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Techniques for Analysis of Mineral Raw Materials

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Series Editor

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Techniques for Analysis of Mineral Raw Materials

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Description of the Handbook

Objective

This handbook presents the content of the course techniques for analysis of mineral raw materials, which aims to present basic concepts in the analysis of raw material characteristics that are defining of technological potential in their industrial application.

The approach to these analysis techniques will be generic and descriptive discussing their main theoretical foundations. Aspects of experimental measurements will be presented, with the aim of providing a contextual view of the techniques, and how to use them as a tool for analysis of mineral raw materials. The description of the techniques will be primarily phenomenological, at the expense of the mathematical formalistic treatment of the physical foundations, necessary for a more rigorous theoretical approach. However, some formulations that support the argumentation of the physical principles and the potentialities of the techniques are inevitable.

At the end of the course, students should have solid knowledge in the main concepts involving the characterization of raw materials and ease in articulating the relationship between the analysis technique and the obtaining of information of industrial and commercial interest.

Contents

1	Introduction	1
2	Chemical and Mineralogical Analysis	5
2.1	Introduction	5
2.1.1	Instrumental Analyses	6
2.2	X-Ray Fluorescence (XRF)	14
2.2.1	Principle of the X-Ray Fluorescence Technique	16
2.2.2	Applications of X-Ray Fluorescence	20
2.2.3	Sample Preparation for XRF	24
2.2.4	Sources of Error in XRF	25
2.3	Atomic Absorption Spectrometry	26
2.3.1	Principle of the Atomic Absorption Technique	27
2.3.2	Applications of AAS	31
2.3.3	Sample Preparation for AAS	31
2.3.4	Sources of Error in AAS	32
2.4	UV/Visible Spectroscopy	33
2.4.1	Principle of UV–VIS Spectroscopy	33
2.4.2	Applications of UV–VIS Spectroscopy	37
2.4.3	Sample Preparation for UV–VIS Spectroscopy	38
2.4.4	Sources of Error in UV–VIS Spectroscopy	38
2.5	Inductively Coupled Plasma Atomic Emission Spectrometry (ICP)	38
2.5.1	Principle of ICP Spectroscopy	40
2.5.2	Applications of ICP Spectroscopy	41
2.5.3	Sample Preparation for ICP Spectroscopy	42
2.5.4	Sources of Error in ICP Spectroscopy	42
2.6	Infrared Spectroscopy (IRS or FTIR)	43
2.6.1	Principle of FTIR Spectroscopy	44
2.6.2	Applications of FTIR Spectroscopy	46
2.6.3	Sample Preparation in FTIR Spectroscopy	48
2.6.4	Sources of Error in FTIR Spectroscopy	48

2.7	Raman Spectrometry	48
2.7.1	Principle of Raman Spectroscopy	50
2.7.2	Applications of Raman Spectrometry	51
2.7.3	Sample Preparation in Raman Spectroscopy	53
2.7.4	Sources of Error in Raman Spectroscopy	53
2.8	Mössbauer Spectroscopy	54
2.8.1	Principle of Mössbauer Spectroscopy	55
2.8.2	Applications of Mössbauer Spectroscopy	57
2.8.3	Sample Preparation in Mössbauer Spectrometry	58
2.8.4	Error Sources in Mössbauer Spectroscopy	59
2.9	Nuclear Magnetic Resonance	59
2.9.1	Principle of Nuclear Magnetic Resonance	61
2.9.2	NMR Applications	70
2.9.3	Sample Preparation in NMR	71
2.9.4	Sources of Error in NMR	72
2.10	X-Ray Diffraction	72
2.10.1	Principle of X-Ray Diffraction	74
2.10.2	Applications of X-Ray Diffractometry	78
2.10.3	Sample Preparation for XRD	83
2.10.4	Source of Error in XRD	83
3	Particle Size Analysis	87
3.1	Introduction	87
3.2	Granulometric Analysis by Sieving	90
3.3	Granulometric Analysis by Laser Diffraction	93
3.4	Granulometric Analysis by Sedimentation	94
3.4.1	Andreasen Pipette	96
3.4.2	Sedigraph	96
3.4.3	Granulometric Analysis by Microscopy	97
4	Surface Area and Porosimetry	99
4.1	Surface Area	99
4.2	Porosimetry	102
4.2.1	Determination of Porosity by Water Absorption	103
4.2.2	Determination of Porosity by Gas Expansion	104
4.2.3	Determination of Porosimetry by Mercury	105
5	Thermal Analysis	109
5.1	Introduction	109
5.2	Thermogravimetric Analysis (TGA)	111
5.2.1	Applications of TGA	112
5.3	Differential Thermal Analysis (DTA)	113
5.3.1	Differential Scanning Calorimetry (DSC)	115
5.3.2	Applications of TDA and DSC	116
5.4	Influence Factors and Sources of Error	117
5.5	Interpretation of Thermal Analysis Data	118

6 Microscopy Analysis	121
6.1 Introduction	121
6.2 Optical Microscopy	121
6.2.1 Petrographic Analysis	123
6.3 Electron Microscopy	126
6.3.1 Scanning Electron Microscopy (SEM)	129
6.3.2 Transmission Electron Microscopy (TEM)	133
Annex I	139
Glossary	143
Bibliography	157

Chapter 1

Introduction



Mineralogy defines mineral as a “solid, inorganic and crystalline substance, with a well-defined chemical composition and physical properties, resulting from a terrestrial or extraterrestrial geological process, without human intervention”.

Mineral raw materials to be used in the industry in general can be characterized in terms of aspects such as:

- (i) Chemical composition: provides the content of each chemical element present in the raw material;
- (ii) Mineralogical composition: describes which minerals constitute the raw material (can be qualitative or quantitative);
- (iii) Granulometric composition: provides the percentage distribution, in weight, of the particle sizes that constitute the raw material.
- (iv) Morphological: informs about the shape and surface area of the particles that constitute the mineral raw material;
- (v) Effect of temperature (thermal analysis): informs about the behavior of the raw material (reactions/transformations) when subjected to heating/cooling;
- (vi) Microscopic Analysis: assists in obtaining information complementary to those previously mentioned.

Knowledge of these characteristics is essential for the control of the extraction process, beneficiation and industrial processing and will decisively influence the financial results of the companies involved in each of the segments that deal with industrial raw materials.

The characterization of raw materials is, therefore, a fundamental step for the exploitation of a mineral resource, as it provides subsidies to the sizing of the beneficiation process or, even, allows identifying inefficiencies and losses in existing processes.

Numerous are the techniques used in the characterization of raw materials. In the past, the chemical analyses of raw materials were done by wet route (acid attack, titrations, gravimetry, borax pearl fusion, flame tests, among others). In addition to

being laborious, the wet route analysis provided a simple list of contents or merely qualitative results.

With the development of instrumental analytical techniques, such as elemental analysis by X-ray fluorescence (XRF), X-ray diffraction (XRD) and scanning electron microscopy (SEM), the work to obtain data was greatly reduced, but the theoretical complexity of interpretation increased greatly.

The use of techniques for raw material analysis goes beyond manipulating samples and equipment, usually performed by trained technicians. Equally or more important is knowing how to interpret the data obtained in order to make decisions from them. Interpreting is generally much more difficult than using the equipment to obtain data.

Figure 1.1 presents a flowchart of the characterization of mineral raw materials for industrial use. The methodology to be adopted in the characterization of a mineral raw material varies greatly with the mineralogy itself and the inherent properties of the ore, as well as with the objectives and scope of the characterization.

Generally, the characterization of a sample begins with its fractionation, done by density or magnetic susceptibility, for example. Afterwards, phase identification takes place, where specific techniques are used, such as X-ray diffraction, in addition to optical and scanning electron microscopies.

The next step, the quantification of minerals, uses various techniques. Depending on the objectives of the characterization, it is possible to group the minerals according to their response to beneficiation or product specification (for example, iron minerals, including hematite, magnetite, goethite and limonites). One of the objectives of characterization may be to determine the liberation grain size of the mineral of interest (or minerals of interest) in relation to the gangue.

From a methodological-experimental point of view in the laboratory, the selection of physical analysis techniques, the establishment of measurement conditions and the interpretation of results depend, obviously, on the purpose of the study, the information sought, the properties of the minerals. They also invariably require clear knowledge of the origin of the sample (type of soil, genetic factors and processes, collection data) and its preparation (granulometric fractionation, magnetic separation, selective chemical treatments, chemical composition).

Generally, ores are characterized as (i) mixtures of phases with varying degrees of crystallinity; (ii) often, strong cementation and mechanically consolidated grains, quite resistant to disaggregation by conventional laboratory methods; (iii) very varied chemical composition, on a short spatial scale; (iv) wide distribution of sizes and shapes of grains (v) significant proportions of small particles, such as the clay fraction (average diameter, $\varphi < 2 \mu\text{m}$), and (vi) isomorphic substitution of iron in iron oxides by Al^{+3} , Ti^{+4} , Mg^{+2} or Cr^{+3} , to name a few more commonly found cations.

Among the most used analytical techniques in the technological characterization of mineral raw materials, we can mention: chemical analysis by X-ray fluorescence spectrometry and by atomic absorption spectrometry; granulometric analysis and thermal analysis, infrared absorption spectroscopy and microstructural analysis by optical microscopy (petrographic analysis) and scanning electron microscopy, complemented by point chemical analysis by energy dispersive detector. These techniques (highlighted in red in Fig. 1.1) are the focus of this course.

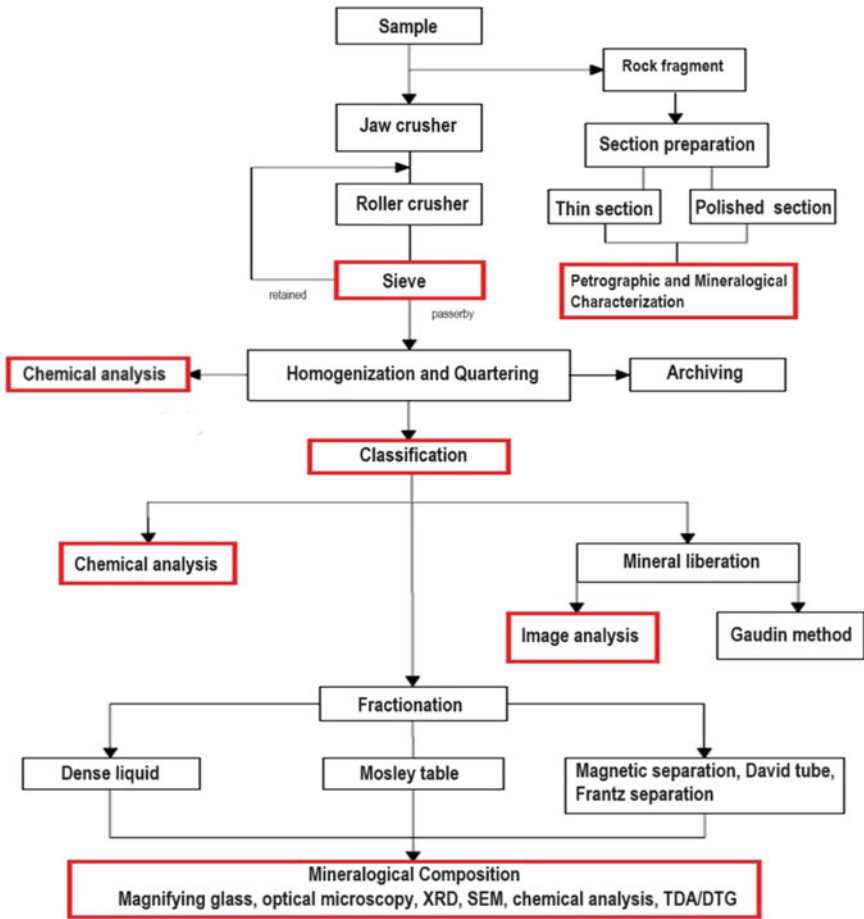


Fig. 1.1 Flowchart of the characterization of mineral raw materials for industrial use (adapted from R. Neumann, C. L. Schneider and A. Alcover Neto CT2004-181-00 Technical Communication prepared for the 4th Edition of the Ore Treatment Book, CETEM, MCT, 2004)

Chapter 2

Chemical and Mineralogical Analysis



2.1 Introduction

The chemical and mineralogical analysis of mineral raw materials is a necessity not always easy to execute, mainly due to the heterogeneous physical nature of the samples. The chemical and mineralogical analysis of ores represents one of the most important pieces of information for the definition of the quality of a raw material. Therefore, chemical and mineralogical analyses are a means and not an end within the industrial process, and the demand and requirements in terms of quality/productivity/technological competitiveness have caused this area to experience exponential growth in recent years.

Chemical and mineralogical analyses are the responsibility of chemists and not engineers, who are only users of chemical laboratories, but some knowledge in this area the engineer must possess to have discernment in the request for analysis and in the interpretation of results. A consistent and accurate exchange of information will facilitate the obtaining of the desired analyses. The engineer, in turn, knowing the analysis technique, will have a clearer notion of the errors and inaccuracies inherent to the analysis, and where the consistency of the results lies in order to use the information obtained appropriately.

The choice of an analysis method should consider the *principle* of the method (detection of atoms, ions, compounds), *what* is desired to analyze, *what precision* (reproducibility) is necessary, *detection limit* (smaller elements), *availability of time and resources* (standards!).

Any analysis technique should consider not only the small aliquot that is submitted to the analysis, but its representativeness of the raw material of interest. The sample sent for analysis must comply with very well defined and described sampling criteria in the literature. When it comes to evaluating raw materials in the mineral industry, a few grams represent tons of material.

Analyses can be **qualitative** and/or **quantitative**. They can be done by traditional methods called **wet route** or classical or by modern **instrumental techniques**, which

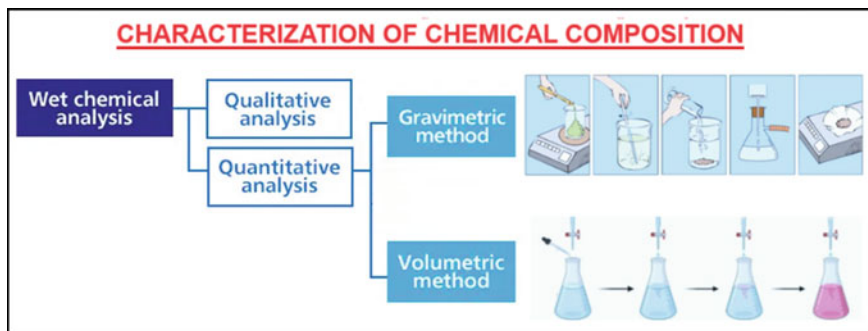


Fig. 2.1 Methods of characterizing the chemical composition of raw materials by wet route

provide quick responses, enabling useful information for research and industrial production.

Until recently, wet route chemical analysis methods were the most common and accurate for determining the chemical composition of a raw material. However, they are generally difficult, time-consuming, expensive, requiring suitable facilities and lengthy training of laboratory technicians. Despite all these difficulties, they are still used in many companies, either because there is no equipment that can replace them, to provide secondary standards for instrumental calibration, as well as to replace equipment during maintenance periods.

Wet route techniques include **titration** (titration of compounds in front of a specific color indicator) **gravimetry** (precipitation of a compound and dosage by the obtained weight) (Fig. 2.1). Trace elements are dosed with great difficulty, with very specific methods. For less precise routine analyses, the duration can be 4 days, while precision ones may require more than a week.

2.1.1 Instrumental Analyses

The development of instrumental analysis equipment intensified from the 1980s, based on the speed and accuracy in obtaining and processing information mainly by the phenomenon of **spectroscopy**. This development led to the emergence of analytical methods **instrumental**, also referred to as methods **spectrometric** or **spectrometric**.

Spectroscopy is the part of Analytical Chemistry for the identification of chemical elements and substances, through the transmission, absorption or reflection of radiant energy incident on a sample. Therefore, when the energy of an electromagnetic radiation is transmitted, absorbed or reflected upon contact with the atoms (or molecules) of a sample, the spectroscopic response of its constituents is a unique characteristic.

Spectroscopic analytical techniques can be classified by wavelengths they work with, the detection principle they use, the way they acquire a spectrum, and intensity of the energy sources they employ. Other important characteristics of spectroscopic techniques include spectral bandwidth and linear range. The simplest measure in spectroscopy is the measurement of light absorption, but it can involve the measurement of diffuse or specular reflectance. The sequence of events in spectroscopy is, as a rule, the following:

- (i) the light source shines on the sample;
- (ii) the sample absorbs part of the radiation;
- (iii) the detector detects the amount of light that the sample absorbed;
- (iv) the detector converts the amount of light absorbed by the sample into a number.
- (v) the numbers are immediately processed, for which, often some treatment is necessary (for example, baseline correction).

This sequence can be preceded by calibration when some standard substance is defined as a base value, by which the measurements of the samples under analysis are referenced.

2.1.1.1 The Electromagnetic Spectrum and Analytical Techniques

Figure 2.2 presents the types of spectra obtained from the decomposition of white light and sunlight. It is possible to identify two types of spectra: the **continuous spectrum** (as in the case of decomposition by a prism of white light); and the **discontinuous spectrum** (as in the case of decomposition by a prism of sunlight), where the spectral lines characteristic of this type of spectrum appear.

The emission of energy by atoms occurs when electrons jump from one energy layer to another. In the case of molecules, the energy emission is based on rotation and vibration movements and on the movement of the electrons of their constituent atoms. The interaction between the **radiation** or **electromagnetic wave** and the matter (atom, molecule or ion) of a sample is analyzed and measured through a device called a **spectroscope**.

There are two major classes of spectroscopic measurements: those obtained by a **single beam or monobeam** (measurement of the intensity of the absolute light) or by **double beam** (relates the intensity of light through two distinct paths, one passing through a standard sample). The result is expressed in the form of a graph of intensity (of the absorbed or emitted energy) as a function of the wavelength—or more commonly the frequency—called spectrum, spectrogram or spectral line width. What will vary is the nature of the measured excitation:

- (i) Absorption spectroscopy: analyzes the amount of energy absorbed as a function of the wavelength of the incident radiation (Fig. 2.3);
- (ii) Emission spectroscopy: analyzes the amount of energy emitted by a sample as a function of the wavelength of the absorbed radiation. It fundamentally consists of the re-emission of energy previously absorbed by the sample (Fig. 2.3);

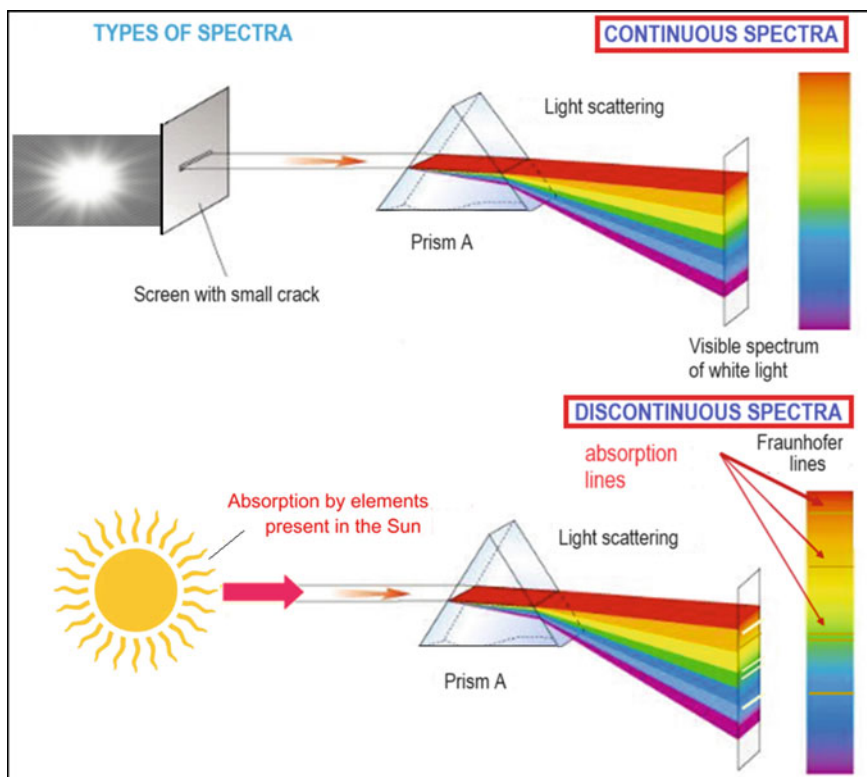


Fig. 2.2 Types of spectra obtained from the decomposition of white light and sunlight. It is possible to identify two types of spectra: the **continuous spectrum** (as in the case of decomposition by a prism of white light); and the **discontinuous spectrum**

- (iii) Scattering spectroscopy: analyzes the amount of energy scattered (dispersed) as a function of parameters such as the wavelength, incidence angle and the polarization angle of the incident radiation.

Thus, according to the interaction of the electromagnetic wave with matter, the electromagnetic spectrum can be divided into regions, for better understanding of the fundamentals of analytical instrumental methods, since physical interactions follow distinct mechanisms and provide different types of information, depending on the transitions that can occur (Fig. 2.4).

Depending on the incident energy and the absorbed energy, atoms emit spectra characteristic of their electron distribution in the electrosphere. The distribution of energy levels in the electrosphere is the “identity” of the chemical element interacting with the incident electromagnetic radiation.

Understanding the interactions between matter and energy, and their applications, becomes easier with knowledge of the **Rutherford-Bohr atomic structure model**: in a neutral atom (not excited), electrons occupy as many levels as necessary, starting