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DETERMINATION OF ALUMINA OXIDE IN BAUXITES BY X-RAY FLUORESCENCE ANALYSIS

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# Determination of Alumina Oxide in Bauxites by X-Ray Fluorescence Analysis

Dragana Keselj<sup>α</sup>, Dragica Lazic<sup>σ</sup>, Jelena Penavin-Skundric<sup>ρ</sup>, Slavica Sladojevic<sup>ω</sup> & Ljubica Vasiljevic<sup>¥</sup>

**Abstract** - This study relates to determination of the content of aluminium oxide (%Al<sub>2</sub>O<sub>3</sub>) in different types of bauxite by the X-ray fluorescence method (XRF). The samples were prepared in the form of beads by the borax method from bauxite, which had been previously annealed. Standard reference samples of bauxite were used to produce a calibration curve and the calibration curve obtained was with very good coefficient of determination  $r = 0.9992$  and standard deviation  $S = 0.091$ . After statistical verification of the method (F-test, reference method and standard sample of bauxite), it was concluded that the method was precise and correct and that there were no systemic errors. In addition to this, by the XRF analysis of different types of bauxite the average value of residuals between percent of Al<sub>2</sub>O<sub>3</sub> determined by the standard method of SRPS B.G8.512 and XRF method was 0.254 with the deviation of 0.191.

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## 1. INTRODUCTION

Bauxite is the aluminium ore which consists of more than a hundred of different minerals, out of which the most significant ones are the minerals of aluminium, iron, silicon, titanium and calcium. Aluminium is present in bauxite mainly in the form of hydrated oxides: hydrargillite (gibbsite)- Al<sub>2</sub>O<sub>3</sub> · 3H<sub>2</sub>O, boehmite- AlOOH and diaspore- AlOOH. In addition to these minerals, aluminium may be found in bauxite to a lesser extent in the form of corundum (Al<sub>2</sub>O<sub>3</sub>) and various aluminosilicates, most often in the form of kaolinite- Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub> · 2H<sub>2</sub>O. Silicon in bauxite is present in the form of free or bonded oxide. Minerals of free oxides, which may be found in bauxite, are crystal forms of SiO<sub>2</sub>, those being: quartz, quartzite, chalcedony or amorphous SiO<sub>2</sub> - opal. Out of free oxides, SiO<sub>2</sub> may most often be found in the form of quartz mineral. As a bonded oxide, silicon is usually found as the mineral of kaolinite- Al<sub>2</sub>O<sub>3</sub> · 2SiO<sub>2</sub> · 2H<sub>2</sub>O. Iron is generally found in bauxites as anhydrous and hydrated oxides, those being : hematite - Fe<sub>2</sub>O<sub>3</sub>, magnetite - Fe<sub>3</sub>O<sub>4</sub>, hydrated

hematite- Fe<sub>2</sub>O<sub>3</sub> · H<sub>2</sub>O, goethite-HFeO<sub>2</sub> and limonite-HFeO<sub>2</sub> · H<sub>2</sub>O. Titanium is most frequently present in bauxites in the form of a free oxide and appears in three allotropic modifications of anatase, rutile and brookite, out of which anatase-TiO<sub>2</sub> is most frequent. Calcium appears in the form of various carbonates, most often as calcite-CaCO<sub>3</sub> and dolomite- MgCO<sub>3</sub> · CaCO<sub>3</sub>. Depending on the mineral form of the present aluminium, as the basic mineral, bauxites are divided into: hydrargillite (gibbsite), boehmite, diaspore and mixed ones (hydrargillite-boehmite and boehmite-diaspore).

Chemical composition of bauxite is presented by the following components: Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, CaO and the loss on ignition at 1075°C. Standard method for chemical determination of aluminium in bauxites is conducted based on the SRPS B.G8.512 standard. By this standard bauxites first were decomposed with acids and Al<sub>2</sub>O<sub>3</sub> were determined by potentiometric method.

X-ray fluorescence analysis (XRF) is one of the most significant emission methods, which enables a quick and multielemental analysis in a very short period of time and requires a minimal preparation of the sample. In case some material gets showered with primary high energy X-rays, it will cause expulsion of electrons from some of inner shells (K,L,M) of atoms in that material, which results in formation of electron holes in one or more atomic orbitals closer to the nucleus, by which appropriate atoms get into an excited state. The atom excited in such a way tends to get into a stable state and therefore the holes in orbitals closer to the nucleus get filled up with the electrons from higher orbitals. This transfer is accompanied with the emission of energy in the form of a secondary, i.e. fluorescent X-ray, which is characteristic of the given atom. The substance of the X-ray fluorescent analysis is measuring the intensity of the developed secondary fluorescence radiation. The method is applicable in a wide scope of concentrations. For determining the components with a high concentration in the examined sample, determination is performed with the help of the calibration curve with the standards of the known composition, where concentration of the appropriate component is generally proportional to the emitted fluorescence radiation by the element that was determined. Due to its advantages, first of all because it is quick, non-destructive and less expensive, the X-ray

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fluorescence analysis is nowadays applied in many fields, where it is particularly necessary to point out its application in everyday analyses in the cement industry and metallurgy.

## II. EXPERIMENTAL PART

According to the research so far (La Tour T.E. 1989, Giles et al, 1995), the best results for determining individual components in the multi-component systems by the X-ray fluorescence method are achieved by dissolving and diluting the sample by some of analytes. When the analysis of rocks is in question, it is customary to prepare the sample by the borax method (Alvarez 1990, Nakayama et al 2007, Hettipathirana et al 2004). Based on this method, borax beads are made so that the examined sample gets destroyed by borax ( $\text{Na}_2\text{B}_4\text{O}_7$ ) or by lithium tetraborate ( $\text{Li}_2\text{B}_4\text{O}_7$ ), with or without oxidizing substance (. Since aluminium is most often present in bauxites as a hydrated oxide, at the high temperatures at which borax palettes are made there will occur its dehydration, so that in preparation of palettes of bauxite of a different type there will occur an error caused by different losses on ignition of different types of bauxite. Therefore, in this study the samples of bauxite, which had been previously crushed up to granulation of less than 200  $\mu\text{m}$  and dried up, were annealed at 1200°C and at the same temperature their loss on ignition was determined. 1 g of the bauxite sample was taken from the sample annealed in that manner and it was mixed with 6 g  $\text{Li}_2\text{B}_4\text{O}_7$ , then it was melted at the temperature of 1200°C for a half an hour with periodical stirring and was poured out into the platinum moulds. The obtained beads in the platinum moulds were recorded on the apparatus.

For measuring the fluorescence radiation the apparatus used was the spectrometer Philips PW1404, where the conditions of recording, i.e. Channelset for aluminium, was: line-  $\text{K}\alpha$ , X-tal – PE, collimator – coarse, detector- FL, kV- 40, mA- 75, angle ( $^\circ 2\theta$ )- 144.8650.

In the experimental part, the certified samples of bauxite were used for making the calibration curve (Table 1.).

The study also used bauxites of various deposits and they were processed in the Factory AD „Birac“ Zvornik, those deposits being: Milici (S1.), Posusje (S2.), Potoci-Mrkonjic Grad( S3.), Liskavica-Mrkonjic Grad (S4.), Citluk (S5.), Bosanska Krupa (S6.), India (S7.) and Guinea (S8.) (Table 2.).

Mineralogical characterization was performed for all samples of bauxite by the X-ray diffraction, where a copper tube was used for an X-ray tube and had the following characteristics: Anode of Cu, K-Alpha1 [ $\text{\AA}$ ]=1.54060, K-Alpha2 [ $\text{\AA}$ ]= 1.54443, K-Beta [ $\text{\AA}$ ]=1.39225, K-A2 / K-A1 Ratio=0.50000, Generator Settings 50 mA and 40 kV.

Table 1: Analysis of standard reference samples of bauxite according to the certificate

Comp.	Standard reference samples of bauxite					
	NBS 696	NBS 697	NBS 698	BCS 395	SB1	SB2
$\text{Al}_2\text{O}_3$	54.5	45.8	48.2	52.4	55.40	48.6
$\text{Fe}_2\text{O}_3$	8.70	20.00	19.6	16.30	24.4	28.2
FeO	-	-	-	-	2.2	3.89
$\text{SiO}_2$	3.79	6.81	0.69	1.24	2.38	7.38
$\text{TiO}_2$	2.64	2.52	2.38	1.93	2.22	3.06
CaO	0.018	0.71	0.62	0.05	1.93	0.39
MgO	0.012	0.18	0.058	0.02	0.14	0.39
$\text{Na}_2\text{O}$	0.007	0.036	0.015	-	-	-
$\text{SO}_3$	0.21	10.13	0.22	-	-	-
S	-	-	-	-	0.33	0.028
GZ1075°C	29.9	22.1	27.3	27.8	12.7	11.7
Gibbsite	80	50	75	-	-	-
Boehmite	-	10	-	-	50-60	45-50
Diaspore	-	-	-	-	-	-
Kaolinite	5	15	-	-	5	To 5
Hematite	-	20	20	-	20-22	28-32
Pyrite	10	-	-	-	0.5-1	0-4
Goethite	-	-	-	-	-	-
Anatase	5	5	5	-	-	-
Calcite	-	-	-	-	3-4	1-2

Table 2: Chemical analysis of different types of bauxites

Com.	Deposits of bauxite							
	S1.	S2.	S3.	S4.	S5.	S6.	S7.	S8.
$\text{Al}_2\text{O}_3$	51.22	54.59	45.56	56.20	49.61	48.16	51.54	59.00
$\text{Fe}_2\text{O}_3$	25.97	20.69	20.00	20.56	19.50	16.16	18.31	6.70
$\text{SiO}_2$	7.93	1.36	6.48	1.52	5.13	3.78	6.18	1.41
$\text{TiO}_2$	2.58	2.87	2.11	2.60	2.69	2.44	2.37	3.77
CaO	0.16	0.58	1.88	4.00	4.50	1.95	4.63	0.28
GZ 1075 °C	11.35	19.90	23.22	14.11	17.70	26.79	15.95	28.64
GZ 1200 °C	11.35	20.04	23.22	14.11	17.70	27.68	15.95	28.64

## III. RESULTS AND DISCUSSION

STANDARD REFERENCE SAMPLES OF BAUXITE, ACCORDING TO THE CERTIFICATE, HAVE A KNOWN MINERALOGICAL COMPOSITION (TABLE 1). THE STANDARD SAMPLE OF BAUXITE BCS 395 IN THE CERTIFICATE DOES NOT CONTAIN THE INFORMATION ON THE MINERALOGICAL COMPOSITION, BUT IT CAN BE SEEN BASED ON THE OBTAINED DIFFRACTOGRAM THAT ALUMINIUM IS PRESENT AS GIBBSITE AND IN VERY SMALL TRACES AS BOEHMITE AND KAOLINITE (PICTURE 1.). BAUXITES NBS 696 AND NBS 698 ARE OF HYDRAGILLITE TYPE, NBS 697 AND BCS 395 ARE OF HYDRAGILLITE-

BOEHMITE TYPE, SB2 IS OF BOEHMITE TYPE AND SB1 IS OF BOEHMITE-DIASPORE TYPE.

Based on X-ray diffraction analysis of the samples of bauxite from different locations (Pictures 2 - 9), it can be noted that the samples of bauxites S7 and S8 are of gibbsite type, S1 and S6 are of boehmite type and the samples of bauxites S2, S3, S4 and S5 are of hydragillite-boehmite type. The chemical analysis for the samples was performed based on the standard SRPS B.G8.512 (Table 2.).

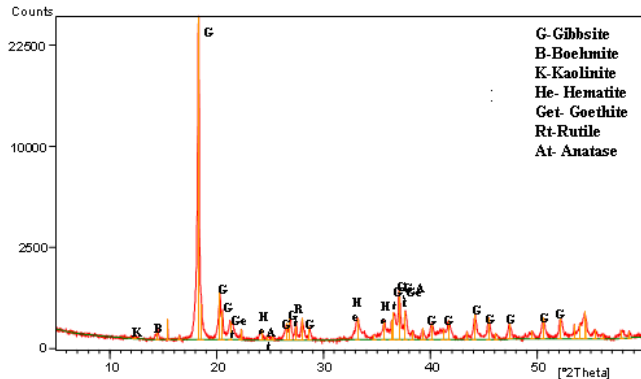


Fig.1 : Diffractogram of the standard sample BCS 395.

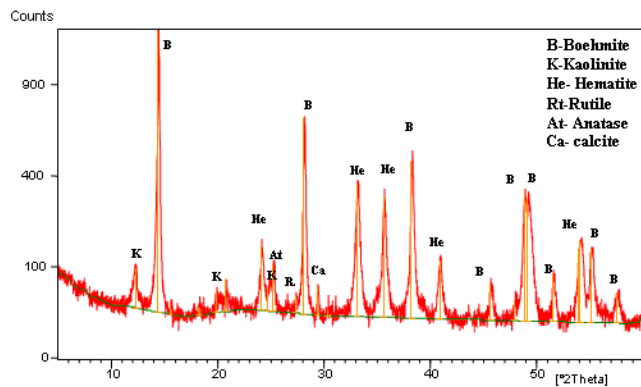


Fig.2 : Diffractogram of the bauxite sample S1.

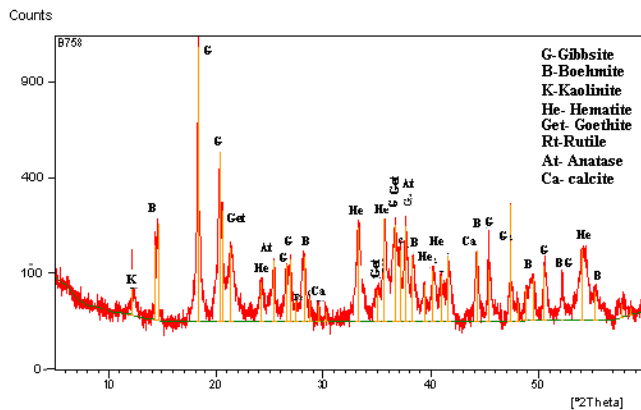


Fig.3 : Diffractogram of the bauxite sample S2.

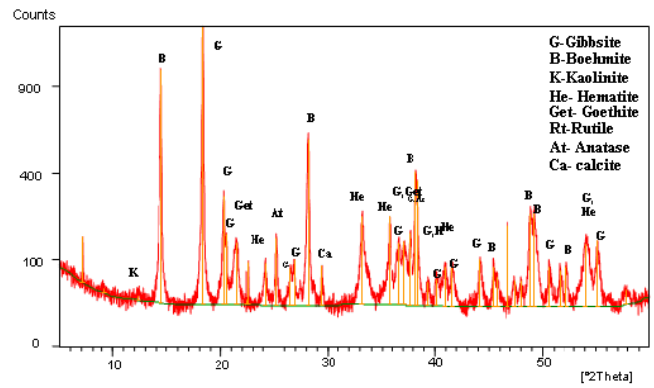


Fig.4 : Diffractogram of the bauxite sample S3.

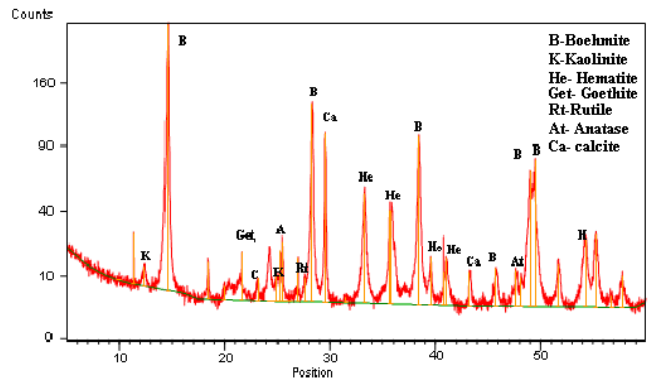


Fig.5 : Diffractogram of the bauxite sample S4.

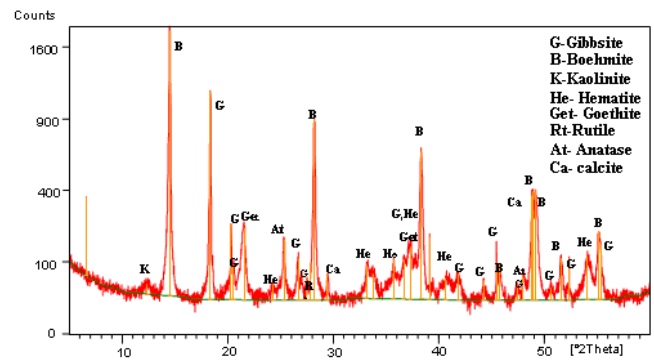


Fig.6 : Diffractogram of the bauxite sample S5.

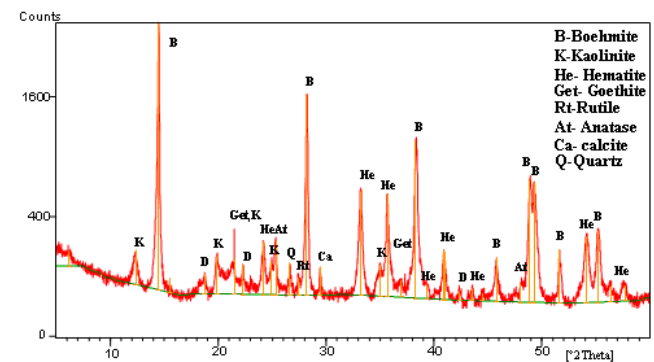


Fig.7 : Diffractogram of the bauxite sample S6.

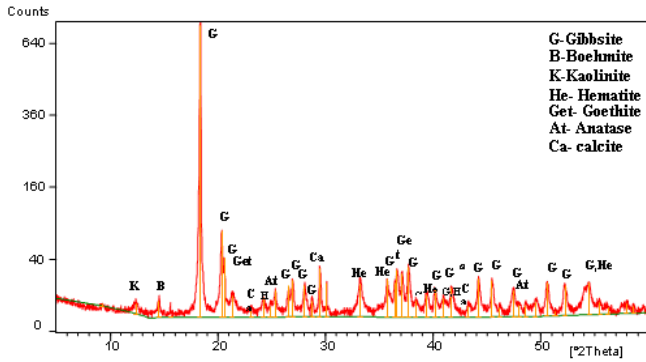


Fig.8 : Diffractogram of the bauxite sample S7.

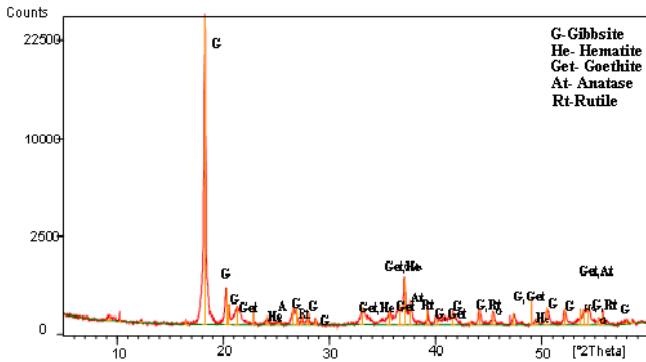


Fig. 9 : Diffractogram of the bauxite sample S8 .

Content of Al<sub>2</sub>O<sub>3</sub> taken in the calibration curve (Picture 10.) is calculated for the absolutely annealed sample.

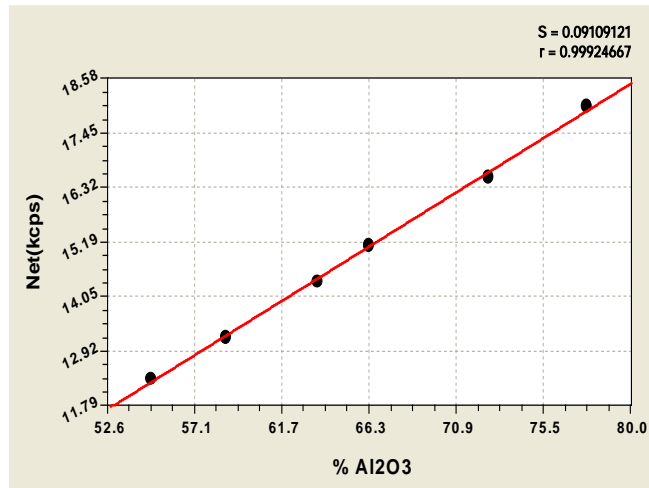


Fig. 10 : Calibration curve .

Based on the calibration curve we got the equation for calculating concentration of aluminium in the annealed bauxite:

$$\% \text{Al}_2\text{O}_3 \text{ annealed} = 4.0714689 * \text{INT} + 4.8320482 \quad (1)$$

Where INT- measured intensity (kcps)

And the true content of Al<sub>2</sub>O<sub>3</sub> in bauxite is further calculated based on the loss on ignition determined at 1200°C (GZ<sub>1200</sub>) based on the formula:

$$\% \text{Al}_2\text{O}_3 = \% \text{Al}_2\text{O}_3 \text{ annealed} * (100 - \text{GZ}_{1200}) / 100 \quad (2)$$

In accordance with the calibration curve, the samples of bauxite in different deposits were also recorded and the content of Al<sub>2</sub>O<sub>3</sub> was determined (Table 3.).

Table 3 : Content of Al<sub>2</sub>O<sub>3</sub> in the bauxites of different locations, which was determined by the standard and XRF method

Sample	Content of Al <sub>2</sub> O <sub>3</sub> in bauxites, %		Residual
	Standard method	XRF method	
S1.	51.22	51.43	0.21
S2.	54.59	54.39	0.20
S3.	45.56	45.04	0.52
S4.	56.20	56.51	0.31
S5.	49.41	49.95	0.54
S6.	48.16	48.09	0.07
S7.	51.54	51.69	0.15
S8.	59.80	59.83	0.03
Average	-	-	0.254
STDEV	-	-	0.191

Within the framework of the experimental part, ten different beads were recorded for the same sample (Table 4.), as well as one bead for ten times (Table 5.).

Table 4 : Content of Al<sub>2</sub>O<sub>3</sub> for ten different beads of the bauxite sample S6

Bead	Net (kcps)	%Al <sub>2</sub> O <sub>3</sub> annealed	% Al <sub>2</sub> O <sub>3</sub>
1.	13.9394	61.586	51.76
2.	14.0227	61.925	52.05
3.	13.8296	61.139	51.39
4.	13.9868	61.779	51.95
5.	13.9333	61.561	51.38
6.	13.9333	61.416	51.62
7.	13.8670	61.291	51.51
8.	13.8952	61.406	51.61
9.	13.9439	61.604	51.78
10.	13.8753	61.325	51.54
Min.	13.8296	61.139	51.54
Max.	14.0227	61.925	52.05
average	13.9227	61.503	51.69
STDEV	0.0576	0.236	0.224

Table 5 : Content of Al<sub>2</sub>O<sub>3</sub> of one bead of the bauxite sample S6 determined ten times by the XRF method

R.B.Measures	Net (ccps)	%Al <sub>2</sub> O <sub>3</sub> annealed	% Al <sub>2</sub> O <sub>3</sub>
1.	13.9723	61.720	51.88
2.	13.8056	61.041	51.30
3.	13.9210	61.511	51.69
4.	13.9672	61.699	51.86
5.	13.9515	61.635	51.80
6.	13.9296	61.546	51.73
7.	13.9645	61.688	51.85

8.	13.9127	61.477	51.67
9.	13.8498	61.221	51.46
10.	13.9127	61.477	51.67
Min.	13.8056	61.041	51.30
Max.	13.9723	61.720	51.88
Average	13.9187	61.501	51.69
STDEV	0.0539	0.219	0.224

Table 6 : Content of Al<sub>2</sub>O<sub>3</sub> of the bauxite sample S6 determined by the standard method of SRPS B.G8.512 for ten samples

5.	59.043
6.	58.909
7.	58.446
8.	58.713
9.	58.867
10.	58.404
Min.	58.404
Max.	59.043
Average	58.7335
STDEV	0.229

R.B.analyses	%Al <sub>2</sub> O <sub>3</sub>
1.	51.50
2.	51.92
3.	51.84
4.	51.61
5.	51.13
6.	51.73
7.	51.23
8.	51.71
9.	51.19
10.	51.53
Min.	51.13
Max.	51.92
Average	51.54
STDEV	0.277

For the verification of correctness of the new non-standard XRF- method F-test was performed, where a zero hypothesis was tested, by which the variants of the standard method for determination of % Al<sub>2</sub>O<sub>3</sub> in bauxites SRPS B.G8.512 and non-standard one are equal.

$$F_{9,9} = \frac{s_1^2}{s_2^2} = \frac{0,277^2}{0,236^2} = 1,378 \quad (3)$$

The critical value is  $F_{tab} = 3,179$  at  $\alpha = 0.05$ , which means that the zero hypothesis on the equality of variants was confirmed. The existing differences are considered to be a cause of accidental errors.

Verification of correctness of the XRF method for determination of % Al<sub>2</sub>O<sub>3</sub> in bauxites was performed by the use of the standard sample of bauxite B697 (Table 6.).

Table 6 : Chemical analysis of the standard sample of bauxite B697 by the XRF-method

Number	%Al <sub>2</sub> O <sub>3</sub>
1.	59.034
2.	58.672
3.	58.532
4.	58.715

For the examined XRF method we got:

$$|t| = \left| \frac{\mu - \bar{x}}{s} \right| \cdot \sqrt{n} = 0.822 \quad (4)$$

where  $|t_{tab}| = 2,262$  at  $\alpha = 0.05$ , which means that the XRF method does not have any systemic errors. For the purpose of verifying the XRF method by the reference method of SRPS B.G8.512, the following values were calculated:

$$Sp = \sqrt{\frac{(n_1 - 1)s_1^2 + (n_2 - 1)s_2^2}{n_1 + n_2 - 2} \left( \frac{1}{n_1} + \frac{1}{n_2} \right)} \quad (5)$$

$$Sp = 0,115$$

$$t = \frac{\bar{x}_1 - \bar{x}_2}{Sp} = \frac{51.693 - 51.539}{0.115} = 1.339 \quad (6)$$

where  $t_{tab} = 2.101$ , so one may conclude that there is no difference between the mean values with the risk of 5 %, i.e. the XRF method does not have any systemic errors.

#### IV. CONCLUSION

The calibration curve obtained by recording the beads of standard reference samples of bauxite, which were obtained from the previously annealed samples and then melted with Li<sub>2</sub>B<sub>4</sub>O<sub>7</sub>, provided the calibration curve with a very good coefficient of determination  $r = 0.9992$  and standard error  $S = 0.091$ . The average value of residuals between % Al<sub>2</sub>O<sub>3</sub> determined by the standard method SRPS B.G8.512 and XRF method in different types of bauxite, was 0.254 with the deviation of 0.191. By the verification of correctness of the XRF method for determination of % Al<sub>2</sub>O<sub>3</sub> in the bauxites of different types by the reference method and standard sample of bauxite NBS 697, one may conclude that the method does not have any systemic errors. Based on the conducted F-test, we may note that the variants of the standard and XRF method are equal. We may also notice that the standard deviation obtained by recording ten different beads of the „Bosanska Krupa“ sample and standard deviation obtained by recording one bead for ten times are the same. The beads prepared by the

borax method could at the same time serve for determining other components in bauxite. This type of preparation of samples for analysis has the advantage compared to the classical analysis, since the method is non-destructive, a lot fewer chemicals and time is necessary, which gives an advantage to this method.

## V. LITERATURE

1. Nakayama K., Shibata Y., Nakamura T., Glass beads/x-ray fluorescence analyses of 42 components in felsic rocks, *X-ray Spectrometry*, 36, 2(2007) 130-140.
2. Alvarez M., Glass disk fusion method for the x-ray fluorescence analyses of rocks and silicates, *X-ray Spectrometry*, 19, 4(1990) 203-206.
3. Giles H.L., Hurley P.W., Webster H.W.M., Simple approach to the analysis of oxides, silicates and carbonates using x-ray fluorescence spectrometry, *X-ray Spectrometry*, 24, 4(1995) 205-218.
4. Hettipathirana T.D., Grey N.A., Naidu R., Analysis of silicates using wavelength-dispersive x-ray fluorescence spectrometry, *X-ray Spectrometry*, 33, 2(2004) 117-123.
5. La Tour T.E., Analysis of rocks using x-ray fluorescence spectrometry, *The Rigaku Journal*, 6,1 (1989) 3-9.