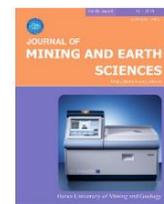




## Journal of Mining and Earth Sciences

Website: <http://jmes.humg.edu.vn>



# X-ray fluorescence major element analyses of silicate rocks by creating a calibration curve with the S2 Ranger instrument

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### ARTICLE INFO

#### Article history:

Received 11<sup>th</sup> July 2019

Accepted 16<sup>th</sup> Nov. 2019

Available online 30<sup>th</sup> Dec. 2019

#### Keywords:

Calibration curve,  
Major elements,  
Silicate rocks,  
Wavelength dispersive,  
X-ray fluorescence.

### ABSTRACT

Japanese silicate rock standard samples and the S2 Ranger XRF Spectrometer are utilized to create a calibration curve for analyzing major element concentrations of silicate rocks. The calibration curve shows strong positive correlations between intensity and concentrations in most of the major elements of standard samples: Si (0.9583), Ti (0.9971), Al (0.9674), Fe (0.9988), Mn (0.9785), Mg (0.9951), Ca (0.9920), Na (0.9710), K (0.9996), and P (0.9199), suggesting a good calibration curve for measuring major elements of silicate rocks. In order to demonstrate the reliability of standard calibration curves, all of the standard samples were tested. The analysis results display narrow analytical deviations, indicating good stability and reliability of the standard calibration curve and analytical instruments. Furthermore, the JA-2 was tested 10 times to examine counting errors of the instrument and avoid instrumental drift. Most of the standard deviation was less than 0.2 wt%, particularly lower 0.05 wt%, such as  $TiO_2$ ,  $Fe_2O_3$ , MnO,  $K_2O$ , and  $P_2O_5$ . The calibration curve created by the S2 Ranger XRF Spectrometer is proved to be suitable for analyzing major element concentrations of silicate rocks.

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## 1. Introduction

The chemical compositions of silicate rocks play important roles in investigating and resolving numerous geological issues. Geological major elements compose 95% of the earth's crust, and they are over 90% of the composition of most silicate rocks. Major elements include the most

abundant elements in the Earth's crust those content exceed 1000 ppm (0.01%) such as Si, Al, Ca, Mg, Na, K, Ti, Fe, Mn, and P. Based on their composition, crystallization history of igneous bodies such as granite or basalt, processes of formation of the seafloor, nature of chemical weathering in various climates, stratigraphic correlation of sedimentary and volcanic rocks, processes of ore generation, and many other features can be clearly studied.

X-ray fluorescence spectrometry (XRF) has been widely utilized to analyze major elements of

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silicate rocks (Schlotz, 2004). The S2 Ranger XRF spectrometer with manual samples loading is an energy dispersive, X-ray fluorescence instrument (Bruker, 2005). The instrument is a good technique for the quantitative determination of major and minor elements from a wide range of sample types. Measurements by the S2 (Solutions Ranger XRF spectrometer are carried out directly on the solid material with little sample preparation. The samples can be measured to allow multi-element determinations from ppm to 100% of elements from sodium (Na) through to uranium (U). Nevertheless, quantitative XRF analysis of samples is accomplished by the use of a comparative procedure, indicating that unknown samples can be analyzed and are compared with samples of well-defined composition. As a result, a calibration procedure must be performed before proceeding to the calculation of unknown sample compositions.

X-ray fluorescence spectroscopy laboratory at Department of Prospecting and Exploration Geology, Hanoi University of Mining and Geology (HUMG) was equipped with the S2 Ranger instrument of Bruker-Germany company. However, developing a process for analyzing specific rock and mineral samples requires a great investment for researchers and time for investigating the procedure of quantitative analysis of samples by x-ray fluorescence with the S2 Ranger instrument. The current requirements are to survey, select, and develop analytical and standardized procedure suitable for the S2 Ranger instrument at the X-ray fluorescence spectroscopy laboratory in the Department of Prospecting and Exploration Geology, HUMG.

In order to promote the efficacious investigation of the X-ray fluorescence spectrometry laboratory at HUMG, 14 Japanese silicate rock standard samples were chosen to investigate and create a calibration procedure on the S2 Ranger XRF spectrometer.

## **2. Materials and methods**

### **2.1. Samples**

To create a good calibration procedure for analyzing major elements of unknown silicate samples, 14 Japanese silicate rock standard samples are utilized in this study (Table 1). These standard samples were provided by the Analysis Centre, Institute of Geological Sciences, Vietnam Academy of Science and Technology (IGS-VAST). They are used as standard samples for constructing a calibration curve on the S2 Ranger XRF spectrometer for major element analyses of silicate rocks.

### **2.2. Instruments**

The S2 Ranger of Bruker company (Figure 1) performs multi-element analysis from sodium (Na) to Uranium (U), from 100% down to the ppm-level in solids, powders, or liquids with little or no sample preparation. Unrivalled analytical performance is ensured by using the highest power in direct excitation geometry. The machine applied up to 50 watts of X-ray power directly to the sample, employs a Silicon Drift Detector (SDD) for the measurement and energy analysis of emitted x-rays. The main advantage of this detector is the ability to operate at or close to room temperature with reasonable resolution. At -25°C a typical detector has a resolution of ca. 150 eV for Mn K- $\alpha$  (5895 eV). By comparison, a Si (Li) detector needs to be operated at liquid nitrogen temperature -196°C to give a similar performance. Moreover, the S2 has the following advantages as no need for moving parts such as primary optics or monochromators and maximum precision thanks to higher intensity resulting from exciting elements at low concentration. Due to Peltier cooling, no liquid nitrogen is required for cooling; this minimizes hassle and significantly reduces operating costs.

The Windows-based software running the Spectra EDX is shared with Bruker's popular Primus series of higher- power WDXRF systems, which means that it has the same advanced algorithms, multiple language support and an intuitive, user-friendly interface that has made Bruker's the world's leader in X-ray instrumentation and industrial applications.



Figure 1. The S2 Ranger instrument and its status display in the laboratory at HUMG.

Table 1. Measurement conditions.

Element	Si	Al	Ti	Fe	Mn
Line	K- $\alpha$ 1 Mn	K- $\alpha$ 1 Mn	K- $\alpha$ 1 Mn	K- $\alpha$ 1 Mn	K- $\alpha$ 1 Mn
kV-mA	20-0.26	20-0.268	40-0.628	40-0.628	40-0.628
Primary Filter	None	None	Al 500 $\mu$ m	Al 500 $\mu$ m	Al 500 $\mu$ m
Absorption correction	None	None	Variable alphas + geometric correction	Variable alphas + geometric correction	Variable alphas + geometric correction
Intensity model	net intensity	net intensity	net intensity	net intensity	net intensity
Mode	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum
Time (s)	30	30	30	30	30
Element	Ca	Mg	Na	K	P
Line	K- $\alpha$ 1 Mn	K- $\alpha$ 1 Mn	K- $\alpha$ 1 Mn	K- $\alpha$ 1 Mn	K- $\alpha$ 1 Mn
kV-mA	40-0.628	20-0.268	20-0.268	40-0.628	20-0.268
Primary Filter	Al 500 $\mu$ m	None	None	Al 500 $\mu$ m	None
Absorption correction	Variable alphas + geometric correction	None	None	Variable alphas + geometric correction	None
Intensity model	net intensity	net intensity	net intensity	net intensity	net intensity
Mode	Vacuum	Vacuum	Vacuum	Vacuum	Vacuum
Time (s)	30	30	30	30	30

### 2.3. Analytical method

#### 2.3.1. Analytical conditions

Major elements were measured by using the S2 Ranger in the laboratory at HUMG. Each sample was analyzed for approximately 30 minutes, and the data were reported as major-element oxides (i.e., SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, MgO, CaO, K<sub>2</sub>O, Na<sub>2</sub>O, P<sub>2</sub>O<sub>5</sub>, TiO<sub>2</sub>, and MnO). Instrumental

conditions for elemental analysis are shown in Table 1.

#### 2.3.2. Construction of standard calibration curve

A calibration curve is created by using the empirical method to determine the chemical concentration for elements in the sample from processed XRF energy count data. This study used the fundamental parameter (FP) method, which was first introduced by Jacob in 1955. The

calibration curves were produced following a guide of Application Wizard to set up an analytical method (Started et al., 2008). Knowledge of instrument and material parameters such as theoretical X-ray beam intensity, beam and detector angles, inter-element effects, and spectral background to estimate elemental concentrations are used in the method. The FP models are computationally demanding and impractical for near real-time applications. Nevertheless, the FP methods require just one reference sample to produce acceptable calibration results. Besides, the reference sample does not have to exactly match the properties of the unknown sample.

### 3. Results and Discussions

#### 3.1. Accuracy of the linear calibration curves

Table 2. Testing results for silicate rock standard samples (unit: mass %).

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
JA-1	63.97	0.850	15.22	7.07	0.157	1.570	5.70	3.84	0.77	0.165
Test v.	65.01	0.82	15.18	6.64	0.14	1.97	5.35	4.00	0.76	0.13
JA-2	56.42	0.660	15.41	6.21	0.108	7.600	6.29	3.11	1.81	0.146
Test v.	55.99	0.68	15.58	6.49	0.11	7.13	6.25	3.56	1.83	0.14
JB-2	53.25	1.190	14.64	14.25	0.218	4.620	9.82	2.04	0.42	0.101
Test v.	51.69	1.19	15.15	14.46	0.22	3.756	9.77	3.22	0.434	0.117
JB-3	50.96	1.440	17.20	11.82	0.177	5.190	9.79	2.73	0.78	0.294
Test v.	49.83	1.44	18.02	11.55	0.17	4.13	9.89	3.81	0.84	0.32
JF-1	66.69	0.005	18.08	0.08	0.001	0.006	0.93	3.37	9.99	0.01
Test v.	65.89	0.11	18.15	0.08	0.003	1.03	1.40	3.52	9.82	0.004
JF-2	65.30	0.005	18.52	0.06	0.001	0.004	0.09	2.39	12.94	0.003
Test v.	63.77	0.02	18.31	0.06	0.00	1.02	1.51	3.00	12.33	0.00
JG-1	72.30	0.260	14.24	2.18	0.063	0.740	2.20	3.38	3.98	0.099
Test v.	71.54	0.508	12.58	2.83	0.1512	1.817	3.18	3	5.33	0.069
JG-2	76.83	0.044	12.47	0.97	0.016	0.037	0.70	3.54	4.71	0.002
Test v.	76.05	0.042	12.82	0.97	0.0138	1.019	0.8	3.63	4.653	0.006
JG-3	67.29	0.480	15.48	3.69	0.071	1.790	3.69	3.96	2.64	0.122
Test v.	66.56	0.486	15.28	3.65	0.0637	3.169	3.87	4.03	2.772	0.117
JGb-1	43.66	1.600	17.49	15.06	0.189	7.850	11.90	1.20	0.24	0.056
Test v.	42.51	1.73	16.98	15.34	0.21	7.98	12.47	1.36	0.30	0.12
JR-1	75.45	0.110	12.83	0.89	0.099	0.120	0.67	4.02	4.41	0.021
Test v.	75.464	0.090	12.574	0.858	0.081	1.044	0.730	3.629	4.148	0.007
JR-3	72.76	0.210	11.90	4.72	0.083	0.050	0.09	4.69	4.29	0.017
Test v.	73.12	0.21	12.24	4.63	0.074	0.849	0.42	4.26	4.14	0.053
Jsy-1	60.02	0.002	23.17	0.08	0.0024	0.016	0.25	10.74	4.82	0.014
Test v.	60.45	0.00	23.20	0.09	0.00	1.11	0.60	9.43	5.12	0.00
JP-1	42.38	0.006	0.66	8.37	0.121	44.600	0.55	0.02	0.003	0.002
Test v.	41.60	0.02	0.98	9.50	0.17	45.35	0.65	1.70	0.01	0.00

The correction coefficients were calculated theoretically by the fundamental parameter (FP) method. The correlation coefficients between the intensity and concentration of each major element of the calibration curve are displayed in Figure 2. The results indicate a very strong positive correlation between intensity and concentration of all major elements, demonstrating that the calibration curve can be used to analyze well major element concentration of silicate rock samples. Furthermore, all of the standard samples were tested using the new calibration, and the results are listed in Table 2. The results show narrow ranges of analytical deviation, confirming the good calibration curve.

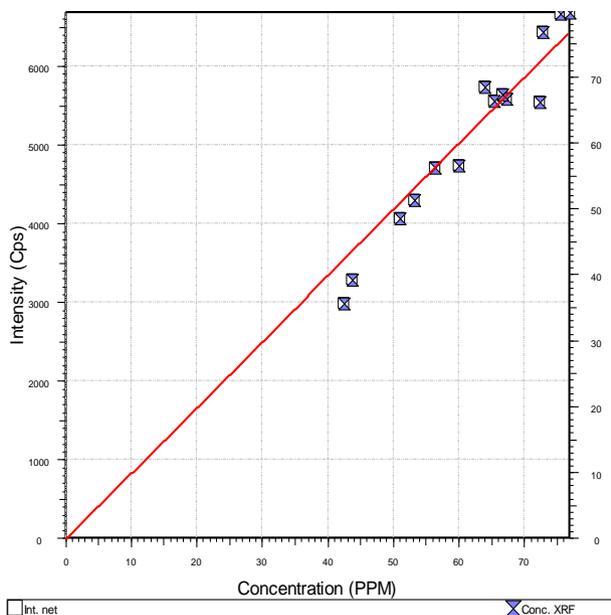
The accuracy of the linear calibration curves ( $\Delta$ ) is calculated by the following formula suggested by Timothy (1989):

$$\Delta = \sqrt{\frac{\sum_i^n (C_i - C_i^*)^2}{n - k}} \quad (1)$$

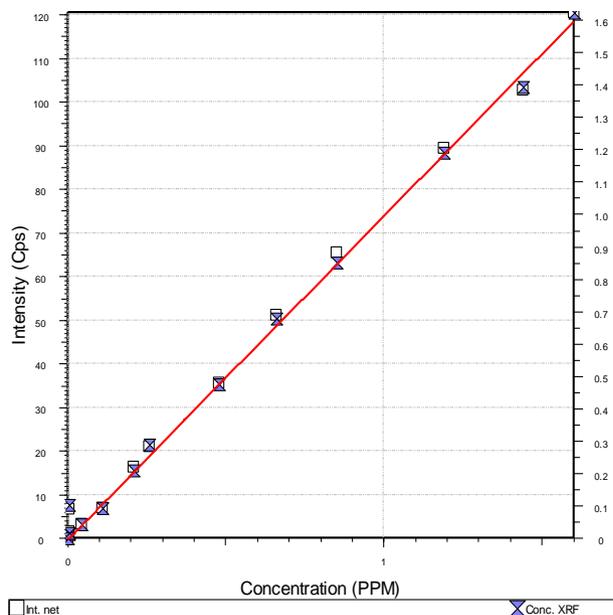
In which,  $C_i$  - the calculated value of the standard sample,  $C_i^*$  - the certified value of the

standard sample,  $n$  - number of standard samples,  $k$  - degree of freedom. In case  $n$  is minimum ( $n = 14$ ) and varies, choose  $k=2$  (Rigaku Corporation), and then the formula becomes as follows:

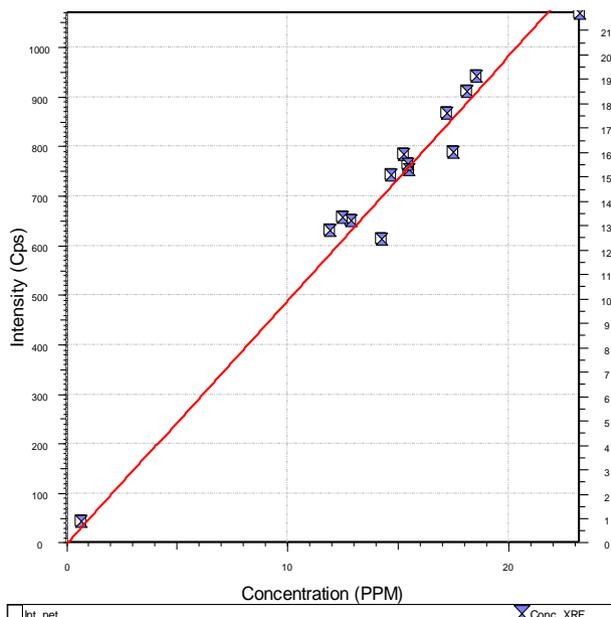
$$\Delta = \sqrt{\frac{\sum_i^n (C_i - C_i^*)^2}{n - 2}} \quad (2)$$



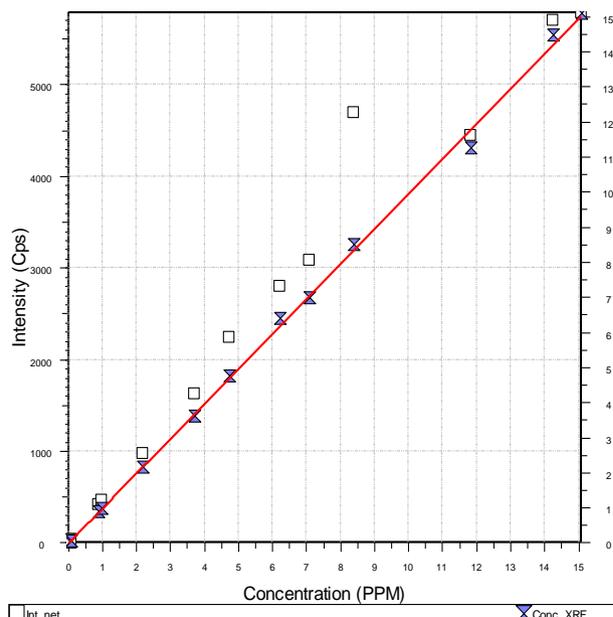
**Si coefficient = 0.9583**



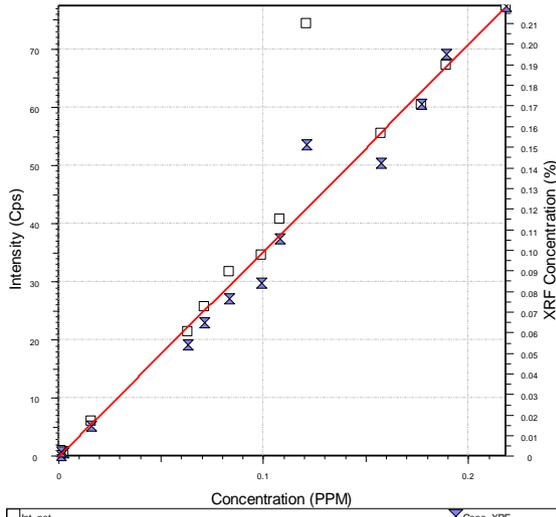
**Ti coefficient = 0.9971**



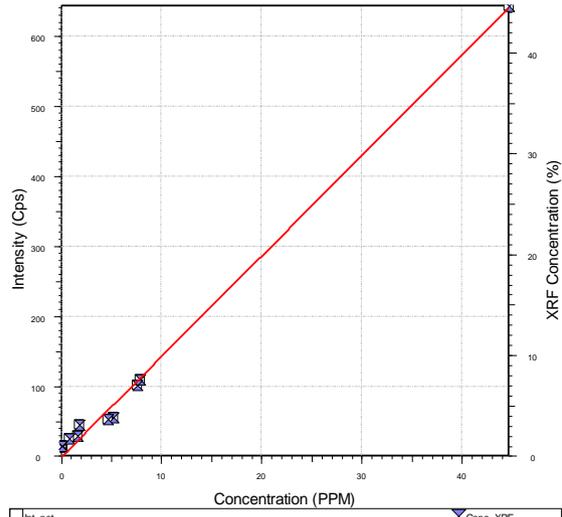
**Al coefficient = 0.9674**



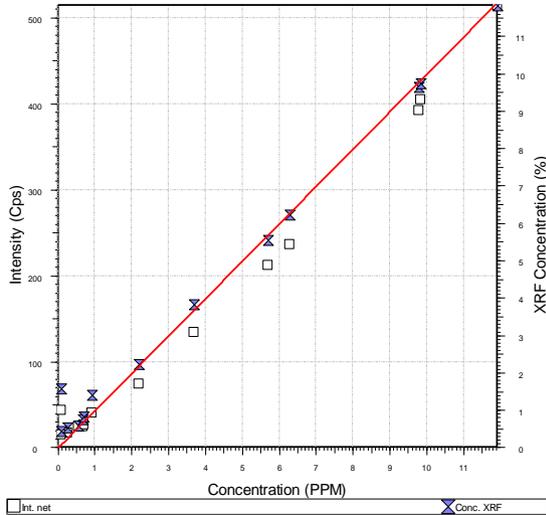
**Fe coefficient = 0.9988**



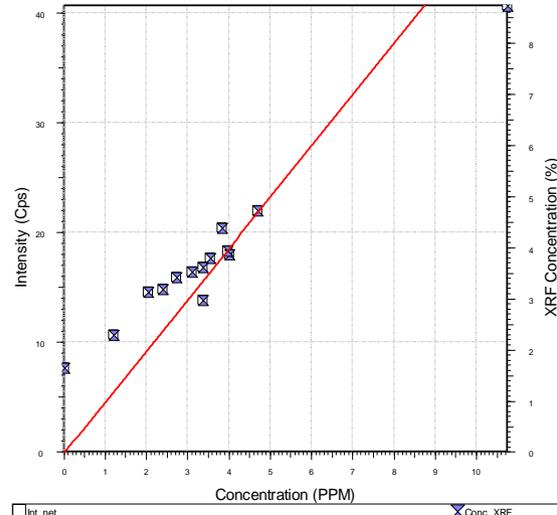
**Mn coefficient = 0.9785**



**Mg coefficient = 0.9950**



**Ca coefficient = 0.9920**



**Na coefficient = 0.9710**

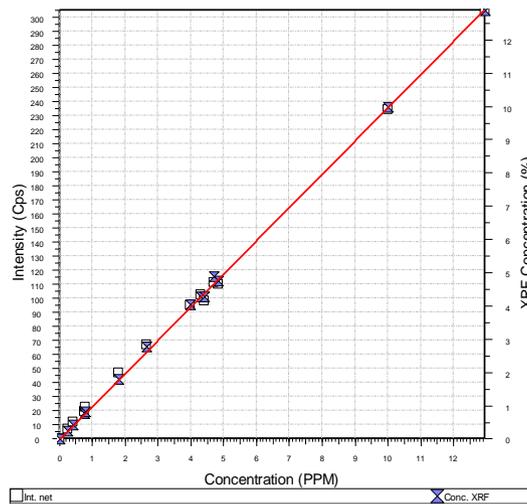


Figure 2. Correlation between intensity and concentration of major elements by using the calibration curve.

Calculated results following formula (2) are listed in table 3.

Tables 2 and 3 show the compositional range covered by the calibration curves and their accuracy of each element. The highest standard deviation (HSD) of SiO<sub>2</sub> content is 1.56wt% and its accuracy ( $\Delta$ ) reaches 0.997wt%; HSD of Al<sub>2</sub>O<sub>3</sub> = 1.66wt%,  $\Delta$  = 0.611wt%; HSD of Fe<sub>2</sub>O<sub>3</sub> = 1.13wt%,  $\Delta$  = 0.425wt%; HSD of K<sub>2</sub>O = 1.35wt%,  $\Delta$  = 0.451wt%, respectively. The accuracy of calibration curves in this study displays the same level as that reported using other instruments (Imai et al., 1995; Goto et al., 2002). Although the accuracy of SiO<sub>2</sub> is relatively larger than that of other elements due to an extreme expansion of the compositional range in relation to synthetic standards, it is not considered to be a severe problem on a practical level.

Table 3. Calibration results (unit: mass%).

Component	Calibration range	Accuracy ( $\Delta$ )
SiO <sub>2</sub>	42.38 ÷ 76.83	0.997
TiO <sub>2</sub>	0.00 ÷ 1.60	0.087
Al <sub>2</sub> O <sub>3</sub>	0.66 ÷ 23.17	0.611
Fe <sub>2</sub> O <sub>3</sub>	0.06 ÷ 15.06	0.425
MnO	0.00 ÷ 0.22	0.031
MgO	0.00 ÷ 44.60	0.984
CaO	0.09 ÷ 11.90	0.573
Na <sub>2</sub> O	0.02 ÷ 10.74	0.828
K <sub>2</sub> O	0.00 ÷ 12.94	0.451
P <sub>2</sub> O <sub>5</sub>	0.00 ÷ 0.29	0.027

### 3.2. Repeatability test results for silicate rocks

The established calibration curve was used to test the concentration of the JA-2 sample (repeated 10 times). For the calibration curve method, lower detection limits (LLD) are essentially defined by the lowest concentration of standard samples for each element. In the cases of TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO, K<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub> used in this study, the lowest content in the standards is <0.1 wt%. Therefore, analytical reproducibility could have affected the quantitative analytical results.

In order to examine counting errors of the instrument and to avoid instrumental drift, the repeated, continuous analysis was carried out in this study. The average composition of analysis repeated 10 times for the JA-2 sample, and its standard deviation is shown in Table 4. This short term reproducibility of essentially the same condition reveals the accuracy of the instrument in repeat analysis. The standard deviation of the analysis repeated 10 times was less than 0.2 wt%, particularly with elements of a lower concentration such as TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO, K<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub>, which were less than 0.05 wt%. Those values were sufficiently smaller than the accuracy of the calibration curves. In the cases of TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, MnO, K<sub>2</sub>O, and P<sub>2</sub>O<sub>5</sub>, the values of the accuracy of the calibration curves are substantially defined as LLD. This indicates that the standard deviations for major and minor components are very small. Therefore, the relative standard deviations of all elements are less than 5%, displaying the stability and reliability of standard calibration curve analysis.

Table 4. Repeatability testing results for silicate rocks (unit: mass %).

	SiO <sub>2</sub>	TiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	MnO	MgO	CaO	Na <sub>2</sub> O	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>
JA-2 (chemical value)	56.42	0.660	15.41	6.21	0.108	7.600	6.29	3.11	1.81	0.146
N=1	55.99	0.68	15.58	6.49	0.11	7.13	6.25	3.56	1.83	0.14
2	55.90	0.681	15.45	6.51	0.10	7.12	6.27	3.52	1.82	0.14
3	57.27	0.698	15.94	6.64	0.11	7.293	6.39	3.64	1.872	0.147
4	57.120	0.654	16.010	6.500	0.120	7.300	6.300	3.620	1.870	0.150
5	56.630	0.689	15.760	6.565	0.110	7.212	6.320	3.600	1.851	0.144
6	56.510	0.668	15.730	6.505	0.110	7.210	6.285	3.570	1.845	0.145
7	55.945	0.681	15.515	6.500	0.105	7.125	6.260	3.540	1.825	0.140
8	57.195	0.676	15.975	6.570	0.115	7.297	6.345	3.630	1.871	0.149
9	56.570	0.678	15.745	6.535	0.110	7.211	6.303	3.585	1.848	0.144
10	56.310	0.685	15.670	6.528	0.110	7.171	6.285	3.580	1.841	0.142
Average	56.544	0.679	15.738	6.534	0.110	7.207	6.301	3.585	1.847	0.144
Maximum	57.270	0.698	16.010	6.640	0.120	7.300	6.390	3.640	1.872	0.150
Minimum	55.900	0.654	15.450	6.490	0.100	7.120	6.250	3.520	1.820	0.140
Range	1.370	0.044	0.560	0.150	0.020	0.180	0.140	0.120	0.052	0.010
Standard deviation	0.5193	0.0119	0.1926	0.0462	0.0053	0.0712	0.0421	0.0389	0.0191	0.0036
RSD%	0.92	1.75	1.22	0.71	4.79	0.99	0.67	1.09	1.04	2.53

#### 4. Conclusion

The S2 Ranger instrument at HUMG and 14 Japanese silicate rock standard samples were utilized to create a calibration curve for analyzing major elements of silicate rock samples. Through the testing results, the conclusions can be drawn as follows:

The intensity and concentration of all major elements in the calibration curve present a very strong positive correlation. The testing standard samples indicate narrow ranges of analytical deviation. Furthermore, the accuracy of calibration curves also shows the same level as that reported using other methods (i.e., chemical analysis). These suggest that the calibration curve be created well.

The calibration curve enables the quantitative analysis of a wide range of compositions ( $\text{SiO}_2$  42.38 ÷ 76.83wt%,  $\text{TiO}_2$  0.00 ÷ 1.60wt%,  $\text{Al}_2\text{O}_3$  0.66 ÷ 23.17wt%,  $\text{Fe}_2\text{O}_3$  0.06 ÷ 15.06wt%,  $\text{MnO}$  0.00 ÷ 0.22wt%,  $\text{MgO}$  0.00 ÷ 44.60wt%,  $\text{CaO}$  0.09 ÷ 11.90wt%,  $\text{Na}_2\text{O}$  0.02 ÷ 10.74wt%,  $\text{K}_2\text{O}$  0.00 ÷ 12.94wt%,  $\text{P}_2\text{O}_5$  0.00 ÷ 0.29wt%). The good analytical precision can related strongly the stability and reliability of the standard calibration curve and analytical S2 Ranger instruments, indicating suitable for practical use in earth science research.

#### Acknowledgments

This work was supported by the basic science project of Hanoi University of Mining and Geology (No.T19-16) and was completed with the valuable assistance of many people to whom the authors wish to extend the sincere thanks.

First of all, we would like to send our deepest thanks to the leaders and staff of HUMG for providing us good facilities in the laboratory and unconditional help to carry on the study.

Besides, our grateful thanks go to Mr. Cu Sy Thang, Vice-director of the Analysis Centre, Institute of Geological Sciences, Vietnam Academy of Science and Technology for the support of 14

silicate rock standard samples and the effective discussions during the time this research was being done.

Finally, many thanks to all of you.

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