0.15^2/5(1) + 0.08^2/5(1) (1) = 0.018$ , then  $\sigma_o = 0.14$ .

**Calculating Statistical Sampling Uncertainties.** Sampling is most important when significant heterogeneity or segregation exists. When  $\bar{x}$ ,  $s$ ,  $K_s$ ,  $A$ , and  $B$  are known exactly, it is easy to calculate the statistical sampling uncertainty and to determine the number and size of the samples needed for a given precision. If, as is more usual, these quantities are known only approximately or not at all, preliminary samples and measurements must be taken, and from these more precise sampling procedures developed.

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## Practical Aspects of Sampling

Chemical analysis is typically performed on a material that is a subset of some other material or even of a system of materials of interest. Although the actual sample analyzed may be so small that its ratio to its parent is almost infinitesimal, for example, a few milligrams of sample as related to thousands of tons of an ore, it must represent the population of interest.

All aspects of the sample must be considered in relation to the model of the analytical problem (Ref 14). It must be taken according to a specific strategy, preserved to minimize deterioration, contained to prevent intrusion of foreign substances or to minimize escape of constituents of interest, processed to retain its integrity, and subsampled as necessary, while maintaining its correspondence to other members of its immediate family. Because all these aspects cannot be guaranteed, it may be necessary to analyze a number of subsamples, to perform related measurements to evaluate the magnitude of any actual or potential complication, or both.

For example, the appearance of a lump of ore under analysis may suggest heterogeneity and that care should be exercised in sampling it. A sample such as a piece of metal may appear uniform and provide no indication of microheterogeneity. Even if the material is uniform in structure, different sized particles or chips obtained by crushing or machining may have significantly different compositions.

**Sampling Protocol.** The model of the problem and planning of the measurement program should specify the location of sampling sites, the number of samples required, and how the actual samples are to be taken. There should be no uncertainty as to what the sample is, which requires that it be taken according to a protocol ideally codeveloped by the problem-area specialist, the analyst, and a statistician. Therefore, a minimum of these three disciplines must be represented in planning.

In many cases, such as failure analysis, field examination of the material or structure being analyzed is required. Such on-site examination frequently reveals information essential to problem solving that may either go undetected or be permanently lost if the description of the incident and sample-taking are left to personnel who are not familiar with metallurgical, analytical, and statistical principles.

**Mechanism of Field Sampling.** Sampling usually requires equipment. Buckets, scoops, or shovels are useful for fluid or granular materials (Ref 15). Special devices called thieves are used to sample granular materials at various levels within a container or mound (Ref 15). Dredges, drills, saws, cutting torches, augers, or corers may be needed to obtain samples from massive materials. In some cases, the sample may be extracted using filters, sieves, or absorption devices. It may be obtained in a form ready for analysis or may require further extraction or processing in the laboratory.

Samples must be taken in a way that does not influence the measurements to be made. For example, the use of cutting for removing samples from metal structures for metallographic examination should be avoided, because the heat generated by cutting can significantly alter the microstructure. If cutting torches must be used, large samples should be taken and subsequent metallography performed at locations where microstructural alteration from the cuts has not occurred.

Similarly, gas samples must be taken in uncontaminated containers that can be subsequently sealed to prevent material leakage into or out of the container before analysis. Many incorrect conclusions have been drawn because samples were altered during sampling. To prevent this, knowledgeable metallurgical and analytical personnel must be involved in sampling.

Any device used for sampling must conform to the sampling protocol. Sampling devices may have critical dimensions or operational parameters, such as those used for sampling respirable matter, or filters used to separate "dissolved" or particulate fractions, or in isokinetic sampling. Failure to conform to critical dimensions or operational parameters can produce erroneous results. Sampling equipment such as pumps and sieves may require calibration to verify their performance characteristics at the time of use. Sampling devices ideally should not be made of or contain the analyte of interest. Therefore, plastic scoops are more suitable when taking metal samples, but metal scoops may be more appropriate for sampling organic materials.

**Preservation** of the sample may be required unless it is measured immediately. Changes in sample composition can result from oxidation, radiation, differential evaporation, loss of volatile constituents, thermally induced degradation, and interaction with other constituents of the sample or the container. Contamination from airborne dust can be important, and the introduction of foreign substances can occur. Protection from airborne contamination may require handling of samples in ultra-clean rooms (Ref 16). Preservation techniques include addition of preservatives, low-temperature storage, enclosure in inert atmospheres, hermetic sealing, and the use of nonactinic glass or opaque containers.

The concept of holding time can be applied to evaluating preservation techniques. Samples preserved in a given way can be analyzed periodically to determine the interval that occurs before a tolerable amount of deterioration has taken place. If this is considered the first indication of significant deterioration, it is equivalent to three standard deviations of the measurement technique used to evaluate it (corresponding to a confidence level of 95%). If unknown, the standard deviation of measurement may be evaluated concurrently with the holding time evaluation by duplicate measurement of subsamples. For some samples, the holding time may be so short as to require field analysis or at least measurement on a rigid time schedule.

**Discrimination.** Decisions should be made that define whether certain constituents of a population should be included or rejected. A particular material may be a foreign object (rejected) or a constituent (included). The model should

anticipate such situations and provide the basis for decision, depending on the use to be made of the data. Thus, sieves may be specified to separate coarse objects or materials from fines if the former are believed to be foreign.

**Moisture.** If the original population contains water, the model should define if the analytical result should be reported on a dry or "as-received" basis. Moisture loss or gain from the time of sampling to analysis also can introduce problems. When different laboratories treat the question of moisture differently (and sometimes in an unspecified manner), disparity in results can occur.

The moisture content may not be theoretically defined, but based on arbitrary considerations. Arbitrary drying procedures must be described or documented. Above all, the basis for the analytical result, such as "as-received," or dried by a specific procedure, must be stated whenever the moisture content of a sample is a significant consideration (Ref 17).

Because of moisture problems, analytical results on solid materials are frequently reported on a dry-weight basis. The sample may be dried before analysis, or the wet sample may be analyzed and corrected for its moisture content, which is measured independently (Ref 17). The nature of the sample may dictate the procedure. Whenever significant volatile components could be lost, the latter approach may be necessary.

**Homogenization or blending procedures** may be required in subsampling and field sampling. Because it may sometimes be difficult or impossible to blend in the field, final homogenization is left to laboratory personnel.

Liquid samples may require only mixing before analysis. However, if immiscible components of differing densities are present, blending may be required continuously during subsampling. The shape of the container and type of mixer may be important in ensuring a proper blending of the constituents.

When the sample contains liquid and solid constituents, the phases may be separated and analyzed separately, in which case the amount and the composition of each phase present may need to be known. Complete separation of the phases could be a problem, and the definition of dissolved and suspended matter may be arbitrary, for example, based on separability by a filter of specified porosity. Filtered solids may contain absorbed or occluded liquids that may be difficult to remove. The alternative of analyzing a suspension could cause even greater problems if any difficulties of maintaining suspendibility are expected.

Blending of heterogeneous solids is frequently performed. Such samples are often crushed to obtain small particle sizes that promote improved mixing. Crushers can range from the familiar mortar and pestle to specially designed mills. They must be made of noncontaminating materials harder than the materials processed to minimize abrasion and should have chemical resistivity to the samples. The fineness of grinding required will depend on the heterogeneity of the sample, but fine grinding is ordinarily preferred. Sieving may be performed at intermediate stages to separate fines and coarses that are later reground. When the coarses differ in composition from the fines, each may be ground using a different process, then combined to compose the analytical sample.

The grinding of soft materials, especially those with appreciable water content, may require special grinders. Special mills have been developed for such materials as food samples and feeds. Cryogenic grinding and blending may also be used (Ref 18). In such cases, prevention of condensation of atmospheric moisture may be a problem. Caking and electrostatic clinging of material to parts of grinders and blenders can cause mixing problems as well.

Blending is often necessary after grinding. Blenders include riffers in which the sample emerges from a container in preset fractions. Cone and V-blenders have been designed for mixing materials. Cones are often double and joined at their bases. Rotation produces swirling or tumbling. V-blenders achieve the same result by alternately pouring their contents from one arm to the other as the device is rotated. For best results, mixers should not be overloaded and should be operated slowly enough to produce alternate interchanges of the contents. Holdup due to caking can decrease their efficiency. The number of cycles required must be determined empirically.

In the simple process of quartering, the sample is placed on a sheet of suitable material, and alternate edges are pulled together to achieve mixing. Shoveling from the edges of a cone of material to the top is sometimes effective.

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## Quality Assurance for Sampling

Many sampling errors can be eliminated or minimized by an appropriate quality-assurance program (Ref 19). Quality control may be achieved by following standard operating procedures and recommended laboratory and measurement practices. Protocols should be developed as part of the planning program to define how each aspect of sampling will be executed. They should specify related calibration procedures and schedules and provide for controls such as field blanks and for the container cleaning process.

**Training of personnel** should provide a thorough knowledge of the elementary statistics of sampling. Specific training should be devoted to the operation concerned with each specific measurement program, including a thorough review of the protocols to be followed. Critical steps should be identified and explained, and any special documentation reviewed.

**Sample uncertainties**, random or systematic, result from the sample or from the sampling operation. Population-related variability has been discussed above. However, unless the entire sample is analyzed, a subsample may be required that may have some of the problems encountered in the original considerations. Thus, subsampling may be considered as sampling the sample. Unless proven otherwise, subsampling error should be assumed to be present (Ref 20).

Sampling can introduce uncertainties superimposed on that of the sample variability. Faulty calibration of sampling equipment, introduction of contamination, malfunction of equipment, and differences between equipment used can introduce systematic errors, and variation of these factors can produce random errors.

Rigorous cleaning of equipment between samples may be necessary to minimize error from contamination or carryover problems. Evaluating the effectiveness of cleaning may be difficult. Containment may contribute to contamination, especially in trace analysis. Virgin containers usually require cleaning. If containers are to be reused, cleaning may need to be monitored. It may be necessary to restrict reuse to a certain class of samples and even to restricted levels within such classes if memory or cross contamination is a possibility.

Rigid calibration programs and checks may be necessary to ensure proper functioning of some sampling equipment. If calibration is performed in the laboratory, periodic field checks may be required to confirm retention of calibration, especially if the usage is severe.

**Sample Identification.** Definite procedures may be required to ensure the identity of samples that are analyzed. Well-designed labels can document the details of sample location and of the sampling operation. Critical aspects of their transport and storage can also be attested. Breakage-proof containers and tamper-proof closures may be required. A sample custodian may be necessary in some cases. There should be no reasonable doubt about the identity and the integrity of any sample analyzed.

**Sampling Specific Materials.** The general principles discussed above apply to the major problems of sampling for chemical analysis. Sources of information on procedures for sampling specific materials are cited in Ref 15, 21, 22, 23, 24, and 25.

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## Optical Emission Spectroscopy

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### General Uses

- Quantitative determination of major and trace elemental constituents in various sample types
- Qualitative elemental analysis

### Examples of Applications

- Rapid determination of concentrations of alloying elements in steels and other alloys
- Elemental analysis of geological materials
- Determination of trace impurity concentrations in semiconductor materials
- Wear metals analysis in oils
- Determination of alkali and alkaline earth concentrations in aqueous samples
- Determination of calcium in cement

### Samples

- *Form:* Conducting solids (arcs, sparks, glow discharges), powders (arcs), and solutions (flames)
- *Size:* Depends on specific technique; from approximately  $10^{-6}$  g to several grams
- *Preparation:* Machining or grinding (metals), dissolution (for flames), and digestion or ashing (organic samples)

### Limitations

- Some elements are difficult or impossible to determine, such as nitrogen, oxygen, hydrogen, halogens, and noble gases
- Sample form must be compatible with specific technique
- All methods provide matrix-dependent responses

### Estimated Analysis Time

- 30 s to several hours, depending on sample preparation requirements

### Capabilities of Related Techniques

- *X-ray fluorescence:* Bulk and minor constituent elemental analysis; requires sophisticated data reduction for quantitative analysis; not useful for light elements (atomic number  $\geq 9$ )
- *Inductively coupled plasma emission spectroscopy:* Rapid quantitative elemental analysis with parts per billion detection limits; samples must be in solution; not useful for hydrogen, nitrogen, oxygen, halides, and noble gases
- *Direct-current plasma emission spectroscopy:* Similar in performance to inductively coupled plasma emission spectroscopy
- *Atomic absorption spectroscopy:* Favorable sensitivity and precision for most elements; single-channel technique; inefficient for multielement analysis

### Introduction

Optical emission spectroscopic methods originated in experiments performed in the mid-1800s, yet they remain some of the most useful and flexible means of performing elemental analysis. Free atoms, when placed in an energetic environment, emit light at a series of narrow wavelength intervals. These intervals, termed emission lines, form a pattern, the emission spectrum, that is, characteristic of the atom producing it. The intensities of the lines are usually proportional to the number of atoms producing them. The presence of an element in a sample is indicated by the presence in light from the excitation source of one or more of its characteristic lines. The concentration of that element can be determined by measuring line intensities. Thus, the characteristic emission spectrum forms the basis for qualitative elemental analysis, and the measurement of intensities of the emission lines forms the basis of quantitative elemental analysis.

### General Principles

The characteristic spectrum an atom produces reflects the electronic structure of the atom. Changes in the energy of the valence or outer shell electrons result in the atomic lines used in emission spectroscopy. Each atom has a ground state in which all of its electrons occupy positions of minimum potential energy. As an atom absorbs energy, one or more of the outer electrons may be promoted to higher energies, producing an excited state. The energy of an atomic state is a function of the energies of the individual electrons and of energy changes resulting from interactions among the electrons. Each possible combination of electron configurations produces a spectroscopic term that describes the state of the atom.

**Electronic Energy Levels.** The simplest atoms, such as hydrogen and the alkali metals, have only one electron outside a filled shell. The simple electron configurations of these atoms produce several possible terms, as illustrated by the energy-level diagram for lithium in Fig. 1. Atomic emission lines result when the atom undergoes a spontaneous transition from one excited state to another lower energy state. Not all possible combinations of states produce emission lines. Only transitions obeying quantum mechanically derived selection rules occur spontaneously. Diverse factors control the relative intensities of the lines. Those transitions between a low excited state and the ground state, termed resonance transitions, generally yield the most intense emission.

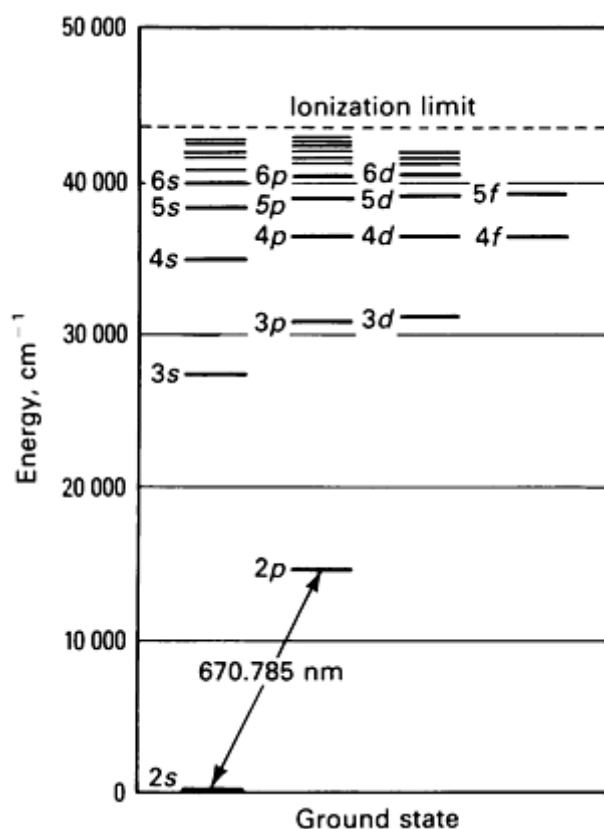


**Fig. 1** Energy level diagram for lithium. With the exception of the s states, each horizontal line corresponds to two closely spaced energy levels. The numbers and letters to the left of the lines are designations for the orbitals that the single electron can occupy. Transitions from the two 2p states to the ground 2s state produce a pair of closely spaced resonance lines at 670.785 nm.

The energy of the excited electron increases with decreasing spacing between excited states until it reaches an ionization limit. At this point, the electron is no longer bound to the atom and may assume a continuous range of energies. Such unbound electrons may undergo transitions to bound states. Because the upper state of the transition is not limited to discrete values, the light from such transitions is spread continuously over a range of wavelengths.

The ionization limit for the atom corresponds to the ground state of the singly charged ion. Excitation of the remaining bound electrons yields a new term system and a new set of lines. Ionization and excitation may continue until an atom is completely stripped of its electrons. In practical emission sources, ionization rarely proceeds beyond removal of two electrons, and in most cases, only the first stage of ionization need be considered. However, a line from the first ion spectrum is commonly used in analysis instead of a neutral atomic line.

**Spectral Overlap.** The use of atomic emission for elemental analysis requires measurability of the emission intensity from a line of interest independent of overlapping emission from other species in the sample. The probability of undesired overlap depends on the number of lines in the spectrum and on the wavelength spread or linewidth of each transition. If all atomic term systems were as simple as that shown for lithium in Fig. 1, the probability of spectral overlap would be low. However, lithium is one of the simplest atoms.

Atoms with more complex electronic structures produce correspondingly complex emission spectra. The iron spectrum, a small section of which is shown in Fig. 2, exemplifies such spectral complexity. The spectrum from one ionization stage of a single element may, given sufficient excitation energy, consist of hundreds of emission lines. The complexity is compounded when several elements are present in a sample, each generating neutral and ionic spectra.