

## ANALYSIS METHODS IN THE MINERALOGICAL LABORATORY OF THE GEOLOGICAL INSTITUTE OF ROMANIA

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**Abstract.** Working in the mineralogical laboratory requires, in addition to processing field collected material, using modern analysis methods and special investigations. The most used methods are X-ray diffractometry and infrared spectrometry in absorption. These two methods, described in detail in this paper, are complemented by thermal analysis and electronic scanning microscopy, enabling the analysis of both crystalline phases of the collected material and the amorphous phase.

**Keywords:** mineralogical analyses, X-ray diffractometry, infrared spectrometry in absorption.

**Rezumat. Metode de analiză utilizate în laboratorul de mineralogie din cadrul Institutului de Geologie din România.** Activitatea desfășurată în cadrul laboratorului de mineralogie, presupune, pe lângă prelucrarea materialului recoltat din teren, și analiza acestuia prin metode moderne de analiză și investigație. Cele mai utilizate metode sunt difractometria de raze X și spectrometria de absorbție în infraroșu. Aceste două metode, descrise pe larg în lucrarea de față, completează de analiza termică și microscopia electronică cu baleiaj, permit analizarea atât a fazelor cristaline din materialul colectat, cât și a fazelor amorfe.

**Cuvinte cheie:** analize mineralogice, difractometria de raze X, spectrometria de absorbție în infraroșu.

### INTRODUCTION

Geological research involves work in the field, thorough laboratory studies, which involves processing and researching the collected material by applying various methods of analysis: physical, chemical or combinations thereof.

Although, the number of such methods is quite high (about 20), not all of these can be successfully applied in the study of minerals.

In the last decades, such methods have considerably broadened the fields of application, now being used as current methods in research laboratories, which study solid substances from areas such as mineralogy, crystallography, mineralurgy, metallurgy and even medicine. The use of these methods also lead to obtaining remarkable results from analysing previously known materials, that were not studied, and the discovery of new minerals.

### MATERIAL AND METHODS

The mineralogical material collected from the usual outcrops and from the less common environments (caves), need to induce the use of analytical methods suitable to highlight the physical and/or specific chemical characteristics of the concerned minerals. This paper aims to present two physical-chemical methods of analysis used in the study of minerals: X-ray diffractometry powder and infrared spectroscopy in absorption.

#### X-ray Diffractometry

X-rays were discovered in 1895 by Roëntgen. In the following years, Laue and his collaborators, by showing that a crystal works as a network for X – ray diffractions, concluded that this could be used to analyze minerals.

X-rays or Roëntgen radiations, represent fields of electromagnetic waves between 0.1 Å and 100 Å (1 Å =  $10^{-10}$  m), arising when high-speed electrons collide with material, transforming their kinetic energy into radiation energy. X radiation frequency is 1,000 times greater than light radiation, while the X photons possess much more energy compared to photons from the visible domain. Because of this, X radiation interaction with materials has special properties given by the small values of the wavelength and the high photon energy. The wavelength of X-rays is at the same order with the dimensions of atoms and distances between the atoms. For these reasons, X radiations pass through opaque bodies, produces black footage, fluorescence of some substances, ionizes gases and it is differently absorbed by materials, depending on density and atomic mass. Its application for studying crystal structures has brought evidence of the internal structure of ordered crystalline solids (IORGA, 1981).

X-ray diffractometry is the most used method to identify mineral species. This method has a number of advantages, namely: it ensures full deciphering of the reticular structure of minerals, gives indications on employment through structural cation positions (in the case of clay minerals), is non-destructive, the quantity of material used is very small (0.1 - 0.5 grams), the exposure time is relatively short (0.5 - 1 hour) and preparation time of samples is short. The study provides minerals static conditions or under constant temperature increase.

The Romanian Institute of Geology has a mineralogical laboratory equipped with an X-ray diffractometer, Bruker D8 ADVANCE (Fig. 1), which is used for studies on mineral dust. The device is composed from a vertical goniometer, a support tube, an evidence holder, a system of two bucks, a slot and a detector. Configuration is a theta/2 theta with a minimum step of 0.0001 degrees and a reproducibility of  $\pm 0.0001$  degrees.



Figure 1. X – ray diffractometer Bruker D8 ADVANCE (photo: Delia Dumitraș).  
Figura 1. Difractometru cu raze X Bruker D8 ADVANCE (foto: Delia Dumitraș).

The X-ray tube, which has a copper anode, releases radiation. Minerals, which in size are up to 0.1 mm, are carefully chosen using binocular magnifying glasses and washed with acetone in order to freeze the organic substance and the sesquioxides amorphous iron. The powder thus obtained is fixed by pressing on the sample and introduced in the device. The laboratory conditions include an electric current with an intensity of 40 mA and a voltage of 40 kV, a kind of standard input, scanning speed of 0.01 degrees per second theta between 4 and 90 degrees. As internal standards, there is also used synthetic corundum, achieving an accuracy of 0.01 degrees 2 theta for the measured interval. In addition, the X-ray results (Fig. 2) can be interpreted with the Diffrac Eva 13, for determining the quality of the crystalline phases, and the Topas program, for quantitative determination, including the amorphous phase.

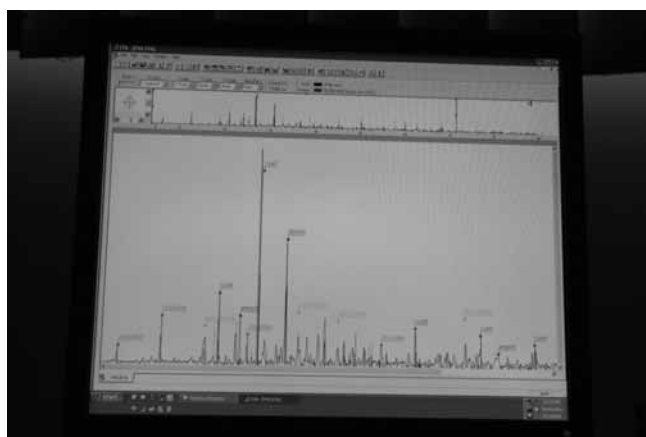


Figure 2. Diffractogram interpreted with the addition Diffrac (photo: Delia Dumitraș).  
Figura 2. Difractograma interpretată cu ajutorul Diffrac (foto: Delia Dumitraș).

### Infrared Spectrometry in absorption

The method aims to study the absorption of the infrared (with wavelength between 0.8 and 1,000  $\mu\text{m}$ , 1  $\mu\text{m}$  = 10,000  $\text{\AA}$  = 10<sup>-4</sup> cm = 10<sup>-6</sup> m). Infrared spectra own the rotation motion and molecular vibration. Infrared spectroscopy in absorption is a physical method of analysis, which is used to obtain molecular absorption spectra that represents the absorption intensity variation depending on the wavelength or wave number. It is based on a principle that underpins all

spectroscopic methods, namely sample irradiation and measurement of radiation absorption incidents. To obtain such molecular absorption spectra showing the variation of absorption intensity depend on the wavelength or wave number.

The absorption phenomenon occurs when the infrared radiation induces vibrations of atoms or groups of atoms in a molecule. Only molecular vibrations, which produce a rhythmic change of dipolar moment of the molecule, produce infrared absorption. From an almost infinite number of vibration that can occur in a crystal, the infrared spectroscopic measurements will detect only those which will induce a change in the timing of some dipolar molecules in the structure, in a field comparable to a characteristic wavelength infrared radiation. The number of the vibration spectrum and the complexity increases with the number of atoms in the elementary cell of a mineral. Depending on their nature, vibration may be stretching (valence of „stretching vibrations”), which correspond to unidimensional movements along the axis of connection, causing a periodic change in the length of connections and the deformation („bending vibrations”), which is two-dimensional movements and causes a change in the angles of connection, molecules distortion. The number of normal vibrations of a molecule depends on the degree of freedom of movement. For linear polyatomic molecules, the number of degrees of freedom is  $3N - 6$ .  $N$  is the number of atoms in the molecule (BECHERESCU et al., 1977). The study of the infrared spectra permits us to obtain data on the structure of the molecule as the distance between atoms, valence angles, symmetry, so the entire ensemble molecular geometry. Although the absorption bands are characteristic of the molecule as a whole, experience shows that molecules with similar chemical structure show similar infrared spectra. Bands in certain areas of the absorption spectrum can be attributed to certain groups of atoms.

High quality of spectra minerals obtained in infrared depends on the preparation of evidence. The physical factor is the most important for obtaining spectra of very good quality in particle size. Theoretically, particle size must be smaller than the wavelength of incident radiation. This will reduce the spreading of radiation and provides increase of the transmitted energy. For the samples examined in the infrared medium region (4,000 - 200  $\text{cm}^{-1}$ ), the particle size should not exceed 2  $\mu\text{m}$ . The break usually runs in the mortar agate in the presence of liquids (alcohol, acetone) to prevent the spreading of the sample.



Figure 3. Absorption spectrometer with infrared Fourier, Bruker Tensor 27 type (photo Delia Dumitraș).

Figura 3. Spectrometru de absorbție în infraroșu Fourier, tipul Bruker Tensor 27 (foto Delia Dumitraș).

As methods of preparation of samples, there are used: the method of pressed disc, the method of mixtures, and films.

The Geological Institute of Romania has a Bruker Tensor 29 type (Fig. 3) infrared spectrometer with a Fourier transformer. The field work in MIR (infrared medium) is equipped with a DTGS detector with window KBR and diffraction of light by KBR. Spectra are recorded in the frequency range between 400  $\text{cm}^{-1}$  and 4,000  $\text{cm}^{-1}$  with a resolution of  $\pm 1 \text{ cm}^{-1}$  and  $\pm 2 \text{ cm}^{-1}$ . When using the external ATR (attenuation of the reflections), the wave field is contained between 600  $\text{cm}^{-1}$  and 4,000  $\text{cm}^{-1}$ . As the dispersion medium is used throughout KBR (2 mg sample in 148 mg KBR), taking into account that this substance does not absorb between 200  $\text{cm}^{-1}$  and 4,000  $\text{cm}^{-1}$  and plasticity that KBR pressure not too high to give pills transparent. The well homogenized mixture is placed in a stainless steel mold and pressed with a force of  $5 \cdot 10^3 - 1 \cdot 10^4 \text{ kgf/cm}^2$  for several minutes so that the pill should be made transparent or translucent at least, thus the resulting pill is introduced in the spectrometer in place. Spectra are recorded automatically on a computer device coupled to the recorded program using the special assignment of absorption bands OPUS 6.5.

The analysis method allows the determination of molecular vibration groups of compounds, and allowing the presence of crystalline water (molecular or OH groups), the presence of ammonium sulphate, carbonate, silicate, etc. giving indications point symmetry of these groups. The spectrometer has in the database a library of 7,000 spectra allows for comparison and analyzed interpretation types of vibration and qualitative and quantitative interpretation of them.

## CONCLUSIONS

By applying diffractometry X-ray, there were analyzed crystallized minerals: spodumene, lithiophilite, or fluorapatite of pegmatite, scheelite of skarn with products resulting from the processing of natural phosphates to

produce synthetic phosphates. Processing diffractometry index by comparison with ICDD sheet, and using the calculation as the starting values obtained for the structure determination of minerals in question could be determined the parameters for each spider species in part. The average values determined for several mineral species are found in Table 1.

Table 1. Average values for parameters reticular minerals determined by X-ray diffractometry.  
Tabel 1. Valorile medii ale parametrilor mineralelor reticulare determinate cu ajutorul difractometriei cu raze X.

Mineral	$a(\text{Å})$	$b(\text{Å})$	$c(\text{Å})$	$\beta(^{\circ})$	$V(\text{Å}^3)$
Spodumene	9,476	8,403	5,227	110,1	390,8
Fluorapatite	9,367	-	6,883	-	522,8
Purpurite	5,831	9,772	4,776	90,3	272,1
Lithiophilite	4,712	10,377	6,043	90,7	295,5
Monazite	6,812	7,002	6,464	103,3	299,9
Gypsum	6,284	15,207	5,667	118,17	493,8
Scheelite	5,243	5,243	11,376	90,02	312,7

Infrared absorption spectrometry allowed the presence of radicals from phosphate pegmatite minerals: fluorapatite, purpurite, lithiophilite, and monazite of sulfate groups in the structure of gypsum, and the ties of Si-O spodumene. Also, there were obtained information on minerals in the structure studies.

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#### REFERENCES

- BECHERESCU D., CRISTEA V., MARX FR., MENESSY I., WINTER FR. 1977. *Metode fizice în chimia silicaților*. Edit. Științifică și Enciclopedică. București. 663 pp.
- IORGA N. 1981. *Metode fizice de studiu a mineralelor și rocilor*. Edit. Universității „Al. I. Cuza”. Iași. 307 pp.

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