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Determination of anatase and rutile in bauxite by means of X-ray diffraction and organic solvent

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Titanium dioxide occurs in bauxites predominantly as anatase and — in much smaller measure — as rutile. Quantitative determination of these two minerals in bauxite by means of X-ray diffraction is not possible in the majority of cases, on one hand on account of their small concentration in bauxite, and, on the other, because their diffraction maxima in the roentgenogramme of bauxite are covered by peaks of other constituents. The only exception are white boehmitic bauxites, that is, bauxites with a very small percentage of goethite and hematite. However, although in the roentgenogrammes of such bauxites the principal diffraction peak of rutile, which occurs through the reflection of X-ray irradiation on planes (110) with interplanar interval d = 3.245 Å is not covered, nevertheless — because of the small concentration of rutile in bauxite — it is usually not sufficiently significant.

Our researches have shown that through extraction of the main mineral constituents of bauxite (hydrargillite, boehmite, goethite and hematite) by means of acetyl-acetone with the addition of catalytic amounts of muriatic and sulphuric acids at 130-150 °C during 5 hours one obtains residues with 15-30 percent of TiO_2. Roentgenogrammes of such residues exhibit clear and uncovered diffraction peaks of anatase and rutile, which makes possible quantitative determination of these minerals. Multiplying the obtained percentages of anatase and rutile by the ratio of the percentages of SiO_2 in bauxite and in the residue, one obtains the percentages of these minerals in bauxite.

Since DTA-grammes of such residues indicate above 700 °C a clear exothermic prominence which belongs to the transformation of anatase into rutile, there exists the possibility that by means of a very sensitive differential calorimeter one should determine the percent of anatase in the residue after extraction, resp. is in the bauxite.

Through the action of acetylacetone at 120-130 °C during 4-5 hours with the addition of catalytically effective amounts of HCl and H_2SO_4, one obtains a solid residue which is largely composed of kaolinite, anatase and rutile. In the roentgenogramme of this residue are now visible significant peaks of these constituents, which may be utilized for their quantitative determination. From the ratio between the percentage of total TIO_2 in bauxite and the percentage of anatase and rutile in the residue and the percentage of anatase and rutile in the residue are computed the percentages of these constituents in bauxite.

1. INTRODUCTION

In Bayer's procedure of producing hydrated alumina from bauxite certain quantities of lye are consumed for decomposing titan-oxide [1]. In bauxite TiO_2 is to be found mainly in the form of anatase and rutile, both of which possess a tetragonal crystal lattice, while here TiO_2 appears but rarely in the form of rhombic brookite. In bauxites rich ib iron also ilmenite $FeTiO_3$ or perovskite $CaTiO_3$ might appear. Since it would seem that anatase and rutile are the most frequent titan constituents of bauxite, it has been of interest to discover an instrumental method for their quantitative determination.

For this purpose the application of X-ray diffraction has proved to be the most suitable method [2]. Namely, through reflection of X-rays on planes of anatase/100/with interplanar spacing d = 3.51 Å one obtains a significant peak, whose size of surface may be utilized for quantitative determination of anatase. By analogy, this rules also for rutile with planes/110/with interplanar spacing d = 3.245 Å.

However, when measuring the surfaces of the aforesaid peaks, we have to face two obstacles in dealing with untreated bauxite. First, these peaks are ordinarily covered by peaks that are produced through X-ray diffraction by gibbsite, boehmite and goethite. A second hindrance is the too low percentage of TiO_2 in bauxite, which usually ranges between 2-5%. Because of such a low percentage of TiO_2 the surfaces of the aforementioned peaks are much too small to be able to serve for quantitative determination of anatase or rutile, as the case may be.

2. THE METHOD FOR DETERMINATION OF ANATASE AND RUTILE

Prior to approaching the determining of the percentage of anatase and rutile by X-ray diffraction, it will be necessary:

a) to determine the percentage of total TiO_2 and total SiO_2 in a bauxite dried up at 106 °C;

b) to scan roentgenogrammes of pure anatase and rutile, and to measure (planimeter) the surface of their significant peaks (in anatase for d = 3.51 Å, in rutile for d = 3.245 Å);

c) to scan roentgenogrammes of mixtures of pure anatase, gibbsite and kaolinite with a percentage of anatase from 1 to circa 30%, and to measure for each of the applied percents the size of the surface of the aforementioned corresponding peak; to do the same also for rutile (Table, Fig. 1);

TABLE

Calibrating mixtures for X-ray determination of anatase in the rests after extraction of Fe from bauxite

Composition of mixture % *an ka gi*	*Ratio of area of the main diffraction maximum of anatase (d = 3.61 Å) in an X-ray diffraction pattern of mixture and in an X-ray diffraction pattern of pure substance* mm^2/mm^2
100 — —	260/260 = 1
16 76 8	160/260 = 0.615
16 16 68	152/260 = 0.585
12 10 78	128/260 = 0,492
8 20 72	112/260 = 0.431
8 10 82	108/260 = 0.415
4 48 48	70/260 = 0.268
4 28 68	64/260 = 0.246
4 8 88	57/260 = 0.219

d) To make a gauging diagramme for anatase, in which are plotted on the axis of the abscisses the ratios of the surfaces of peaks of anatase in the roentgenogramme of the mixtures as well as the surfaces of the same peak in the roentgenogramme of an analytically pure anatase, and on the axis of the ordinates the corresponding percentages of anatase (see fig. 1); the same is to be done for rutile.

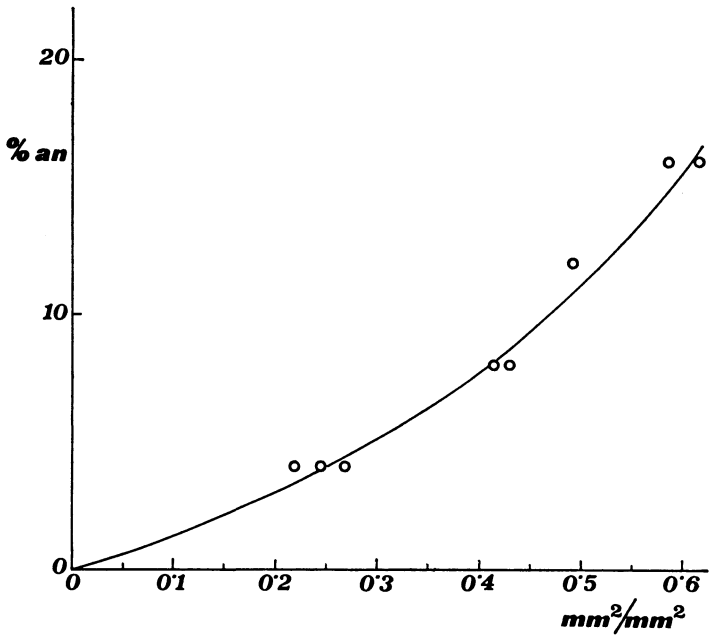

Fig. 1

In order to effect scanning of roentgenogrammes of anatase or rutile in bauxite, it is imperative to eliminate from bauxite those constituents whose roentgenographic peaks cover the most marked peaks of anatasé and rutile. For this purpose we submitted bauxite to the extractive action of acetylacetone.

We performed [3] the extraction of bauxite by means of acetylacetone in the following way:

10-20 g of bauxite was crushed to the size of grains d = 80/um and dried at 106 ± 2 °C. The extraction was carried out by means of 150 ml of acetylacetone (purum, 99 %, Ferric Co. London) along with a catalytically effective addition of 0.2 ml conc. HCl and 0.2 ml H_2SO_4 1: 1 in a thermostat with rotating glass autoclaves of 200 ml at a temperature of 150 °C during 6 hours.

By such extraction are eliminated from bauxite the more or less quantitative oxides and oxidehydrates of iron as well as oxidehydrates of aluminium, in the main goethite, hematite, gibbsite and boehmite. Titan-oxide, quartz, silicates and alumosilicates reamin untouched in the solid phase. In the liquid phase are now to be found ferum- and aluminium-acetylacetonates dissolved in excess of acetylacetone.

The extraction completed, the contents of the autoclaves are filtered through a round unbent filter-paper (Schleicher-Schüll, blue ribbon), which is placed on the horizontal perforated bottom of the glass funnel. In so doing, one should be careful that along with the application of a weak vacuum the filter-paper remain steadily well-adhering to its base. The residue on the filter are rinsed with about 100 ml of hot acetylacetone, and on the end with 50 ml of hot chloroform, for the purpose that the acetylacetone and acetilaceto-nates should be pressed out from the residue.

The filter-paper with the residue is then dried at 106 °C and weighed. The weight of the residue is obtained from the difference between the weight of dried filter-paper with

the residue and the weight of this same filter-paper before filtration, dried preliminarily also at 106 °C.

In one part of the obtained residue we determine the percentage of SiO_2, while the other part is submitted to roentgenographic scanning.

In the thus obtained roentgenogramme we measure the size of the surface of the significant peak. The ratio between this size and the size of the same peak in the roentgenogramme of pure anatase (comp. what is stated under *b*) yields a value which, plotted on the axis of the abscisses of the gauging diagramme (see what is stated under *d*) and Fig. 1), makes it possible to read off from the axis of the ordinates the percentage of anatase in the residue after extraction.

By multiplying this percentage by the ratio of the percentage of SiO_2 in the bauxite to the percentage of SiO_2 in the residue, one obtains the percentage of anatase in bauxite.

In the case when by first extraction the disturbing components have not bee sufficiently removed, extraction should be repeated under the same conditions on the first obtained residue, while the second residue should again be rinsed, dried up and weighed.

The percentage of rutile may be determined either through planimetering the surface of its peak (d = 3.245 Å) along with the application of the corresponding gauging curve, or from the difference between the total percentage of TiO_2 and the percentage of anatase. The latter procedure is valid under the assumption that bauxite contains TiO_2 only in the form of anatase and rutile.

3. EXAMPLES OF APPLICATION

As an example of the application of the described method we mention one gibbsitic and one boehmitic specimen of bauxite.

Our scannings were performed using an apparatus of the General Electric Co., U.S.A. We applied CuKα-radiation (d = 1.5071 Å) with a discriminator and Ni-filter; the speed of the goniometer amounted to 1°/min; the time constant = 2.0 sec, the intensity range 1 000 c/s, horizontal divergence 1°, receiving-slit width 0.2 mm.

The gibbsitic bauxite (Obrovac, Dalmatia) contained 3,36% TiO_2 and 2,38% SiO_2.

The roentgenogramme of this bauxite is shown in Figure 2-1. Here are prominent only the peaks of gibbsite, goethite, boehmite and hematite, whilst the peaks of kaolinite, anatase and rutile cannot be visualized at all.

However, the remains after a two-time extraction yielded the roentgenogramme presented in Figure 2-2, in which have altogether vanished the peaks of gibbsite, goethite and hematite, with the peaks of boehmite still visible, while very prominent are the peaks of kaolinite (e.g. d = 3.570 Å, preferable orientation), then anatase (e.g. main diffraction maximum at d = 3.51 Å), and rutile (e.g. main diffraction maximum at d = 3.245 Å).

The surface of the main diffraction maximum of anatase (d = 3.51 Å) in the residu II amounted to 150 mm_2.

This value, divided by the size of the surface of the same peak in the roentgenogramme of pure anatase (260 mm^2) was 150: 260 = 0.578 mm^2/mm^2, which, according to the gauging curve in Figure 1, corresponds to 15,4% anatase in the residu III.

This percentage, multiplied by the ratio $(\%\ SiO_2)_b/(\%\ SiO_2)_{II}$ gives the following percentage of anatase in bauxite:

$$\%\ A_b = 15.4\ (2.38 : 13.40) = 2.7\%$$

The percentage of rutile in the bauxite was determined also here from the difference between the percentage of total TiO_2 and the percentage of anatase in the bauxite:

$$\%\ R_b = 3.4 - 2.7 = 0.7\%$$

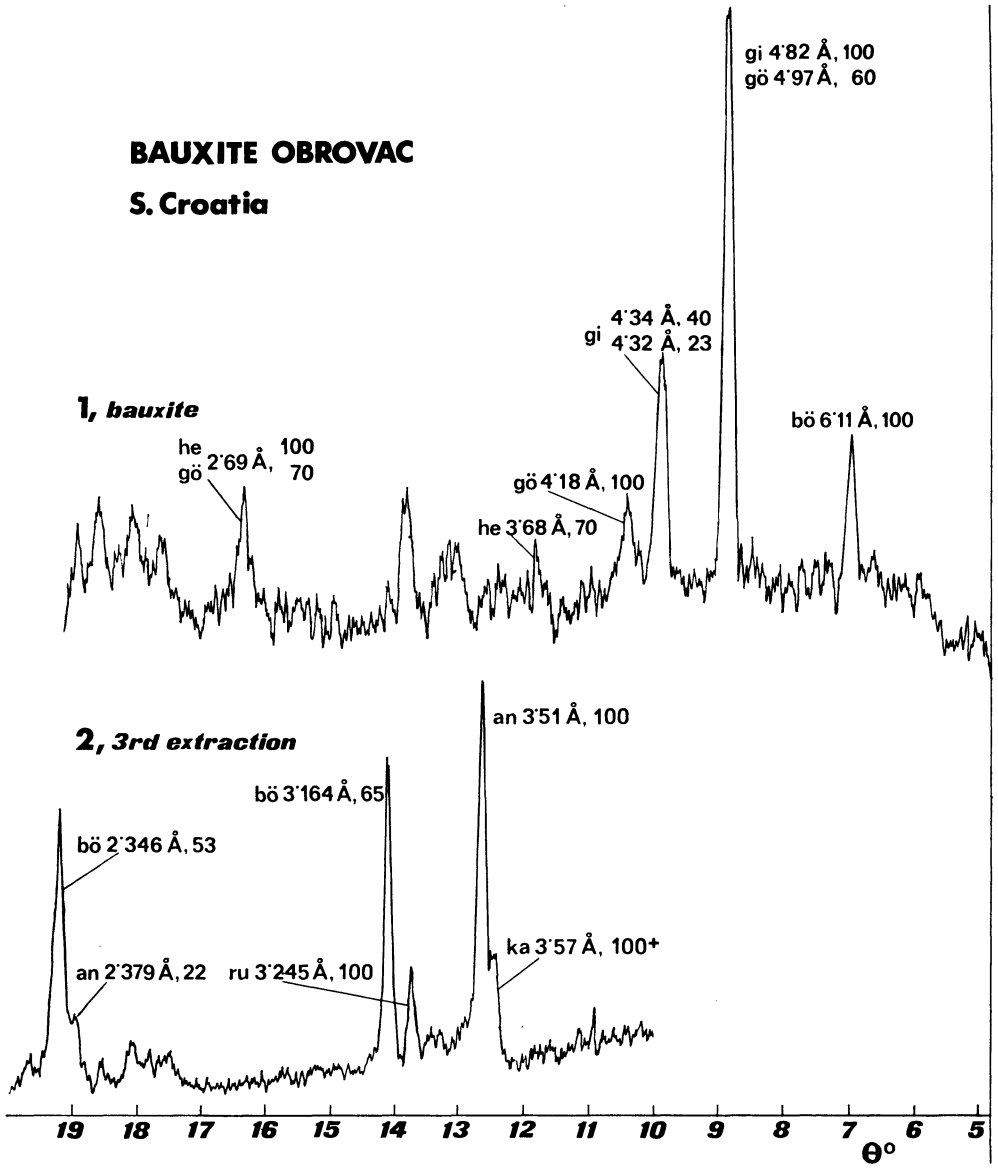

Fig. 2

The boehmitic bauxite (Kržljak, Istria) contained 3.93% TiO_2 and 4.39% SiO_2.

Roentgenogramme of this bauxite is exhibited in Figure 3-1, while roentgenogramme of the residu in the first extraction is seen in Figure 3-2.

The surface of the main diffraction maximum of anatase amounted to 69 mm^2. The ratio of this size to that of the same peak in pure anatase yelded the following value: 69: 260 = 0.265 mm^2/mm^2. From the gauging curve in Figure 1 it is visible that to this ratio corresponds 4.5% anatase (in the residue).

This percentage, multiplied by the ratio $(\%\ SiO_2)_b/(\%\ SiO_2)_1 = 4.39/6.76 = 0.633$, yields the following percentage of anatase in the bauxite:

$$\%\ A_b = 4.5\ .\ (39: 6.76) = 3.3\%$$

The percentage of rutile in bauxite will accordingly be:

$$\%\ R_b = 3.9 - 3.3 = 0.6\%$$

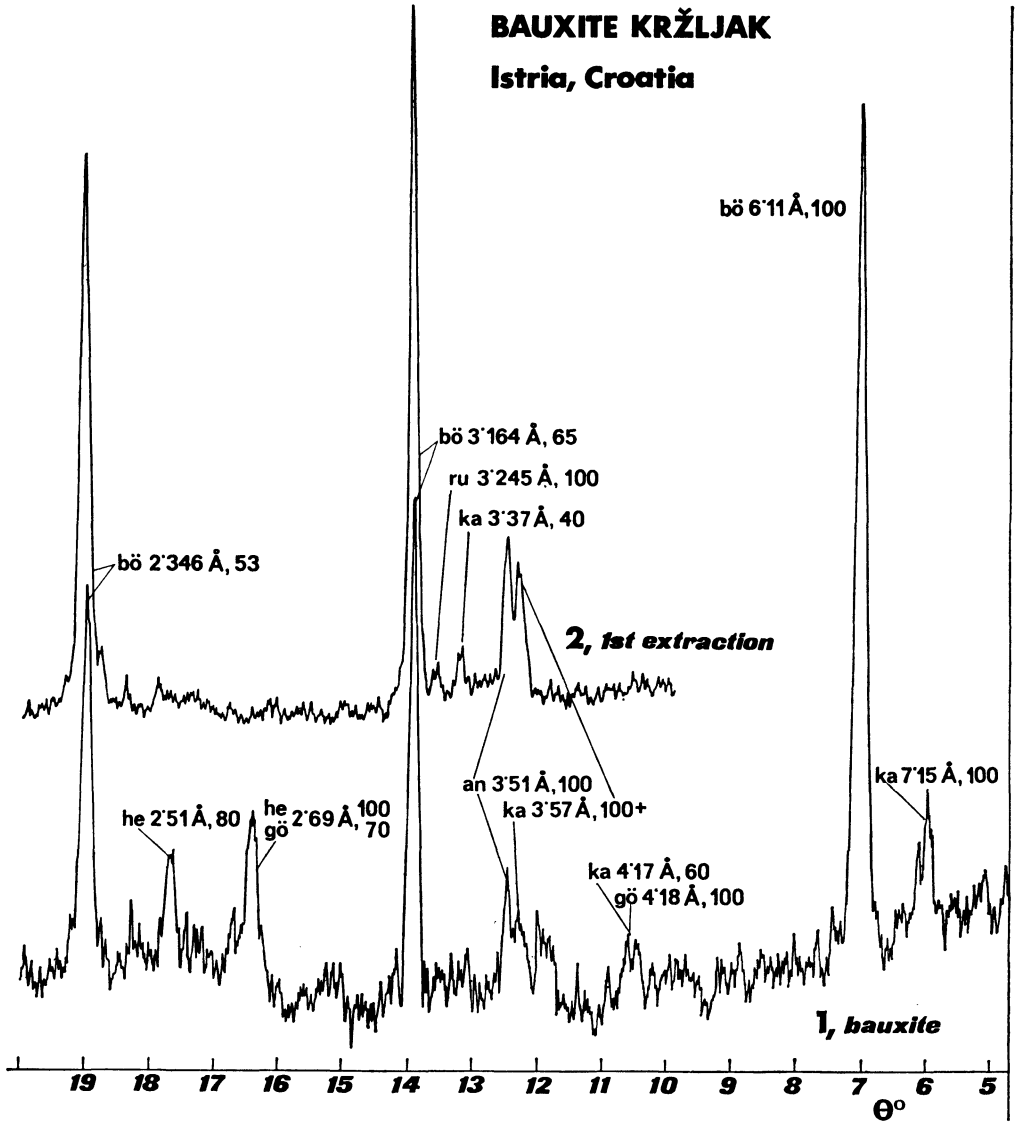

Fig. 3

As the residu obtained by drastic extraction of bauxite through acetylacetone frequently contain even up to 30% TiO_2, there exists a possibility that by means of a very sensitive differential calorimeter one should establish the percentage of anatase by utilizing the peak in the temperature interval of 700-870 °C, which is produced by exothermic transformation of anatase into rutile.

As a third example we are going to mention a specimen of white boehmitic bauxite (Cetinje, Montenegro). On account of a very low content of goethite (1.5%) and gibbsite (6.5%) already in the roentgenogramme of untreated bauxite are visualized the main diffraction maxima of anatase and rutile (see Fig. 4-1). Through the effect of acetylacetone there appear in the remains after extraction the mentioned significant peaks with a yet more marked prominence (see Fig. 4-2). Thus it has been possible to establish the percentage of anatase and rutile with greater accuracy than it would have been feasible using roentgenogrammes of bauxite itself. By an analogous procedure carried out as in the first two aforementioned bauxites we established the percentage of anatase (3.6%) and rutile (0.5%) in this bauxite.

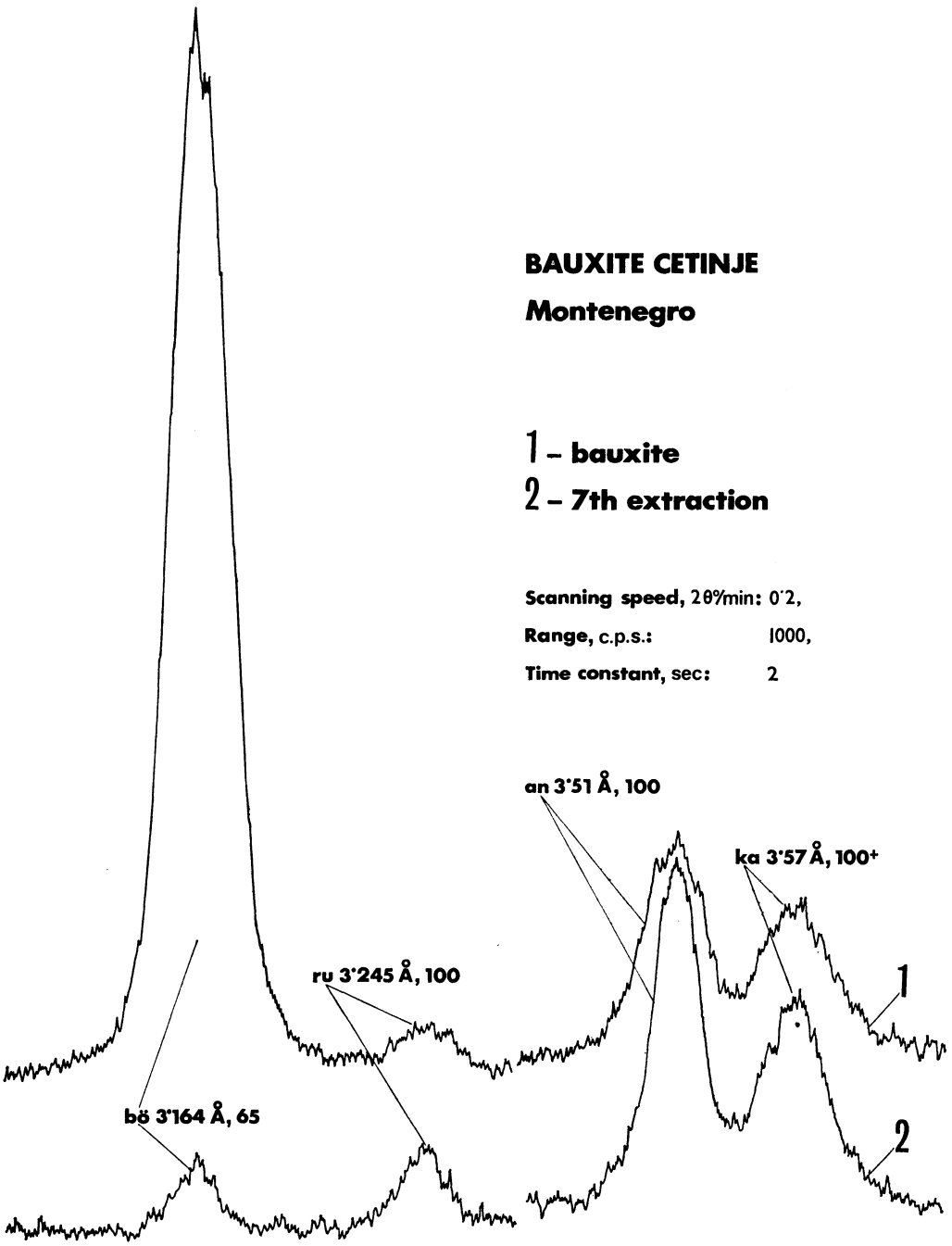

Fig. 4

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