

USE OF A LINEAR LOCALIZATION DETECTOR FOR X-RAY DIFFRACTION OF VERY SMALL QUANTITIES OF CLAY MINERALS

Key Words—Alcohol, Corrensite, Instrumentation, Linear localization detector, X-ray powder diffraction.

X-ray powder diffraction patterns of very small quantities of mineral materials (10^{-1} to 10^{-2} mg) could be obtained, until recently, only by a step-scanning method (Meunier and Velde, 1982; Beaufort *et al.*, 1983). Accurate determinations of the d -values in the small-angle range were effective using a counting-time of 200 s for each scanning step. Several problems, however remained unresolved: (1) Using the above conditions, the acquisition time was about 16 hr 40 min for a $15^\circ 2\theta$ scan. (2) Ordinary proportional detectors were not sensitive enough to provide an accurate resolution (peak/background ratio) for the weak-intensity reflections. (3) Peak resolution in the vicinity of the incident beam ($<3^\circ 2\theta$) could not be improved even with highly energetic $\text{CoK}\alpha$ radiations.

To overcome these problems, a linear localization detector of X-rays (Elphyse) in place of a proportional detector (Philips 1965/60) was developed. The present report describes the apparatus and compares the results obtained with it with those obtained with a classical proportional detector.

EXPERIMENTAL

Principle of the linear detector

The linear detector consists of a detection cell containing two amplifiers. The detection cell is composed of a resistive cathode surrounding an anode wire which is connected to high voltage (1720 V); the detector gas is xenon (90%) and carbon dioxide (10%). The anode signal created by X-ray photons controls the exact count-rate of X-rays radiating over the detector. The pulses from both sides of the cathode serve to calculate the position of the X-ray photon impact (delay-line readout method). The pulses pass through the two amplifiers; the difference in time between the two signals created is first converted into a voltage and then into binary values coded on 12 bits.

Experimental assembling

The linear localization detector was fixed on the worm wheel (2θ movement) of a Philips 1050/25 vertical goniometer. Experiments were performed with a Philips 1730 generator. The X-ray incident beam ($\text{CoK}\alpha$, 40 mV, 40 mA) was focused using a collimator 0.8 mm in diameter which gives a $8 \text{ mm} \times 2 \text{ mm}$ irradiated area at $2^\circ 2\theta$.

Sample holder

The sample was placed into the specimen holder (Figure 1). The solid angle explored by the detector

varied with its distance from the goniometer axis (d'). It was equal to $14^\circ 2\theta$ when the detector was located at 20.05 cm from goniometer axis (d). Under these conditions, each degree 2θ was represented by 73 dots on the spectra (distance between two successive dots corresponded to $0.014^\circ 2\theta$). The real intensities of peaks were recorded if the sample oscillated regularly around the position. The oscillations of θ movement were derived by a programmable controller (Omrom Sysmac S6) to select the central point, the amplitude, and the oscillation speed.

A lead thin plate was fixed on a micrometric movement perpendicular to the sample to avoid scatter near the direct beam near $3^\circ 2\theta$ and to improve the peak/background ratio. Micrometric movement allowed the exact and reproducible location of the lead plate above the sample.

Data processing

Spectrum data were stored in a 512 to 4096 multi-channel analyzer and processed using a Victor (Sirius) microcomputer. The diffraction patterns were analyzed into a 1024 channel system and were treated by programs which allowed the peaks to be indexed, background subtraction, and peak deconvolution. Spectra were reproduced using a dot-matrix printer.

EXPERIMENTAL RESULTS

To estimate the possibilities of the linear localization detector in the classical angular range for the identification of clay minerals (2° – $16^\circ 2\theta$), experiments were performed using oriented specimens of an organic product ($\text{C}_{18}\text{H}_{37}\text{OH}$) and a regular chlorite/smectite mixed-layer mineral: corrensite from altered granite (Langenberg, Vosges, eastern France). The 060 corrensite reflection was also recorded in the 68° to $74^\circ 2\theta$ angular region.

The use of the long-chain alcohols $\text{C}_{18}\text{H}_{37}\text{OH}$ was recommended by Brindley and Wan (1974) to test the accuracy of X-ray powder diffraction (XRD) peak position at small angles. An oriented sample was prepared from a solution. The organic chains crystallize in very thin layers; and reflections, at small angles, may be recorded at 49.9 and 41.3 Å. The XRD patterns obtained with the linear detector (Figure 2a) suggest that the 49.9-Å reflection was clearly distinct from the incident X-ray beam; the same reflection could not be differentiated from the incident X-ray beam by means of a proportional counter detector (Figure 2b).

XRD patterns of clay minerals usually require sev-

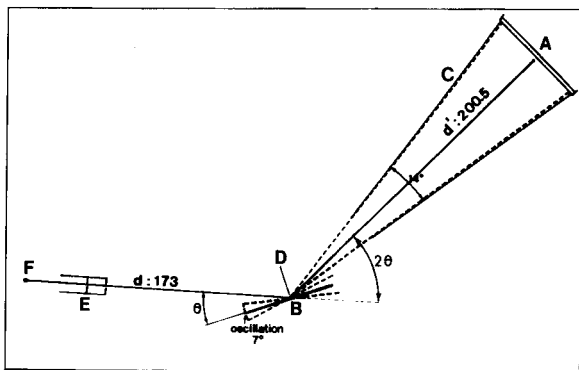


Figure 1. Diagram of the experimental apparatus showing linear localization detector (A), goniometer axis (sample holder—B), anticatter apparatus (C), thin lead plate (D), the collimator (E), and X-ray source (F). *d* and *d'* are the distance from source to goniometer axis, and goniometer axis to counter cell (unit = mm), respectively.

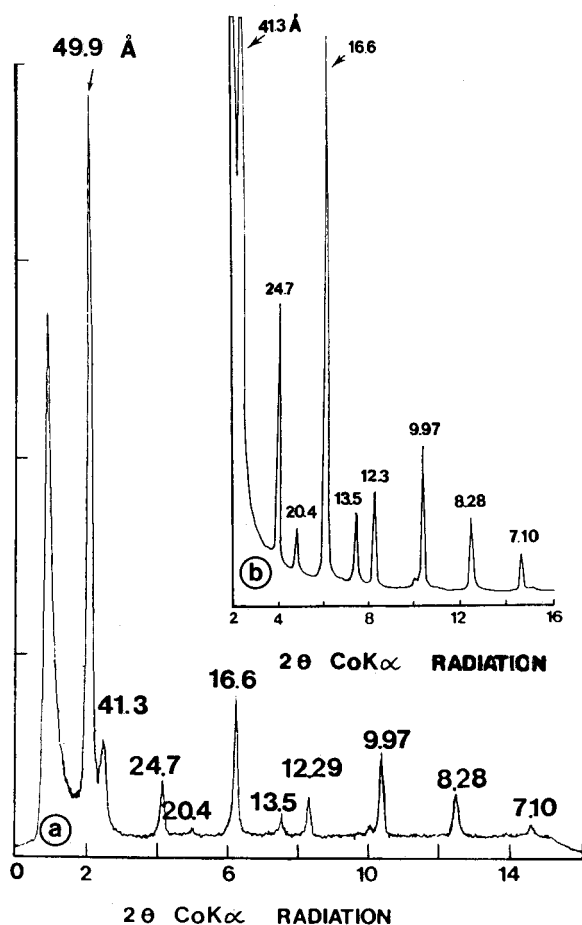


Figure 2. (a) X-ray oriented powder diffraction diagram of the alcohol $C_{18}H_{37}OH$ recorded by the linear detector between 1° and $15^\circ 2\theta$. (b) X-ray oriented powder diffraction diagram of the alcohol $C_{18}H_{37}OH$ recorded with a proportional detector (PW 1965/60) between 2° and $18^\circ 2\theta$.

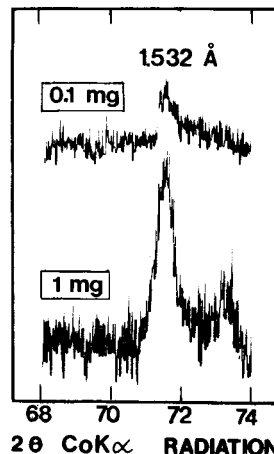


Figure 3. X-ray powder diffraction diagram of corrensite (1 and 0.1 mg) showing the 060 reflection measured with the linear detector between 68° and $74^\circ 2\theta$.

eral milligrams of material (Paterson *et al.*, 1986). XRD analyses were made for the 68° – $74^\circ 2\theta$ region to allow the determination of the weak 060 corrensite reflection (Figure 3). The 060 reflection obtained with 0.1 mg of corrensite material required 2 hr of exposure.

Oriented corrensite preparations

To test the performances of the linear detector on very small samples, experiments were performed on a series of corrensite quantities. Oriented samples yielded increased intensities for the 001 reflections and,

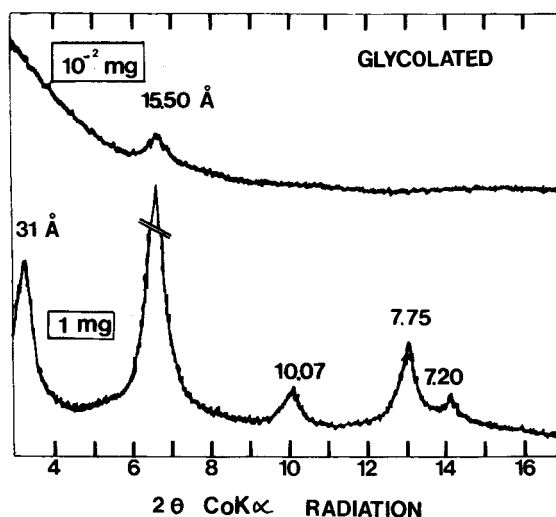


Figure 4. X-ray diffraction diagram of corrensite (1 and 0.01 mg) from an oriented sample recorded with a classical proportional detector (PW 1965/60). Ethylene glycol-solvated samples. Analyzing time = 1 hr. $CoK\alpha$ radiation $\frac{1}{4}^\circ 2\theta/\text{min}$, $\frac{1}{4}$ cm/min. This sample contains small amounts of illite (10.07 Å) and kaolinite (7.20 Å).

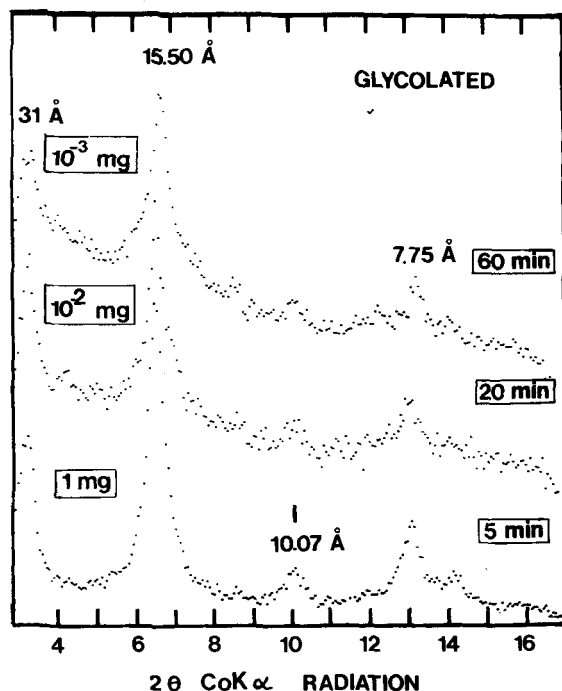


Figure 5. X-ray diffraction diagrams of corrensite from an oriented sample with decreasing quantities (1, 0.01, 0.001 mg) obtained with the linear detector. Analyzing times are indicated.

therefore, less material was required for XRD patterns of oriented samples. It was necessary to concentrate these preparations on an area equal to $\frac{1}{3}$ of the irradiated area (2×8 mm).

The diagrams given in Figure 4 (1 and 0.01 mg of corrensite) were obtained after 1 hr of exposure with a classical proportional detector. The results with 0.01 mg were not resolved sufficiently for identification of the corrensite structure: a band was found instead of the most intense reflection (15.5 \AA), and the other reflections were not present.

Figure 5 shows XRD patterns of decreasing corrensite quantities (1, 0.01, 0.001 mg) obtained with the linear detector. The resolution of reflections with 0.001 mg of material allowed on accurate identification of the corrensite structure; compared to basal reflections, the low intensities of the long-spacing reflection (31 \AA) may be due to very thin stacking sequences of clay layers.

CONCLUDING REMARKS

Compared with the results obtained using a classical X-ray powder diffraction apparatus, the method proposed in this paper allows definite improvements:

1. The lower limit of detection by X-ray powder diffraction is about 0.1 mg using a proportional detector and 0.001 mg using the linear detector. Consequently, the acquisition time is much reduced for routine XRD (e.g., 1 mg of material analyzed in 5 min over $14^\circ 2\theta$) by the use of linear detector.
2. The greater utility of this method results from the use of powder preparations similar to those employed in classical powder X-ray diffraction. The improvement is provided by the quantity of matter which is decreased by a factor of 100.
3. In petrology this new method allows the identification of clay minerals in their microsites if they are concentrated by microdrilling from areas selected under the optical microscope (Beaufort *et al.*, 1983); e.g., an extraction of 0.001 mg of material corresponds to a volume of $100 \mu\text{m}$ by $30 \mu\text{m}$.

This method complements chemical microanalyses (e.g., microprobe analyses) and allows an accurate determination of mineral species at the microsite scale.

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