Determination of silicon dioxide content in bauxite: comparing the ICP-OES method with the UV-VIS method

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Abstract

In this paper, the ICP-OES method (induced coupled plasma optical emission spectrometry) was used to determine the content of silicon dioxide in bauxite, as an important impurity that affects the quality and application of bauxite in alumina production by the Bayer process. Twenty bauxite samples from seven different deposits were analysed. The results were compared with the reference spectrophotometric UV-VIS method. The mean relative difference between the silicon dioxide content determined by the ICP-OES method and the reference method is found to be 4.88 %. Statistical tests were used to assess the comparability of the two methods, followed by a scatter plot, the Bland Altman, Passing-Bablok, and the "Mountain" plot. Graphical comparisons generally do not show statistically significant differences between methods. The accuracy and precision of the ICP-OES method were verified by using the standard reference material SRM NIST 697, Dominican Bauxite. Recovery and repeatability values, expressed as relative standard deviation (RSD), are within the acceptance criteria. Based on the t-test, there is a statistically significant difference between the mean value of ICP-OES measurements and the certified value of silicon dioxide, which can be attributed to the effect of systematic error of ICP-OES analysis.

Keywords: impurities; sample preparation; precision; X-ray analysis; alumina.

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1. INTRODUCTION

Bauxite is the most important aluminium ore presently serving as a source of almost the entire world production of alumina and aluminium. Bauxites are a complex multi-component raw material with the basic components being the minerals of aluminium, iron, silicon, titanium, calcium, and magnesium [1]. The quality of bauxite and the choice of process parameters are determined by the content of impurities in addition to the percentage content of Al_2O_3 and the mineral form in which it is found. Silicon occurs in bauxite in the form of clay minerals of kaolinite and halosite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) and quartz SiO_2 [2]. The presence of SiO_2 in bauxite in the form of chamosite $4FeO \cdot Al_2O_3 \cdot 3SiO_2 \cdot 4H_2O$ [3] is also possible. Based on these facts, for the assessment of bauxite quality in laboratory conditions, methods for fast, accurate, and precise characterization of bauxite are extremely important. In numerous papers, different methods have been used to quantify silicon and other impurities in bauxite, such as spectrophotometry [4,5], X-ray fluorescence (XRF) [4], *Fourier transform infrared spectroscopy* (FTIR) [1], and laser-induced plasma spectroscopy (LIBS) [6,7]. Combinations of LIBS, energy-dispersive X-ray *spectroscopy (EDS)*, X-ray diffraction (XRD), and *scanning electron microscopy* (*SEM*) [8] methods were used for the chemical-mineralogical analysis of high silicate bauxite. The previously frequently used gravimetric method, is not practical for the silicon dioxide determination [3] as it is time-consuming. Although it is a more expensive analysis compared to most of the others, the method of inductively coupled plasma emission spectrometry (ICP-OES) [9,10] is increasingly used. The advantages of this method are low detection limit,

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stability and reproducibility of excitation sources, efficient atomization, speed of analysis, wide dynamic range, and the possibility of multi-element analysis.

This study aimed to evaluate the possibility of using the ICP-OES method as an alternative method for the determination of silicon dioxide in bauxite, by comparing the results with the reference spectrophotometric method and the use of a standard reference material. The used method of sample preparation was the same as for the spectrophotometric method, therefore not requiring additional time or material consumption.

2. EXPERIMENTAL

2. 1. Materials, standard solutions and reagents

Twenty bauxite samples from several different deposits from Bosnia and Herzegovina (Milići, Posušje, Jajce, Srebrenica, Široki Brijeg and Mrkonjić Grad) and from Montenegro (Nikšić) were analyzed. A standard bauxite sample SRM NIST 697, Dominican bauxite (National Institute of Standards and Technology, USA), was used to assess the accuracy and precision of the ICP-OES method.

All chemical reagents used were of analytical grade: sodium carbonate anhydrous, CAS 497-19-8 (Merck KGaA, Germany), sodium tetraborate decahydrate, CAS 1330-43-4 (Merck KGaA, Germany), ammonium molybdate tetrahydrate, CAS 12054-85-2 (LobaChemie PVT, Mumbai, India), ascorbic acid, CAS 50-81-7 (LobaChemie PVT, Mumbai, India), monoelement ICP standard silicon solution of 1000 mg dm^{-3} (Certipur Merck, KGaA, Germany), Specto Genesis ICAL solution (Bernd Kraft GmbH, Germany), HCl acid 37 % (m/m), CAS 7647-01-0 (Zorka Pharma, Šabac, Serbia) and H_2SO_4 acid 96 % (*m/m*), CAS 7664-93-9 (Zorka Pharma, Šabac, Serbia). Argon gas purity of 5.0. (99.999 %), CAS 7440-37-1 (Messer, B&H) was used for ICP-OES analyses. A standard solution concentration of 0.04 g dm^{-3} SiO_2 for spectrophotometric measurements was prepared from powdered SiO_2 *p.a.*, CAS 60676-86-0 (Fisher Scientific, Germany). Ultrapure water (resistance 18 MΩ cm^{-1}) was used for all analyses.

2. 2. Methods and instruments

2. 2. 1. Determining the silicon dioxide content by the ICP-OES method

The concentration of silicon dioxide was determined by using the ICP-OES spectrometer SPECTRO GENESIS, Spectro Analytical Instruments GmbH, Kleve, Germany in radial plasma mode. Calibration, measurements and data processing were performed by using the Smart Analyzer Vision 5.0 software package, which also served to record and control the instrument itself. Disassembly torch with 1.8 mm diameter Al_2O_3 injector, nebulizer, and spray chamber is adapted to work with HF. The continuous flow of the sample was achieved by using a peristaltic pump. The power of the radiofrequency generator was 1400 W, the flow rate of the cooling gas 12 dm^3 min^{-1}, the flow rate of the nebulizer gas 0.90 dm^3 min^{-1}, and the flow rate of auxiliary gas 0.90 dm^3 min^{-1}.

All laboratory glassware used for quantification of the silicon oxide content by the ICP-OES method was previously immersed in 10 % (v/v) HNO_3 for 24 h, washed with high purity distilled water, and dried with dry air at room temperature. Set-up method, ICALization (Intelligent Calibration and Logic) of the optical system of the ICP-OES spectrometer, calibration and measurement of control samples were performed according to the appropriate instructions [11].

The following equipment was used for sample preparation: VIMS Elektrik dryer (Tršić, Serbia) with a maximum temperature of 200 °C, analytical balance Entris (Sartorius, Germany with the precision of 0.1 mg, annealing furnace up to 1100 °C and laboratory stove (ELEKTRON, Banja Koviljača, Serbia), pipettes and burettes of AS class and other common glass laboratory accessories. Ultrapure water (resistance 18 MΩ cm^{-1}) for all analyses was provided by using the Milli-Q Reference system, Merck Millipore, Germany.

2. 2. 2. Measurements by the reference method

Analysis of the ICP-OES results were performed with respect to the spectrophotometric method MA.BM.006, following the method "VAMI" St. Petersburg and JUS B.G8.518 (ISO 6607). Spectrophotometric analysis was performed by using a double-beam UV-VIS spectrophotometer Shimadzu UV 1800 (Shimadzu, Japan) with UV Probe software. The pH value was measured by using a Five Esay pH meter (Mettler Toledo, Germany).

Silicon is characterized by the formation of a yellow silicomolybdate complex under strictly controlled conditions of acidity, reagent concentration, temperature, and time. The addition of ascorbic acid in the sulphuric acid environment reduces the resulting complex to a blue colour. The absorbance of this coloured complex was measured at 810 nm and the results were calculated and related to the calibration curve in the SiO_2 concentration range of 0.4-2.8 mg dm^{-3}.

2. 2. 3. Mineralogical characterization of samples

Qualitative mineralogical characterization of bauxite samples was performed by X-ray diffraction using a powder diffractometer D8 ENDEAVOR Minerals (BRUKER, Germany), under the following conditions: radiation of cobalt anticathode wavelength CoKα = 0.178897 nm, current and voltage of the generator 35 mA and 40 kV, respectively, angular range 10-90° 2θ, variable divergent slit, step size 0.02°, step time 1 s. Interpretation of diffractograms was performed by using the software package EVA.DIFRAC (BRUKER, Germany) with an integrated database.

2. 3. Sample preparation

Bauxite samples were homogenized, dried at 105 °C, and ground to a particle size below 200 μm. For both methods the samples were prepared in the same way, by melting with a mixture Na_2CO_3: $Na_2B_4O_7$ in a ratio of 3:1 and by dissolving the molten mass in hydrochloric acid (1:3), according to the method MA.BM.004, and modified methods JUS B.G8. 520/92 and ISO 6994/86. The bauxite specimen mass of 1 g was mixed with 6 g of Na_2CO_3:$Na_2B_4O_7$ mixture (3:1) in a Pt-crucible. Sodium tetraborate decahydrate, $Na_2B_4O_7 \cdot 10\ H_2O$, was previously annealed for two hours at 400 °C, after which it was cooled and ground to powder. The sample with the mixture was melted in a covered crucible at 1000 °C for 30 min. The molten mass was dissolved in 60 cm^3 of HCl 1: 3, taking care not to boil. The solution was transferred to a normal 500 cm^3 vessel, filled up to the mark with water, and well homogenized. The prepared samples were analysed by spectrophotometry and ICP-OES methods, at appropriate dilutions. For the ICP-OES analysis samples were diluted 10 times. The blank probe was prepared in the same way, but without a sample, and measured with each series of samples. Three samples of each bauxite specimen were prepared for the analyses. To assess accuracy and precision, the standard bauxite specimen SRM NIST 697 was prepared in the same way and measured ten times.

2. 4. Statistical processing

Microsoft Excel with the Analysis ToolPak (Microsoft, US) and MedCalc Statistical Software version 19.3.1 (MedCalc Software Ltd, Ostend, Belgium) were used for statistical data processing. The scatter plot, Bland Altman, Passing-Bablok, and "Mountain" plots were used to process and display the data obtained by the two analytical methods.

Bland Altman difference plots are used to describe agreement between two quantitative measurements by constructing limits of the agreement. These statistical limits are calculated by using the mean and the standard deviation of the differences between two measurements (SD). Bland-Altman recommended that 95 % of the data points should lie within ± 1.96 SD of the mean difference. The normal distribution of the differences must always be verified. If the line of equality (differences=0) is not in the confidence interval for the mean, the bias between the two measurements is statistically significant [12].

The Passing-Bablok regression is a linear regression model that assumes that neither of the two variables is either dependent or independent. The result is presented through a graphical representation of the value of the intercept and the slope, with a confidence interval that indicates the existence of a constant or proportional difference between the measurement results [13].

A "Mountain" plot is a complementary plot to the difference plot. It shows the distribution of differences between the two methods with an emphasis on the center and the tails of the distribution [14].

The measurement uncertainty according to the certified SiO_2 value was calculated based on the European Reference Materials [15].

3. RESULTS AND DISCUSSION

Diffractograms of bauxite samples from the seven deposits and of the standard bauxite sample are shown in Figures 1-7. According to the results of the X-ray analysis, the Milići, Jajce, Nikšić, Srebrenica, Široki Brijeg and Mrkonjić Grad bauxite deposits are of boehmite type, while bauxite from the Posušje deposit is of the mixed boehmite-gibbsite type. In addition to boehmite (AlOOH) and gibbsite ($Al(OH)_3$), the samples contain hematite (Fe_2O_3), goethite (FeOOH), kaolinite ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$), anatase ($TiO_2$), rutile ($TiO_2$), calcite ($CaCO_3$), and quartz ($SiO_2$). The bauxite from Jajce deposit also contains a small amount of diaspore (AlOOH). Silicon dioxide (SiO_2) is predominantly present in the form of kaolinite. Within bauxite obtained from Milići (samples 2 and 3), Posušje (samples 1 and 3), and Srebrenica (samples 1, 2 and 3), apart from kaolinite, there was also a certain amount of quartz. The standard bauxite sample NIST 697, Dominican bauxite [16] is a gibbsite type with a boehmite content of up to 10 %. Apart from gibbsite and boehmite, this bauxite contains hematite, goethite, kaolinite, anatase and calcite.

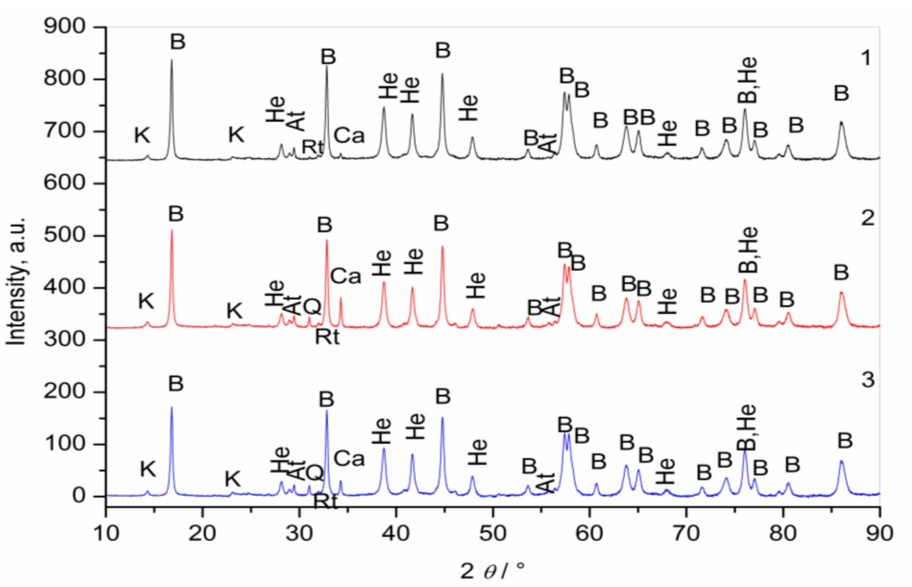

Figure 1. Diffractogram of the bauxite samples Milići (1-3): B-boehmite, He-hematite, At-anatase, Rt-rutile, Ca-calcite, Q-quartz and K-kaolinite

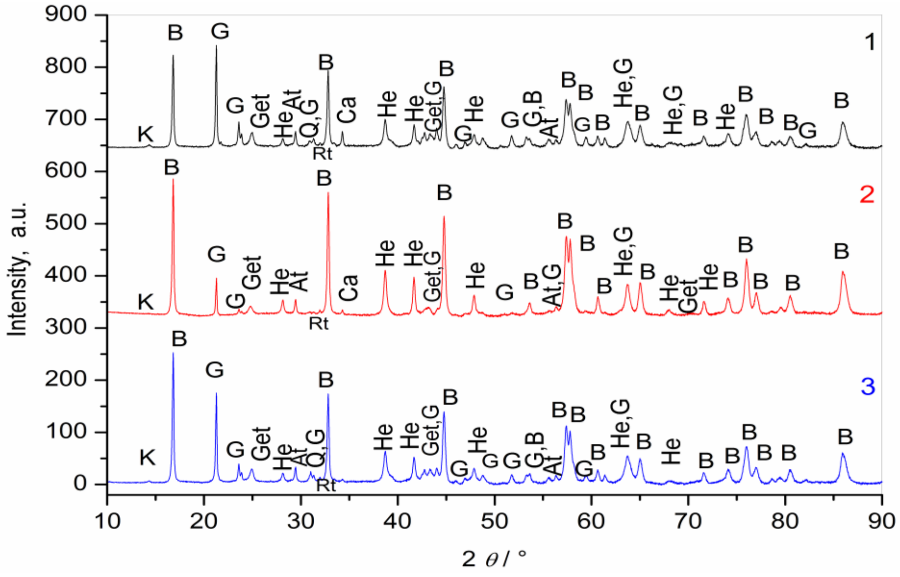

Figure 2. Diffractogram of the bauxite samples Posušje (1-3): B-boehmite, G-gibbsite, He-hematite, Get-goethite, At-anatase, Rt-rutile, Ca-calcite, K-kaolinite and Q-quartz

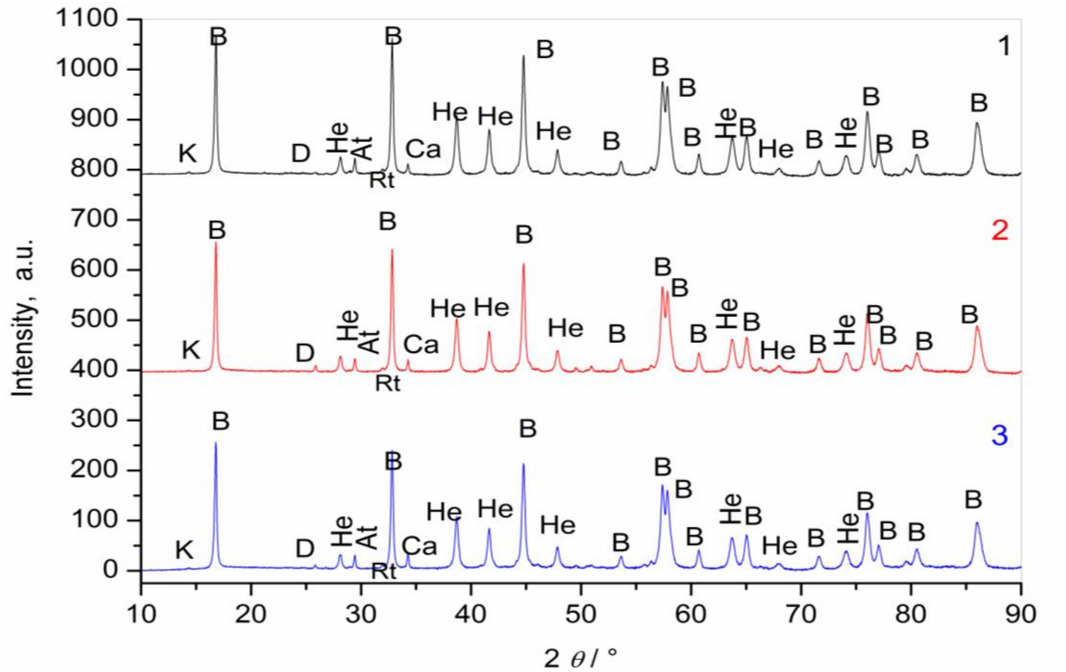

Figure 3. Diffractogram of the bauxite samples Jajce (1-3): B-boehmite, He-hematite, At-anatase, Rt-rutile, Ca-calcite, K-kaolinite and D-diaspore

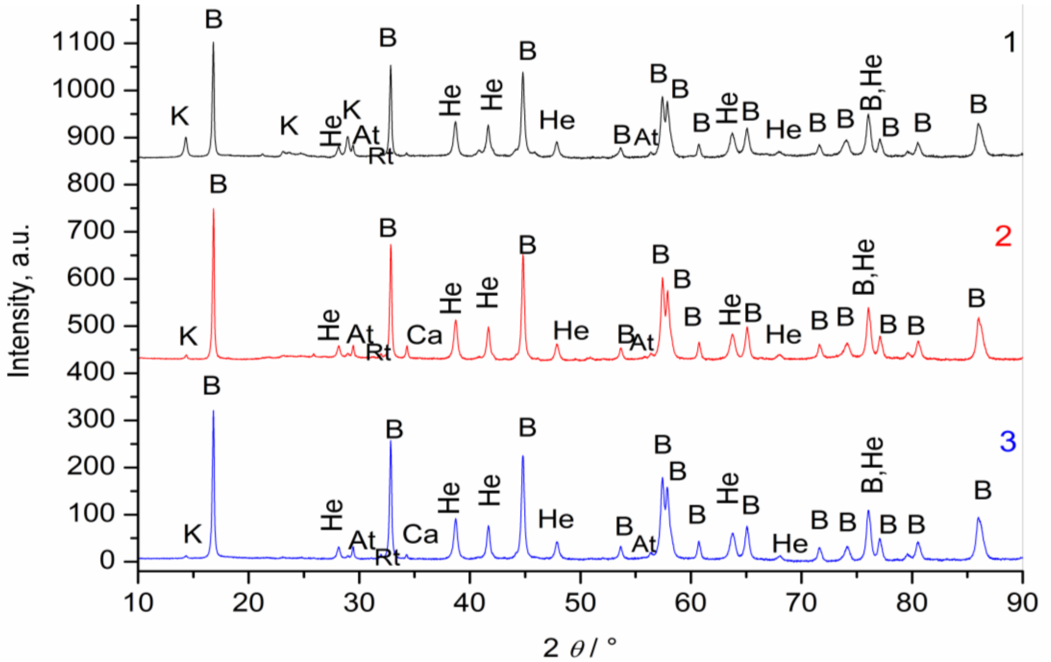

Figure 4. Diffractogram of the bauxite samples Nikšić (1-3): B-boehmite, He-hematite, At-anatase, Rt-rutile, Ca-calcite and K-kaolinite

Calibration curve for the ICP-OES analysis was constructed using eight points in the range of 0-80 mg dm^{-3} Si by a serial dilution of the standard solution with ultrapure water to the desired concentrations, with three measurements for each concentration level. According to the literature data [17], a line of wavelength 288.158 nm is recommended for the determination of silicon by this method. In this paper, three Si wavelengths were observed simultaneously: 212.412, 251.612 and 288.158 nm, as it was also reported in literature [18]. For further processing of the results, a wavelength of 251.612 nm was used because it is the most sensitive line with a BEC (*Background Equivalent Concentration*) value of 0.645 mg dm^{-3}, as compared with 0.865 mg dm^{-3} on 212.412 nm and 1.15 g dm^{-3} on 288.15 nm, Table 1.

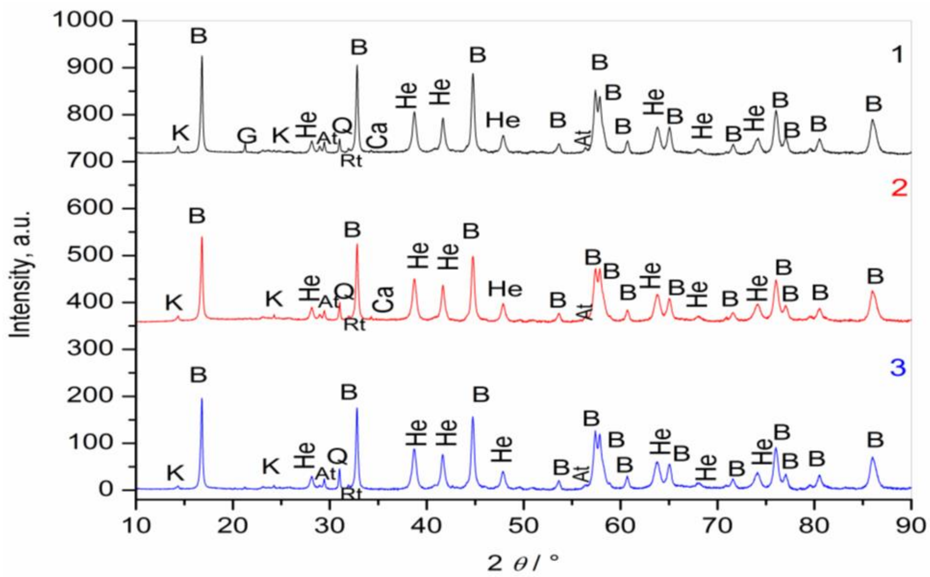

Figure 5. Diffractogram of the bauxite samples Srebrenica (1-3): B-boehmite, He-hematite, At-anatase, Rt-rutile, Ca-calcite, Q-quartz, K-kaolinite and G-gibbsite

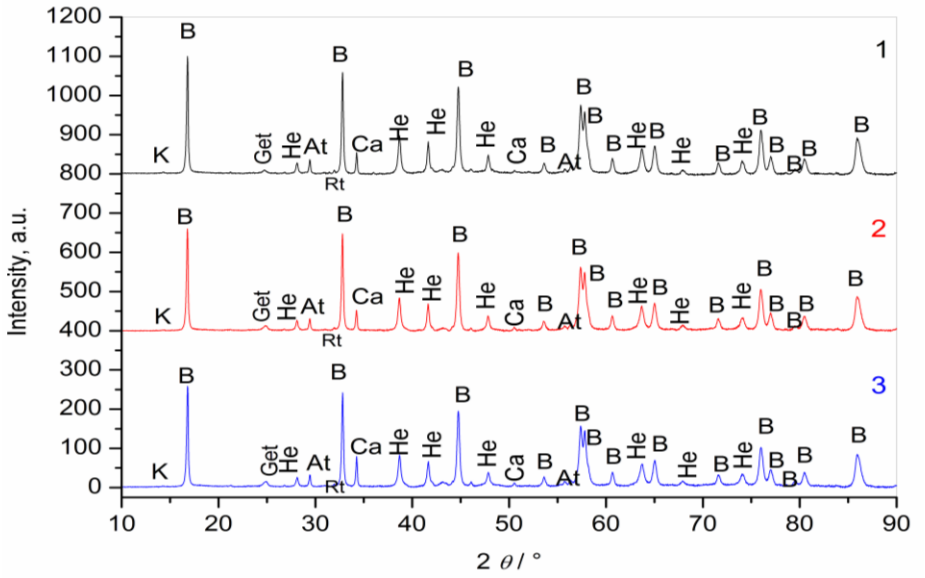

Figure 6. Diffractogram of the bauxite samples Široki Brijeg (1-3): B-boehmite, He-hematite, At-anatase, Rt-rutile, Ca-calcite, K-kaolinite, G-gibbsite and Get-goethite

Table 1. Calibration data of silicon emission lines determined by regression analysis. Correlation coeficient is 1 for all lines.

Si wavelength line, nm	LOD[a], mg dm^{-3}	BEC, mg dm^{-3}	Standard error, mg dm^{-3}	Detection range, mg dm^{-3}
212.412	0.0136	0.865	0.0788	0.0136-96
251.612	0.00168	0.645	0.0592	0.00168-96
288.158	0.0221	1.15	0.0765	0.0221-96

[a]LOD - limit of detection

For verification of calibration, a solution of silicon concentration of 20 mg dm^{-3} with a tolerance of ± 10 % to the expected value was used as an ICV (*Initial verification calibration*) control sample [11,19], Figure 8. Bauxite NIST 697 was analysed with each series of samples as a laboratory control sample (LCS) [11,19] and the measurement results are shown in Figure 9.

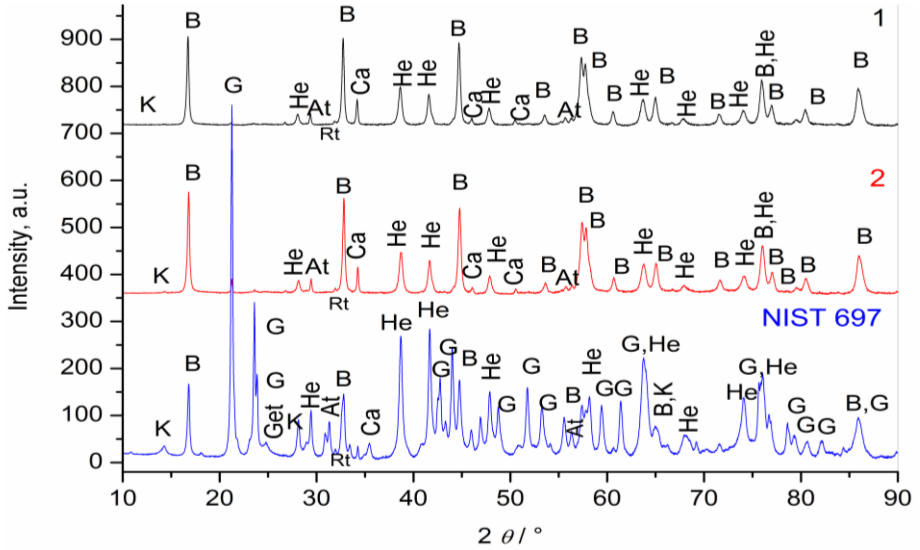

Figure 7. Diffractogram of the bauxite samples Mrkonjić Grad (1-2) and bauxite standard reference material NIST 697: B-boehmite, G-gibbsite, He-hematite, At-anatase, Rt-rutile, Ca-calcite, K-kaolinite and Get-goethite

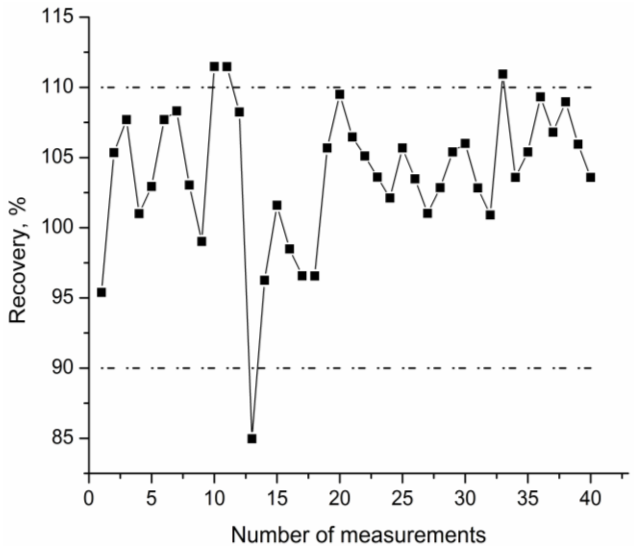

Figure 8. Recovery of Si concentration in ICV control sample (concentration 20 mg dm^{-3} Si) according to the reference value (acceptance recovery criteria: 90-110 %) [11]

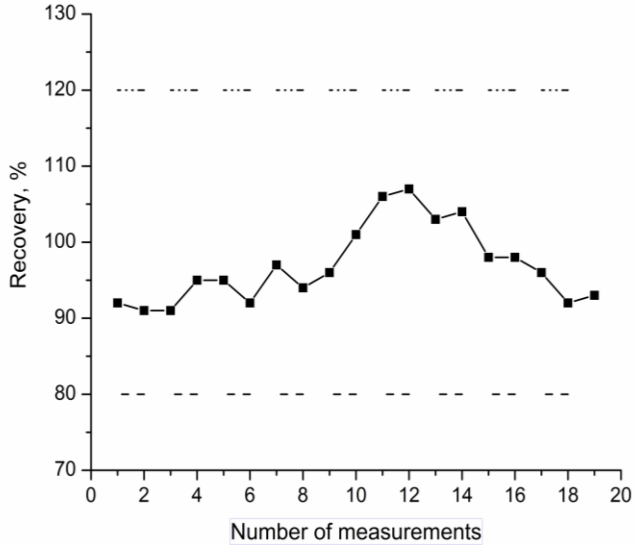

Figure 9. Percentage recovery of SiO_2 concentration in LCS control sample. Bauxite standard NIST 697 measured as a Laboratory Control Sample (LCS) during the period of measuring samples, acceptance recovery criteria: 80-120 % [11]

The silicon dioxide content determined by ICP-OES was calculated by multiplying the results (mg dm^{-3}) with a conversion factor of 2.14 (SiO_2/Si) and a dilution factor. The results of ICP-OES silicon dioxide content determination in comparison with spectrophotometric methods are presented in Table 2. Each result is the average value of three samples (preparation and measurement), with an error in the form of one standard deviation. Bias and recovery values were calculated related to the spectrophotometric method.

The mean relative deviation (bias) of ICP-OES results compared to UV-VIS spectrophotometry results is 4.88 %, and the mean recovery value of ICP-OES results compared to spectrophotometric results is 97.83 % (from 85.56 to 107.04 %). The scatter-plot diagram shown in Figure 10 shows that there is a good and strong correlation between the results of the two methods: correlation coefficient, R = 0.9993, determination coefficient R^2 = 0.9987, p-value <0.0001. The relationship between the results of the two methods is defined by the direction equation: $C_{\mathrm{SiO_2\,(ICP\text{-}OES)}} = -0.1984 + 1.0647 C_{\mathrm{SiO_2(UV\text{-}VIS)}}$.

The correlation of the results is not sufficient to conclude the comparability of the two methods [20]. Further comparison and evaluation are performed by applying the Bland Altman, Passing-Bablok, and "Mountain" plots [12-14], as well as statistical tests. The Shapiro-Wilk test (W = 0.92262, P = 0.11764, α = 0.05) confirms the normal distribution of differences between the two methods, Figure 11, thus fulfilling the condition for the Bland Altman analysis.

Table 2. Content of SiO_2 in bauxites from different deposits, determined by the ICP-OES method and compared to the results obtained by the spectrophotometric UV-VIS method

Bauxite sample	Concentration of SiO_2 ± SD, %		Bias, %	Apsolute bias*, %	Recovery, %
	ICP-OES	UV-VIS			
Milići 1	4.74±0.066	4.75±0.057	-0.01	0.21	99.79
Milići 2	6.33±0.034	6.12±0.057	0.21	3.43	103.43
Milići 3	6.49±0.089	6.36±0.184	0.13	2.04	102.04
Posušje 1	1.79±0.003	1.95±0.042	-0.16	8.21	91.79
Posušje 2	0.75±0.004	0.85±0.078	-0.10	11.76	88.24
Posušje 3	2.46±0.043	2.59±0.085	-0.13	5.02	94.98
Jajce 1	1.67±0.022	1.92±0.106	-0.25	13.02	86.98
Jajce 2	1.25±0.014	1.24±0.071	0.01	0.81	100.81
Jajce 3	1.54±0.017	1.80±0.198	-0.26	14.44	85.56
Nikšić 1	11.62±0.064	11.13±0.106	0.49	4.40	104.40
Nikšić 2	3.28±0.052	3.20±0.156	0.08	2.50	102.50
Nikšić 3	2.33±0.055	2.35±0.042	-0.02	0.85	99.15
Srebrenica 1	5.47±0.069	5.27±0.000	0.20	3.80	103.80
Srebrenica 2	6.72±0.028	6.52±0.064	0.20	3.07	103.07
Srebrenica 3	6.69±0.020	6.25±0.042	0.44	7.04	107.04
Široki Brijeg 1	1.51±0.008	1.61±0.007	-0.10	6.21	93.79
Široki Brijeg 2	1.15±0.013	1.21±0.028	-0.06	4.96	95.04
Široki Brijeg 3	1.57±0.015	1.60±0.014	-0.03	1.88	98.13
Mrkonjić Grad 1	1.59±0.007	1.61±0.014	-0.02	1.24	98.76
Mrkonjić Grad 2	1.82±0.010	1.87±0.046	-0.05	2.67	97.33
Average				4.88	97.83
Standard deviation				4.13	6.10

*[(Bias$_{\text{ICP-OES}}$- Bias$_{\text{UV-VIS}}$) / Bias$_{\text{UV-VIS}}$] 100

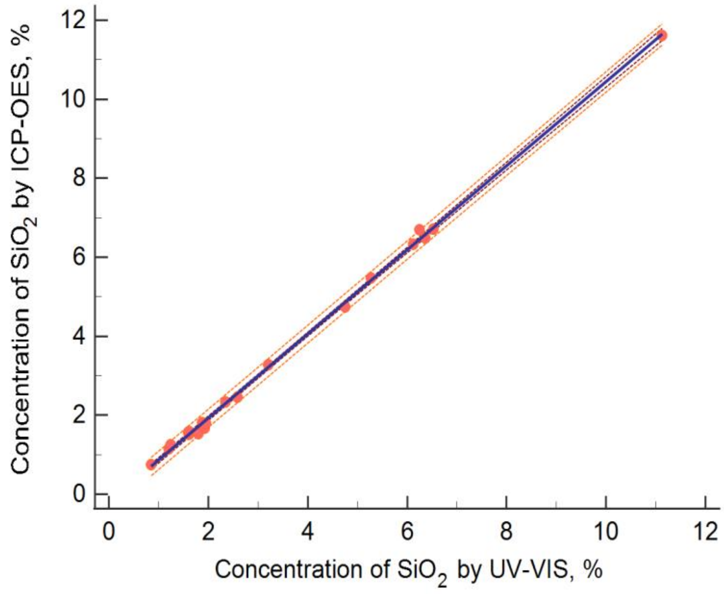

Figure 10. Correlation results of ICP-OES and spectrophotometric method for determination of SiO_2 content in bauxite samples. The solid line represents regression direction and dashed lines represent the 95 % confidence interval

The correlation of the results is not sufficient to conclude the comparability of the two methods [20]. Further comparison and evaluation are performed by applying the Bland Altman, Passing-Bablok, and "Mountain" plots [12-14], as well as statistical tests. The Shapiro-Wilk test ($W = 0.92262$, $P = 0.11764$, $\alpha = 0.05$) confirms the normal distribution of differences between the two methods, Figure 11, thus fulfilling the condition for the Bland Altman analysis.

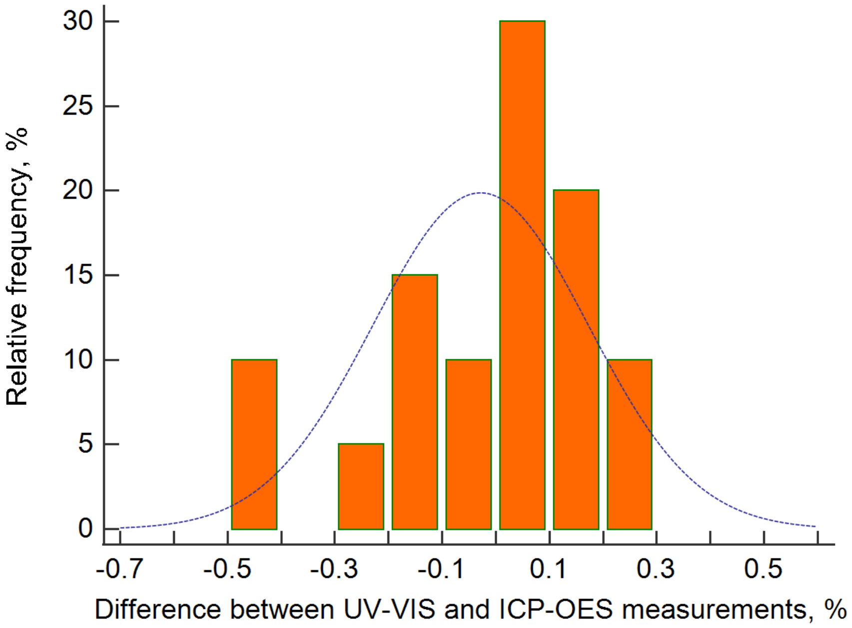

Figure 11. Distribution plot of differences between measurements by ICP-OES and UV-VIS methods. The dotted line represents normal distribution. Shapiro-Wilk test for normal distribution accepted normality (W = 0.92262, P = 0.11764)

By using the Bland Altman plot of the difference between the obtained measurements, it can be seen whether there is a difference in the measurements of the two methods in different concentration ranges, *i.e.* whether there is a constant or proportional difference in the measurements by a different method. The Bland Altman plot displayed in Figure 12 shows the difference between the measurement results of the two methods for determining SiO_2 in bauxite depending on the mean value of the measurement by the two methods for each sample. The solid center line represents the mean value of the difference measured by different methods for each sample (-0.03), with a 95 % confidence interval (CI) above and below the mean value line (CI from -0.1224 to 0.0654), while the dotted line represents the zero differences. The dashed lines represent the range of values or agreement limits ± 1.96 SD (from -0.42 to 0.36). Two points are outside these control limits. The regression direction of the measurement difference $y = 0.1946-0.0633x$ has a slightly negative slope depending on the mean value. This indicates that the differences decrease proportionally and move towards negative values with increasing SiO_2 concentration. The value of the zero difference is within the confidence interval of the mean value, based on which it can be concluded that the mentioned difference between the methods is not statistically significant.

A similar conclusion can be drawn from the analysis of Figure 13. This figure represents a Bland Altman graph comparing the relative differences of the two methods for determining SiO_2 in bauxite depending on the mean value. It is obvious that there is a proportional difference with a negative slope of the regression line, $y = 7.8642-1.5562\,x$, and one point is outside the range of ± 1.96 SD (from -10.09 to 14.92). The value of the zero difference is within the confidence interval of the mean value, based on which it can be concluded that the mentioned difference between the methods is not statistically significant.

Figure 14 shows the results of the Passing-Bablok regression, where the relationship between the methods is given by the equation:

$$y = -0.157\ (-0.2376-0.1066) + 1.058\ (1.0374-1.0833)\ x \qquad (1)$$

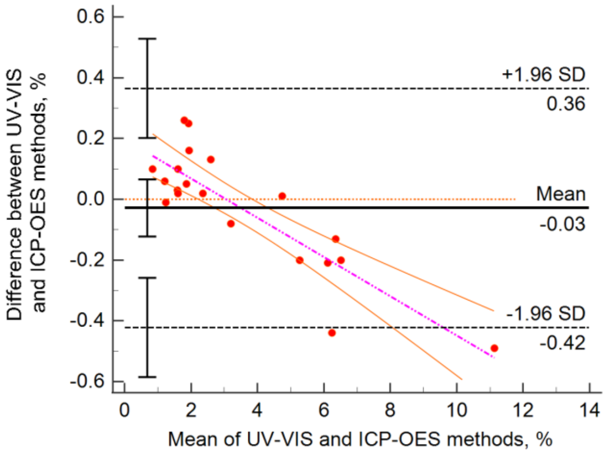

Figure 12. Bland Altman plot of absolute differences between the results of two methods from Table 2. Dashed black lines represent limits of agreement from -1.96 SD to +1.96 SD. Dashed pink line represent direction equation y=0.1946-0.0633x, confidence interval limits are pre- sented as continuous line. Error bars with horizontal lines showa 95 % confidence interval of mean and limits agreement

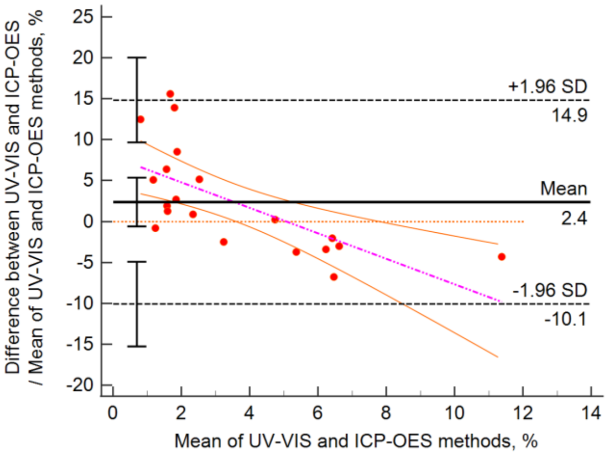

Figure 13. Bland Altman plot of the relative differences between the results of two methods from Table 2. Dashed lines represent limits of agreement from -1.96 SD to +1.96 SD. Dashed pink line represent direction equation y=7.8642-1.5562x, confidence interval limits are pre- sented as continuous line. Error bars with horizontal lines showa 95 % confidence interval of mean and limits agreement

The Cusum linearity test (*P* = 0.36) shows that there is no significant deviation from linearity. To confirm the agreement between the two methods, the values 0 and 1 for the section on the ordinate and the slope of the direction must be within 95 % confidence intervals. If the zero is not within the 95 % confidence interval of intercept, there is a constant difference between methods. In the case that the value of 1 is not within the 95 % confidence interval for the slope confidence interval, there is a proportional deviation. In this paper, the 95 % confidence interval of the section does not contain zero, and the 95 % confidence interval of the slope does not include the value 1, which indicates the existence of slight systematic (constant) and proportional differences between ICP-OES and UV-VIS methods. The distribution of concentration differences between measurements of the two methods is additionally described by using the "Mountain" graph, Figure 15, where it is clear that the top of the graph is close to zero, indicating a good agreement between the results of the compared methods.

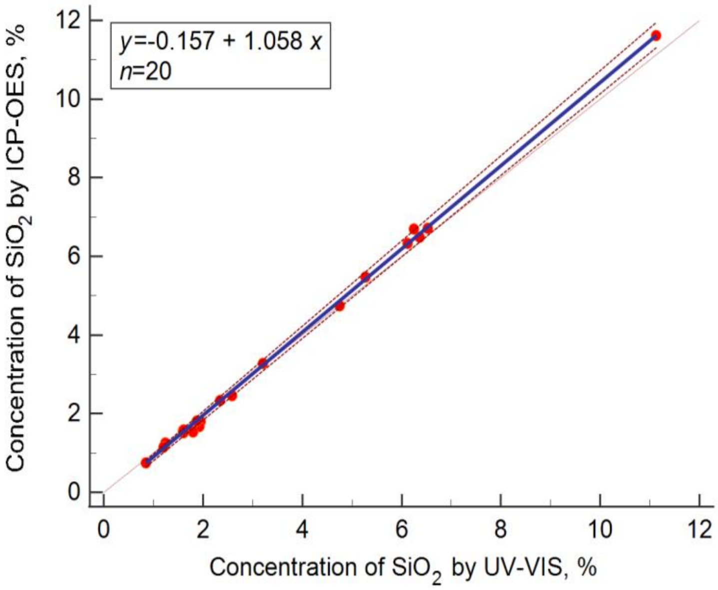

Figure 14. Passing-Bablok regression. The solid line represents regression direction. Regression equation is expressed as y= -0.157+1.058 x. Reggresion line has a slope of 1.058 (1.0374 to 1.0833) and an intercept of -0.157 (-0.2376 to -0.1066). Dashed lines represent the 95 % confidence interval

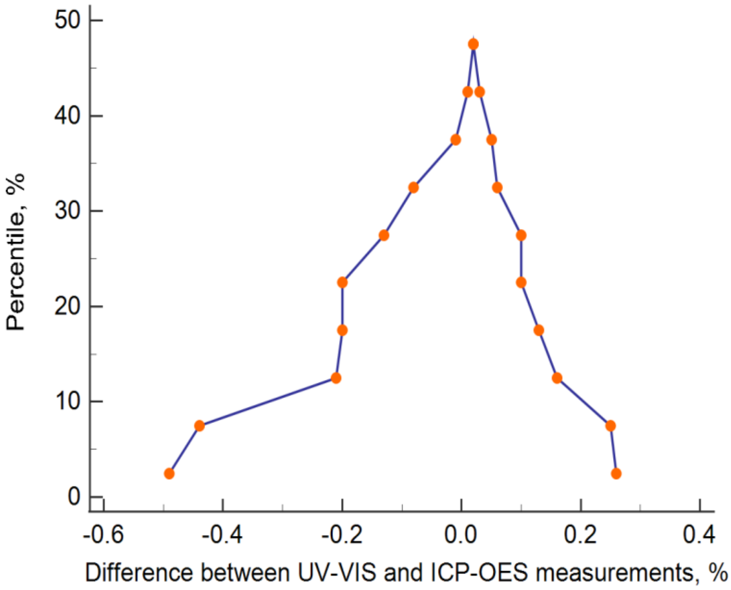

Figure 15. "Mountain" plot of differences between the results of two methods from Table 2

Further, a paired *t*-test was used to compare the mean values of the methods. The calculated value of the parameter *t* (0.635) is lower than *t* critical (2.093), so it can be concluded that there is no statistically significant difference between the mean values of the ICP-OES and UV-VIS methods, Table 3. As *F* is calculated (1.135) to be lower than the critical value of $F_{19,19}$ at $\alpha = 0.05$ (2.12), it can be concluded that there is no statistically significant difference in the precision of the two methods when measuring routine bauxite samples.

Table 3. t-test paired two samples for means of SiO_2 content measurement by UV-VIS and ICP-OES methods

	ICP-OES	UV-VIS
Mean, %	3.5385	3.51
Variance	8.091224	7.129052632
Observations	20	20
Pearson correlation	0.999352	
Hypothesized mean difference	0	
df	19	
t-stat	0.635	
P(*T*<=*t*) one-tail	0.266499	
t critical one-tail	1.72913	
P(*T*<=*t*) two-tail	0.53299	
t critical two-tail	2.093024	

In the next step, the accuracy assessment of the ICP-OES method was performed by successively measuring ten different samples (each time newly prepared) of the standard reference material, SRM NIST 697, Dominican bauxite, with a SiO_2 content of 6.81 ± 0.07 % [16]. Recovery values are in the range from 95.45 to 98.53 %. According to literature [21], the mean value of 96.51 % is slightly lower than the acceptance criteria of 97-103 %. Additionally, and according to [22], for this level of concentration this result is within the acceptability value of 95-102 %, Table 4. By using the *t-test*, it is determined that t calculated (11.499) is greater than *t* critical (2.262) for df-9, at α= 0.05. At the same time, the mean value of ten measurements and the certified value differs significantly, which can be attributed to the effect of a systematic error of the ICP-OES analysis. The calculated value for the 95 % confidence interval (6.53-6.61 %) does not include the certified value of the standard bauxite sample. The measurement uncertainty calculated in relation to the SRM [12] is 0.082 %. On the other hand, compared to the reference method, t calculated (2.305) is slightly higher than t critical (2.262), so it can be concluded that there is a good correlation of SRM NIST 697 measurement results using both methods, as well as for measuring routine samples, Table 4.

Table 4. Assessment of the accuracy of the ICP-OES method by using the standard reference material NIST 697

Number of measurements	ICP-OES		UV-VIS	
	C_{SiO_2} / %	Recovery, %	C_{SiO_2} / %	Recovery, %
1.	6.71	98.53	6.46	94.86
2.	6,.56	96.33	6.50	95.45
3.	6.65	97.65	6.50	95.45
4.	6.58	96.62	6.54	96.04
5.	6.55	96.18	6.53	95.89
6.	6.54	96.04	6.47	95.01
7.	6.52	95.74	6.55	96.18
8.	6.60	96.92	6.50	95.45
9.	6.50	95.45	6.58	96.62
10	6.51	95.59	6.42	94.27
Average	6.57	96.51	6.51	95.52
Standard deviation	0.066	0.971	0.047	0.693
RSD	1.01	1.00	0.73	0.73
t-calculated, SRM	11.498			
t-calculated, ref. method			2.305	
t-critical (df-9, α-0,05)	2.262		2.262	
95 % confidence interval	±0.0409 (6.53 - 6.61 %)			
Measurement uncertainty according to the certified value=0.082 %				

Table 5 shows the estimation of precision in repeatability. For this purpose, the solution of molten control bauxite samples SRM NIST 697 was measured in one day as follows: three repeated measurements during aspiration of the same solution, measuring the same sample ten times consecutively in the series and measuring the same sample several times in one day, every 30 min. Repeatability expressed as RSD is 0.48, 0.66, and 2.10 %, respectively.

Table 5. Assessment of repeatability of the ICP-OES method by measuring NIST 697 samples

Measurement number	Concentration of SiO_2, %		
	The same aspiration, measuring 3 times	Measurement in the series	Periodic measurement during day
1.	6.65	7.00	6.96
2.	6.66	6.96	6.78
3.	6.60	6.97	6.68
4.		7.02	6.55
5.		6.99	6.69
6.		6.94	6.89
7.		7.08	6.86
8.		7.01	
9.		6.92	
10.		7.02	
Average	6.64	6.99	6.77
SD	0.032	0.046	0.142
RSD	0.48	0.66	2.10
Precision limit based on measurement in the series, r=2.8·SD=2.8·0.046 = 0.129 %			

The precision of the method was checked against the Horwitz limit for intra-laboratory repeatability [21] for this concentration level, according to the equation (2):

$$\mathrm{PRSD_r} = 2^{(1-0.5\log C)} \quad (2)$$

which has been modified as Equation (3):

$$\mathrm{RSD_r} = 0.67\ \mathrm{PRSD_r} \quad (3)$$

where: $\mathrm{PRSD_r}$, % is the predicted relative standard deviation, *C* is the concentration expressed as mass fraction, RSDr is an acceptable limit for repeatability

The Horwitz's equation (2) represents an exponential relationship between the laboratory determined relative standard deviation (RSD) and concentration. This equation has emerged from sever al inter-laboratory studies conducted by the AOAC (American Association of Official Analytical Chemists). The Horwitz's PRSDr limit for SiO_2 concentration of

6.57 % is 3.01 %, while the modified value of the Horwitz's limit RSDr is 2.02 %. The repeatability in the series (RSD = 0.66 %) meets this criterion, and the RSD of periodic measurements during the day between analyses of other samples (2.10 %) differs slightly from the mentioned criterion. As a result, it can be concluded that the repeatability of the ICP-OES method is good. The repeatability of measurements of ten newly prepared samples of the same specimen (RSD = 1.01 %), Table 4, is within this criterion. The absolute difference between the two measurements in repeatability conditions (*r*) is 0.129 %, and according to the Horwitz's equation should not be greater than 0.372 %. Intermediate precision was determined by measuring one sample of SRM NIST 697 in a period of seven days (three times during each day), Table 6. In this period the calibration curve was not recalibrated, and different days of analyses were included as an additional factor of variability.

Table 6. Intermediate precision by measuring NIST 697 samples during 7 days

Measurement number	Concentration of SiO_2, %						
	1. day	2. day	3. day	4. day	5. day	6. day	7. day
1	6.90	7.05	6.65	6.42	6.49	6.79	6.70
2	6.73	6.99	6.72	6.42	6.79	6.48	6.67
3	6.71	7.49	6.46	6.42	6.39	6.39	6.92
Average	6.78	7.18	6.61	6.42	6.56	6.55	6.76
Standard deviation	0.104	0.273	0.135	0.000	0.208	0.210	0.137
Average value of all measurements							6.69
Standard deviation							0.275
RSD							4.11

Mean and relative standard deviations are calculated for each day. The total accuracy expressed as the value of RSD is 4.11 % and this value is about 50 % higher than the RSD measurements for one day, as well as the calculated predicted Horwitz's value of PRSDr [21]. In previous research [22-25], precision as RSD of <10 % and recovery of 90-110 % are generally considered satisfactory.

Intermediate precision was also observed over a longer period. During that time, the sample introduction system and torch were cleaned. The recalibration of the calibration curve was performed to the same standards. A control laboratory sample (LCS) NIST 697 was measured every day and the obtained results are presented in Table 7.

Table 7. Intermediate precision after 19 days, torch and sample introduction system was cleaned

Measurement	I series-before cleaning		II series-after cleaning	
	c_{SiO_2} / %	Recovery, %	c_{SiO_2} /%	Recovery, %
1.	6.26	92.00	6.46	94.81
2.	6.20	91.04	6.08	89.23
3.	6.20	91.04	5.94	87.22
4.	6.49	95.37	6.43	94.49
5.	6.49	95.31	6.23	91.44
6.	6.27	92.01	6.10	89.61
7.	6.59	96.97	6.27	92.09
8.	6.41	94.05	6.51	95.61
9.	6.53	95.94	7.35	107.90
10.	6.86	100.72	6.81	99.93
11.	7.23	106.20	5.71	83.78
12.	7.31	107.30	5.97	87.71
13.	6.99	102.71	6.26	91.88
14.	7.05	103.57	6.02	88.41
15.	6.65	97.68	7.10	104.30
16.	6.66	97.86	7.13	104.71
17.	6.53	95.89	5.40	79.27
18.	6.27	92.01	5.59	82.06
19.	6.35	93.31	5.39	79.17
Average	6.60	96.88	6.25	91.77
Standard deviation	0.343	5.041	0.559	8.216
RSD	5.20	5.20	8.94	8.95
t-test: *t* calculated = 2.304, *t* critical = 2.042				
Anova single factor: *F* = 5.309, *F* critical = 4.113, *p*-value= 0.027				

Recovery values are in the acceptable range, 80-120 %, except in two cases in the second series of measurements. Precision during the first 19 working days was 5.20 %, while it was 8.95 % during the next 19 days, after cleaning the instrument. Values of the paired *t*-test (*t* calculated > *t* critical) and the ANOVA test ($F > F$ critical, *p*-value $< \alpha = 0.05$) indicate that there is a statistically significant difference between the mean values and the precision of these two series of results. It can be concluded that RSD increases over time and that intermediate precision is deteriorating. The results are indicating that the ICP-OES method is sensitive to the variability of experimental measurement conditions (next working day, new argon bottle, memory effect, cleaning torch, and sample introduction system) [19], leading to random and systematic errors. This is implying that the determination of silicon dioxide by the ICP-OES method requires control of operating conditions, high purity of reagents, and measurement of a control sample, prepared according to the same procedure as the tested samples.

The errors of the reference method are not discussed in the paper. The fact that there is an agreement between the results of both methods, as well as the use of the same method of sample preparation, indicates the existence of several factors during the analysis that can be a source of errors in both methods.

4. CONCLUSION

The SiO_2 content in the analyzed bauxites, according to ICP-OES, ranges from 0.75 to 11.62 %. The emission line of 251.612 nm was selected for the determination of silicon dioxide by the ICP-OES method due to the lowest BEC values and standard error. Based on a graphical comparison of ICP-OES and UV-VIS results of bauxite analysis, there is a good correlation and comparability of analysis results of reference material and bauxite samples from different deposits. The values of the *t*-test and *F*–test indicate that there is no statistically significant difference in measurements by the two methods while the Passing-Bablok regression indicates slight differences between the methods. The value of the *t*-test shows that there is a statistically significant difference to the certified value of the NIST 697 standard, while the recovery values are in the acceptable range for a given concentration level. The repeatability of determination of the SiO_2 concentration in bauxite by the ICP-OES method, consecutively, in series (0.66 %) and over one day (2.10 %), is within the acceptable Horwitz's limit. RSD values that represent intermediate accuracy over 7 days (4.11 %), over a longer period of 19 days (5.2 %), and after instrument cleaning and measurement concerning the new calibration (8.94 %), are above the predicted RSDr limits but are still less than 10 %. The ICP-OES method shows greater sensitivity to experimental conditions and lower precision over time. Errors of the reference UV-VIS method are not considered and discussed in this paper. In the absence of another alternative method, the ICP-OES method can be applied with control of measurement conditions, system cleanliness, and measurement of the bauxite control sample (SRM or internal standard) with each group of unknown samples, with correction factor relative to the reference value.

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Određivanje sadržaja silicijum-dioksida u boksitu: poređenje metode ICP-OES sa metodom UV-VIS

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(Naučni rad)

Izvod

U ovom radu metoda optičke emisione spektrometrije sa induktivno spregnutom plazmom (engl. inductively coupled plasma - optical emission spectrometry, ICP-OES) korištena je za određivanje sadržaja silicijum-dioksida u boksitu, kao važne primese koja utiče na kvalitet i primenu boksita u proizvodnji glinice po Bajerovom (Bayer) postupku. Analizirano je dvadeset uzoraka boksita iz sedam različitih ležišta. Rezultati su upoređivani sa referentnom metodom UV-vidljive spektroskopije. Srednja relativna razlika između sadržaja silicijum-dioksida određenog pomoću ICP-OES metode i referentne metode je 4.88 %. Za procenu usporedivosti metoda korišteni su statistički testovi, zatim grafikon raspršenosti (engl. scatter plot), te Bland - Altman, „Passing-Bablok“ i "Mountain" grafikoni. Grafičke komparacije uglavnom ne pokazuju statistički značajne razlike između metoda. Tačnost i preciznost ICP-OES metode proverena je pomoću standardnog referentnog materijala SRM NIST 697, boksit Dominikan. Vrednosti iskorištenja (engl. recovery) i ponovljivost, izražena kao relativna standardna devijacija (RSD), su u okviru kriterijuma prihvatljivosti. Na snovu t-testa postoji statistički značajna razlika između srednje vrednosti ICP-OES merenja i sertifikovane vrednosti sadržaja silicijum-dioksida, što se može pripisati efektu sistematske greške ICP-OES analize.

Ključne reči: primese; priprema uzoraka; preciznost; rendgenska analiza; glinica