

PROCESS AND APPARATUS FOR X-RAY CRYSTALLOGRAPHY

This invention concerns an X-ray crystallography process, and an apparatus comprising two measurement instruments, one for diffracted radiations and the other for Compton scattered radiations.

Various methods already exist for measuring the X-ray absorption coefficient of a sample. These aim at reducing the most serious error affecting diffractometry measurements, caused by the presence of non-crystalline elements alongside the crystalline elements, which makes it almost impossible to measure the fraction of amorphous matter in a sample.

External reference samples, similar in composition to the substance for analysis, can be used, if the approximate composition of the sample for analysis is known, and in particular if it is certain that the elements not detected in the diffractogram do not include any significant quantities of strongly disturbing minerals.

In this method, however, analysis of elements in the specimen sample that are not contained in the reference sample is lengthy and costly, and it requires the preparation of specific reference samples.

Finally, the unreliability of the results obtained by this method increases in direct proportion to the size of the non-analyzed fraction, although, for sedimentary rocks, Ferrero's method can be used with the unanalyzed fraction considered as a clay of average absorption, overcoming this difficulty to a certain extent.

There are also drawbacks in the method involving internal reference materials, in which the sample is mixed with a known compound, the intensity of the diffracted radiation is measured, and the absorption coefficient of the sample is deduced from this: very thorough homogenization of the mixtures is required, and the diffraction peaks of the reference materials have to be superimposed on others peculiar to the unknown fraction, unless prior diffractometric examination of the sample has been done before the known compound is added, so that the results before and after mixing can be compared. This is lengthy and expensive procedure.

The use of the sample-holder diffraction lines constitutes a variant on this method. A sample in the form of a thin film is placed on a sample-holder, and the incident X-ray beam diffracts through this film, being partly absorbed. This method is attractive, but also has major drawbacks: the radiations diffracted by the film are of very low intensity compared with those from the sample-holder, and a homogenous film of uniform thickness is needed, which usually cannot be prepared satisfactorily, particularly when the film is approximately the same thickness as the grains of the sample.

The process offered by the present invention provides a way of overcoming the difficulties involved in the various methods described above. It involves no restrictive assumptions, for samples of any kind, does not require preliminary diffractograms, and uses samples prepared in the standard way.

In this new method, the absorption coefficient of the sample for analysis is determined by measuring the Compton scattered intensity on a wavelength close to the diffracted wavelength, but incoherent, and accordingly unaffected by diffraction phenomena, so that it is separable from the diffracted beam.

The diffracted intensity is expressed, in A. Guinier's "Théorie et technique de la Radiocristallographie," page 239, formula 5.22 (ed. Dunod 1964), as follows:

$$I_d = K_1 \times C / \mu$$

where:

C = the mass concentration of the mineral being analysed

μ = the absorption coefficient of the sample

The Compton scattered intensity is calculated as follows. For an atom with atomic number Z , it is expressed as:

$$I_{cz} = I_0 r e^2 \frac{(1 + \cos^2 \theta)}{2} \left[Z - \sum_{n=1}^{n=Z} F n^2 - \sum m \sum n F m n \right] R$$

as given in the work already referred to (first member on page 24- Thomson's formula; second member on page 30, formula 1.30; third member on page 26, line 13- Breit-Dirac coefficient), where:

θ = angle of diffraction

I_0 = intensity per unit of surface area of the incident beam

$$r e^2 = 7.9 \times 10^{-26} \text{ cm}^2$$

$F n$ = scattering factor of the electron of order n

$F m n$ = correction factors based on Pauli's exclusion principle

$$R = \text{Breit Dirac coefficient} = (V/V')^3$$

Next comes the Compton volume intensity dI_c for n atoms in an elementary sample volume dv with mass dm and density ρ :

$$dI_c = \sum_{z=1}^{z=92} n_z i_{cz} = I_e R \left(\sum_{z=1}^{z=92} F z \frac{C z}{A z} \right) \rho^{dv}$$

Calculation of F/A for all the elements in the periodic table gives: (where A = atomic mass)

$$F/A = 0.3 \pm \epsilon \quad \epsilon \text{ maximum} = 0.12$$

or $F/A = 0.3$ approximately,

$$\text{giving: } dI_c = I_e R \times 0.3 \rho dv$$

The re-emitted elementary intensity, corresponding to the angle of incidence θ , can be calculated from this intensity per unit of volume: $dI'_c = 0.3 I_e \cdot R \cdot \rho \cdot \exp. [-\mu \rho X (1/\sin \theta + 1.03/\sin(\theta - \theta))](S/\sin \theta) dx$ after integration into the total thickness of the sample for the incident radiation:

$$I'_c = 0.3 I_e R (S/\mu) [(1 + \cos^2 \theta/1 + 1.03 \sin \theta)] [\sin(\theta - \theta)]$$

This equation can be further simplified.

Since there is a relation between μ Compton and μ diffraction:

$$\mu_c = K_2 \mu \quad K_2 = 10.3 \text{ to } 2 \% \text{ approximately.}$$

Under given instrument conditions, the apparatus constant K_3 can be brought in, so that:

$$I'_c = K_3 / \mu$$

It is then possible to calculate with a very low residual error:

$$C = K X I_d / I_c \quad \text{where } k = K_3 / K_1$$

The absorption coefficient of the sample can be eliminated by calculation.