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Phase analysis and characterization of bauxites and red muds by infrared spectrophotometry

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1. *Quantitative phase analysis of bauxites and red muds; the comparison of the applicability and efficiency of the X-ray, thermal and infrared methods.*
2. *The effect of the grain size (milling) on the phase analysis data.*
3. *The significance of the correct choice of the standard materials in the phase analysis.*
4. *Some other applications:*
   The role of isomorphous substitution in the phase analysis; aluminium substitution in the iron minerals.
   Hydrogen bridge bond strength in, and digestibility of bauxite.

For the quantitative phase analysis of bauxites and red muds first of all X-ray and thermal methods are applied. IR spectrophotometry has been proposed only in the last years due to the problems arising in the registration of the spectra of solid materials. There are however many parameters -e.g. the crystalline state, purity (isomorphous substitution) grain size ect. of the mineral—which have significant effect on the analysis in all the mentioned methods. The very complex effects of these lead to the fundamental problem of the quantitative analysis, namely to the proper choice of the standards.

There are several isomorphous aluminium-iron mineral pairs in the bauxite, thus the theoretical basis of the mutual substitution exists. Certain other foreign ions might have also role. A lot of work has been done and published concerning the determination of the fact and degree of substitution, both in synthetic and in natural samples, based mostly on the phenomenon that X-ray peaks are displaced gradually on the action of the inbuilded cation. The occurence of substitution is quite unambiguous in the case of the iron minerals, but it is questionable concerning the aluminium minerals. Caillere and Pobeguin describe boehmite (and diaspore) of very high iron substitution in certain French bauxites, without finding any modification of the lattice parameters [1], [2], [3].

Due just to the absence of systematic lattice parameter changes many authors dispute the existence of iron-substituted boehmite or diaspore. In addition to the effect of the foreign ion on the lattice structure itself, it influences also the grain size and crystallinity of the sample. The grains of the substituted minerals (especially of the iron minerals) are usualy extremely fine and so the X-ray peaks are broad, have often asymmetric character, and the determination of the peak position is difficult. To evade that problem Janot and coworkers propose and use the Mössbauer spectrometry for the determination of the substitution in iron and aluminium minerals [4], [5]. Very fine particle size and weak

X-ray crystallinity has been reported e.g. for substituted lepidocrocites [6]. It might be even supposed that the lepidocrocite is a much more common mineral in the nature than it has been suggested by X-ray evidence, but being substituted it is nearly X-ray amorphous, and other detection methods are needed.

The thermal behaviour (DTA, TG curves) of the substituted minerals is also altered. It is well known e.g. that alumo-goethite dehydrates on higher temperatures than pure goethite does. The magnetite-lepidocrocite, lepidocrocite-maghemite, maghemite-hematite transformation temperatures and rates are significantly influenced by foreign cations [6], [7].

The effect of the particle size and lattice distortion on the X-ray spectrum and on thermal curves is well demonstrated directly on crushed samples. Schrader and coworkers [8], [9], [10], [11] stated that intensively milled boehmite, gibbsite, corundum and bauxite gave X-ray and thermal curves resembling those of amorphous materials.

Our investigations aimed at the study of the effects of these parameters on the infrared spectra and at the elaboration of quantitative infrared analysis methods.

Goethites were synthetized in presence of aluminium, lepidocrocites in presence of aluminium, chromium and manganese and boehmites in presence of aluminium and chromium by different methods known from the literature. IR spectra were registered in KBr disc with UR 10 (Zeiss) spectrophotometer. The aluminium content of the synthetic and natural alumo-goethites was determined by chemical analysis and by X-ray method using Thiel's calibration curve [12]. It was found that the intensity (extinction measured at the band maximum) of the Fe-O-H deformation bands (at about 800 and 900 cm^{-1}) is gradually increasing, the wave number of the band maxima is gradually increasing due to aluminium substitution (fig. 1, 2) [13].

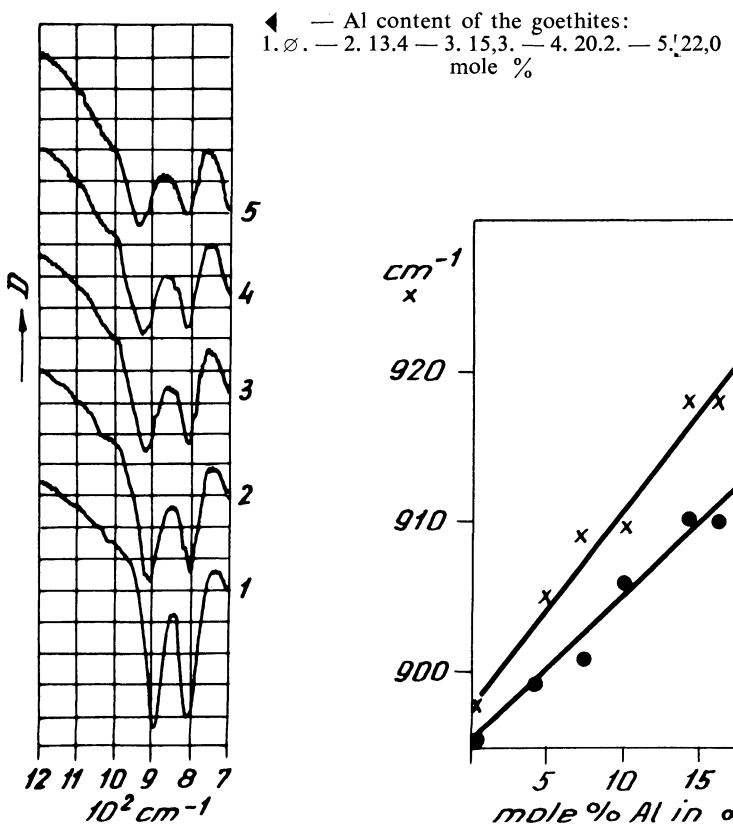

Fig. 1.

Fig. 2

The wave number-aluminium mole % curve might be used also for quantitative determination of the aluminium in goethite. Unfortunately these bands are overlaped by strong aluminium mineral bands in the spectrum of bauxite. In the spectrum of the red mud the 800 cm^{-1} band is undisturbed (the 900 cm^{-1} band is still masked by sodalite or cancrinite).

The position and very low intensity of the 800 cm^{-1} band in the spectra of red muds of goethite containing Hungarian bauxites indicate that the goethites in these contain significant amount of aluminium. That was proved by X-ray analysis too [14]. Taking into consideration that in some Hungarian bauxites there is a high percentage of goethite (18-20%) and that the aluminium substitution attains in certain cases even the 20-22 mole %, great aluminium losses are to be encountered in the Bayer process.

Some X-ray, and IR data concerning syntetic lepidocrocites are summarized in Table 1.

TABLE I

Sample *	*Wave number* cm^{-1}	*log (Io/I) g FeOOH*	I_{x}*-ray mm (1,937 Å)*
FeOOH	1019	132	185
Fe/Al/18	1022	110	130
Fe/Al/33	1022	107	120
Fe/Mn/5	1022	130	160
Fe/Mn/10	1023	103	153
Fe/Cr/10	1022	86	107
Fe/Cr/20	1023	48	70

(*) The meaning of our sample notations: Fe/Al/18, a lepidocrocite produced in presence of 18 mole % Al; Al/Fe/18, a boehmite produced in presence of 18 mole % Fe.

The lattice parameters do not show a well measurable systematic shift compared to the pure lepidocrocite, and there is practically no change in the wave number of the most characteristic IR band. The crystallinity is however influenced, as it is shown by the intensity change of the IR bands and X-ray peaks. The chromium is a crystallization inhibitor. The effect of manganese is small, aluminium takes a middle position in that respect.

Not so much the lepidocrocite dehydration peak temperature, but rather the beginning of that process is shifted toward higher temperatures ou the action of foreign ions. The maghemite-hematite exothermic transformation peak temperature and intensity is greatly altered. It is even absent in some aluminium or chromium containing samples indicating that the transcrystallization is extended over a wide temperature interval.

We found that the wave number of the infrared bands of pure boehmites synthetized hydrothermaly at different ageing conditions changes according the degree of crystallinity. The better is the crystallinity the stronger are the hydrogen bridge bonds, and correspondingly the O-H stretching bands are shifted towards lower, the Al-O-H deformation bands toward higher wave number values. The intensity of the bands (and also that of the X-ray peaks) is increasing with increasing crystallinity (Table 2).

Boehmites synthetized in presence of iron showed increasing crystallinity with increasing iron content of the original hydroxide mixture, as proved by the gradual intensity increase of the IR and X-ray bands and by the shift of the wave number of the IR bands (Table 3). At the same time however systematic lattice parameter changes were not found. A free iron phase (alumo-hematite) was present in all the produced samples. Iron is —according to our oppinion—a crystallization catalyst (not only for boehmite but also for diaspore), but it does not substitutes the aluminium (or at least only in very low concentration). The chromium is however crystallization inhibitor, a fact which has been already mentioned in the case of lepidocrocite. It is interesting that a definite systematic X-ray peak

TABLE II

Ageing conditions of γ-AlOOH	*Wave number of deform. band. (cm^{-1})*	ε *
240°, 12 hours	1068	700
300°, 12 hours	1070	775
300°, 26 hours	1085	1040

(*) For the characterization of the intensity of the I.R. band we introduced the « Specific extinction » ε:

$$E = \frac{\log (Io/I) \text{ measured at band max.}}{\text{mg sample in KBr disc}}$$

$$\varepsilon = \frac{E.\ 1000}{\text{cc. of the mineral in sample (weight fraction } Al_2O_3)}$$

TABLE III

Ageing cond.	*Al/Fe/X X*	*IR band (cm^{-1})*	ε	*X-ray peak (Å)*	*(mm)*
300 °C	0	1070	775	6,0798	344
	3	1075	770	6,0869	410
12 hours	5	1080	1080	6,0798	660
300 °C	0	1085	1040	6,0339	560
	3	1085	1100	6,0233	560
26 hours	5	1085	*	6,0656	*
	Al/Cr/X				
240 °C	0	1069	700	1,3098	110
	5	1068	623	1,3115	49
12 hours	10	1068	436	1,3125	23

* That sample contained about 8% diaspore too.

displacement could be measured in Cr containing samples, and this was observed also in certain Russian bauxites of high chromium content [15]. Therefore we do not exlude a possible substitution of Al by Cr in boehmite.

It is very evident on the basis of the above presented data that the intensity of the boehmite (and kaolinite and gibbsite) IR bands in bauxites of different origin might be very different (See fig. 3).

We found that the intensity (ε) of properly selected IR bands of these minerals in the bauxite is a characteristic parameter, a measure of the crystalline state and grain size of the mineral in question. We proved that on numerous bauxites and found that there are indeed only small differences in ε values of samples from related or similar occurence territories. We must underline however that the IR band intensity is related not only to the crystallinity but also to the grain size. If we mill intensively a solid crystalline material than the intensity is at first increasing—due to particle size reduction—but after a certain milling time the intensity begins to decrease, because the individual crystals are already destroyed, they (or at least their surface) begin to be amorphous. We accomplished milling experiments with bauxites in a vibration ball mill. We found that the course of the ε-milling time curves depended on the original state of the mineral. If it was originally fine disperse (high ε)—like most minerals in Hungarian bauxites—than the crushing resulted just in the beginning intensity decrease, showing that further size diminution was not possible, but the individual grains were already distorted. In the case of minerals composed of coarser and harder grains (low ε)—e.g. the boehmite in some Greek and Yugoslav bauxites—at first particle size reduction (ε increase) was measured (fig. 4).

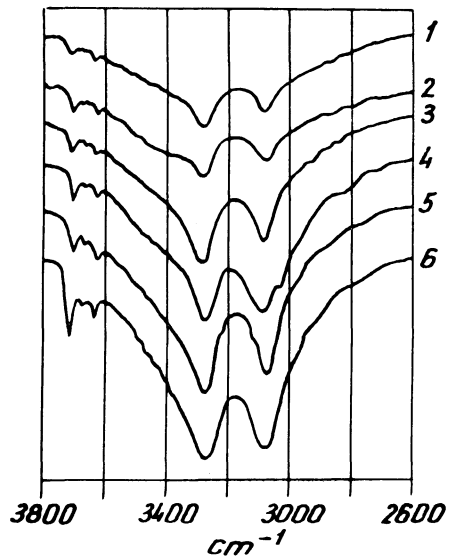

Fig. 3. — IR sprectra of boehmitic bauxites of different origin but of nearly the same composition
(46-52% Al_2O_3 in boehmite)
2 mg sample in 800 mg KBr
1. Hung. Nagyharsany. — 2. Greek. — 3. Yugoslav. — 4. French. — 5. Yugoslav. — 6. Hung. Halimba

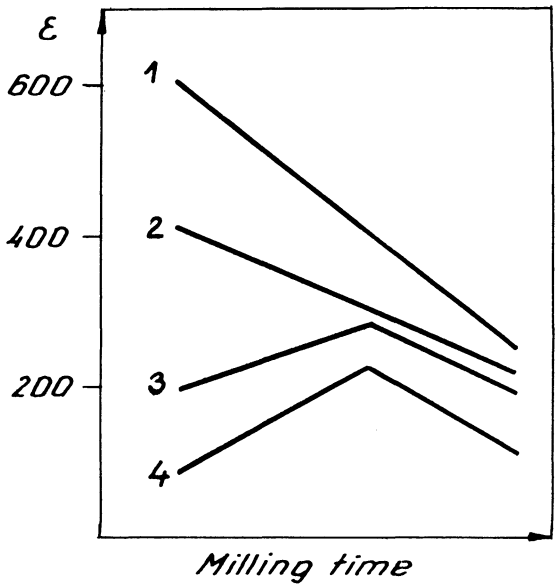

Fig. 4. — ε milling time curves
(3100 cm^{-1} boehmite band)
1. Hung. Halimba. — 2. Hung. Iszkaszentgyürgy. — 3. Yugoslav. — 4. Greek bauxite

Taking into consideration the presented experimental data it is evident that synthetic samples or pure concretions cannot be used as standards in the plotting of calibration curves because their crystalline state, grain size, purity etc. is surely quite different from those, being present in natural samples.

We elaborated a quantitative IR phase analysis method for the determination of boehmite, kaolinite and gibbsite in bauxite [16]. The calibation curves were made always with bauxites of known composition originating from the same or related territory as those to be analyzed. Separate calibration curves are needed for bauxites containing boehmite only, and for those containing boehmite and gibbiste. The same principle was applied in the case of quantitative determination of cancrinite and undissolved boehmite in red mud [17]. Mixtures containing the standard bauxite processed in the factory in question, and red mud produced from the standard bauxite in the factory were used for calibration. If that basic principle of the calibration is applied—as a key of a good IR method—than solid materials can be analyzed also quantitatively even if they are as complex ones as the bauxites are.

REFERENCES

[1] Caillère (S.) et Pobeguin (T.), 1961. — *C.R. Acad. Sc.*, Paris, *253*, p. 288.

[2] Caillère (S.) et Pobeguin (T.), 1966. — *C.R. Acad. Sc.*, Paris, Ser. D, *263*, p. 1349.

[3] Caillère (S.) et Pobeguin (T.), 1962. — *C.R. Acad. Sc.*, Paris, *254*, p. 137.

[4] Janot (C.), Gibert (H.), Gramont (X. de) et Biais (R.), 1971. — *Bull. Soc. fr. Mineral. Cristallogr.*, *94*, p. 367.

[5] Biais (R.), Bonemayre (A.), Gramont (X. de), Michel (M.), Gibert (H.) et Janot (C.), 1972. — *Bull. Soc. fr. Mineral. Cristallogr.*, *95*, p. 308.

[6] De Villiers (J. M.), van Rooyen (T. H.), 1967. — *Clay Minerals, 7*, p. 229.

[7] Basta (E. Z.), 1959. — *Econ. Geol., 54*, p. 698.

[8] Schrader (R.), Arnold (M.) et Rump (H.), 1967. — *Z. anorg. allg. Chem., 350*, p. 120.

[9] Schrader (R.), Rump (H.) et Sanner (G.), 1967. — *Z. anorg. allg. Chem., 350*, p. 130.

[10] Schrader (R.) et Rump (H.), 1967. — *Z. anorg. allg. Chem., 350*, p. 137.

[11] Schrader (R.), Rump (H.) et Kressner (R.), 1967. — *Chem. Ing. Techn., 39*, p. 843.

[12] Thiel (R.), 1963. — *Z. anorg. allg. Chem., 326*, p. 70.

[13] Jónás (K.) et Solymár (K.), 1970. — *Acta Chimica, 66*, p. 383.

[14] Solymár (K.) et Jónás (K.), 1971. — *Bányászati és Kohászati Lapok*, Kohászat, *104*, p. 226.

[15] Solymár (K.), Bárdossy (Gy.) et Jónás (K.), 1972. — *Acta Geologica Academiae Hung., 16*, p. 83.

[16] Jónás (K.) et Solymár (K.), 1970. — *Acta Chimica, 66*, p. 1.

[17] Jónás (K.), Solymár (K.) et Orbán (M.). — *Acta Chimica* (*in press*).

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