

A METHOD TO ELIMINATE THE BACKGROUND IN X-RAY DIFFRACTION PATTERNS OF ORIENTED CLAY MINERAL SAMPLES

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(Received 15 June 1981)

ABSTRACT: A method is described for calculating, and then subtracting, the background from X-ray diffraction patterns of oriented clay mineral samples. Ti- $K\alpha$ radiation is used and, to minimize the absorption of this radiation by air, a vacuum and helium-flushed device has been developed. This device can be used with other X-ray sources, offering a considerable increase of intensity—e.g. Co- $K\alpha$ radiation is increased by 125%. With the background-eliminated patterns a better semi-quantitative estimate of the composition of clay mineral mixtures is possible. Small differences in composition of two samples can be identified by subtracting one of the background-eliminated patterns from the other. Using this method, peak maxima of smectite-group minerals can also be accurately determined.

In order to estimate the clay mineral composition of sediment or soil samples, the intensities of some low-angle basal reflections of clay minerals on their X-ray diffraction patterns are usually measured. At these low angles, the reflections are superimposed on a sharply decreasing background that has to be subtracted from the reflections. To improve this method, determination of the background is necessary.

In normal X-ray patterns measured with a suitable divergence slit (which provides a constant radiated volume at all angles), the background is composed of (Fig. 1)—(a) incoherent radiation: Compton diffusion (3), fluorescent radiation (4) and temperature-diffuse scattering (3) (Cullity, 1967); (b) apparatus-dependent factors: incident beam (5) and air scatter (6); (c) total reflection (7) (Guinier, 1956). The reflections in the X-ray pattern caused by coherent radiation result not only from the 00 l reflections of the clay minerals but also from diffraction by small particles (1), micro-pores (1) (Tchoubar & Méring, 1969) and crystal defects (2) (Pons, 1980; Pons *et al.*, 1980). Although the last three effects cannot strictly be regarded as background, they often are regarded as such because they cannot be distinguished from the real background. The background effects mentioned above are also influenced by the Lorenz-polarization factor (6), the absorption factor (4) and the atomic scattering factor (8). On X-ray diffraction traces, the sum of the effects 1 to 8 results at low angles in a curve more or less represented by curve 9 of Fig. 1.

On X-ray patterns obtained with Co- $K\alpha$ radiation, the true background is often only visible from $\sim 16^\circ 2\theta$. To estimate the background on the low-angle side of the 00 l reflections of clay minerals in X-ray diffraction patterns we chose Ti- $K\alpha$ radiation ($\lambda = 2.74973 \text{ \AA}$). Measured at 50% relative humidity (r.h.), the 001 smectite reflection then gave its maximum at $\sim 11^\circ 2\theta$. This peak shift makes part of the background on the low-angle side of the pattern visible. To obtain a suitable diffracted intensity at the angles

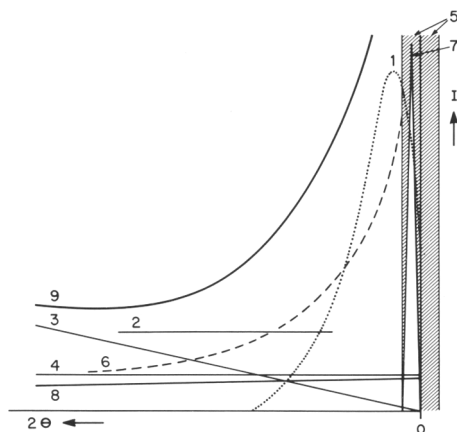


FIG. 1. Factors contributing to 'background' in normal X-ray diffraction patterns. It is assumed that the irradiated volume is kept constant at all angles and the total reflection peak is overlapped by the incident beam. (1) small particles, micro-pores; (2) crystal defects of large spacing minerals; (3) Compton diffusion, temperature diffuse scattering; (4) fluorescent radiation, absorption factor; (5) incident beam; (6) Lorenz-polarization factor, air scatter; (7) total reflection; (8) atomic scattering factor; (9) 'background' resulting from the combined effects 1-8.

at which the clay mineral reflections are measured, and also to avoid the influence of the incident beam on the pattern, an automatic divergence slit system (ADSS) was used. This device varies the divergence continuously, so that, whatever the angle of the goniometer, the same area is irradiated; this results in a decreasing irradiated volume with decreasing angle. Thus with decreasing angle there is: (a) a progressive decrease of the temperature-diffuse scattering; (b) a slowly increasing Lorenz-polarization factor effect; (c) a decrease in the absorption factor effect; (d) a slight decrease in the atomic scattering factor effect. This 'ADSS effect' is also accompanied by a decrease in the diffracted intensity from the small particles, micro-pores and crystal defects. With the method described in this paper, Compton diffusion and fluorescent radiation were prevented from reaching the counter by using a crystal monochromator between the sample and the detector. Air-scatter was avoided by flushing the specimen chamber with helium.

To determine the form of the background curve, we analysed the X-ray patterns of a kaolinite, two smectites of different crystallinity, some size fractions from two sediment

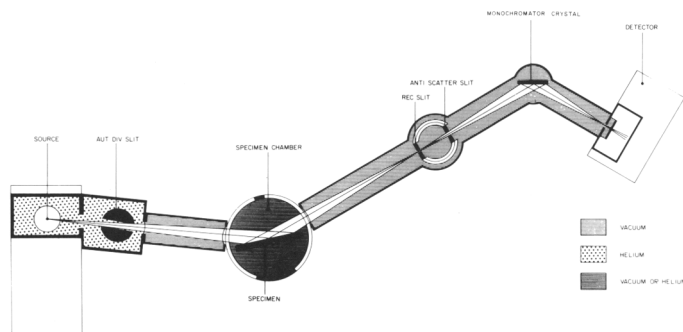


FIG. 2. Schematic view of the vacuum-helium device.

samples and a ceramic tile sample holder. Using a computer, the background was calculated for all patterns from the formula $y = Ax^B$. The background values were subtracted from the original pattern and the background-eliminated pattern plotted.

If the peak to background ratio is low in normal X-ray patterns, the peak values are often shifted to higher \AA values. With this method more accurate peak values were obtained.

Because of the high level of absorption of $\text{Ti-K}\alpha$ radiation by air, a device was developed in which a part of the X-ray path is evacuated and another part is helium-flushed (Fig. 2). With this device the intensity of the $\text{Ti-K}\alpha$ radiation was increased 200 times. An increase of this magnitude was necessary to obtain a workable pattern.

MATERIALS AND METHODS

The background was determined on $<2\ \mu\text{m}$ fractions of a kaolinite from Provence, France, a montmorillonite from Wyoming, USA, a smectite from Ethiopia, 2–0.5, 0.5–0.2, <0.2 and $<0.05\ \mu\text{m}$ fractions from a sediment 50 cm from the top of a core from the North Atlantic, $<2\ \mu\text{m}$ fractions from this sediment and also from a sediment 25 cm from the top of the same core, and, finally, a ceramic tile sample holder. The sediment and smectite fractions were Ca-exchanged. Oriented samples were prepared on polished porous ceramic tiles (Dümmler & Schröder, 1965) and dried at room temperature. X-ray runs were carried out at 50% r.h. and also after glycolation. The r.h. was kept constant with a humidity generator developed at our institute. An X-ray generator PW 1730 with

TABLE 1. Apparatus and experimental conditions.

X-ray tube	Broad focus Co-tube, PW2256/20 (Philips)	Broad focus Ti-tube, PW2250/22 (Philips)
Rating	40–50 kV and 40–50 mA	25 kV and 48 mA
Window tube	Be, 300 μm	Be, 150 μm
Divergence slit	0.5°	ADSS PW1386/50 (Philips) open at 0.3° 2θ
Receiving slit	0.2 mm	0.2 mm
Anti-scatter slit	1°	1°
Monochromator	Graphite, AMR	Graphite, AMR
Counter	Proportional, PW1965/60 (Philips)	Proportional krypton counter with a signal amplifier, 60 \times
Counter window	Mica	Be, 150 μm
X-ray path	Vacuum (1 mm Hg)	Vacuum (1 mm Hg)
Window vac. part	6 μm Mylar foil	6 μm Mylar foil
Specimen chamber flushed with	Air, 50% r.h., 150 ml min^{-1}	Helium, 50% r.h., 150 ml min^{-1}
Scanning speed	0.5° $2\theta\ \text{min}^{-1}$	Stepscan, 4 sec 0.02° $2\theta^{-1}$
Scanning range	3–16° 2θ	0–30° 2θ
Scanning time	26 min	140 min
Recording	Recorder PM 8203 (Philips)	Computer, Tektronix 4051, floppy disc unit (File Manager Tektronix) and plotter

channel control PW 1390 and motor control PW 1394 (Philips) was used; apparatus constants are given in Table 1. The Simple Linear Regression Program (*Statistics 1*, Tektronix) was used to estimate the shape of the background.

RESULTS

Using the reflection method in combination with the ADSS implies that the irradiated sample volume decreases with decreasing angle. Because small particles, micropores and crystal defects show their diffraction effects at low angles, they will only slightly affect the part of the X-ray diffraction pattern studied. To eliminate any interference from these low-angle diffraction effects, a well-ordered kaolinite sample was chosen as a starting point for determining the background. Applying the ADSS, the graphite monochromator and the vacuum-helium device, the background on this sample comprises only the temperature-diffuse scattering, the absorption factor, the Lorenz-polarization factor and the total reflection, influenced by the ADSS effect.

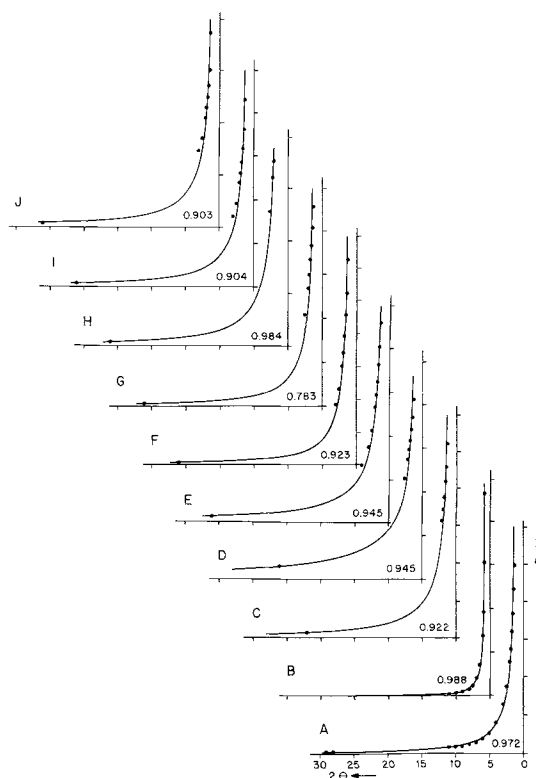


FIG. 3. Background curves calculated from X-ray diffraction pattern values, represented by dots, compared with curves calculated from the formula $y = Ax^B$. A = kaolinite, Provence; B = ceramic tile; C = montmorillonite, Wyoming; D = smectite, Ethiopia; E = $2-0.5 \mu\text{m}$, F = $0.5-0.2 \mu\text{m}$, G = $<0.2 \mu\text{m}$, H = $<0.05 \mu\text{m}$ sediment fractions; I = $<2 \mu\text{m}$ sediment fraction (E-I all from 25 cm depth in North Atlantic core); J = $<2 \mu\text{m}$ sediment fraction from 50 cm depth in the same core. The values shown are R^2 values, which reflect the fit of the calculated curve with the measured values.

For smectite-containing samples, the r.h. strongly influences the effects caused by 1 and 2 in Fig. 1. Both low and high humidities result in an increase of the diffracted intensity in the $1-4^\circ 2\theta$ region.

This was not found with the kaolinite sample and only a small deviation was observed from $1-2.5^\circ 2\theta$ when it was glycolated. Glycolation of the smectites and the smectite-containing sediment samples masked the background between the 001 peak and $1^\circ 2\theta$. Because this part of the pattern is very important for obtaining background values, we decided to carry out the measurements for estimating the background at 50% r.h. Under these conditions the background is least obscured by the coherent radiation caused by the clay minerals. The background measurements were started at $0^\circ 2\theta$, although below $1^\circ 2\theta$ the measured values are influenced by inaccurate opening of the ADSS. In the patterns of the $>0.05 \mu\text{m}$ sediment fractions in Figs 5, 6 and 7 and that of the smectite in Fig. 5, the total reflection peak can be seen at about $1^\circ 2\theta$ where the background is not eliminated. In some cases a peak, caused by a part of the incident beam, can be seen at about $0.5^\circ 2\theta$ (in Fig. 5, $2-0.5 \mu\text{m}$ sediment fractions; in Fig. 6, <0.2 and $<0.05 \mu\text{m}$ sediment fractions and the Ethiopian smectite). The peak caused by the total reflection is partly included in the background measurements. The incident beam had no influence on it.

The formula $y = Ax^B$, in which x and y represent the coordinates of the measured values in the diagrams and A and B are constants, appeared to describe the background most accurately (Fig. 3).

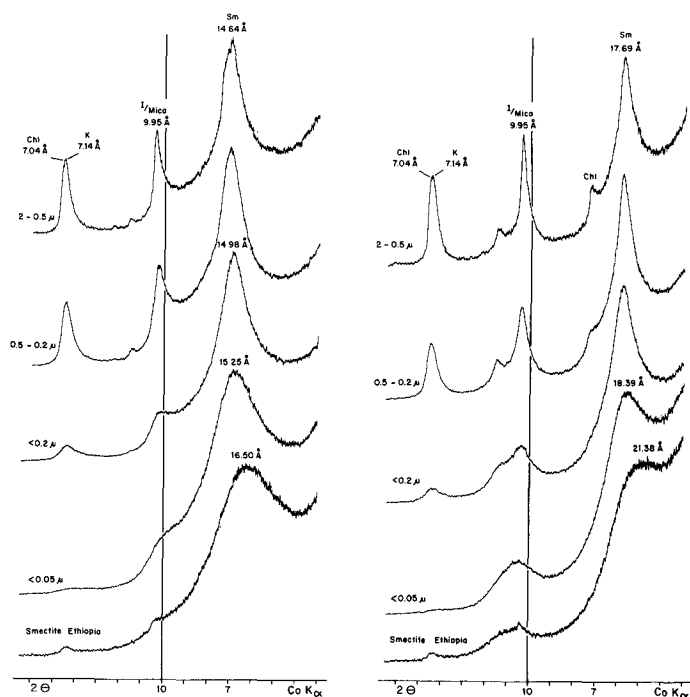


FIG. 4. X-ray diffraction patterns of the sediment fractions and the Ethiopian smectite, run with Co-K α radiation at 50% r.h. (left) and after glycolation (right). Chl=chlorite, K=kaolinite, I=illite, Sm=smectite.

Fig. 3, curve A, shows the very good fit of the diffraction curve of the kaolinite sample with the curve calculated from the measured values. A near perfect fit was also found for the empty ceramic tile (Fig. 3, curve B). In this case we were able to measure the background from 0.7° 2θ , probably due to the very flat surface of the tile. At angles $>6^\circ$ 2θ , the background increased because of the temperature-diffuse scattering, the absorption factor and the atomic scattering factor influenced by the ADSS effect. In this curve we measured the background between 0.7° and 6° 2θ . The slight background increase was also observed in the X-ray patterns of Figs 5, 6 and 7 but could be ignored in

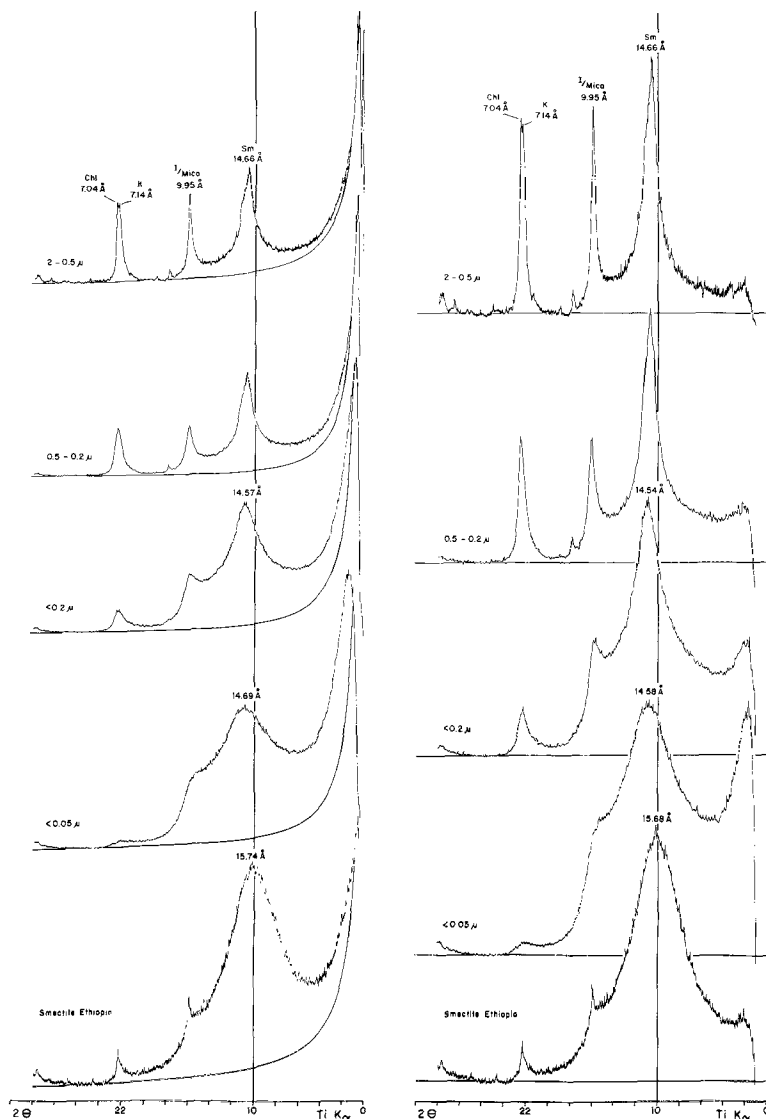


FIG. 5. X-ray diffraction patterns of the sediment fractions and the Ethiopian smectite, run with Ti-K α radiation and the vacuum-helium device at 50% r.h. before (left) and after (right) background elimination. Chl=chlorite, K=kaolinite, I=illite, Sm=smectite.

background calculation. With decreasing particle size a smaller part of the X-ray pattern could be used for background values, due to the increase in width of the smectite peak and an increasing amount of this mineral in the sample. Thus one background value between 3° and 4° 2θ on each of the curves E, I and J (Fig. 3) showed a small deviation because of this. The calculation of curve H (Fig. 3) from only the four values 1.8 , 2.0 , 2.5 and 26° 2θ , yielded a very good R^2 value (the R^2 values reflect the fit of the calculated curve to the measured values). However the X-ray pattern from this sample shows a peak at about 1.4°

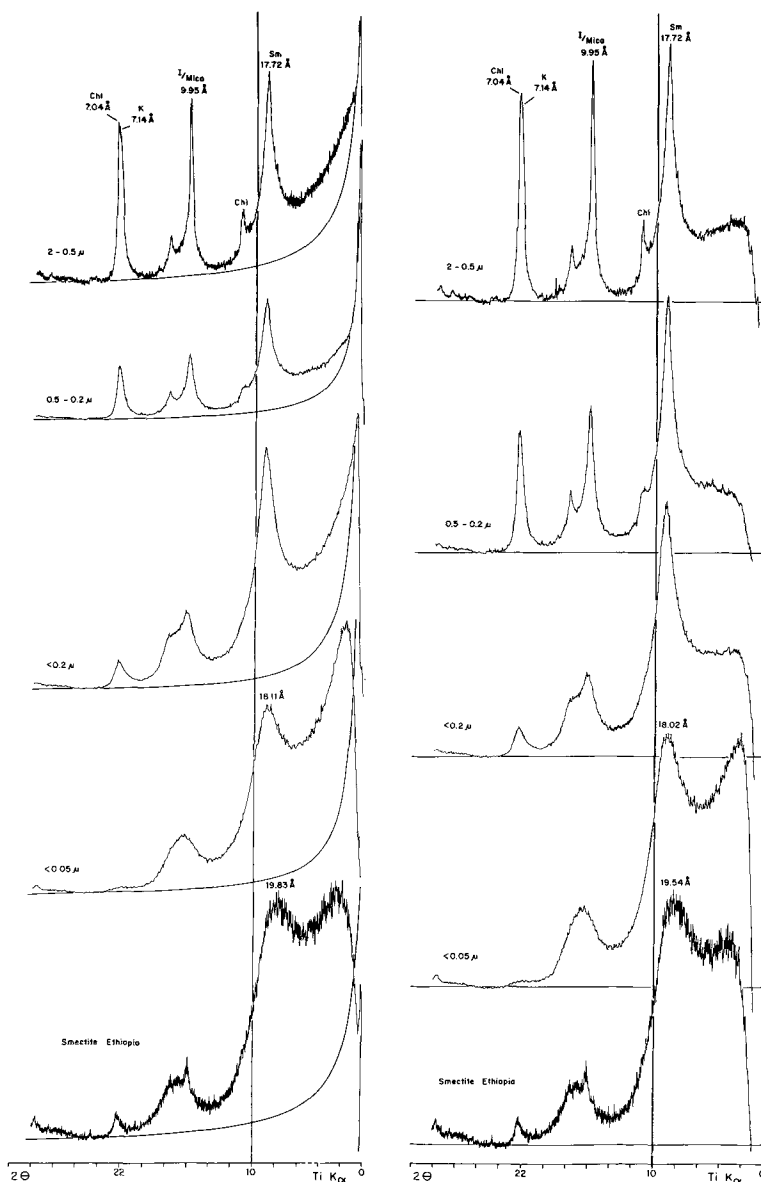


FIG. 6. Same samples as in Fig. 5 after glycolation before (left) and after (right) elimination of the background. Chl=chlorite, K=kaolinite, I=illite, Sm=smectite.

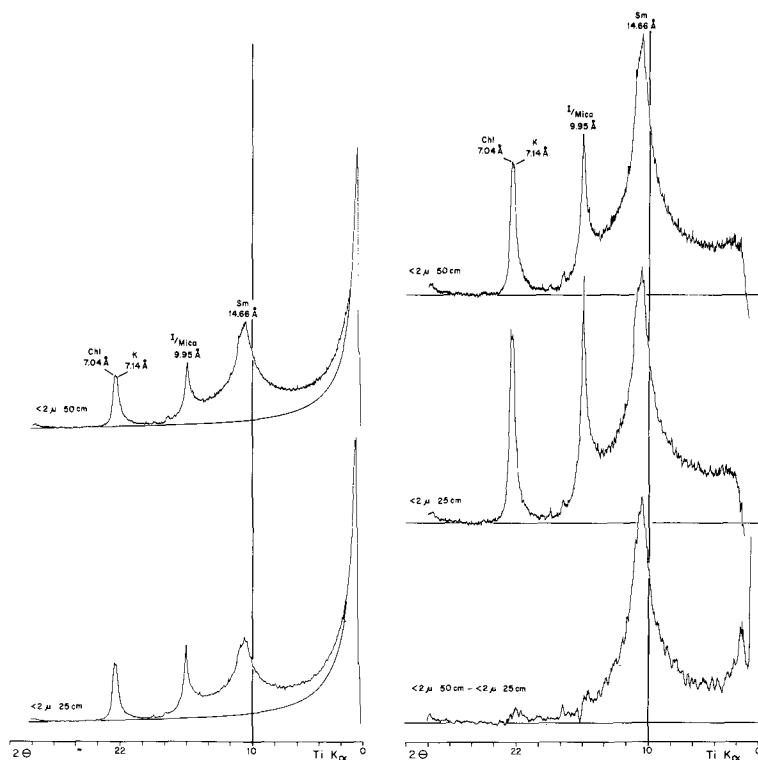


FIG. 7. X-ray diffraction patterns of the $< 2 \mu\text{m}$ sediment fractions from 25 and 50 cm depth run with $\text{Ti-K}\alpha$ radiation and the vacuum-helium device at 50% r.h. Left side before and right side after background elimination. The vertical scale of the background-cleared patterns was 'equalized' with the 001 kaolinite reflections and subtracted.

2θ , which slightly obscures the $1^\circ 2\theta$ background value. This peak, caused by coherent radiation from small particles, micro-pores and crystal defects, cannot be regarded as belonging to the background. In such a case the $1^\circ 2\theta$ value has to be used as this approaches the real background much closer than the 1.8 , 2.0 and $2.5^\circ 2\theta$ values.

Figs 5 and 6 show the patterns of the sediment samples and the Ethiopian smectite obtained with $\text{Ti-K}\alpha$ radiation and the vacuum-helium device, with and without background. The $\text{Ti-K}\alpha$ radiation, gives much better peak resolution, as can be seen by comparing the patterns in Fig. 4.

The result of subtracting the background-eliminated patterns of two $< 2 \mu\text{m}$ sediment fractions is shown in Fig. 7. Peak value corrections are shown in Table 2. Using $\text{Ti-K}\alpha$ radiation with the whole vacuum-helium device, the intensity was increased 200 times. $\text{Co-K}\alpha$ radiation, in combination with the vacuum part of the device, showed an intensity increase of 90%. When the other part was simultaneously flushed with helium, the intensity increase was 125%. The intensity of $\text{Co-K}\beta$ radiation increased about 100% using both vacuum and helium. The specimen chamber can also be evacuated or flushed with other gases, provided that they do not attack the Mylar windows.

The scanning time for one sample is 140 min (Table 1). This long scanning time is due to: (1) the stepscan method, because for computer calculations the counts have to be in

TABLE 2. Ångstrom values of the smectite peaks from the sediment samples and the Ethiopian smectite run Co-K α radiation and Ti-K α radiation. Δ = values with background, — = values without background.

	Co-K α radiation		Ti-K α radiation			
	50% r.h.	glycolated	50% r.h.		glycolated	
	Δ	Δ	Δ	—	Δ	—
2-0.5 μm	14.66	17.69	14.66	14.66	17.72	17.72
0.5-0.2 μm	14.64	17.69	14.64	14.64	17.66	17.66
< 0.2 μm	14.98	17.69	14.57	14.54	17.70	17.66
< 0.05 μm	15.25	18.39	14.69	14.58	18.11	18.02
Smectite, Ethiopia	16.50	21.38	15.74	15.68	19.83	19.54
< 2 μm , 25 cm	14.66	17.69	14.66	14.66	—	—
< 2 μm , 50 cm	14.70	17.72	14.66	14.66	—	—

digitized form; (2) the number of counts required to obtain a workable difference pattern; (3) the large scanning range (from 0–30° 2 θ). Because of the digitized storage of the counts by the computer, the X-ray generator can constantly be used at a maximum rating, i.e. the rating is not any longer constrained by the size of the X-ray pattern in relation to the width of the recorder paper.

DISCUSSION

Using the method described above, the background of X-ray patterns from oriented clay mineral samples can be calculated accurately from the formula $y = Ax^B$, utilizing the diffraction curve values between 1–1.5° 2 θ and 26° 2 θ . The best results are obtained when the samples are measured at 50% r.h. With samples containing considerable amounts of very small particles, the 1° 2 θ value of the diffraction curve may be somewhat high, resulting in a small deviation of the calculated background at the lower angles.

After the background is calculated it can be subtracted from the original pattern. The method was applied to the sediment fractions and to the Ethiopian smectite, run at 50% r.h. (Fig. 5). As can be seen in the patterns after background elimination, the diffracted intensity between 1 and 5° 2 θ increases with decreasing fraction size. This effect can be caused by: (1) a decrease in particle size; (2) an increase in the amount of micro-pores and a decrease in micro-pore size; (3) increase in amount of crystal defects. The phenomena mentioned under (1) and (2) shift their reflections towards larger angles with decreasing fraction size, resulting in a diffraction maximum at 1.8° 2 θ in the < 0.05 μm fraction of the North Atlantic sediment. Phenomenon (3) decreases with decreasing angle, due to the ADSS effect. The curve of the Ethiopian smectite is nearer to the baseline at the same low-angle region than the curve of the < 0.05 μm sediment fraction, although their smectite peak size and peak width are about the same.

With the glycolated samples this same increase, somewhat enhanced, can be observed (Fig. 6). Due to glycolation, the reflections caused by the phenomena mentioned above

shifted. The smectite peak also shifted toward lower angles, causing peak overlap with the low-angle maximum.

The advantage of eliminating the background of X-ray patterns is shown in Fig. 7. To calculate the difference in clay mineral composition, the background-eliminated pattern of the $< 2 \mu\text{m}$ fraction of the sediment from 25 cm in the core was subtracted from that at 50 cm and the difference curve, smoothed over five measurements, plotted (Fig. 7). Before subtraction the vertical scale of the two curves was determined in order to equalize the average value of the peak interval between 22.30 and $22.42^\circ 2\theta$ (the 001 kaolinite reflection).

The resulting difference curve, assuming equal amounts of kaolinite in both fractions, shows that the fraction from 50 cm depth contains more smectite than that from 25 cm depth. This curve shows also that a small peak remains at the low-angle side of the kaolinite and illite/mica reflections. This is probably due to a small difference between the properties of these minerals in the two samples. The peak at $1.5^\circ 2\theta$ indicates a small difference in the low-angle phenomena.

Due to the rapidly decreasing background, a smectite peak shift was observed with decreasing particle size in the X-ray patterns of the sediment samples obtained with Co- $K\alpha$ radiation (Table 2). This shift was absent in the X-ray patterns obtained with Ti- $K\alpha$ radiation. Both with Co- $K\alpha$ and Ti- $K\alpha$ radiation the Ethiopian smectite showed a peak shift; this was completely corrected after background subtraction of the X-ray pattern obtained with Ti- $K\alpha$ radiation.

To check that the amount of kaolinite was constant in the two sediment samples, an orienting internal standard was added. We obtained encouraging results with molybdenite, which with Ti- $K\alpha$ radiation gave its main peak at $\sim 26^\circ 2\theta$. In this case the $27\text{--}28^\circ 2\theta$ region was used for background calculations. Molybdenite has also been used as an internal standard in quantitative X-ray diffraction of clay minerals by Quakernaat (1970) and Cody & Thompson (1976).

CONCLUSIONS

A device has been developed to measure, at a few predetermined points, the background on the X-ray pattern of an oriented clay mineral sample. From the measured background values a background curve can be calculated with a formula $y = Ax^B$ and this subtracted from the original X-ray pattern. Slight differences in clay mineral composition can be detected by subtracting one of the two background-cleared patterns from the other. The advantages of this approach are enhanced when an orienting internal standard, such as molybdenite, is used.

Due to the rapidly decreasing background of X-ray patterns obtained with Co- $K\alpha$ radiation the smectite peak sometimes shifts to higher values. This effect is prevented by using the background elimination method on the X-ray patterns obtained with Ti- $K\alpha$ radiation.

The long wavelength Ti- $K\alpha$ radiation also gives better resolution. For all X-ray sources a considerable gain in intensity is obtained when the vacuum-helium device is used. $K\beta$ lines from X-ray sources can be used if the $K\alpha_1\alpha_2$ doublet hinders accurate measurements of the X-ray reflections.

This method and device offer interesting possibilities to clay mineralogists, sedimentologists and soil scientists interested in improving their quantitative analytical techniques.

ACKNOWLEDGMENTS

Thanks are extended to Mr F. Eijgenraam for devising the computer program; Mr F. Schilling for assistance in constructing the humidity generator; Dr D. Spitzer for his help in solving the mathematical problems; Mr B. Verschuur for drawing the figures and Drs D. Tchoubar and C. H. Pons of the University of Orléans, France, for their stimulating discussions. The manuscript was critically read by Drs J. H. F. Jansen and D. Eisma and typed by Mrs J. Hart. The authors are especially appreciative of the helpful comments of the staff of the X-ray application division, Philips, Almelo and of Dr W. H. Diemer of I & S, Philips, Eindhoven.

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RÉSUMÉ: On décrit une méthode de calcul du fond continu que l'on peut ensuite soustraire du cliché de diffraction X d'un échantillon d'argile orientée. On utilise le rayonnement Ti-K α ainsi qu'une enceinte étanche soit sous vide soit balayée par l'hélium afin de diminuer l'absorption de ce rayonnement par l'air. Cet appareillage peut être utilisé avec d'autres sources de rayons X permettant un accroissement important de l'intensité diffractée recueillie, par exemple l'efficacité du rayonnement CoK α est accrue de 125%. Les diagrammes corrigés de leur fond continu permettent une meilleure estimation quantitative de la composition de mélanges d'argiles. Des petites différences de composition de deux échantillons peuvent être identifiées en soustrayant l'un des diagrammes ainsi corrigés de l'autre. En utilisant celle méthode les maxima des raies des minéraux d'un groupe de smectites peuvent être déterminés avec précision.

KURZREFERAT: Es wird eine Methode zur Ermittlung und anschließender Subtraktion des Untergrundes von Röntgendiagrammen orientierter Tonmineralproben beschrieben. Angewendet wird Ti-K α Strahlung, und um die Absorption dieser Strahlung durch Luft zu minimieren, wurde eine vakuum- und heliumgespülte Apparatur entwickelt. Diese kann mit anderen Röntgenstrahlungsquellen benutzt werden, wobei ein beträchtlicher Intensitätsgewinn auftritt — z.B. wird CoK α — Strahlung um 125% verstärkt. Mittels untergrundbereinigter Diagramme ist eine bessere halbquantitative Abschätzung der Zusammensetzung von Tonmineralgemischen möglich. Kleine Unterschiede in der Zusammensetzung zweier Proben können durch die Subtraktion eines untergrundbereinigten Diagramms von anderen erkannt werden. Die Anwendung dieser Methode ermöglicht die genaue Bestimmung des Peakmaximums von Mineralen der Smektitgruppe.

RESUMEN: Se describe un método para calcular y posteriormente sustraer el fondo de los diagramas de difracción de muestras orientadas de minerales de la arcilla. Se usa radiación Ti-K α , y para minimizar la absorción de esta radiación por el aire, se utiliza su montaje a vacío y con flujo de helio. Este montaje puede ser usado con otras fuentes de rayos X, ofreciendo un considerable aumento de intensidad, p.e., la radiación Co-K α aumenta su intensidad en un 125%. Con el fondo eliminado es posible mejorar las estimaciones semicuantitativas sobre la composición de las mezclas de minerales de la arcilla. Pequeñas diferencias en composición de dos muestras pueden ser determinadas por diferencia entre los dos diagramas eliminando previamente el fondo. Usando este método los máximos de difracción de los minerales del grupo de las esmectitas pueden ser determinados con precisión.