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Quantitative Analysis of Clay Minerals and their Admixtures

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Abstract. Clay minerals are of non uniform composition and particle size. Also their identification and nomenclature have given much confusion. Examples are given.

Quantitative analysis of clay minerals from deposits and soils, by X-ray, thermo- and infrared analysis is treated. Examples are given of the large variability in the results; even for X-ray and electron microscope pure- and 85 to 90% chemical pure samples of kaolinite a well defined clay mineral. They are caused mainly by varying conditions of crystal growth from which result differences in isomorphous replacements, structure, ordering and strain.

An amorphous weathering substance coating the mineral particles (Beilby layer) upsets in particular quantitative analyses of the finer kinds of clay minerals.

Clay minerals from soils have, as compared to those from pure deposits, in particular formed by hydrothermal action, only poor characteristics of small intensity. Examples are given.

Quantitative analyses are further hindered by specific characteristics for a certain mineral being masked by those of other minerals which usually occur in the same sample. Examples are given.

Introduction

About 150 well defined types of clay minerals and their admixtures are known to occur in the clay separate of soils. Because there exists non uniformity in the methods of their identification and the interpretation of the results, various names for one and the same mineral are synonyms.

Quantitative analysis of even the well defined types is largely disturbed because they do not have constant composition, shape, X-ray, infrared and thermal characteristics. Other difficulties arise from the way the sample is prepared before it is investigated by the instrument.

In the following is an outline of the many difficulties in quantitative analysis which may be encountered when samples are investigated with various mineral composition from various origin.

A. Nature of Clay Minerals in Sediments

I. Identification and Nomenclature

The minerals of the chlorite group have on a total of 88 names, 52 synonyms (59%) — for details van der Marel (1964). For the minerals of the illite group is found 84 synonyms on a total of 120 names (70%) — to be published. The names and their identification characteristics of both groups are spread over 180 and 240 papers respectively.

In the 1951—1960 period 419 "new" minerals in all branches of mineralogy mentioned in literature, 44% of them were synonyms (53% over 1941—1950 period) — Fleischer (1961).

II. Chemical Composition

The chemical composition of 85 to 95% X-ray pure minerals is even for well defined clay minerals variable — see literature. Quantitative analysis of clay minerals based on their chemical composition, f.i. the K_2O% of illite thus are not allowed.

The differences are caused by isomorphous substitutions, replacement of K^+ by $(H_3O)^+$, of O by OH and of vacant holes with non compensated charges at crystal dislocations. For the chlorite-related minerals, the intermediates and the badly defined minerals formed by interlayering of Fe and Al hydroxides in expanded illite, swelling illite or soil montmorillonite, the differences are much larger.

The variation in chemical composition cause differences in particle shape and size, heat of conductivity, heat of reaction, intensity of X-ray diffraction and infra-red extinction.

See for E.M.: BATES (1959) *for d.t.a.:* ORCEL (1935), BUDNIKOV and BOBROVNIK (1938), GRIM and ROWLAND (1942), KELLEY and PAGE (1943), PAGE (1943), CAILLÈRE and HÉNIN (1948, 1949), KULP et al. (1951), GRAF (1952), EARLEY et al. (1953), FÖLDVARI-VÖGL and KOBLENCZ (1955), MUMPTON and ROY (1956), WEBER and GREER (1965). *For X-ray:* GRIM et al. (1951), BROWN (1955), BRINDLEY and GILLERY (1956), PETRUCK (1959), MITCHELL (1960), WIEGMANN and KRANZ (1961), SCHOEN (1962), DE MUMBRUM (1963), LAPHAM and JARON (1964). *For I.R.:* TUDDENHAM and LYON (1959), SAKSENA (1960), LYON and TUDDENHAM (1960), STUBIÇAN and ROY (1961), VEDDER (1964), HAYASHI (1965).

III. Particle Size and Shape

Electronmicrographs of clay minerals show wide variations in particle size and shape. After BATES (1959) the relation between ion composition and morphological structure for minerals of 1:1 type layer lattices can be indicated by a SiO_2-R″ (MgO, FeO, MnO)-H_2O diagram. The morphological index $M = \sin 45°. (x - y - 0.285). 1000$ (x and y are the average radii of the octahedral and tetrahedral cations respectively), measures the amount of misfit of the two sheets within the layer.

Thus small variations in mineral composition caused by small differences in environmental conditions at their growth, may considerably effect shape and particle size of a mineral. Crystal structure will also be the most ordered, e.g. the "period bond chain vector" — HARTMAN and PERDOK (1955) — the highest in pure dilute solutions with only a small number of non complicated ions.

Soil clay minerals are formed under various conditions. Consequently the same mineral may be found in various particle size and shape e.g.:

Kaolinite in the clay separate of soils may have a diameter and thickness of only 0.1 μ and 0.005 μ respectively, thus escaping quantitative estimation by the X-ray method. Perfectly crystallized kaolinite, but very fine from Provence has a disordered structure after X-ray and I.R. analysis. Also halloysite is found in various particle sizes and shapes from tubular to fibrous and conchoidal. The latter is an intermediate product between halloysite and uprolled kaolinite.

Montmorillonite and soil montmorillonite have about the same morphological habit; only the latter is coarser and thus appears less fluffy. Also illite may be found in various sizes and shapes depending on the conditions during their growth.

Thermal products are better crystallized than those formed by authigenic action. Thus the sample from Sarospatok formed hydrothermally, is very well crystallized.

Such in contrast to the "Hudig biogene" illite resulting from plant debris in marshes.

Many examples are given by BEUTELSPACHER and VAN DER MAREL (1966) in their "Atlas of electronmicroscopy of clay minerals and their admixtures" which contains 240 selected micrographs out of a total of about 4000 samples (published by Elsevier Publ. Comp., Amsterdam, New York). The E.M. method is very suited to identify certain clay minerals in mixtures; even in very small amounts. Rather this method is not suited for quantitative analyses because the very small amount which can be investigated = only some 10^{-6} g.

B. Thermo Analysis

I. Theoretical Approach

After SPEIL (1944, 1945), KERR and KULP (1948) the peak area (°C sec) enclosed by base line and curve of differential temperature (ΔT — °C) versus duration of thermal reaction ($t_2 - t_1$ sec), is related to the specific heat of reaction (ΔH — cal g^{-1}) released (exothermal) or absorbed (endothermal) when the sample is heated in an oven in a nickel sample holder (block):

$$\text{Peak area} = \int_{t_1}^{t_2} \Delta\, T\, dt = \Delta H\, M/g\, \lambda.$$

M = mass of sample (g), g = geometrical (body) factor (cm) accounting for temperature gradient distribution in sample, λ = thermal conductivity of sample in sample holder (cal $\sec^{-1}$ $°C^{-1}$ cm^{-2} cm).

Thus the "calibration factor"

$$(\psi) = \frac{\text{peak area}}{\Delta H} = M/g\, \lambda.$$

KRONIG and SNOODIJK (1951) and ERIKSSON (1952, 1953, 1954) found the following equation for a sample in a cylindrical metallic (nickel) block:

$$\text{Peak area} = L\, \varrho\, r^2/4\, \lambda.$$

L = heat of reaction per unit volume of sample; r = radius of sample holder (cm); ϱ = density of sample (g cm^{-3}).

Its derivation was more complicated as given by SPEIL, KERR and KULP. The physical character of the dissipation process of heat in the sample as outlined by CARLSLAW and JAEGER (1947) was regarded. It is not proportional to the temperature difference between centre of sample and nickelblock and also the sample temperature during the thermal process is not uniform throughout as was assumed by SPEIL, KERR and KULP. BOERSMA (1955) avoiding the use of Bessel functions came to the same result. SEWELL (1952, 1955) arrived at a similar equation:

$$\text{Peak area} = L\, \varrho\, a^2\, w_0/\lambda.$$

a = radius of cylindrical sample; w_0 = a factor determined by the shape of the sample.

The above equations are similar to the SPEIL, KERR and KULP one, when for g the body factor in their notation is read $4\pi h$ and $\pi h/w_0$ respectively but they both contain the factor L = the heat of reaction per unit volume.

Also the experiments prove that peak area depends on the sample's dimensions and the place of the thermocouple in the sample holder. If the sample height surpasses a certain limit, the surplus material is even almost out of the influence zone of the thermocouple — Smyth (1951), Barshad (1952), Talibudeen (1952), Eriksson (1952, 1953, 1954), Josselin de Jong (1957), Cole and Rowland (1961).

From the above follows that, to obtain quantitative analysis of minerals, the heat flow (λ) through the samples and the reference material usually Al_2O_3, must be a constant during the whole thermal traject investigated.

Heat conductivity of different clay minerals and reference material, at various temperatures and packing densities are not constant either — see literature. Moreover heat is also transferred along the thermocouples — Soulé (1952), Sewell (1955), Boersma (1955), Josselin de Jong (1957), Cole and Rowland (1961). Variations of 20 to 30% are observed for different thermocouples and the peak area registrated may even be reduced to 20 to 50% of its theoretical value.

By introduction of the thermocouple influence the calibration factor can after Boersma (1955) be represented by the equation:

$$\psi(^\circ\mathrm{C}\,\mathrm{sec}\,\mathrm{gcal}^{-1}) = \frac{\varrho a^2}{4\lambda}\left\{\left(1-\frac{r_0^2}{a_2}\right)\left(1+2\ln\frac{a}{r_0}\right)\right\}\Big/\left(1+\frac{\Lambda}{\lambda}\ln\frac{a}{r_0}\right).$$

r_0 = radius of thermocouple junction (cm), Λ = heat transfer through the thermocouple wires (cal sec^{-1} $^\circ\mathrm{C}^{-1}$ cm^{-2} cm).

II. Determination of Intensity of Thermal Reaction

1. Directly from peak area (°C sec), radius of sample holder, density and specific conductivity of sample. The latter was determined separately from a sample equally packed — Rey and Kostomaroff (1959).

2. Calibration of sample against a reference sample of well known heat capacity at various temperatures and both samples packed in the crucibles of same density — Cohn (1924), MacGee (1926), Allison (1954), etc.

3. Determination of electrical energy to maintain a temperature difference = 0, between sample to be investigated and the reference by a recording wattmeter. Both samples are mixed before with 25% graphite — Lakodey et al. (1956).

4. Determination of peak area enclosed by base line and curve of the differential temperature when heating sample in an oven at a constant heating rate. Peak areas in cm^2 are converted to cal/g by:

a) Electrical calibration at different temperatures with a certain current of well defined caloric heat flowing through a coil placed in sample holder — Fischer and Lorenz (1956), Lehmann and Haszler (1958).

b) Calibration with substances of well known heats of reaction, heats of fusion or heats of transfer and with thermal reactions at different temperatures — Barshad (1952), Sabatier (1954), de Bruin and van der Marel (1954).

To avoid differences in heat conductivity between reference sample and sample to be investigated, the sample is diluted with an excess of the inert reference material — Grim and Rowland (1944), Eriksson (1952), Soulé (1952), Grimshaw and Roberts (1953), Sabatier (1954).

It is further packed in the same way as the reference sample to such a degree (volume) that their densities and porosities and therefore their heat conductivities and heat capacities also at the higher temperatures ($> 800°$ C with radiation effects of T^3) are determined principally by that of the inert material — dilution technique. Thus heat transfer (the geometrical factor) will hardly change during analysis; this regardless of shrinking, sintering, gasevolution or liquefaction of sample which phenomena would otherwise completely change heat conductivity.

5. Exponential decay of differential temperature curve after thermal reaction has ceased delivering the thermal conductivity of sample. An air oven is used which, because of bad conductivity, delivers a relaxation time large enough to be interpretable after reaction has ceased — Vold (1949). Because of the air heating, this method is only suited for low temperature reactions e.g. melting points of organics. Moreover heat capacity of the sample which is determined separately is not constant but changes because of loss of reaction products.

6. Vapour pressures (p) at isothermal temperatures (T) by thermovolumetry, which by a graphical plot delivers the heat of dissociation Q/kcal mole^{-1} after the Van't Hoff equation:

$$\frac{d \ln Kp}{dT} = \frac{Q}{RT^2}$$

or in its integrated form:

$$\ln p_{H_2O} = -\frac{Q}{nRT} + C\cdot$$

n = number of H_2O molecules lost on 1 molecule of reaction material: kaolinite = 2, calcite = 1. Kp = equilibrium constant, R = gas constant, T = absolute temperature. p_{H_2O}, P_{CO_2} = vapour pressure H_2O and CO_2.

— Pieters (1928), Bischoff (1950), Schwob (1950), Rowland and Lewis (1951), etc.

7. Reaction rate constants (k) of unit order at isothermal sample temperatures (T) by thermogravimetry which by a graphical plot of log k_T against $1/T$ delivers the activation energy E (k cal mole^{-1}) after Arrhenius: $k_T = A \exp - E/RT$ (A = frequency factor of effective collisons).

— Murray and White (1949a, b, 1955), Vaughan (1955), Kissinger (1956), Brindley and Nakahira (1957, 1958), etc.

8. Reaction rates at isothermal sample temperature by conductivity measurements and which by a graphical plot delivers E — Fripiat and Toussaint (1963).

9. Reaction rates at isothermal sample temperatures calculated from specific heat calibration curves of sample against calcined alumine the heat capacity of which is known and sample temperatures which by a graphical plot delivers E — Allison (1954).

10. Reaction rates calculated from the exponential decay of the differential temperature curve after the thermal reaction has ceased and sample temperatures which by a graphical plot deliver E — Allison (1954).

11. Heating rates (dT/dt) and sample peak temperatures (T_m) by differential thermal analysis and by a graphical plot delivering E after the Kissinger (1956) equation:

$$\frac{d \ln \left(\frac{dT}{dt} T_m^{-2}\right)}{d \frac{1}{T_m}} = -\frac{E}{R}.$$

12. Reaction rates (dw/dt), total weight loss (w_r) and sample temperatures (T) by thermogravimetry delivering by a graphical plot x = the order of the reaction and E after the FREEMAN and CARROLL (1958) equation:

$$\frac{\Delta \log dw/dt}{\Delta \log w_r} = x + \frac{\frac{-E}{2.3\,R}\,\Delta T^{-1}}{\Delta \log w_r}$$

— see also JACOBS (1958, 1961) and own analyses.

From the above follows that the thermal effect of a heated mineral can be estimated in several ways and based on several principles, although theoretically not always justified e.g. the thermal reaction of kaolinite etc. is not reversible (condition for Q) and does not begin at any temperature (condition for E) but only from a certain temperature. Moreover the methods used are not always accurate enough for their particular purposes — see 1, 2, 3, 9, 10.

The results obtained are very variable — Table. Even for pure well crystallized "standard" kaolinite when conditions are uniform and which mineral is the simplest of structure and the most homogeneous of composition.

III. Quantitative Analysis — General

For quantitative analyses the magnitude of the thermal reaction registered by a dta or dtg (tg) apparatus when the mineral is heated in an oven, should be strong, not overlapped by that of neighbouring reactions of the same mineral or of other minerals. It should further be constant for each mineral, regardless of its origin or particle size. Fig. 1 represents the dta results of the commonest clay minerals and their admixtures. The samples were diluted before with Al_2O_3 150:250 and moreover the same pair of thermocouples were used for the sample or the calibration substance and the reference material. Many thermal reactions overlap each other; even those of the same minerals but of various origin. Their intensity is also variable — see also literature.

Particle size. A particle size effect has been observed by various investigators. For coarse particles, the reaction rate when heated is decreased, the peak is broadened and its area decreased f.i. coarse samples of calcite magnesite and dolomite when finely ground, give an increase in the heat of reaction of 40%, 34% and 77% (first peak), 61% (second peak) respectively — WEBB (1958). In particular chlorite has a large particle size effect — SABATIER (1950). In literature likewise examples are found for biotite, vermiculite, muscovite, dickite, kaolinite, antigorite, goethite, lepidocrocite, quartz, talc, diaspore, etc.

For very fine particles there is a decrease in thermal effect because of an amorphous (BEILBY) layer coating the minerals when ground or when they weather under natural conditions (chemical processes, mechanical disruptions). Its thickness is for coarse ground quartz 0.03 to 0.15 μ — see literature. For common kaolinite was found 1 to 10 Å — ENGELHARDT (1955). Fine kaolinites with a specific surface of 75 m^2/g thus will contain 1.5 and 15% amorphous matter respectively assuming a density of 2.

A negative particle size effect is also caused by a decrease in the structural ordening of the various components of the mineral.

Heat of reaction. The thermal reaction of a mineral when heated is not a constant either. It will be largest when the mineral occurs in its most perfect state of

Table. *Thermal Effect of Various Minerals when Heated Determined after Several Methods*

Method used	Authors	quartz	kaolinite	halloys.	montmor.	illite	hydrarg.	calcite
1. Heat conductivity (*H*)	REY, 1959						272	
2. Heat capacity (*H*)	COHN, 1924	4.1—4.2	91.8—92.6					
	MACGEE, 1926		118—150					
	ALLISON, 1954		104—115	91	23—44		ball clay = 71	
3. Electrical energy (*H*)	LAKODEY, 1956	1.75						
4. Calibration against minerals of well known reaction heats (*H*)	BARSHAD, 1952		253	166	67	64	259	
	SABATIER, 1954	1.5	114—130				276	1
	BRUYN, 1954	0—4	100—180	110—145	20—60	25—45	200—240	and many others
	SCHWIETE, 1958		186		58.5	43.2		
	REY, 1959			151				417
	ELLIS, 1962		154					
	KARSCH, 1964		154—170					
6. Vapour pressures at isothermal temperatures (*Q*)	PIETERS, 1928		305					
	BISCHOFF, 1950			dolomite = 240				476
	SCHWOB, 1950							401
	ROWLAND, 1951			magnesite = 325				432
	STONE, 1952—1954		145	magnesite = 120				
	WERNICK, 1954			dolomite = 234				460
	ZAGAR, 1962							391
	ELLIS, 1962		157					
7. Reaction rate constants at isothermal temperatures by gravimetry (*E*)	MURRAY, 1949—1955		145—175	143—165	48—77		ball clay = 134—159	
	VAUGHAN, 1955		149—159	136			fire clay = 100—103	
	KISSINGER, 1956		152—164					
	BRINDLEY, 1957—1958		254	215				
	FERRANDIS, 1959			125				
	REY, 1959		143—145	121—143				
	BIRCH HOLT, 1962		170					
	TOUSSAINT, 1963		98	at low vapor pressure				
8. As 7 but by electric conductivity (*E*)	FRIPIAT, 1963		70					

9. As 7 but by calibration against Al_2O_3 (*E*)	ALLISON, 1954	308—314			ball clay = 373
10. As 7 but from the exponential decay of the reaction (*E*)	ALLISON, 1954	215—223		72	ball clay = 167
11. Heating rates and peak temperature (*E*)	KISSINGER, 1956	137—152	141—148		
12. Reaction rates by gravimetry and sample temperature (*E*)	FREEMAN, 1958				390
	JACOBS, 1958—1961	148		[2]	
	VAN DER MAREL this paper	170—220	150—200		fire clay, ball clay = 160—210

[1] Diaspore = 166, goethite = 90, brucite = 285. [2] $H^+ = 56$, $Ca^{++} = 66$, $Na^+ = 73$.

ordering. Thus e.g. aragonite may be distinguished from calcite by the small (3 to 6 cal/g) exothermal reaction in the 350 to 550° C traject caused by recrystallization to calcite — PRUNA et al. (1949), GRUVER (1950). Disordered calcite (vaterite) and disordered dolomite (protodolomite) have their thermal reactions at a lower peak temperature as the better ordered forms — PRUNA et al. (1949) and GRAF and GOLDSMITH (1956) respectively.

The α/β transition reaction of quartz, commonly = 4.2 cal/g, may largely be decreased and even suppressed — BERKELHAMER (1944), TUTTLE (1949), MIDGLEY (1951), SABATIER (1954), etc. in fine grained X-ray positive cryptocrystalline samples, called chalcedonite — FIELDES (1952). It is caused by crystal defects from which results a strained lattice. Thus when the mineral is powdered, the transition effect may appear again — PELTO (1956). Pure calcite of various origin, but ground to about the same particle size ($< 149\ \mu$) delivered a peak area varying from 62.8 to 80.8 cm^2 — WEBB (1958), etc.

Small differences in chemical composition may largely change the heat of reaction — e.g. dolomite — BUDNIKOV and BOBROVNIK (1938), BERG (1943), CAILLÈRE and HÉNIN (1948), KULP et al. (1951), GRAF (1952), FÖLDVARI-VÖGL and KOBLENCZ (1955), WEBB (1958). Small amounts of Fe increase the area of the second endothermic peak of dolomite — KULP et al. (1951) and hematite that of goethite — KULP and TRITES (1951). Well-defined and well-crystallized pure chlorites of igneous origin show considerable variations in their thermal effects even in samples of a certain type — ORCEL (1927).

Heat of reaction per gram mass and per gram H_2O evaporated of X-ray and electron microscope pure kaolinites $< 2\ \mu$ of 85 to 95 % chemical purity varying from 100 to 180 and from 800 to 1400 respectively, is inversely related to their specific surface — Fig. 2 — VAN DER MAREL (1960).

After CARTHEW (1955) for kaolinite a direct relation exists between the ratio peak area/width of the peak at half its height = (A/W) and the slope ratio tan α/tan β. This relation should be independant of the particle size and the degree of crystallinity. As furthermore the A/W ratio is proportional to the amount of kaolinite, it should

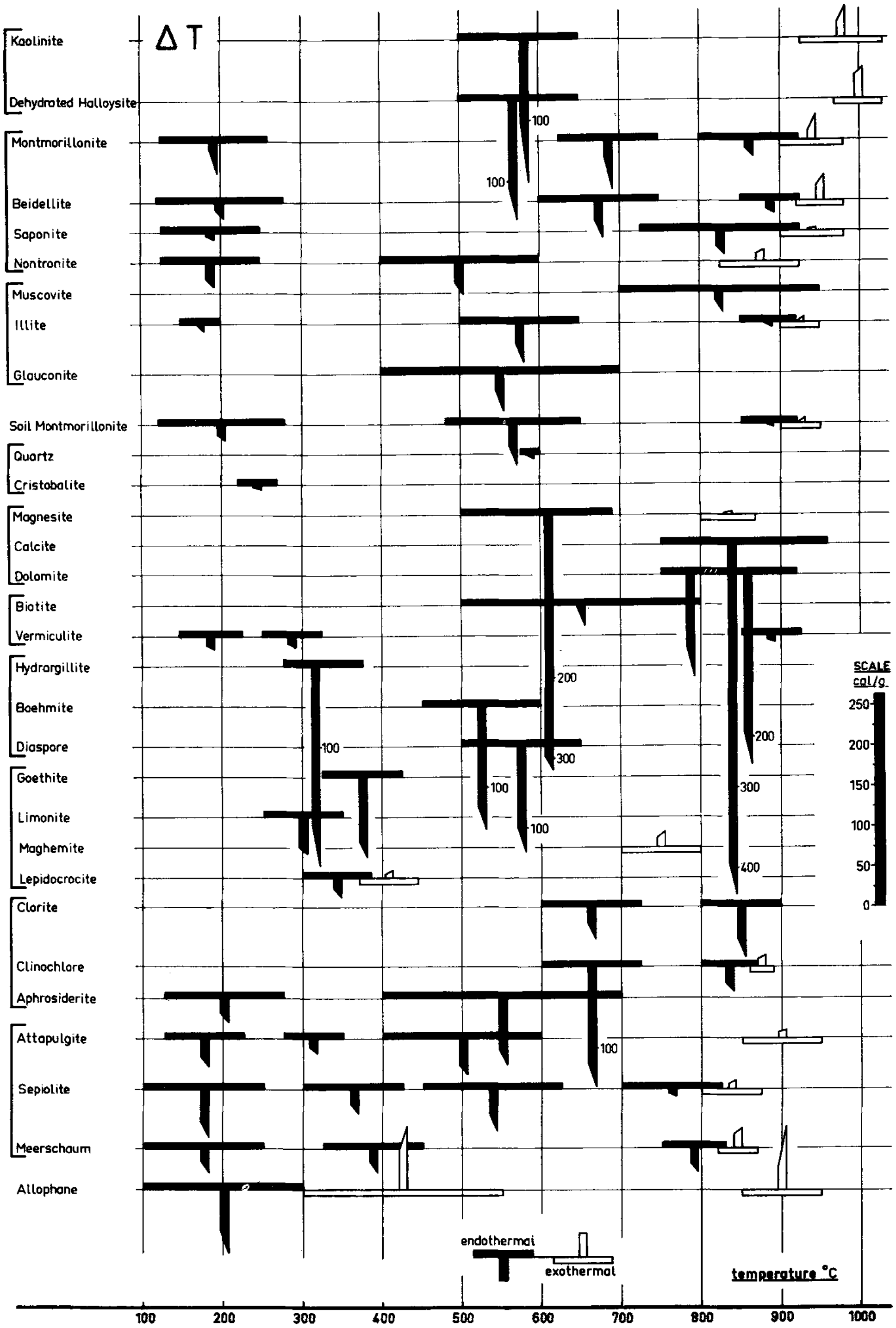

Fig. 1. Peak intensity and peak temperature limits between which thermal reactions may proceed for most common clay minerals and their admixtures in sediments. — After DE BRUYN and VAN DER MAREL (1954) — improved. — With permission of Geologie en Mijnbouw, Netherlands

be possible to estimate the percentage of kaolinite in any sample regardless of its particle size or degree of crystallinity.

By application of this method to a large number of the samples, there was a wide spreading of the observations, although the slope of the line representing the above equation was similar — van der Marel (1960).

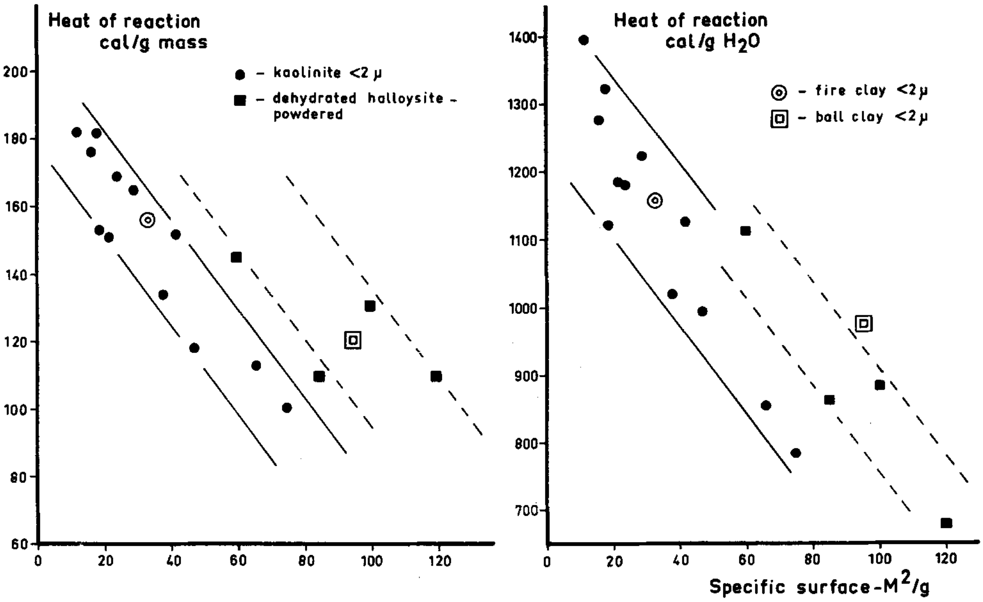

Fig. 2. Heat of reaction and specific surface for endothermal reaction (± 600° C) of various kaolin minerals. — With permission of Silicates Industr., Belgium (1960)

IV. Application to Clay Mineralogy

Fig. 3 represents dta results of some pure clay minerals and the clay separate ($< 2\,\mu$) of some soil types. Their composition was verified by X-ray analysis. All diagrams show very poor thermal effects as compared to those of minerals from pure deposits formed under optimal conditions. Consequently the minerals are better ordered, not so fine and will thus give thermal reactions of larger intensity. The figure moreover shows that the occurrence of many common clay minerals in soils is masked by that of others.

For mixtures of minerals the overlapping effect is increased partly by changes in the peak temperatures of minerals with their thermal effects close to each other e.g. small amounts (5%) of calcite decrease the first endothermic 770° peak of dolomite to 850° C — Heady (1952). The shape and intensity of the exothermic peak of kaolinite is largely decreased by iron oxides and mica. The overlapping effect is also caused by differences in the amount of a certain mineral in the mixture investigated. The smaller the amount the lower its peak temperature.

Attempts have been made to increase the thermal reaction by use of high heating rates, piperidine — Allaway (1949), Carthew (1955), vacuum — Whitehead and Breger (1950), Linseis (1951), Wittels (1951), or to better separate thermal reactions close to each other e.g. addition of ethyleneglycol to hydrated halloysite

halloysite — kaolinite mixtures — SAND and BATES (1953), use of high CO_2 pressures for calcite-dolomite mixtures — ROWLAND and LEWIS (1951), ROWLAND and BECK (1952), HAUL and HEYSTEK (1952), and calcite-magnesite mixtures — STONE (1954).

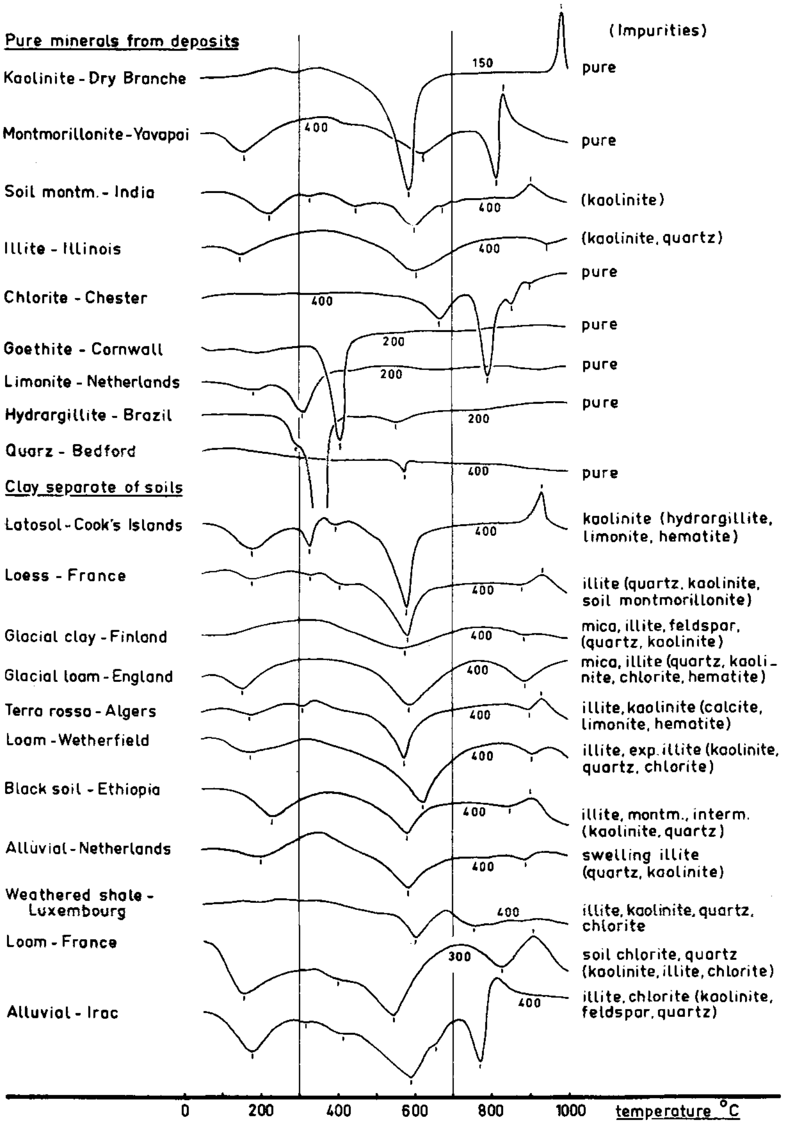

Fig. 3. D. t. a. of pure minerals from deposits and of the clay separate (< 2μ) of soils from various origin

But all these methods are only successfull for some particular minerals and some particular combinations of minerals which are rare in soil clays, and therefore of very restricted application. As a result many of the commonest minerals in the clay separate of soils cannot be distinguished from each other e.g. illite and expanded illite, soil montmorillonite and swelling illite, soil chlorite and sedimentary chlorite, chrysotile, antigorite, lizardite. Nor can the numerous types of interstratifiedm inerals, regular or non regular, which are so frequently found in soil clays, be distinguished from each other and from their bases components.

Therefore the thermal method is unsuited for quantitative analysis of soil clays; — VAN DER MAREL (1956, 1960, 1961) such notwithstanding the great perfection of the modern dta equipment and the great propagation made for it. The successes are based mainly on examples of pure minerals of non complicated mixtures e.g. circumstances mostly absent in the clay separate of soils of various origin and type. About 20 years ago SPEIL the grounder of quantitative dta, already warned for the doubtful existence of "Standard minerals" with well defined constant thermal effects — see p. 24.

Quantitative dta determinations are only possible for samples with high thermal reactions and coming from a certain locality e.g. a hydrargillite pit defiled with kaolinite, a kaolinite pitd efiled with quartz, etc.

C. X-ray Diffraction

I. Theoretical Approach

When X-rays of intensity I_0 and wave length λ (Å) fall on a small area of randomly oriented crystalline particles as conditions prevailing in the goniometer diffraction technique, the following relation exists for the intensity I of a certain reflection minus its background (white radiation, Compton- and air scattering, noise) — see literature:

$$I = I_0 k \psi j P L N^2 O A F^2$$

k = constant depending on slit width, current density, effective surface of the incident rays.

j = multiplicity factor accounting for the number of superposing crystal planes delivering a certain reflection.

ψ = factor for preferred orientation of the sample.

P = polarization factor accounting for the amount of partly polarized radiation = $= \frac{1 + \cos^2 2\Theta}{2}$.

L = Lorentz factor accounting for the partly, non equal strong radiation of the incident X-rays $= \frac{1}{2} \cdot \frac{1}{\sin^2 \Theta \cos \Theta}$.

N = number of unit cells per cm^3.

O = effective surface of the incident rays diffracted by the sample.

A = absorption factor accounting for the amount of absorbed radiation when the X-rays penetrate the sample.

F = structure factor accounting for the amount of diffracted radiation by a certain crystal because of scattering of the X-rays by atoms in different positions in the unit cell.

When a certain mineral is investigated under standardized circumstances of wave length, intensity of the incident rays and their effective surface and sample mounting represented by the factor K, the above equation is simplified to $I = I_0 K \psi A F^2$.

a) Absorption factor (A). Absorption of X-rays by a solid medium can be represented by the equation:

$$I = I_0 e^{-\frac{\mu}{\varrho} \varrho l}$$

μ/ϱ = mass absorption coefficient (cm^2/g); μ = linear absorption coefficient; ϱ = density. l = depth to which the X-rays have penetrated (cm).

Tables of mass absorption coefficient of various elements for various wave lengths are given in the International Tables for X-ray Crystallography Vol. III, 1962. Thus e.g. for $\lambda = 1.55$ Å (Cu radiation $= 1.54$ Å): Li $= 0.72$, Na $= 30.6$, K $= 145$, Mg $= 39.2$, Ca $= 164$, Mn $= 289$, Fe $= 313$, Si $= 61.6$, Al $= 49.4$, H $= 0.44$, C $= 4.67$, O $= 11.7$.

To obtain maximum diffracted intensity the sample's thickness must exceed a certain minimum e.g. $\geqq \frac{3.2}{\mu} \frac{\varrho}{\varrho_1} \sin \Theta$.

ϱ = average density of the solid sample, ϱ_1 = density of sample powder including the interstices — ALEXANDER and KLUG (1948).

b) Structure factor (*F*). The scattering power of an unit cell for a wave in a crystal direction defined by *hkl* is given by: see International Tables for X-ray crystallography etc.

$$F = \Sigma_n f_n \exp 2\pi i \,(h x_n + k y_n + l z_n)$$
$$= [\{\Sigma_n f_n \cos 2\pi \,(h x_n + k y_n + l z_n)\}^2 + \{\Sigma_n f_n \sin 2\pi \,(h x_n + k y_n + l z_n)\}^2]^{\frac{1}{2}}$$

$f = f_0 \times$ temperature factor.

f_0 = the scattering intensity of a single atom at rest at the point x, y, z, relative to that of a single electron($\frac{e^2}{m c^2} = 2.819 \cdot 10^{-13}$; e = charge of electron $= 4.802 \cdot 10^{-10}$ e.s.u.; c = velocity of light $= 2.9986 \cdot 10^{10}$ cm sec^{-1}, m = mass electron $= 9.108 \cdot 10^{-28}$ g.)

Temperature factor $= e^{-B\left(\frac{\sin \Theta}{\lambda}\right)^2}$ which accounts for the temperature dependent thermal vibration of the atoms (B = a constant depending on temperature and mass atom).

Tables of f_0 ratios which depend on $\sin \Theta/\lambda$ for several atoms and ions are given in the International Tables of X-ray Crystallography Vol III, 1962 p. 202—206. Thus e.g. for small angles and Cu radiation ($\lambda = 1.54$ Å) and $\sin \Theta/\lambda \cdot 10^{-8} = 0.1$ and non ionized elements: Li $= 2.21$, Na $= 9.76$, K $= 16.73$, Mg $= 10.51$, Ca $= 17.33$, Mn $= 22.61$, Fe $= 23.68$, Si $= 12.16$, Al $= 11.23$, H $= 0.81$, C $= 5.13$, O $= 7.25$; $H_2O = 8.87$ and $(H_3O)^+ = 9.68$.

Therefore substitutions of (Al/Fe), (K/H_3O), (Mg/Ca), (Ca/Na) in crystal structures may produce appreciable differences in the intensity of the observed reflections. The other members of the above structure factor equation contain terms which are a measure of the arrangement of the atoms in the crystal planes of the unit cell and their mutal influence — see for values of cos 2 (...) and sin 2 (...) for various space groups the structure tables of LONSDALE (1936) etc. In the ideal case of a perfect crystal F stands in the intensity equation as F, but as F^2 in case of an ideal mosaic crystal. The latter consists of a large number of small perfect blocks each of which being so small that absorption and extinction can be neglected and each independently scattering the X-rays. For Al and calcite the intensities of the integrated reflections may vary 30 × and 5 × — JAMES (1934) and for diamond 50 × — LONSDALE (1949).

In an ideal lattice, identical atoms occupy equivalent sites. Each atom encountered by the incident X-rays is in the correct position to reflect it. Slight differences in the arrangement of these elements, will broaden the Bragg reflections. If these deviations are sufficiently large, there is no loss of intensity as the effect can be measured by integration. If not there is a decrease in intensity since the effect cannot be discerned from background radiation. Strain greatly increases the ability of a crystal to diffract X-rays — WHITE (1950).

Crystals are of varying degree of structure, strain and mosaic constitution; especially those as are found in the clay separate of sediments. Therefore the intensity factor of the diffracted radiation for a certain Bragg reflection is not a constant for a certain mineral species.

c) Factor for Preferred Orientation (ψ). Platy minerals may be orientated along their basal planes when they are investigated in the sample holder. Even fine particles when dried before and pressure is not applied to fill the sample holder may do so.

II. Determination of the Intensity of an X-ray Reflection

Best suited for lattice cell dimensions are determinations of the higher angle reflections. This follows from the Bragg relation $2d \sin\Theta = n\,\lambda$ delivering: $\delta\Theta = -\operatorname{tg}\Theta\;\delta\,d/d$ when its first differential is equalized to zero.

However, for quantitative analyses the lower reflections are better suited as they are the least overlapped by those of other minerals.

For a powder sample infinitely thick for the incident radiation with no appreciable extinction or preferential orientation of the particles, the latter consisting of several minerals of weight fraction $x_1, x_2, \ldots, x_i$, density $\varrho_1, \varrho_2, \ldots, \varrho_i$ and linear absorption coefficient $\mu_1, \mu_2, \ldots, \mu_i$, the following relation exists for the intensity I_1 of a certain reflection of the sample component x_1 — Alexander and Klug (1948).

$$I_1 = \frac{K\,x_1}{\varrho_1\left[x_1(\mu_1^* - \mu_M^*) + \mu_M^*\right]}\,.$$

K = a constant depending on instrumental equipment, crystal structure of the sample component.

μ_1^* = mass absorption coefficient of sample component $= \frac{\mu_1}{\varrho_1}$; $\mu_2^* = \frac{\mu_2}{\varrho_2}$ etc.

μ_M^* = ditto of matrix (other components than x_1) $= \mu_2^*\,x_2 + \mu_3^*\,x_3 + \cdots \frac{\Sigma_2^n \mu_i\,x_i}{(1 - x_1)}$

Mass absorption coefficients (cm²/g) for Cu radiation (1.5418 Å) vary for several minerals: quartz = 34, kaolinite = 30, illite = 51, montmorillonite = 38, mica = 42, Na feldspar = 33, K feldspar = 48, Ca feldspar = 50, calcite = 71, goethite = 198, hematite = 219, cellulose = 8. Moreover most clay minerals are of non uniform composition — Chapter I.

Thus great errors may be made in quantitative analyses of complicated minerals by direct intensity measurements. A solution is to dilute the sample with an excess of inert material e.g. gum arabic to 80% by volume — Mitchell (1960) which is only possible at high intensities of the sample reflections.

Quantitative analyses can also be obtained by mass absorption — diffraction analysis if the sample consists of binary mixtures of well defined components — Leroux et al. (1953). Intensities of the reflections and mass absorption coefficients of the sample components were used for quantitative analyses by Engelhardt (1955) and Sehlke (1963).

However the estimation of packing densities and the production of a certain radiation of constant intensity, create other problems. Therefore a certain amount of a Standard mineral is added to the sample for calibration. The Standard may thereby serve as a diluent if its intensity is weak compared to that of the mineral to be investigated. Recommended Standards with only few reflections (cubic crystals), their use depending on the kind of mineral to be investigated (reflection of Standard and of mineral should be very near but not overlapping) are stearic acid, LiF, NaF, Al_2O_3, $Sr(NO_3)_2$, CaF_2, KCl, etc. with $\mu/\varrho = 5, 12, 24, 31, 58, 91, 125$ respectively. Artificial AlOOH (cerahydrate) recommended by GRIFFIN (1954) has 28 which is about that of various clay minerals and thereby its most intensive reflection $d = 6.06$ Å (020) is nearest to that of the basal spacing of the layer silicate clay minerals. Cholestrine has strong low angle reflections (33.2 Å, 17.1 Å) but μ/ϱ is only 4.4.

The goniometer is run 4 × over the specified 2Θ range and an average value is calculated from the countings. The registered intensities are corrected for base line (background). The latter depends on optical conditions of the instrument (surface of the focus, intensity of the current, thickness of the metalfilter, slit width, discriminator system); also on properties inherent to the sample (particle size, amorphous matter).

Preferred orientation of the sample in the sample holder can be decreased by dilution of the sample, first with ethylcellulose (dissolved in toluene) and thereafter by evaporation of the latter — REDMOND (1947), cork meal — ENGELHARDT (1955), FLÖRKE and SAALFELD (1955), or a thermoplastic cement — BRINDLEY and KURTOSSY (1961) which materials also act as diluents. For cork meal (100:100 volume %) was found for 5 kaolinites a spreading in the intensity of the (001) reflection of 177:100. For the thermoplastic cement (1:5) was found for 15 kaolinites calibrated against AlOOH (boehmite) a decrease in the limits of the I (001, K)/I (020, B) quotient from 167:100 to 147:100 (without sample G = 135:100).Analogous results were found for the paired reflections: I (002, K)/I (021, B) = from 185:100 to 178:100 (without G = 143:100) and the I (001, K)/I (060, K) reflections = from 233:100 to 151:100 and I (002)/I (060) from 193:100 to 157:100. The disorientation effect of the cement is perfect.

III. Quantitative Analysis — General

For quantitative analyses the intensity of the reflection of the sample registered by the instrument should be strong, not overlapped by that of other minerals and constant for each mineral, regardless of its origin or particle size.

Fig. 4 represents the X-ray data of the commonest clay minerals and their admixtures. Many reflections overlap each other. Their intensities are also variable, even for kaolinite which mineral has still the most uniform composition of all clay minerals. In particular kaolinite in the clay separate of soils gives weaker intensities and several reflections are lacking in the diagram. The same holds for halloysite.

a) Particle size. Coarse crystallites > 5 to 10 µ lose diffracted radiation by reflection, interaction of incident and reflected rays which differ $\pi/2$ in phase, entrapment of the rays in crevices, rays prevented to reach crystals in lower layers which are in the right position to give a Bragg reflection by absorption of crystals in upper layers. When the sample is rapidly rotated in its own plane, more crystallites are allowed to participitate in diffraction. The intensity of the reflections is increased and the statistical fluctuations in the intensities are

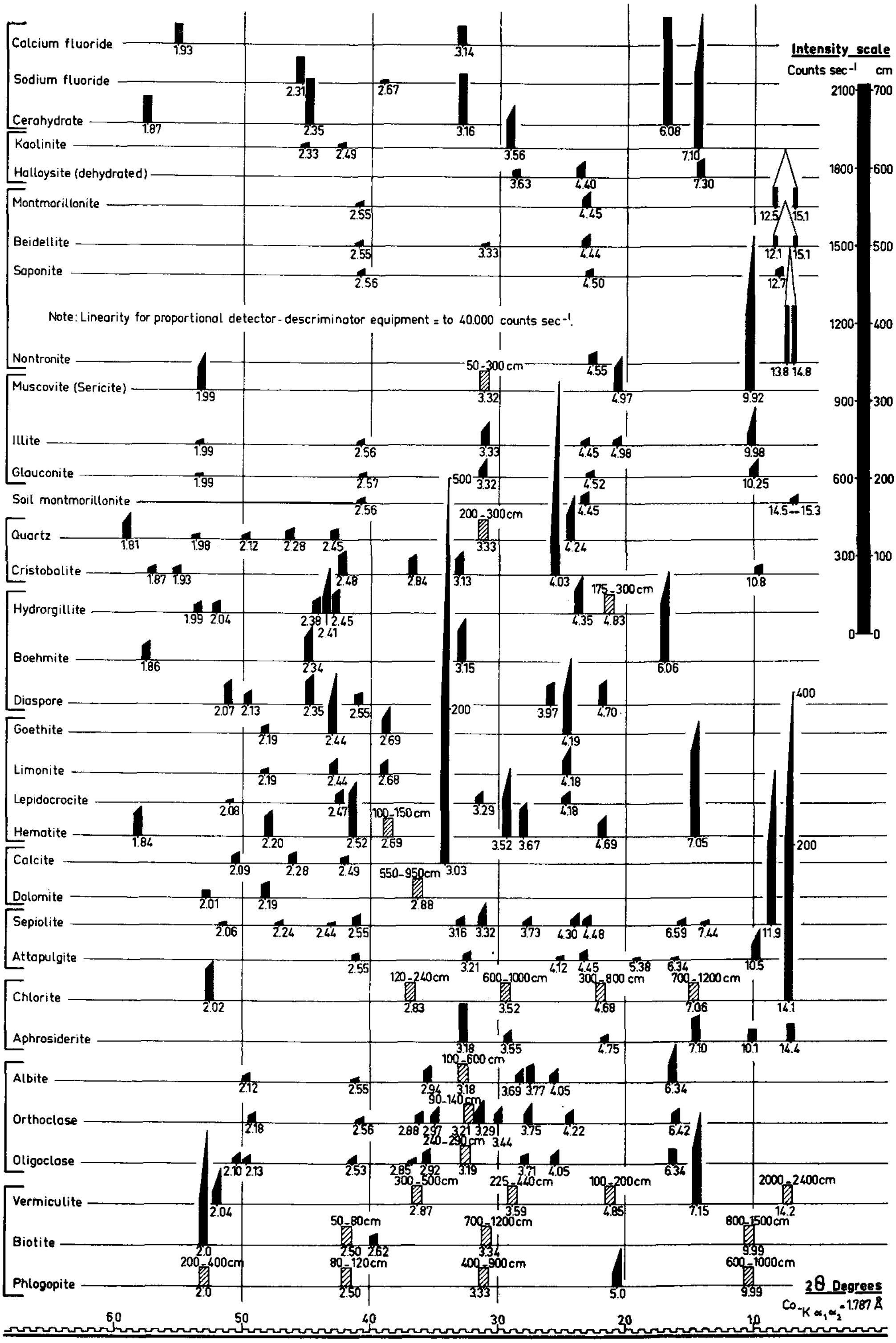

Fig. 4. X-ray spectra (Co-radiation) of main reflections of most common clay minerals and their admixtures in sediments. *d* spacings in Å. — With permission of Acta Universitatis Carolinae, C.S.R. (1961)

greatly reduced. Various equations have been suggested to determine particle size in the range 0.1 to 10 μ from loss of intensity — see literature.

It is recommended to dry grind the 200 mesh quartz to be measured and the standard quartz from about 0.5 to 1 hour in a mill — Brindley and Udagawa (1959). After Gordon and Harris (1955) the errors with quartz particles of 1 to 20 μ are in the order of 12%. Alexander et al. (1948) and Lonsdale (1949) suggest using a crystallite size $< 5\ \mu$. For silica was found 5 to 10 μ the best size for quantitative analyses — de Wolff et al. (1959).

sipart from this the quantitative estimation of mixtures of coarse, irregularly Azed minerals with different linear absorption coefficient is a complicated problem. Failures to 30% can be made, unless the particle size of the several constituents of the sample and their absorption coefficient are standardized.

If the crystallite size decreases to below 0.1 μ depending on absorption coefficient, crystallite size and shape and grade of distortion of the lattices, the Bragg reflections are broadened with decreasing particle size. This effect (directly related to $1/\cos\Theta$), is caused by small deviations from the path of the mean diffracted X-ray direction which are not ruled out or intensified by accumulation in successive underlying planes. Various equations have been suggested to estimate the crystallite size of the sample from line broadening — Scherrer (1918), etc. At a particle size of 0.01 μ and below the method is very inaccurate. Line broadening which may also be caused by strain and stress or crystal defects, means loss of intensity when the effect is large because too weak intensities cannot be measured and thus fade away in the background.

Decrease in intensity at decreasing particle size is also due to a Beilby layer (1921) effect — Gordon et al. (1952), Gordon and Harris (1955). For quartz as measured from the decrease in density, the decrease in dta reaction and the amount of SiO_2 dissolved by a borate buffer the thickness should be 0.03 to 0.05 μ, 0.11 to 0.15 μ and 0.02 to 0.03 μ respectively — Dempster (1951), Clelland et al. (1952), Clelland and Ritchie (1952), Dempster and Ritchie (1952, 1953). By extraction with HF Nagelschmidt et al. (1952) found 0.03 μ. Gibb et al. (1953) found by extraction with HF and borate buffer 0.03 to 0.06 μ, Jensen (1954) by etching with increasing HF concentrations 0.01 to 0.09 μ. Rieck and Koopmans (1964) even found 0.4 μ from X-ray line profiles for wet ground quartz particles of 3 μ size.

But also the surface of clay minerals is coated with an amorphous layer. It should be formed however by hydrolysis as a result of weathering action and not by deformation as a result of grinding. Engelhardt (1955) estimated for kaolinite particles a thickness of 1 to 10 Å. When calculated on a specific surface of 100 m^2/g (fine illite) and 400 m^2/g (montmorillonite) thereby assuming a sp. w. of the amorphous matter to be about 2 as in permutites and the thickness of the layer to be 10 Å, the clay particles should contain 20% and 80% amorphous matter.

b) Intensity. Many authors have already pointed to the large variability of the intensity of the Bragg-reflections of clay minerals — Dyal and Hendricks (1952), Schroeder (1954), Griffin (1954), Gordon and Nagelschmidt (1954), Engelhardt (1955), Jarvis et al. (1957), Galan et al. (1958), van der Marel (1960).

Isomorphous replacements to varying degrees as common in feldspars, micas, mica-related, chlorite and chlorite-related minerals change the intensity of the reflections — see also Grim et al. (1951), Brown (1955), Brindley and Gillery (1956), Petruck (1959), Mitchell (1960), Wiegmann and Kranz (1961), Schoen (1962). When K^+ of muscovite or illite is replaced by $(H_3O)^+$ because of weathering action, its (001) reflection is increased — Brown (1955), White et al. (1961). However when K_2O is lost the reflections are broadened and peak intensities decreased — Lapham et al. (1964). X-ray diffraction intensity decreases also by K loss from *K*-feldspars — de Mumbrum (1963).

The intensity of the basal reflections of interstratified minerals is lost to about 30% as compared to those of their single components — Mac Ewan (1961). Vermiculite, montmorillonite and expanded illite when saturated with several cations have varying intensities of their basal reflections — Barshad (1950).

Interlayering of $Fe(OH)_2^+$, $Fe(OH)^{++}$, $Mg(OH)^+$, $Mg(OH)_2$ and to a less degree $Al(OH)_2^+$, $Al(OH)^{++}$ between expanded layers of montmorillonite and the illite-related minerals, also change their intensities. Even kaolin minerals which have the most homogeneous composition and structure of all clay minerals, show large differences in the relative intensities of the reflections of samples from various origin for each group — Fig. 5. Badly crystallized kaolinite (fire clay mineral) cannot be distinguished from better ordered halloysite.

By calibration of the (001) reflection of kaolinite $d = 7.09$ Å against the (020) reflection of Cerahydrate (trade name for AlOOH) $d = 6.08$ Å, an inverse relation was found between the peak intensity or the integrated peak intensity and the specific surface of the kaolinite investigated — van der Marel (1960). The samples investigated were all from well known deposits, not defiled with other minerals after X ray- analysis and after chemical analysis containing only 5 to 15% impurities.

For kaolinite with a specific surface of about 70 m^2/g the decrease in peak intensity or integrated intensity was from 1.5 to 0.5 and from 1.8 to 0.9 (relative values) respectively as compared to that of well crystallized kaolinite with a specific surface of about 16 m^2/g. These large differences are not relative to the small differences in the amount of impurities.

Brindley and Kurtossy (1961) believe that preferred orientation effects are the main cause of the above results. But the remaining spreading of the cement treated (disoriented) samples = 147:100, and 178:100 for the (001) and (002) reflection of kaolinite respectively, is too large to be tolerated in quantitative analyses.

When using the (060), $(3\bar{3}\bar{1})$, $(33\bar{1})$ reflection, which is less affected by preferented orientation owing to the $b_0/3$ displacements in disordered kaolinites, better results are obtained — Engelhardt (1955), Wiegmann and Kranz (1961).

Fig. 6 gives the results for several types of pure to nearly pure (85%) kaolin minerals from various origin for which the (001), (002), and (060), $(3\bar{3}\bar{1})$ $(33\bar{1})$ reflections were calibrated against the (111) reflection of 10% CaF_2. Further the results of the same samples but treated before with Vertex Sc.[1] a polymerizable harshon two component basis.

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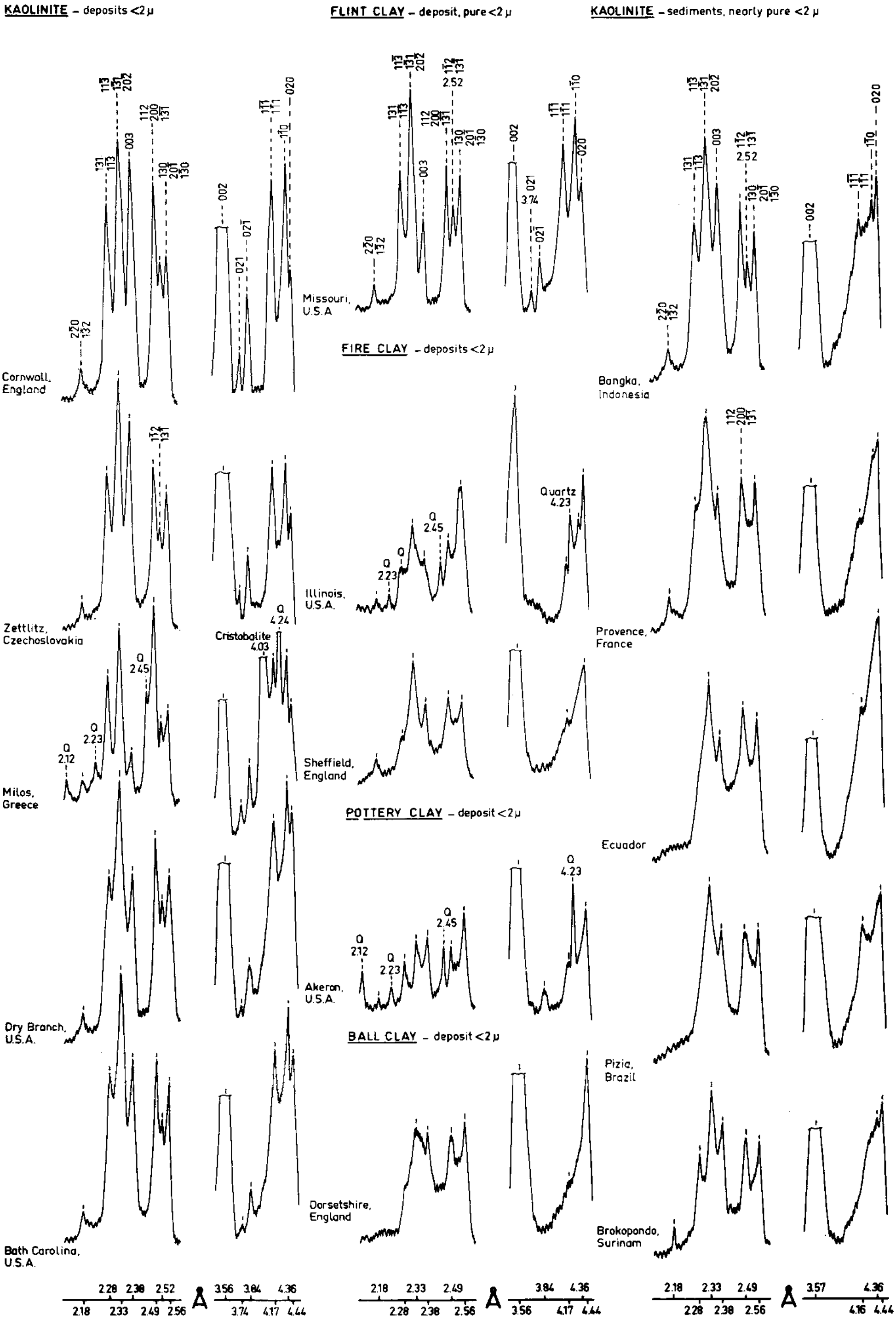
[1] Vertex selfcuring wax (methylmetacrylate) on two component basis fabricated by Kunstharsfabriek DIVO, Zeist, Netherlands.



a

Fig. 5. Most characteristic X-ray reflections of kaolin minerals from various origin

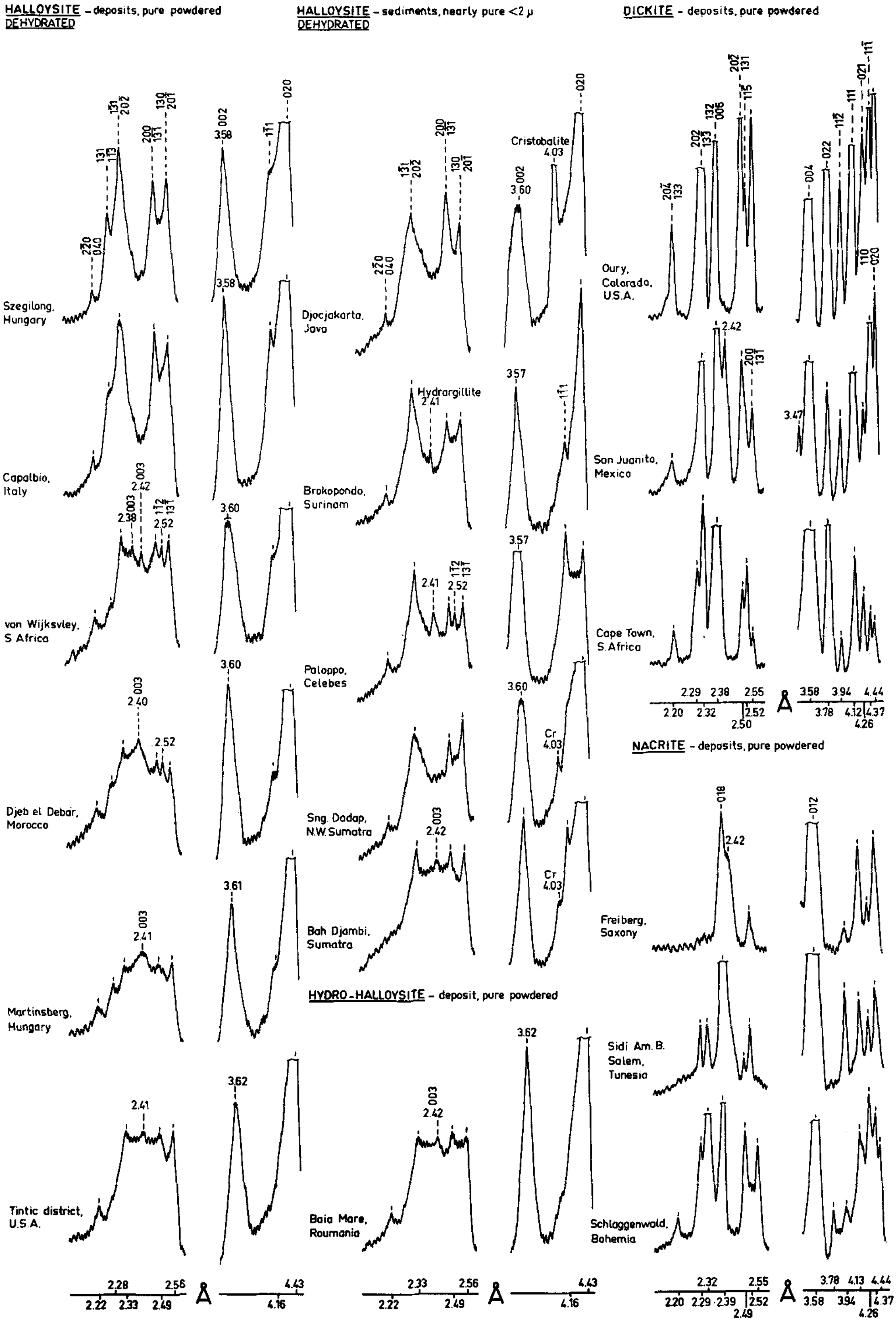

HALLOYSITE - deposits, pure powdered
DEHYDRATED
HALLOYSITE - sediments, nearly pure <2 μ
DEHYDRATED
DICKITE - deposits, pure powdered
Szegilong, Hungary
Capalbio, Italy
von Wijksvley, S Africa
Djeb el Debar, Morocco
Martinsberg, Hungary
Tintic district, U.S.A.
Djocjakarta, Java
Brokopondo, Surinam
Paloppo, Celebes
Sng. Dadap, N.W. Sumatra
Bah Djambi, Sumatra
HYDRO-HALLOYSITE - deposit, pure powdered
Baia Mare, Roumania
Cristobalite 4.03
Hydrargillite 2.41
Cr 4.03
Oury, Colorado, U.S.A.
San Juanito, Mexico
Cape Town, S. Africa
NACRITE - deposits, pure powdered
Freiberg, Saxony
Sidi Am. B. Salem, Tunesia
Schlaggenwald, Bohemia
Å
2.28 2.56
2.22 2.33 2.49
4.43
4.16
2.33 2.56
2.22 2.49
2.29 2.38 2.55
2.20 2.32 2.52 2.50
3.58 3.94 4.44
3.78 4.12 4.37 4.26
2.32 2.55
2.20 2.29 2.39 2.52 2.49
3.78 4.13 4.44
3.58 3.94 4.37 4.26

Fig. 5b

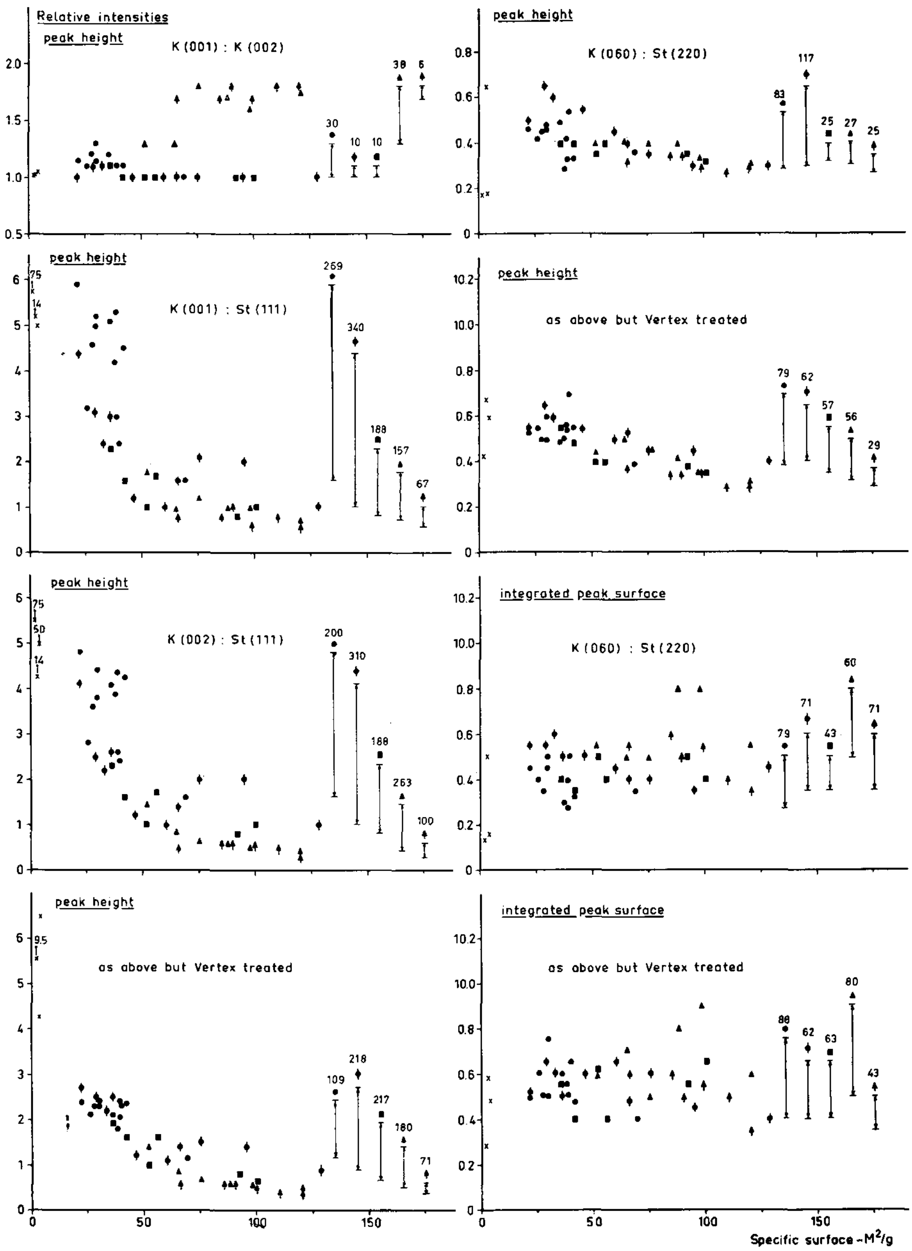


Fig. 6. Intensities of (001), (002), (060) $(3\overline{31})$ $(33\bar{1})$ reflections of various pure to nearly pure (85%) kaolin minerals at $d = 7.1$ Å, 3.6 Å, 1.48 Å respectively relative to intensities of CaF_2-Standard 10% at $d = 3.15$ Å (111) and 1.93 Å (220) and their specific surfaces (m^2/g). ● well crystallized kaolinite from deposits $< 2\mu$. ⧫ kaolinite from soils $< 2\mu$. ■ fire clay, ball clay, pottery clay. ▲ halloysite from deposits. ▴ halloysite from soils $< 2\mu$. × dickite, nacrite. Samples non treated and treated before with Vertex Sc. (mineral + standard : polymer : activator = 1:1:1)

The analyses show that notwithstanding the excellent disorientation effect of the harsh, there still remains a large spreading in the intensities of various samples for each kaolin type. For the (002) reflection of kaolinite from deposits, the spreading of the peak intensities (between bracelets = peak surface) of the harsh treated kaolinite samples = 109% (100%), for ditto from soils = 218% (185%), for fire clay, ball clay = 217% (234%), for halloysite—7 Å from deposits = 180% (150%), for ditto from soils = 71% (83%). The intensities of the (060) reflection is even somewhat increased by the harsh treatment; in particular for kaolin minerals with a large orientation effect. Such because by the disorientation relative a larger number of (060) layers are available for the X-rays to produce a reflection.

For the (060) intensities of the harsh treated samples is found for kaolinite from deposits = 79% (88%), ditto from soils = 62% (62%), fire clay, ball clay = 57% (63%), halloysite from deposits = 56% (80%), ditto from soils = 29% (43%).

There is a decrease of the intensities with breadth and particle size — see also van der Marel (1960, 1961).

Apparently the smallest particles are the less ordered, the most strained and have the largest thickness of amorphous Beilby material coating their surface. For, when the crystal is highest ordered there will only be a minimum of loss of X-rays which do not participipitate at a Bragg reflection as a result of atoms which are situated at regular distances from each other and also in planes parallel to each other. Assuming a Beilby layer of 1 and 10 Å, the finest kaolinite sample investigated (128 m^2/g), should consist of 2.56 and 25.6% amorphous material.

Fig. 7 shows the results of analogous experiments with several pure to nearly pure (85%) Na-saturated montmorillonites of various origin. In this case of fine particles the orientation effect is absent. The Vertex treated samples even show an increase of the intensities of their basal spacings which is caused by a better orientation of the plates.

The remaining variability is for the (060) reflection, which is the least affected by orientation, still 36% (peak height) and 77% (peak surface). Surface intensities are for weak reflections less accurate as peak height intensities because of instrumental errors in the readings and the unsharp border of the background.

This figure further shows that a particle size/X-ray intensity relation for the various samples investigated is absent.

But also non platy minerals like hydrargillite, boehmite, goethite, limonite, hematite show a large variability in the intensities of their X-ray reflections — van der Marel (1961).

Even non complicated minerals like rock salt — Renninger (1934), quartz — Pollack et al. (1954), Despujols (1957), Legrand and Nicolas (1958), tridymite and cristobalite — Swindale (1955), Flörke (1955) show appreciable variations in the intensities of their reflections from one individual to another. In this case they are mainly caused by differences in their mosaic character. If the particles are too small or if the crystallites have crystal defects (mosaic structure) there is increased scattering of the X-rays — Despujols (1957).

IV. Application

Fig. 8 shows the X-ray spectra of the organic poor clay ($<2\,\mu$) separate of various soil types. The reflections are all broad at their base and of an intensity of maximal 30 cts/sec = 10 cm on the diagram.

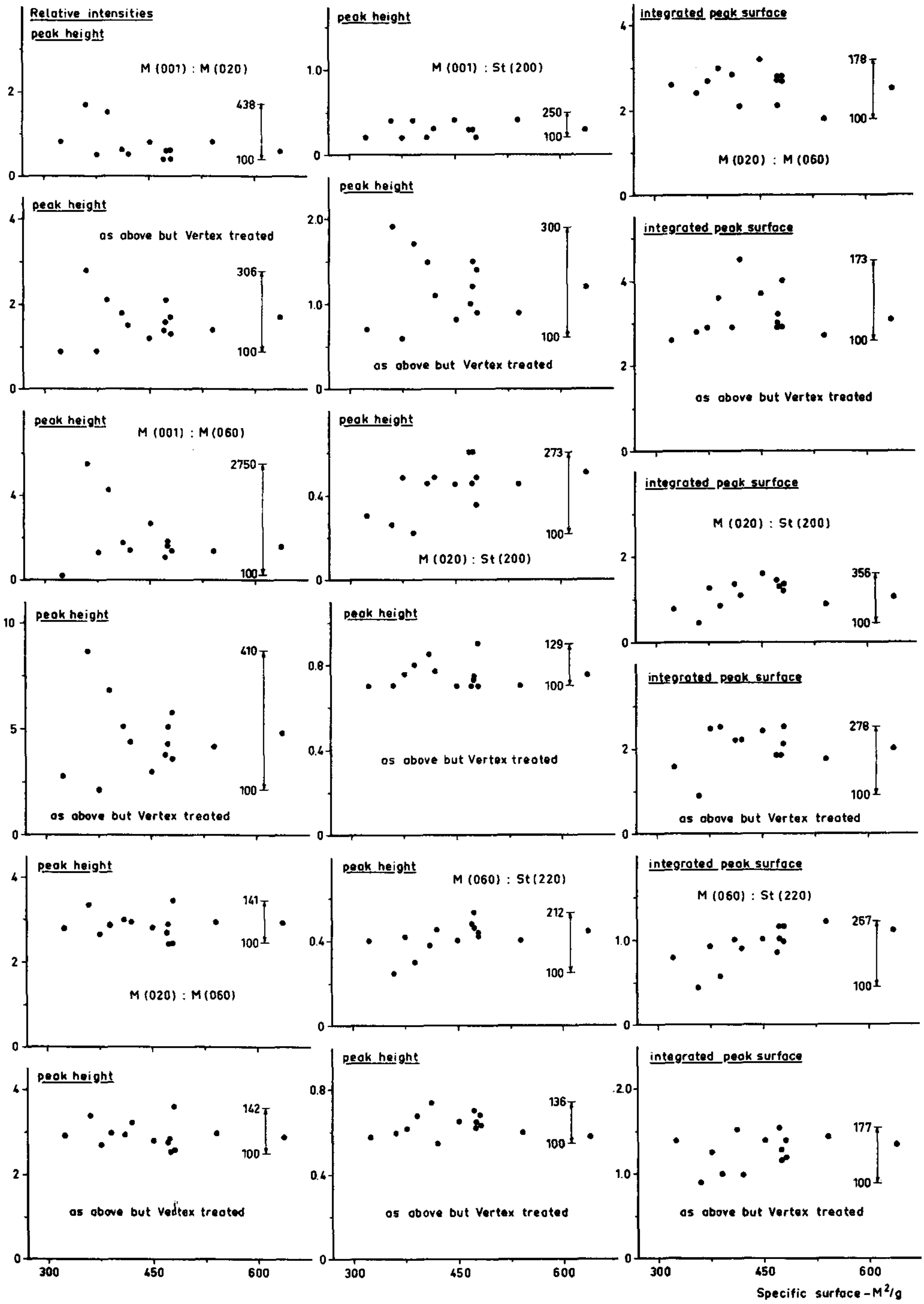


Fig. 7. Intensities of (001), (020), (060) (33) reflections of pure to nearly pure (85 %) Na-saturated montmorillonites $< 2\mu$ at $d = 10$—13 Å, 4.46 Å, 1.50 Å respectively relative to intensities of NaF-Standard 10% at $d = 2.31$ Å (200) and 1.64 Å (220) and their specific surfaces (m^2/g). Samples non treated and treated before with Vertex Sc. (mineral + standard : polymer : activator = 1:1:1)

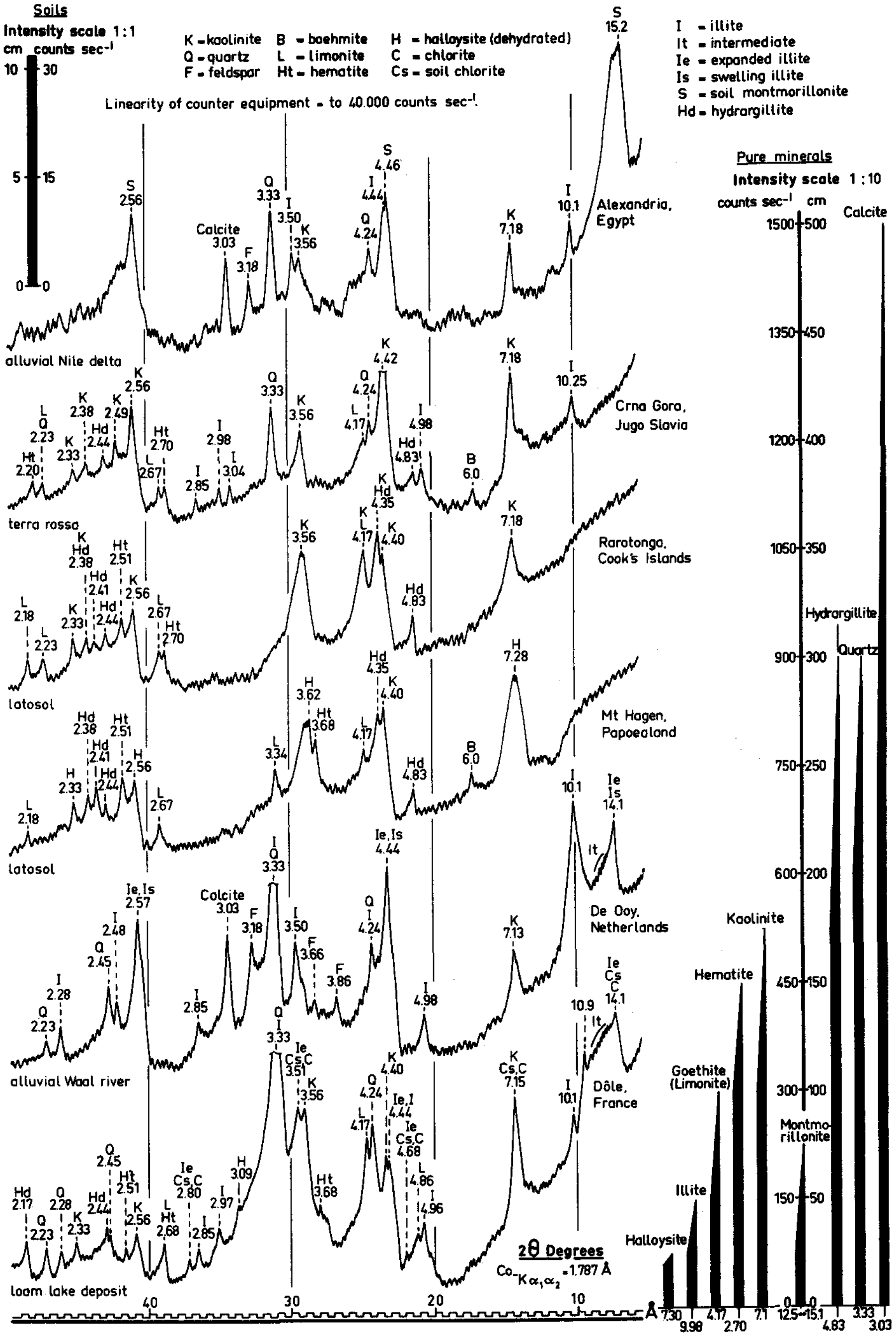


Fig. 8. Intensities of Bragg reflections of minerals in the organic poor clay separate ($< 2\mu$) of some soil types compared with those of pure minerals. — With permission of Acta Universitatis Carolinae, C.S.R. (1961)

As a contrast those of pure minerals are much stronger: halloysite = 25, illite = 50, montmorillonite = 75, kaolinite = 175, quartz = 300 cm. Vermiculite has, when measured with the X-ray equipment used, even a peak of 2400 cm.

The poor spectra of the clay separates of the soils are caused by bad ordering, isomorphous substitutions and defects in the crystals. The latter are partly of primary (inherent to the minerals) and partly of secondary (caused by weathering) origin — see also Clark et al. (1937). Another cause is small particle size (broadening, loss intof ensity) and contamination with fine amorphous inorganic and organic matter (scattering of the rays). The latter can be removed by 10% H_2O_2 which gives an improvement — for details of various treatments — Beutelspacher and van der Marel (1961a, 1961b).

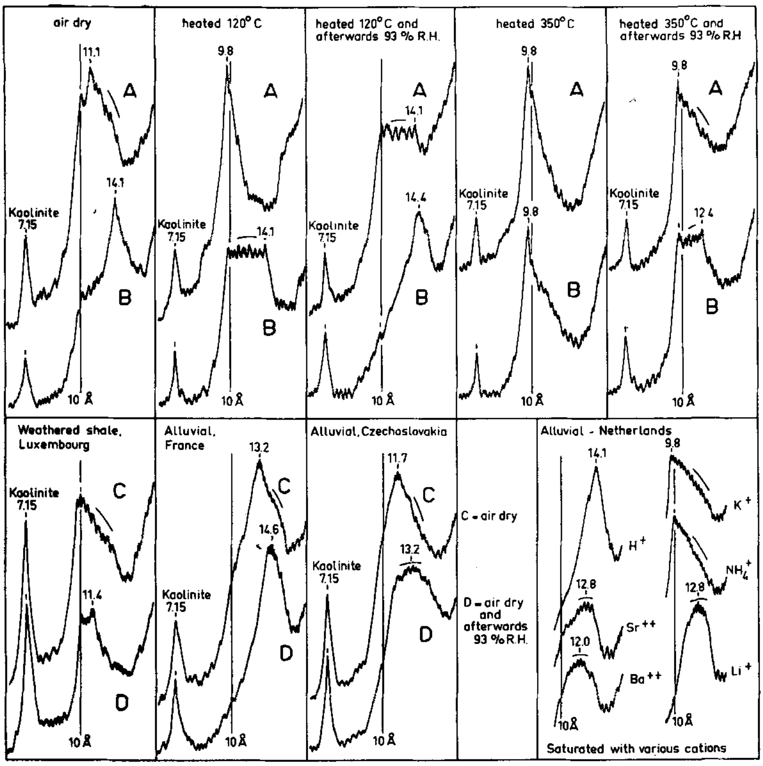


Fig. 9. Basal spacings of the clay separate ($< 2\mu$) of some soil types (*A* Loess-Netherlands, *B* Alluvial-Netherlands) as related to their pretreatment

Also the line which can be drawn through the bases of the separate reflections is very irregular. This is caused by overlapping of several reflections. In particular when the diffraction maxima are close together and the concentration of one mineral far exceeds that of the other, the effect is large.

Apart from the above difficulties there is the severe problem of finding one and the same mineral in various sediments. Even kaolinite which still has the most uniform composition and structure has a large variability. For the interstratified minerals which are very common in the clay separate of soils, this will be even larger. The same holds for various mineral types which are formed by deposition of Al- and Fe hydroxy groups in the interlayers of expanded illite, swelling illite and soil montmorillonite by weathering action.

All these expanded minerals with various charge densities of their interlayers and the latter filled to various extents with cations of various polarizability, hydroxides of various composition or H_2O molecules have (001) reflections which position and intensity moreover depend on conditions during the separation of these minerals from the sediments and the preparation of the sample afterwards before its spectrum is registered by the instrument. This is illustrated by Fig. 9.

Peak intensities of montmorillonite which contain a large amount of exchangeable cation between the layers surrounded by hydrated H_2O molecules, depend largely on the amount of oriented H_2O layers — Barshad (1950). The Ca and Mg saturated samples with 2 oriented H_2O layers give the highest intensities, because parallelism and preferential orientation are enhanced — Talvenheimo and White (1952).

Other examples of the influence of pretreatment of the sample on the shape of the spectra are given by Milne and Warshaw (1956), Warshaw (1960), Heller (1961). Beutelspacher and Fiedler (1963), Sayegh et al. (1965). By different mounting techniques the results may vary in the order of even 250% — Gibbs (1965).

D. Infrared Analysis

I. Theoretical Approach

When under normal (room) temperature conditions atoms and molecules which continuously vibrate at 10^{12} to 10^{14} Hz around their equilibrium positions, are radiated with electromagnetic rays of the infrared range 3 to 30 μ (10^{13} to 10^{14} Hz), they will absorb energy when the energy of the rays is in resonance with the energy needed for their vibration. Only those vibrations are infrared active where the dipole moment of the atoms or molecules is changed in direction and magnitude by the vibrational movement (non active I.R. vibrations may be Raman active for which a change in polarizability is needed). In the ideal case of two free moving atoms of small amplitude and a highly symmetrical stretching path, the following relation exists — Barnes et al. (1944).

$$E = (v + {}^1/_2)\frac{h}{2\pi}\sqrt{\frac{k}{u}} = (v + {}^1/_2)\, 5.11 \times 10^{-4} \sqrt{\frac{k}{u}}\,.$$

E = vibration energy (eV mole^{-1} = 23.04 k cal atom^{-1}).

k = bond force constant between the two atoms (dyne cm^{-1}) = $1.86 \cdot 10^5/(r - d_{ij})^3$ in which r = interatomic distance (Å), d_{ij} = a characteristic for a diatomic molecule consisting of an atom of the i-th and the j-th row respectively in the periodic system — Badger (1934).

u = the reducing mass = $\frac{m_1 \times m_2}{m_1 + m_2}$ (m_1 and m_2 = mass atom m_1 and m_2 respectively in g.

h = constant of Planck = $6.625 \cdot 10^{-27}$ erg sec.

v = vibrational quantum number (0, 1, 2, 3, ...).

The vibration energy is commonly expressed in the frequency ν of the rays = $1/\lambda$ in which λ = the wave length in Å. Thus when $1/\lambda = 1$ cm^{-1} also called Kaiser (K) unit:

$$K = \frac{1}{\lambda} = h\,c = 1.986 \times 10^{-6}\,\text{erg}.$$

Ideally the vibrating frequency of two atoms varies inversely with the root of their atomic mass. Thus if Al is replaced by Fe, the absorption band shifts to a lower energy (cm^{-1}) level. Vibrational energy depends also on the bond force constant (k) between the two atoms. For atoms in tetrahedral configuration (AB_4) the following relation exists — GORDY (1946):

$$k(AB) = 3.29\left(\frac{x_A\,x_B}{r^2}\right)^{3/4} - 0.40\;\cdot$$

x_A and x_B are electronegativities of the bonded atoms; r = internuclear distance.

For tetrahedral configuration $k(\text{Si—O}) = 5.85 \cdot 10^5$ dynes/cm and $k(\text{Al—O}) = 5.06 \cdot 10^5$ dynes/cm ($r = 1.62$ Å, $x_{Si} = 1.8$ eV, $x_{Al} = 1.5$ eV, $x_O = 3.45$ eV) there will be a shift of the I.R. band to lower cm^{-1} values when Si is replaced by Al in increased amounts.

However, in reality the above equations for a stretching vibration give only a simple representation of what actually happens e.g. the repulsing forces between the atoms considerably increase at small distances. A crystal consists of a framework of densely compacted atoms and atomgroups with numerous types of vibrations in case of polyatomic structure. Thus the vibration energies of two atoms in a crystal may be changed and even damped because of dipolar association effects from surrounding atoms and molecules. For bending and wagging, rocking, twisting movements indicated by δ and γ, vibrating in a direction parallel and perpendicular or oblique to the molecule plane respectively, the calculations of the vibrational energies are very complicated and mostly impossible. Apart from the fundamentals and their weaker sums (CO_2: $\nu_1 + \nu_3 = 3716\ cm^{-1}$ and multiple overtones (H_2O: $2\nu_1 = 7251\ cm^{-1}$, $3\nu_1 = 10631\ cm^{-1}$) also vibrations of somewhat higher or somewhat lower energy level may exist. They result from perturbations by neighbouring components, anharmonic coupling, interactions, crystal dislocations, strain, stress, vacant holes, Frenkel and Schottky crystal defects, isomorphous substitutions of incidental character (impurities), disorder in the arrangement of the atoms which all modify the electronic structure in their neighbourhood. The effect is a broadening of the bands.

Crystals have a large number of low level ($< 300\ cm^{-1}$) lattice (skeletal) vibrations. They also broaden the bands of sharp harmonic vibrations by anharmonic coupling with lattice vibrations or even cause forbidden vibrations to appear in the spectrum by combination e.g. that of the strong NH_4-ion band at 1754 cm^{-1} of NH_4Cl or NH_4Br crystals — HORNIG (1948).

By association with other atoms or atomgroups, the bands move to lower energy levels e.g. the 3300 cm^{-1} polymer of the O—H stretching vibration of ethylalcohol moves to 3630 cm^{-1} of its monomer thereby increasing in intensity when this liquid is largely diluted with an inert solvent like CCl_4 or CS_2. The O—H stretching band at 3756 cm^{-1} of monomeric H_2O molecules in vapour or in inactive solvents, is replaced by an intensive doublet at 3515 and 3575 cm^{-1} of its polymer, when water is dissolved in dioxane or pyridine — ERRERA and SACK (1938). The O—H stretching vibration may even fail in organics like m-nitrophenol, salicylic aldehyde and 2.6-dihydroxybenzoic-acid as the protons are in this case in a "chelated" position between two oxygen ions — HILBERT et al. (1935). Also in spectrography of crystals analogous association effects are known — see further.

II. Determination of the Intensity of a Vibration Band

After Lambert-Beer's law the intensity of the transmitted rays of a certain frequency (ν) at a certain temperature is related to the concentration of the sample absorbing the rays in the inert solvent in which the sample is homogeneously dissolved:

$$I = I_0 \exp^{-\varepsilon_\nu c l}$$

which delivers:

$$E\,(\text{extinction}) = -\log I/I_0 = A\,(\text{absorbance}) = \log I_0/I = \varepsilon_\nu c l.$$

I and I_0 = intensity of the transmitted and incident radiation.
c = concentration of the sample (mole/liter).
ε_ν = molar extinction coefficient (liter cm^{-1} mole^{-1}).
l = thickness of the sample (cm).

From the above follows that, given a certain thickness of the sample, a linear relation exists between extinction and concentration. For spherical particles of diameter d when pressed in a non absorbing medium like KBr can be written:

$$E = -\frac{3}{2}\,\frac{m}{F\varrho K d}\log\left[(1-K)+K\Theta\right]\cdot$$

m = mass of the sample dispersed in the KBr disc.
ϱ = density of the particles.
d = diameter of the particles.
F = cross sectional area of disc.
Θ = transmittance of the particles = $\dfrac{1-(kd+1)\,e^{-kd}}{k^2 d^2/2}$ (k = linear absorptivity).
K = the geometrical fraction of the surface normal to the incident rays that is covered by the particles.

As particle size increases there is a decrease in the extinction. For calcite particles to about $< 10\,\mu$ the effect however is small, but it increases largely for coarser sizes.

For molecular dispersion of the particles ($kd \to 0$) in the KBr pellet the relation exists:

$$E_{(kd\to 0)} = \frac{m}{F\varrho} \times \frac{k}{2.3}$$

which equation is similar to that of Lambert Beer for absorbing liquids in a solvent when read for $\frac{k}{2.3} = \varepsilon$ and for $\frac{m}{F\varrho} = c\,l$ — for details Otvös et al. (1957) and Duyckaerts (1959).

If a double beam instrument is used with always the same slit width and pellet surface, addition of a standard mineral is superfluous unless Lambert-Beer's law is not followed. Non linearity of the law is caused by non linearity of the photocell, asymmetric vibrations, association effects from other atoms and atomgroups.

For mixtures with non linearity of the Lambert-Beer's law calibration curves should be made by a plot of the ratios for E mineral to be investigated/E internal standard against their weight ratios. The amount of the internal standard added to the samples should be taken constant and that of the mineral to be investigated variable. Another procedure is to calibrate the % of the unknown component in the mixture against increasing amounts of the pure component in the reference sample = differential absorbance method — HAMMER and ROE (1953). An estimation of the maximum extinction of a band for quantitative purposes can be obtained by the WRIGHT (1941) and HEIGL et al. (1947) procedure for base line correction. In the Nujol technique a certain amount of the sample is mulled together with a certain amount of a Standard mineral e.g. dl-Alanine = 851 cm^{-1} — BARNES et al. (1947), $CaCO_3$ = 875, 1435 cm^{-1} — KUENTZEL (1955), KCNS = 2041 and 2127 cm^{-1} — WIBERLEY et al. (1957), $Pb(SCN)_2$ = 2041 cm^{-1} — BRADLEY and POTTS (1958). The spectrum of this mixture is compared to similar mull spectra in which a pure compound of the sample replaces the unknown in increasing amounts.

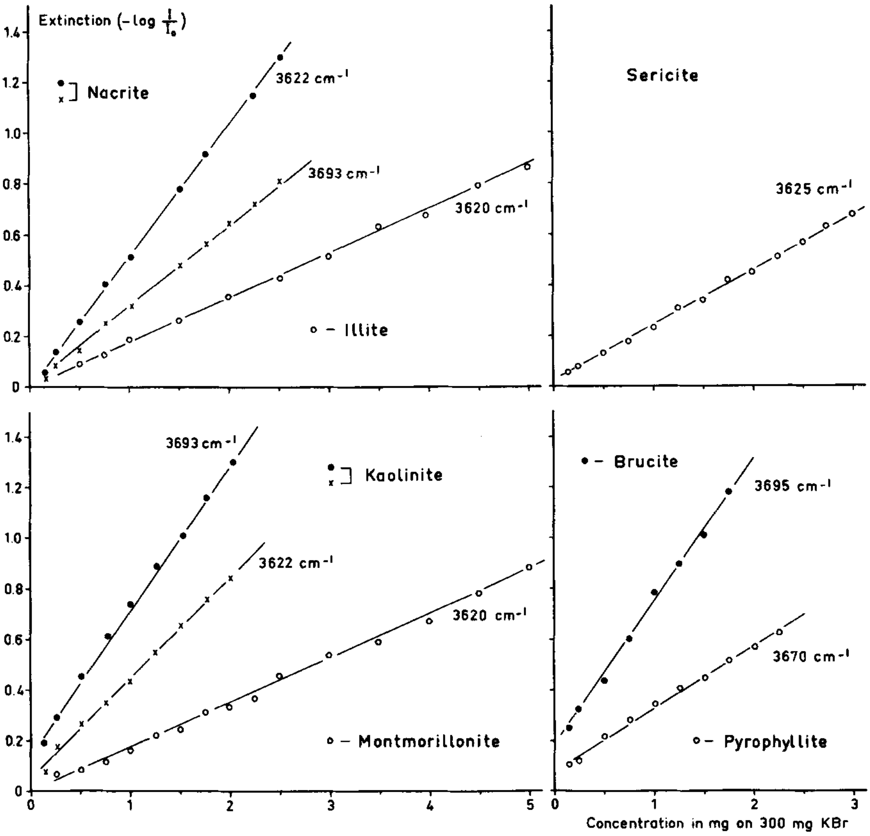


Fig. 10. Mineral concentration in mg on 300 mg KBr and extinction — Lambert-Beer law

In the KBr pellet (disc) technique of STIMSON and O'DONNELL (1952) and SCHIEDT and REINWEIN (1952) a certain amount of the sample is first mixed and slightly ground with infrared pure KBr (for spectroscopy) in a mullite mortar. After drying at 120° C the mixture is pressed (ca. 10 $tons/cm^2$) in an evacuated die to transparent pellets of a certain constant diameter inherent to the instrument used.

Fig. 10 shows the extinctions at increasing concentrations for kaolinite ($< 2\,\mu$) and powdered pyrophyllite, talk, brucite, nacrite. Lambert-Beer's law is followed.

Only at high extinctions there is some deviation. A measurement of the integrated intensity of an absorption band provides a closer approach to the real intensity of the vibrational movement; such in particular for broad, asymmetric bands. Its calculation by graphical way is very tedious however, but modern instruments may be provided with an automatic integrator.

III. Quantitative Analysis — General

Absorption bands suited for quantitative analyses should be of high intensity and not be overlapped by neighbouring bands of other minerals. Moreover the band should be small and deep so that the exact point where resonance absorption caused by a vibrational movement of atoms or atomgroups has started and ended, can clearly be distinguished from background absorption caused by noise of the detector circuit and conversion of absorbed radiation in unordered thermal motions of the crystal components. The background base line should be of minimum elevation at either side of the peak. Finally the bands of a mineral should be reproducible regardless of its origin or particle size.

The I.R. spectra of most common clay minerals and their admixtures mainly show broaded bands of small intensity overlapping each other even for the minerals apart — Fig. 11.

Particle size. When particle size is much larger than or about equal to the wave length of the incident transmitted infrared rays, in this case = 2.6 to 24 μ, there will be a decrease of the intensity of the absorption band mainly because of non wavelength selective reflection and diffraction respectively — see for calcite: Duykaerts (1959). Smooth (polished) surfaces and large differences in refractive index (Fresnel equation) give increased reflection and therefore poorly developed infrared spectra. The Christiansen effect which is characterized by an asymmetrical shape of the band at its higher frequency side from which results a non linearity of the Lambert-Beer's law, is only negligible for particles smaller as their wavelength. This is caused by a rapid change of the refractive index in the vicinity of an absorption band.

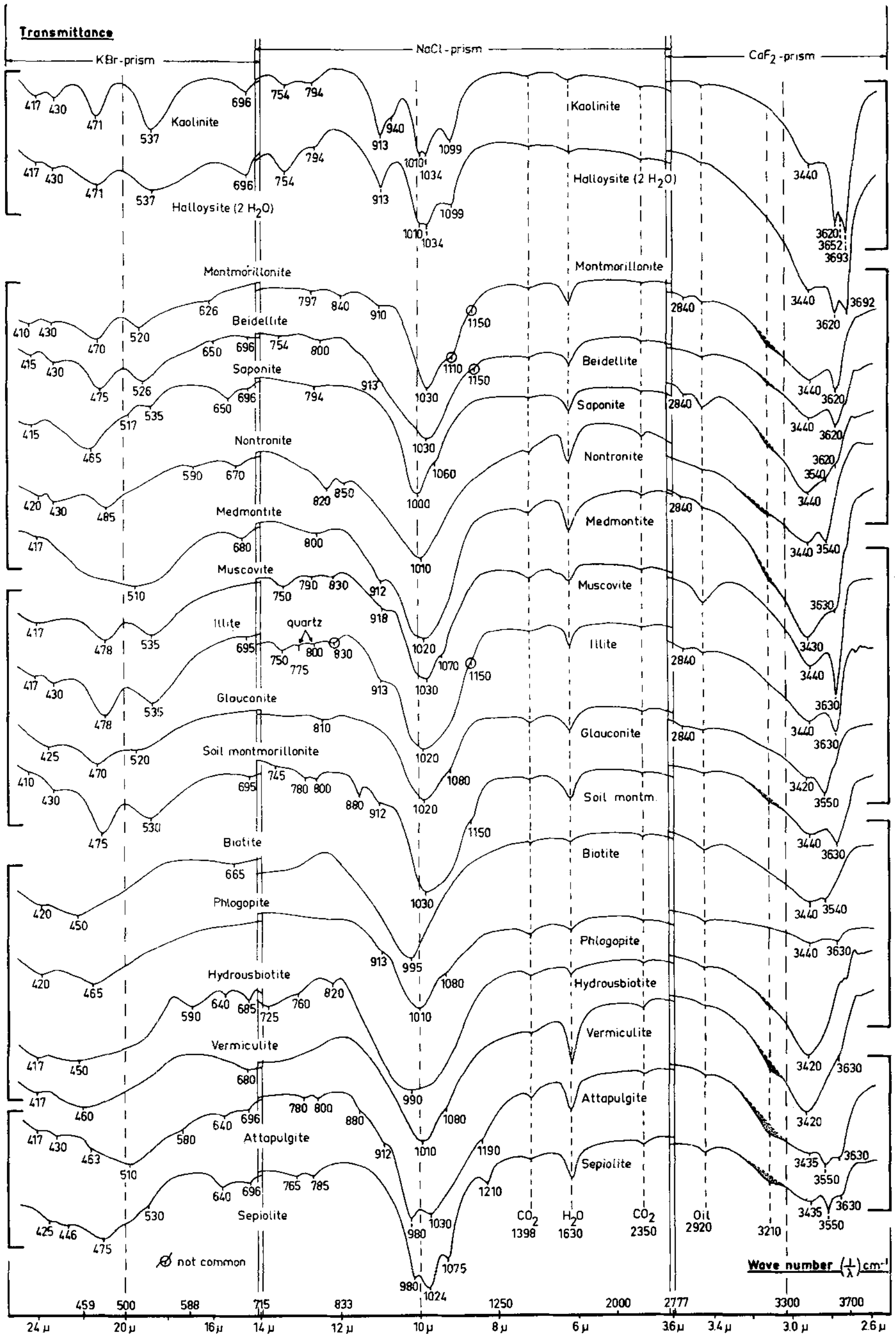
If the particles are < 0.1 to 0.3 of λ the intensity of the transmitted rays is decreased (base line = background absorption increased) by allside, wavelength selective Tyndall scattering. After Rayleigh's scattering equation — see Valesek (1960), the intensity of scattering is inversely related to the 4th power of λ and reversely to the 6th power of the radius.

$$I_s = I_0 \frac{(n^1 - n)^2}{n^2} (1 + \cos^2 \Theta) \frac{\pi N V^2}{R^2 \lambda^4}.$$

I_s = intensity scattered rays; I_0 = intensity incident rays.
n^1 = refractive index of scattering particle; n = ditto of embedding medium.
N = number of scattering particles; V = volume of ditto.
λ = wave length used; Θ = scattering angle.
R = distance from the sample to the observer.

The above equation is only valid if the amount of light scattered per particle is small and the phase shift of the scattered light can thus be neglected — Zimm and Dandliker (1954).

Scattering of ZnO ($n = 2.0$) in water ($n = 1.33$) was found to be negligible for particles > 0.9 μ at $\lambda = 0.48$ to 0.63 μ.



a

Fig. 11a and b. Infra-red spectra of most common minerals and their admixtures in the clay separate of soils. — With permission of Acta Universitatis Carolinae, C.S.R. (1961)

Maximum scattering occurred at about 0.25 μ. For smaller particles at equal concentrations by weight, scattering decreases because of the V^2 factor — Stutz (1930), Clewell (1941).

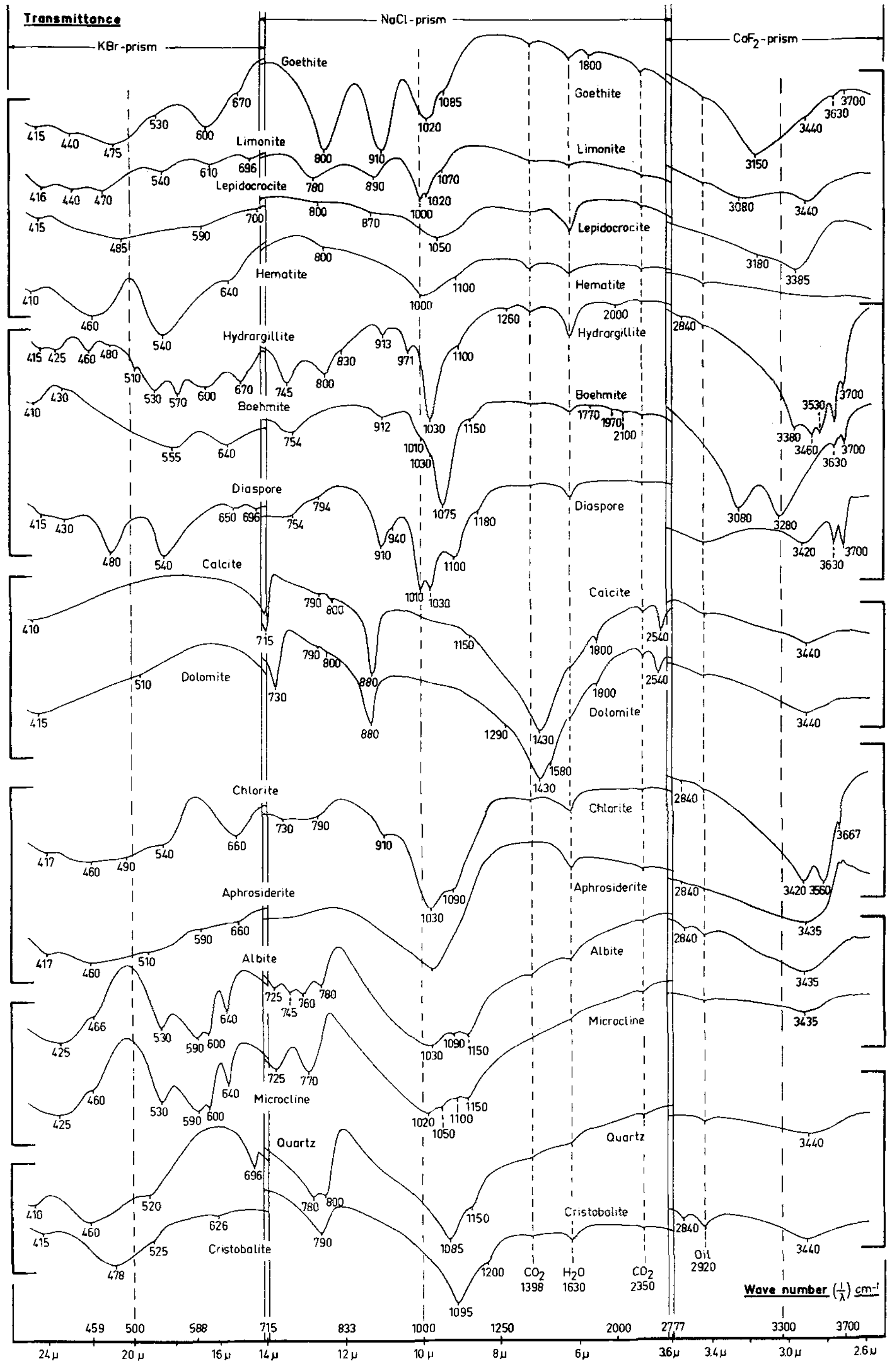


Fig. 11 b

For clay particles ($n = 1.56$) with a maximum specific surface of 60 to 450 m^2/g (equivalent particle $\varnothing = 0.04\,\mu$ to $0.005\,\mu$ respectively) embedded in KBr

($n = 1.56$) there will be some scattering only in the shortest range of their I.R. bands at ca 2.7 to 3 μ. Fine amorphous admixtures (Si, Fe, Al-gels) and organic matter (humus) will also give some scattering (background) in that traject — Beutelspacher and van der Marel (1961). The latter can be removed by previous oxidation with H_2O_2.

Intensity of a vibration. The intensity of an absorption band (E) depends on the magnitude of the dipole moment (μ) change of the atomgroups (atoms) during the vibrational movement. Therefore E of HCl is stronger than that of HJ ($\mu \cdot 10^{18} = 1.08$ and 0.38 e.s.u. respectively).

If the polarity of one of the two vibrating atoms (or atomgroups) is increased by coordination with another atom (atomgroup), the intensity of the vibration increases too because of an increase in the dipolemoment — see N—H in ethylenediamine and ethylenediaminebromoplatinum — Svatos et al. (1955). Irregularities in the crystal caused by incidental isomorphous substitutions, crystal defects and impurities, change the electronic structure in their neighbourhood and therefore the magnitude of the dipolemoment transition. The frequency and intensity of a certain vibration depends on the nature of the components, the surrounding components, their distances and the degree of association or chelation; in general on their geometric arrangement. In a highly ordered crystal there will be a maximum of resonance absorption of I.R. rays for a certain vibration of two atoms (or of an atom and an atomgroup etc.). For, the deviations in the distances between these atoms (or atoms and atomgroups etc.) are the smallest and their surroundings are in this case also the most constant as compared with those of a badly ordered crystal. In literature many examples are given — Laves and Hafner (1956, 1957), Serratosa and Bradley (1958), Bassett (1960), Milkey (1960), Lyon and Tuddenham (1960), Liese (1963), Manghnani and Hower (1964) — see further A.

The spectra of the same mineral but of various origin are not always constant either. This is demonstrated in Fig. 12 for the bands of free O—H, octahedral O—H and O—H between the plates — see also Beutelspacher (1956), van der Marel and Zwiers (1959), etc. for 85 to 95% pure kaolin minerals of various origin.

There is an inverse relation between extinction and particle size for the 795, 754 and 698 cm^{-1} bands of kaolinite. Also halloysite shows this relation — van der Marel (1960). Its specific surface however is relatively larger, because of strongly bonded ethyleneglycol molecules (Dyal-Hendricks method) between the layers. The same holds for the 3693 cm^{-1} band of free O—H. The 3622 cm^{-1} band of octahedral O—H is influenced by the strong 3440 cm^{-1} band of O—H of absorbed H_2O molecules and therefore has a large spreading — Fig. 13.

In this case of well defined pure minerals of non scattering particle size (specific surface = 20 to 100 m^2/g or with equivalent ⌀ = 0.11 to 0.022 μ) differences in the I.R. traject investigated are mainly caused by differences in crystal ordering in such a way that the magnitude of the dipolemoment decreases as particle size decreases; for the rest by a Beilby layer coating the particles with amorphous — non I.R. active material. Assuming a thickness of 1 and 10 Å the decrease is 0.4 to 2% and 4 to 20% respectively. Of the existing clay minerals the above example of kaolinite is still the best ordered and of most uniform composition.

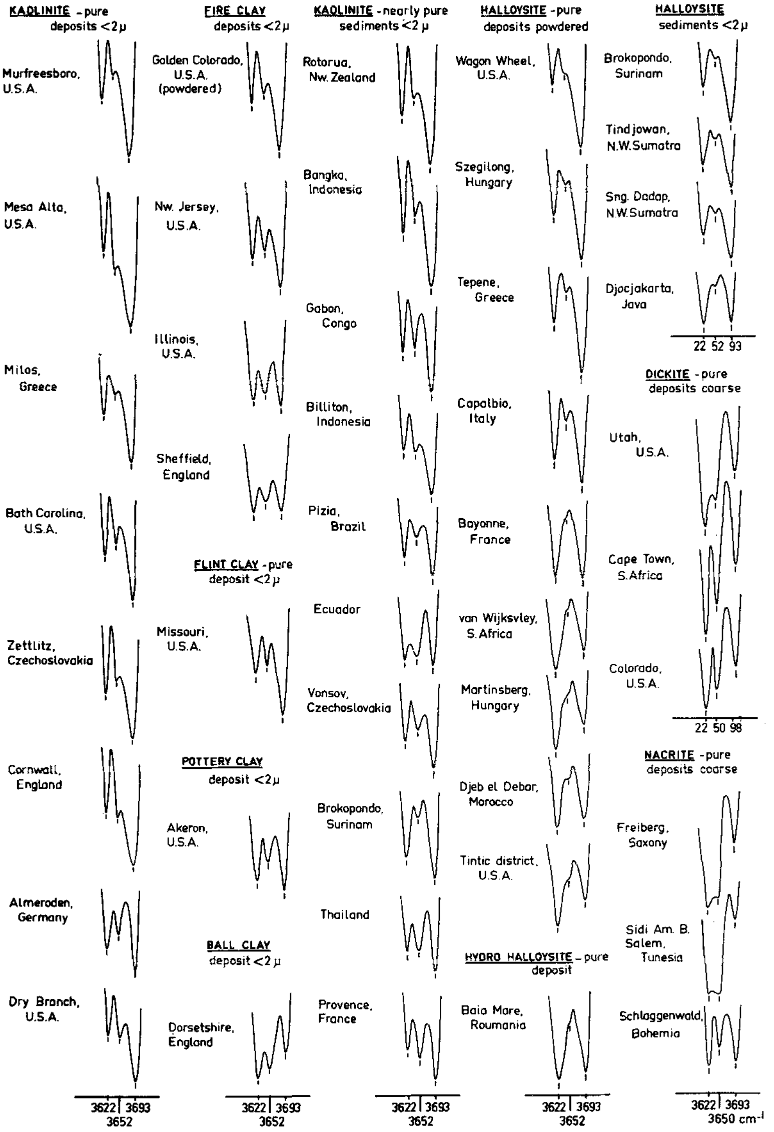


Fig. 12. Infra-red spectra CaF_2-prism of various kaolin minerals 0.58% in KBr pellets

IV. Application

Fig. 14 demonstrates I.R. analyses of the clay separate ($< 2\,\mu$) of various soil types — VAN der MAREL (1961). — Their composition was verified by X-ray analysis. The spectra mainly show broaded bands of small intensity overlapping each other moreover. Their intensities are also smaller than those of minerals from pure deposits particularly those of organic liquids e.g. benzene; such by disorder in the crystals, scattering effects, the prevailing of an amorphous Beilby layer — see before. The CaF_2 traject is not suited for quantitative analyses of minerals with a large surface because of the strong 3430 cm^{-1} band, which largely deform the O—H stretching vibrations of various minerals in the 3400 to 3700 cm^{-1} traject. It is caused by losely absorbed water molecules on the particle surface with O—H . . . O distance = 2.87 Å. (Strongly absorbed monolayered H_2O molecules on the particle surfaces, hydrated H_2O molecules of cations and H_2O molecules in narrow pores have 3220 cm^{-1} with O—H . . . O distance = 2.77 Å. H_2O molecules in ice have 3180 cm^{-1} with O—H . . . O distance = 2.76 Å).

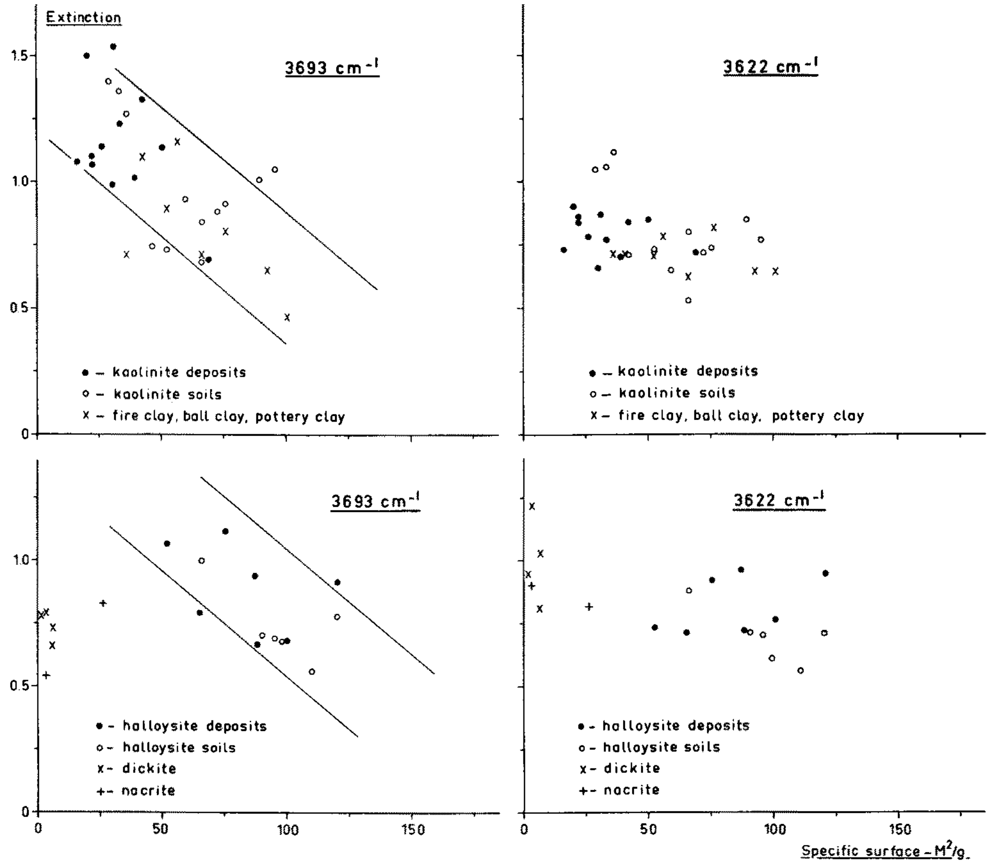


Fig. 13. Extinction (—log I/I_0) at 3622 and 3693 cm^{-1} (CaF_2-prism) of various kaolin minerals and their specific surface. Samples (0.58%) pressed with KBr to pellets

In the higher frequency level occur free O—H, O—H—O and M(metal)—O—H stretching bands of high energy. In the middle level are O—H, O—H—O, bending and M—O—H, M—O, M—O—M stretching and ditto bending vibrations of lower energy level. In the lower regions are mainly M—O, M—O—H and M—O—M bending vibrations of lowest energy level.

The spectrum of goethite is far better developed than that of the less ordered limonite. Bayerite, hydrargillite and boehmite, common minerals in bauxite deposits may easily be distinguished from each other. Also in this case the bands are overlapped by neighbouring bands of other minerals. Quartz and cristobalite may be distinguished from each other by the 780 cm^{-1}, 800 cm^{-1} doublet and 790 cm^{-1} band. Quartz amounts of 1% may be detected when not overlapped

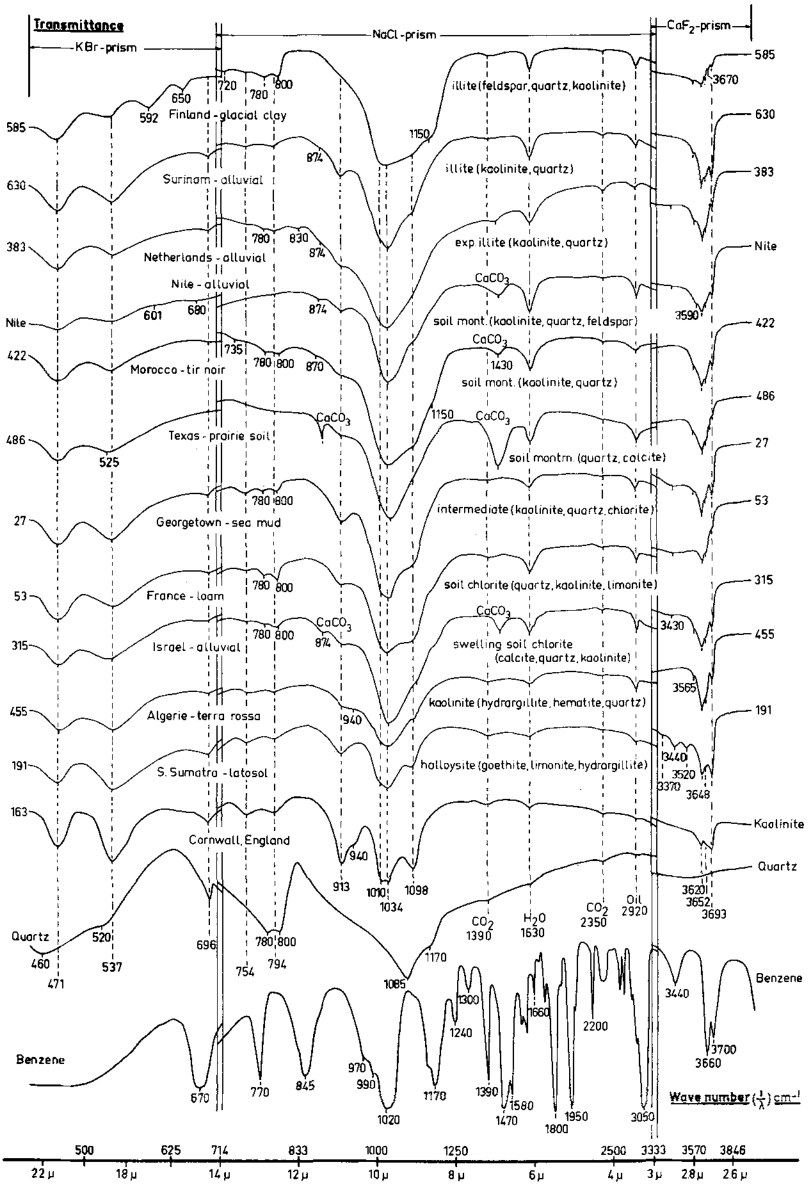


Fig. 14. Infra-red spectra of separate $< 2\mu$ from various soil types, kaolinite, quartz and benzene. Impurities between bracelets. — With permission of Acta Universitatis Carolinae, C.S.R. (1961)

by other bands and when particles are of uniform size — Hunt and Turner (1953).

Calcite may be distinguished from aragonite by the 880, 1430 and 859, 1480 cm^{-1} bands respectively. Aragonite however is a rare mineral in the clay separate of sediments. Dolomite may be distinguished from calcite and magnesite by the 730, 715 and 750 cm^{-1} band respectively. As these bands are sharp and not overlapped by others, they are — if particle size thereby is uniform — best suited for quantitative analysis. From the above follows that (semi) quantitative analyses by the I.R. method will be restricted to non complicated mixtures of the better ordered minerals of well defined composition, particle size and sample locality and thereby with narrow bands of high intensity and sharpness e.g. quartz, hydrargillite, carbonates, sulfates, etc.

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