

[54] **PROCESS AND APPARATUS FOR X-RAY CRYSTALLOGRAPHY**

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[51] Int. Cl. **G01n 23/00**

[58] Field of Search **250/273, 276, 277, 278,**
250/272; 235/151.35

[56] **References Cited**

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position of Diffraction Lines." Levin Industr. Lab., Vol. 36, Jan. 1970.

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[57] **ABSTRACT**

An X-ray crystallographic process, in which the intensity of the radiation (I_d) diffracted by each constituent element, identified qualitatively by its angle of diffraction, and the intensity of the Compton radiation (I_c) scattered by the whole sample, are measured, and the content C of each element is calculated by working out the ratio of the two measurements according to the formula $I_d/I_c = K.C$.

9 Claims, 5 Drawing Figures

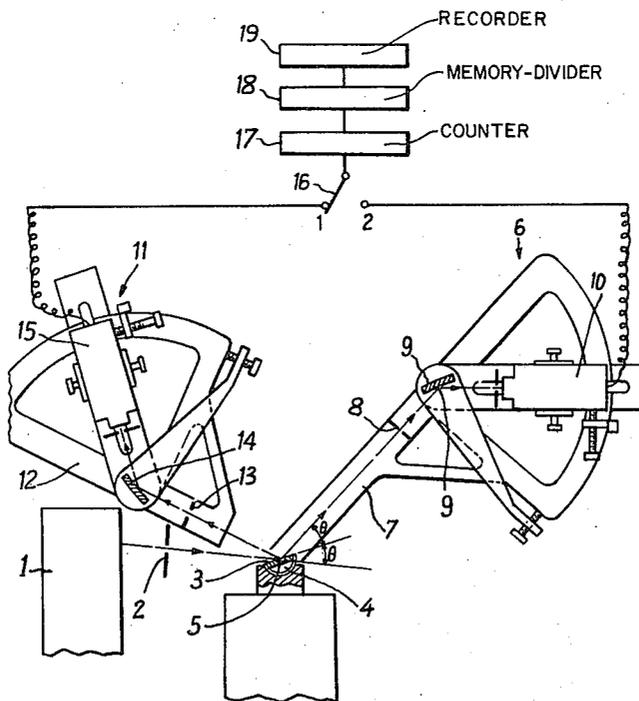


Fig:1

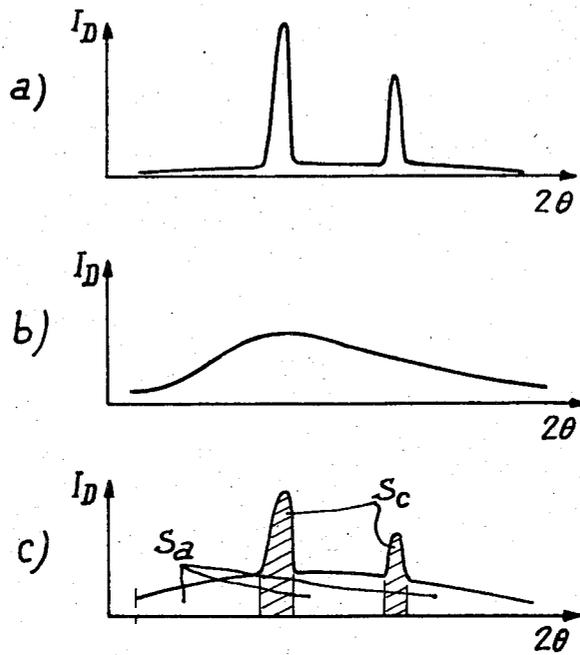


Fig:2

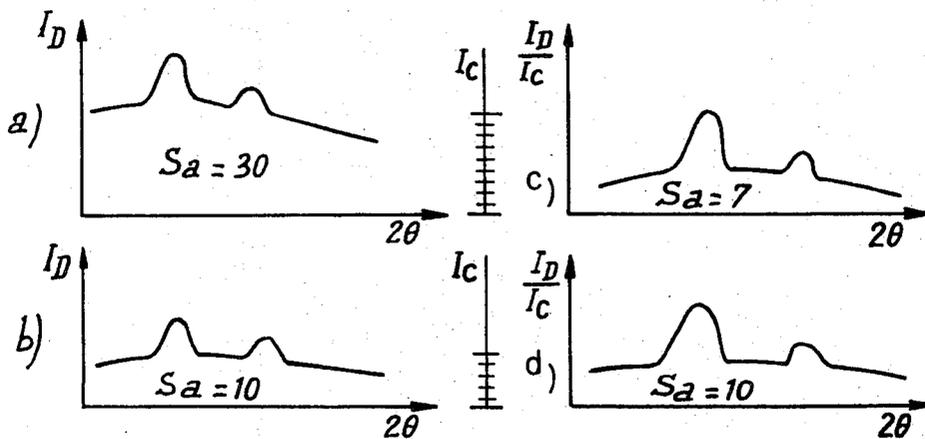
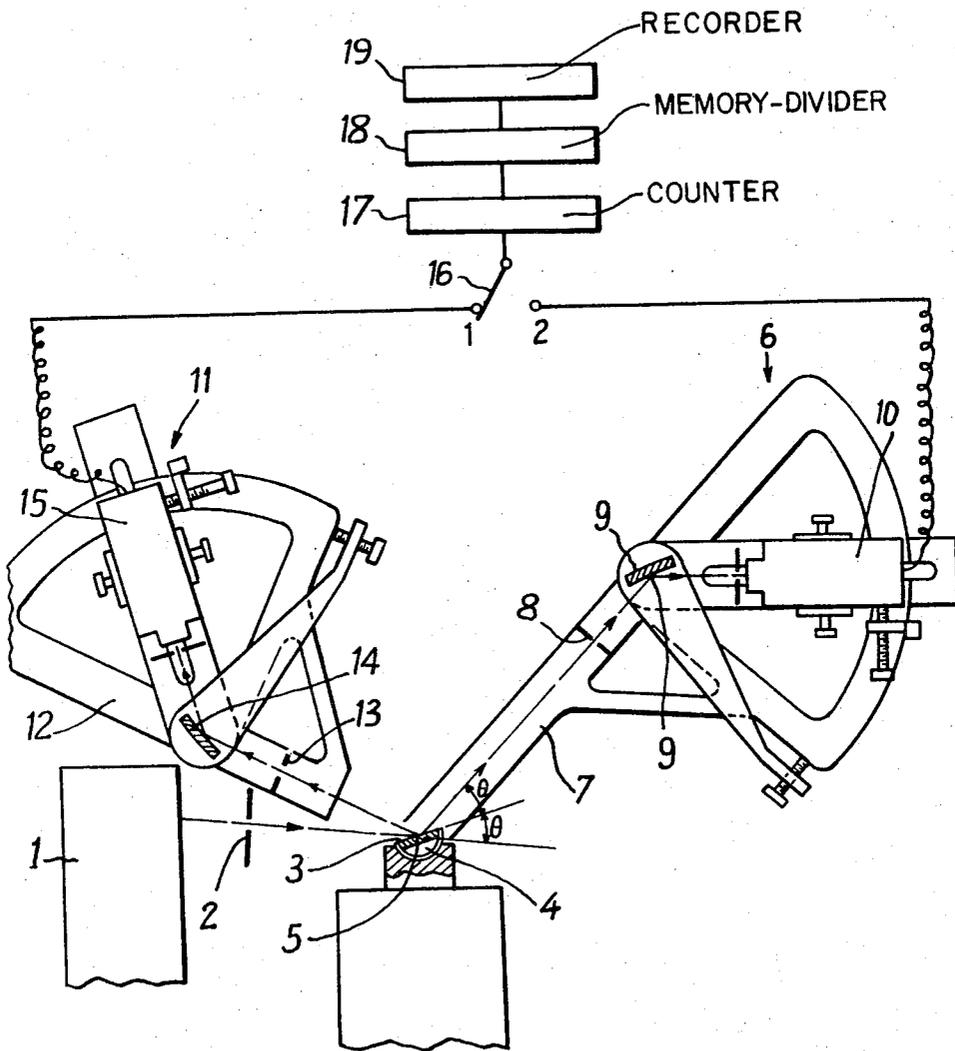


Fig. 3



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_{mn} = correction factors based on Pauli's exclusion principle

R = 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 :

$$dI_c = \sum_{z=1}^{z=92} n_z I_{ez} = I_e R \left(\sum_{z=1}^{z=92} F_z \frac{C_z}{A_z} \right) \rho^{dv}$$

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: $dI'_c = 0.31 I_e \cdot R \cdot \rho \cdot \exp. [-\mu \rho \chi (1/\sin \theta + 1.03/\sin(\theta - \theta))](S/\sin \theta) dx$ 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.

Numerous other features and advantages of this invention will become apparent from the drawings, in which:

FIGS. 1a - 1c show plots of intensity of diffracted radiation (I_d) in relation to angle of diffraction θ , where:

FIG. 1a shows the relation for a crystalline body;
 FIG. 1b shows the relation for an amorphous body;
 FIG. 1c shows the relation for a mixture of crystalline and non-crystalline elements;

FIGS. 2a and 2b show plots of intensity of diffracted radiations (I_d) in relation to angle of diffraction (θ) for two different non-crystalline substances, whereas

FIGS. 2c and 2d show plots of the ratio of intensity of diffracted radiation to the intensity of Compton scattered radiation i.e. I_d/I_c , in relation to angle of diffraction (θ);

FIG. 3 is a plan view of one embodiment of apparatus according to the invention;

FIG. 4 is a plan view of a second embodiment of apparatus; and

FIG. 4a is a pictorial view of a double Ross filter.

In the X-ray crystallographic process offered by this invention, the intensity of the radiation (I_d) diffracted by each constituent element, identified qualitatively by its angle of diffraction, and the intensity of the Compton radiation (I_c) scattered by the whole sample, are measured, and the content C of each element is calculated by comparing the two measurements in accordance with the formula:

$$C = K \cdot I_d / I_c.$$

When the diffracted intensity I_d is shown in relation to the angle of diffraction θ (see FIG. 1):

for a crystalline body FIG. 1a different peaks appear for the diffraction lines;

for an amorphous body FIG. 1b, a curve appears, forming a scatter halo;

for a mixture of crystalline and non-crystalline elements FIG. 1c, peaks are superimposed on the halo curve.

In the case of polymers in the same family, the ratio of the mass of non-crystalline matter to the mass of crystalline matter is given by the ratio of the surface areas S_a/S_c as defined in FIG. 1c.

For samples other than polymers in the same family, and notably for mineral samples, the surface area of non-crystalline matter S_a varies considerably depending on the nature of such matter, for the same concentration.

FIGS. 2a and b show different non-crystalline substances, at 100 percent concentration, with the result that the surface area S_a is 30 for a and 10 for b. With these substances, measurement of the non-crystalline matter by means of the ratio S_a/S_c would involve a 300 percent error.

If instead of showing I_d in relation to θ , I_d/I_c is shown in relation to θ , the surface area of non-crystalline matter S_a is found to be much less dependent on its nature: in FIG. 2c, S_a is 7 and in FIG. 2d S_a is 10. In this case, measurement of the non-crystalline matter by means of the ratio S_a/S_c would involve an error of 30 percent.

In the process offered by the invention, used in measuring the non-crystalline fraction of a material, the value of I_d/I_c is entered on a diagram in a continuous curve, related to the angle of diffraction, and the ratio of the mass of non-crystalline matter to the mass of

crystalline matter in the sample is calculated, working out the ratio of the surface area between the scatter halo curve and the abscissa axes, to the surface area between the diffraction peaks and the same abscissa axes.

The apparatus proposed by the invention comprises an X-ray glow-tube and a sample holder, an instrument to measure the intensity of the diffracted radiation, consisting of a diaphragm, monochromating crystal and radiation counter, attached to a goniometer arm with the same rotational axis as the irradiated sample, with means of adjusting the angle of the monochromating crystal and radiation counter in relation to the goniometer arm, an instrument to measure the intensity of the Compton scattered radiation, consisting of a diaphragm, frequency-band selector, and radiation counter, attached to an arm that is adjustable in the direction of the irradiated sample, forming a fixed angle with the incident beam, with means of adjusting the angle of the frequency-band selector and radiation counter in relation to the adjustable arm.

The instrument to measure the Compton scattered radiation is attached to an adjustable arm, such as a goniometer arm, and is placed in a fixed position in which it will receive a wave-band of the Compton scattered radiation in the furthest possible wave-length zone from that of the diffracted radiation.

In one recommended embodiment, the frequency-band selector on the path of the Compton scattered radiation consists of a monochromating crystal preceded by an inlet diaphragm, the width of which is such that the monochromating crystal will select a wave-band comprising at least 80 percent of the Compton radiations emitted by the sample.

The intensity of the Compton scattered radiation is fairly low compared with that of the diffracted radiation, so that measurement of it must comprise most of the scatter.

To ensure maximum efficiency in irradiation, the divergent slit in the X-ray glow-tube is preferably wide enough to allow irradiation of the total surface area of the sample.

Furthermore, to allow the sample to receive irradiation as close as possible to normal incidence during measurement of the intensity of the Compton scatter, the position of the sample should be maintained throughout the measurement operation at an angle corresponding to the maximum angle of diffraction.

In another embodiment, the frequency-band selector on the path of the Compton scatter consists of a double Ross filter, preceded by a plane diaphragm bounded by the envelope of straight lines resting on the outlines of the sample and the inlet aperture in the Ross filter.

In one recommended embodiment, each counter to measure the intensity of the diffracted and Compton scattered radiations contains two separate time-measurement instruments, one making an absolute measurement and the other operating in relation to the periodicity of the electrical current.

In apparatuses to analyze samples weighing considerably less than 1 gram, the sample holder may consist of a thin film of a material with a very low scatter coefficient, such as a sheet of polypropylene approximately 0.5 microns thick.

It will be easier to understand the invention from the following description of two possible embodiments of the X-ray crystallographic apparatus.

FIG. 3 shows an assembly of means of measuring the intensity of diffracted X-rays and Compton scattered X-rays.

The plan of the figure is the optical symmetry plane of the assembly, which comprises an X-ray glow-tube (1), with a divergent slit (2), a sample (3) on a sample-holder (4), which can rotate about an axis (5) situated in the plane of the irradiated surface of the sample and perpendicular to the plane of the figure.

A device (6) to receive and measure the diffracted X-rays is fixed to a goniometer arm (7), which can rotate on the same axis (5). This device consists of three components: an inlet slit (8), a curved monochromating crystal (9), and a radiation counter (10). The relative positions of these components are fixed by setting the device (6) for a given wavelength, such as that of the diffracted line for copper, $\text{Cu K}\alpha$. By means of a mechanism not shown here, the goniometer arm (7) revolves round the axis (5) at an angle of 2θ when the sample turns on the same axis by an angle of θ .

A device (11) to receive and measure the Compton scattered X-rays is fixed to an adjustable arm (12), which also rotates on the same axis (5). This arm (12) is adjusted in such a way that the angle of deviation between the prolongation of the incident beam striking the sample and the Compton scattered beam is as wide as possible (approximately 160° on this figure).

This device consists of three components: an inlet slit (13), a curved monochromating crystal (14), and a radiation counter (15).

The relative positions of these three components are adjusted by setting to the Compton scattered wavelength corresponding to the incident wavelength $\text{Cu K}\alpha$.

The radiation counters (10 and 15) are connected alternately, by means of a double contactor (16) to a counting cell (17), followed by a memory cell (18). These two cells are equipped with means of processing the data collected by the radiation counters, so that results can be stored in the recording unit (19).

An electronic control unit, not shown here, emits the orders for the various phases of the measurement and processing program.

FIG. 4 shows an assembly of means of measurement, comprising a device (6) to receive and measure diffracted X-rays identical to the one in FIG. 3, and a device (11) to receive and measure the intensity of Compton scattered X-rays, the three components of which are an inlet slit (13) a double Ross filter (20) and a radiation counter (15), on the path of the Compton scattered X-rays forming the largest possible angle with the incident X-ray beam (approximately 160° in FIG. 4).

The means of processing and using the measurements taken by the radiation counters (10 and 15) in FIG. 4 are the same as those in FIG. 3.

FIG. 4a shows a double Ross filter.

The principle of this double filter is to carry out two successive measurements, using a radiation counter, of the intensity of radiations not stopped by each of the filters, and work out the difference. The material for the two filters is selected so that their respective absorption edges or discontinuities occur on each side of the wavelength of the radiation to be isolated.

The two filters (21 and 22) are fixed in two apertures cut from a plate, which can be moved lengthwise between two slides (24 and 25), under the influence of an

electro-magnet (26), so that they are placed in turn on the path of the scattered radiation beam, as defined by the inlet slit (13).

Any other mechanical device producing the same result can be used, such as a revolving circular plate containing two apertures in which the filters are fixed, and which can be made to revolve.

When the scattered radiation corresponding to the diffracted line $\text{K}\alpha\text{Cu}$ has to be isolated, the first filter (21) is of gadolinium with a discontinuity (LII at 1510 A) or dysprosium with a discontinuity (LIII at 1577 A), and the second filter (22) is of cobalt, with a discontinuity (K at 1600 A).

When the scattered radiation corresponding to the diffracted line $\text{K}\alpha\text{Mo}$ is to be isolated, the filters (21 and 22) are selected from the following materials:

uranium with a discontinuity (LIII 0.720 A)

yttrium with a discontinuity (K 0.728 A)

protactinium with a discontinuity (LIII 0.742 A)

strontium with a discontinuity (K 0.770 A).

With apparatuses constructed in this way, diffraction measurements are recorded, with the contactor (16) in position 2, during the period in which the angle 2θ is increasing from 15° to 35° , with the sample turning from 7.5° to 17.5° , for instance.

Measurements of the intensity of the Compton scattered radiation are recorded, with the contactor (16) in position 1, as follows:

In the apparatus shown in FIG. 3, with a monochromating crystal of low luminosity, to obtain the highest intensity the measurement process consists first of maintaining the diffraction goniometer arm in the position in which the angle of deviation 2θ is maximum, and second of opening the divergent slit in the glow-tube to its maximum width.

When the measurement time has elapsed, the divergent slit in the glow-tube is reduced to its initial width, the diffraction goniometer arm returns to the minimum angle, by means of a fast return, and the sample is changed.

In the apparatus shown in FIG. 4, comprising a double Ross filter, which retains high luminosity, measurement of the scattered energy can take place during the period when the angle 2θ decreases from 35° to 15° , with the divergent slit in the X-ray glow-tube kept at the same width as during the diffraction measurement.

In both apparatuses, when changing from diffraction measurement to scatter measurement, the electronic control unit alters the sensitivity of the counting unit from about 4,000 pulses per second to about 50 pulses per second, and increases the time constant, from 2 to 8 seconds for instance. At the end of the measurement cycle it reduces the sensitivity and the time constant of the counting unit to their original values.

In addition to controlling the various measurement operations on a sample, the electronic control unit transfers measurements to a conventional recording system, such as a graph recording unit or a punched-card or magnetic-tape recording system, for use in a computer.

In this case, the counting cell comprises a device to integrate data for equal lapses of time, such as two seconds.

The starting impulse for a time unit triggers off a quartz clock and a decimal or binary counter, which receives the pulse. At the end of 2 seconds, the clock

blocks the counter and orders transfer of the number of pulses counted to a store, resetting of the counter and the start of scanning of the store. Each figure read is immediately transferred to the punched card or magnetic tape. The reading-writing operation lasts approximately 0.3 seconds, ending 2.3 seconds after the start of the time unit.

The starting impulse for the first diffractogram-counting time unit is given by the first pip from the angle marker on the goniometer, after it changes direction.

The time units follow one another every two seconds, until arrival at the limit stop on the goniometer arm. This stop causes blocking of the counting and data-output system.

The different phases of diffraction and scattering measurements take place according to the process selected, the limits being fixed by a clock connected to the supply current, which thus controls the duration of the measurement phases.

The purpose of using two time bases, one absolute, using a quartz clock for instance, and the other relative to the current, is to ensure that despite variations in the current frequency (± 2 percent), there is both a measurement of the number of pulses counted for a given time unit, which must be independent of these variations (the effective duration of counting must be absolute) and a correspondence between the goniometer angle and the serial number of the time unit involved, which remains perfect despite these variations, in order to determine the precise angle at which the diffractogram peaks appear.

Since the velocity of the motor driving the goniometer varies with the frequency of the current, the order of the time lapses must vary in the same way, and this is why the total duration of the cycle is set to the current.

A computing programme has been drawn up, for functions culminating in the recording of mass concentrations. This involves the following operations.

A diffractogram, cleared of stray impulses, and with the tops of the peaks smoothed into parabolae, is drawn. The beginnings and ends of the peaks are determined by detecting the slope variation after smoothing of the bottom. A sub-programme allows peaks that are not completely separated to be distinguished. After subtracting the base, one obtains a precise measurement of the net surface-area of each peak.

The total number of Compton pulses is calculated after removal of stray impulses.

The surface-area of each peak is divided by the Compton measurement, giving the equation defined above

$$(C = K I_d/I_c)$$

This quotient is compared with the reference curve for the corresponding constituent element, identified by means of the abscissa at the top of its characteristic peak. The percentage finally obtained is sent to the printing machine.

Analyses using copper radiation ($K \alpha$ Cu) or molybdenum ($K \alpha$ Mo) have been carried out on samples prepared with 20 percent quartz in a wide variety of materials, ranging from lithium tetraborate ($\mu = 8\text{cm}^2 \cdot \text{g}^{-1}$) to ferric oxide ($\mu = 215\text{cm}^2 \cdot \text{g}^{-1}$) whereas, with very few exceptions, μ is between 20 and $150\text{cm}^2 \cdot \text{g}^{-1}$ for

rocks. The results obtained are at most about 2.5 away from the real value.

Analysis of the non-crystalline fraction, using the process proposed by the invention, is carried out by taking surface-area measurements of the halo for values of 2μ between 0° and 180° .

In practice, measurement from 10° to 100° is satisfactory and in some cases a much smaller range, for example 15° to 40° , is enough.

FIG. 2a corresponds to an organic material with an absorption coefficient μ of $7\text{cm}^2 \cdot \text{g}^{-1}$ and 2b corresponds to an amorphous silica with an absorption coefficient μ of $32\text{cm}^2 \cdot \text{g}^{-1}$

Analysis of the amorphous fraction of samples containing these constituent elements is possible with an error of 30 percent, whereas earlier results were barely qualitative.

Insufficiently thick samples, which means that the thickness cannot be regarded as infinite for Compton scattering, like samples with a smaller surface-area than the sample-holder, affect the two measurements, of the intensity of diffracted energy and of Compton scattered energy, in the same proportion. This results in compensation for these effects at the stage of calculation of the percentage of constituent element in the sample, since this percentage is obtained by the ratio between the two energy intensities:

$$I_d = K \cdot m \cdot C / \mu \text{ and } I_c = K' \cdot m / \mu, \text{ whereas } I_d/I_c = K'' C$$

The process and device offered by this invention can be used both for reflection diffractometry, as described earlier, and for transmission diffractometry.

What is claimed is:

1. An x-ray crystallographic process comprising, measuring the intensity of the radiation (I_d) diffracted by each constituent element of a sample, identified qualitatively by its angle of diffraction, measuring the intensity of the Compton radiation (I_c) scattered by the whole sample, and determining the content C of each element as the ratio of the intensity I_d with respect to the intensity I_c .

2. A process for analyzing the amorphous fraction of a sample, as defined in claim 1, in which the value of the ratio of I_d to I_c , namely, I_d/I_c is entered on a diagram in a continuous curve, related to the angle of diffraction, and the ratio of the mass of non-crystalline matter to the mass of crystalline matter in the sample is determined as the ratio of the surface area between the scatter halo curve and the abscissa axes to the surface area between the diffraction peaks and the same abscissa axes.

3. An x-ray crystallographic apparatus, comprising an x-ray glow-tube for irradiating a sample with an incident beam, a sample holder, and instrument to measure the intensity of the diffracted radiation, comprising a diaphragm, monochromating crystal and radiation counter, attached to a goniometer arm with the same rotational axis as the irradiated sample, means for adjusting the angle of the monochromating crystal and radiation counter in relation to the goniometer arm, an instrument to measure the intensity of the Compton scattered radiation, comprising a diaphragm, frequency-band selector and radiation counter, attached to a second arm means for adjusting the second arm in the direction of the irradiated sample to a certain angle with the incident beam, means for adjusting the angle

of the frequency-band selector and radiation counter in relation to the adjustable arm, and means to determine the content of a constituent element of the sample in response to the measured intensities.

4. An apparatus as defined in claim 3, in which the frequency-band selector of the Compton scattered radiation comprises a monochromating crystal preceded by an inlet diaphragm, the width of which is such that the monochromating crystal will select a wave band comprising at least 80 percent of the Compton radiation emitted by the sample.

5. An apparatus as defined in claim 3, in which the X-ray glow-tube has a divergent slit wide enough to allow irradiation of the total surface area of the irradiated sample.

6. An apparatus as defined in claim 3, in which during measurement of the intensity of the Compton scat-

tered radiation the position of the sample is maintained at an angle corresponding to the maximum angle of diffraction.

7. An apparatus as defined in claim 3, in which the frequency-band selector of the Compton scattered radiation comprises a double Ross filter.

8. An apparatus as defined in claim 3, in which each counter to measure the intensity of the diffracted and Compton scattered radiations contains two separate time-measurement instruments, one making an absolute measurement and the other operating in relation to the periodicity of the electrical current.

9. An apparatus as defined in claim 3, in which the sample holder consists of a thin film of a material with a very low scattering coefficient.

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