JTE
HCMUTE
ISSN: 2615-9740

JOURNAL OF TECHNOLOGY EDUCATION SCIENCE
Ho Chi Minh University City of Technology and Education
Website: https://jte.hcmute.edu.vn/index.php/jte/index
Email: jte@hcmute.edu.vn

Determination of Essential Element and Titanium Contents in Rocks using Flame Atomic and Molecular Absorption Spectrometry

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ARTICLE INFO

Received:	05/05/2022
Revised:	31/08/2022
Accepted:	14/10/2022
Published:	28/12/2022

KEYWORDS

Rock analysis;
Microwave;
Titanium;
AAS;
UV-Vis.

ABSTRACT

Rocks contain a large number of elements such as Na, K, Ca, Mg, Fe, Mn, and Ti. The determination of those element contents is important in geological and geographical exploration as well as the original identification and classification of rocks. Currently, the analysis of the elemental composition of rocks can be carried out on equipments such as ICP-OES, ICP-MS,... However, in some laboratories with limited conditions, the analysis has many difficulties. In the present study, we analyzed rock samples after being treated by microwave using flame atomic and molecular absorption spectroscopy. The results showed that the content of elements in the range of Na (0.31 – 2.46%), K (1.38 – 3.71%), Ca (0.08 – 0.23%), Mg (0.16 – 0.69%), Fe (2.38 – 5.19) %), Mn(0.08 – 0.1%) and Ti(0.12 – 0.36%). The study provides a simple and cost-effective method for rock analysis.

Doi: https://doi.org/10.54644/jte.73.2022.1207

1. Introduction

Rock is a combination of minerals[1]. There are many ways to classify rocks based on origin, mass, volume-strength, silicon oxide content, etc. In geology, rocks are classified into three large groups based on their structure, origin, and formation conditions, including igneous, sedimentary, and metamorphic rocks [2]. Most rocks are composed mainly of inorganic minerals [3]. The difference in structures, compositions, and proportions of inorganic minerals creates the diversity of rocks. Studying the chemical compositions of rocks on the Earth's crust, scientists have identified 8 elements that account for average mass proportion: O (46.60%), Si (27.72%), Al (8.13%, Fe (5.0%), Ca (3.63%), Na (2.83%), K (2.59%) and Mg (2.09%) [2]. Besides, titanium in rocks was also found in the form of rutile and ilmenite [4], the minerals distributed in the Earth's crust and lithosphere. For applications in aerospace, manufacturing, medical, etc.[5] - [6], the determination of titanium content in rocks is also a necessity. Currently, inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS) are often used to analyze the compositions of elements in rocks after the samples are prepared by alkaline infusion or wet acid digestion. However, in some laboratories, those methods are difficult to apply because of limitations in sample preparation and analytical equipment.

In the present study, we proposed a simple and cost-effective method for analysis of rock compositions, where the content of Na, K, Ca, Mg, Fe, and Mn was determined using a flame atomic absorption spectrometry (FAAS) while Ti content was employed using a molecular absorption spectroscopy method.

2. Materials and Methods

2.1. Chemicals and equipments

The stock solutions of Ti, Fe, Na, K, Ca, Mg, Mn 1000 mg/L, HNO_3 (68%), H_2SO_4 (98%), HF (≥ 48%), H_3PO_4 (85%), H_2O_2 (30%), and H_3BO_3 (99%) were purchased from Merck (Germany).

Microwave Processor (Multiwave 3000, Anton Paar GmbH, England), Flame atomic absorption spectrometer (AA 6300, Shimadzu, Japan), UV-Vis Spectrophotometer (UV-190, Shimadzu, Japan), other glassware (Isolab, England) were employed in the study.

2.2. Sample preparation

2.2.1. Sampling and pre-treatment

Three rock samples named NC1, NC3, NC6 and four geological drilling samples named CL1-1-3, CL1-6-3, VL39-2, and VL34-2 were provided by the Faculty of Geology, University of Sciences, Vietnam National University, Ho Chi Minh City. In brief, NC1, NC3, and NC6 were taken directly from the surface, existing in a monolithic state, with very high hardness. These samples are composed mainly of inorganic minerals, contain no or very little organic components and do not contain water (moisture = 0%). Geological drilling samples CL 1-1-3, CL 1-6-3, VL 39-2 and VL 34-2 were drilled up from the ground and compressed into a cake-shaped block with a diameter of 10 cm, thick 3-4 cm. These samples have a rather complicated composition, including soil, rock, sand, and a small number of organic impurities, with a moisture content of 20-30%.

Samples were dried at 105 °C to constant weight, crushed, finely ground and sieved through a 140-mesh. The fine powders that passed through the sieve were collected for further analysis.

2.2.2. Microwave digestion

The samples were digested using a microwave instrument following previous reports [7] - [9] and the procedure is summarized in Figure 1. The parameters set for the microwave conditions were as follows: the instrument power was increased from 0 to 800W in 15 minutes, kept for 30 minutes, then cooled for 15 minutes. The temperature and pressure of the system were limited at 200 ^oC, and 25 bar, respectively, while the pressure rising rate should not exceed 0.5 bar/sec.

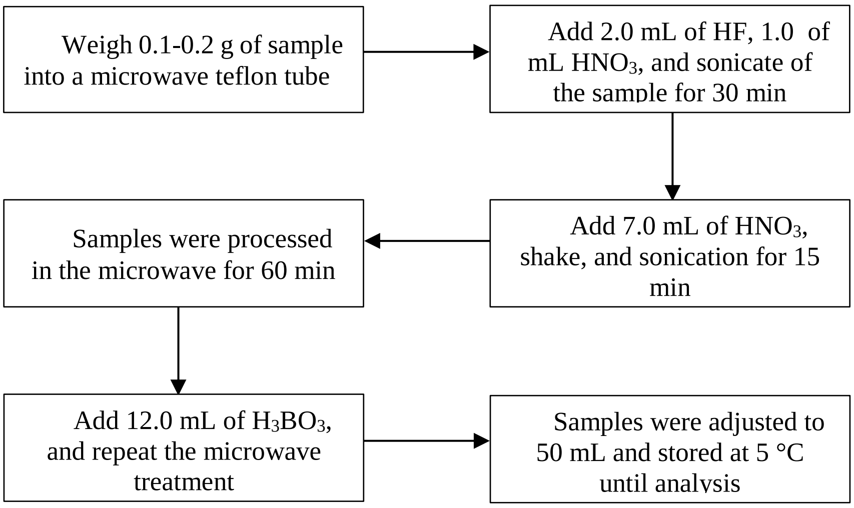

Figure 1. *The diagram of sample preparation using microwave.*

2.3. Titanium analysis

Titanium content was determined using molecular absorption spectrometry. Titanium ion forms a yellow complex $[TiO(H_2O_2)]^{2+}$ with H_2O_2 and is measured at the maximum absorption wavelength of 410 nm [10] - [11]. In brief, a 50 mL flask containing an aliquot of a treated sample was subsequently added with 1 mL of concentrated H_3PO_4 and a predetermined volume of 3 % (v/v) H_2O_2. The flask was then marked up to 50 mL using 1% H_2SO_4 solution, and the absorbance was recorded after 10 min. The influence of H_2O_2 concentration was performed between 0.06 to 1.2 % (v/v).

Fe^{3+} ions present in the sample solutions could affect the absorption measurement of the $[TiO(H_2O_2)]^{2+}$ complex due to its yellow color availability. The influence of Fe^{3+} ions was also investigated with concentrations from 0 to 50 mg/L as fixing Ti concentrations of 5.0 mg/L.

2.4. Essential element analysis

Other elements including Fe, K, Na, Ca, Mg and Mn were determined using the FAAS instrument. The operating conditions of the instrument are shown in Table 1.

Table 1. *Operating conditions of FAAS.*

Parameters	**Elements**					
	Fe	**K**	**Na**	**Ca**	**Mg**	**Mn**
Wavelength (nm)	248.3	766.5	589.0	422.7	285.2	279.5
Light source	HCL	HCL	HCL	HCL	HCL	HCL
Lamp amperage (mA)	12	10	12	10	8	10
Slit width (nm)	0.2	0.5	0.2	0.5	0.5	0.2
Burner height (mm)	7	7	7	7	7	7
Background correction	BGC-D_2	N-BGC	N-BGC	BGC-D_2	BGC-D_2	BGC-D_2
Acetylene flow (L/min)	1.5	1.6	1.5	1.8	1.0	1.8
Air flow (L/min)	15	15	15	15	15	15

2.5. Method validation

The linear ranges of Ti, Fe, Na, K, Ca, Mg, and Mn were investigated in ranges of 0.5–10 mg/L, 0.5–5 mg/L, 0.5–7 mg/L, 0.2–3.5 mg/L, 0.02-0.5 mg/L, and 0.2–2 mg/L, respectively. The limit of detection (LOD) and limit of quantification (LOQ) were calculated based on the calibration curves. The influence of the sample matrix in the determination of elements was determined by the standard addition method.

3. Results and discussion

3.1. Titanium analysis using UV-vis spectrometry

3.1.1. Effects of H_2O_2 concentration

Figure 2 shows the effect of H2O2 concentration on the absorbance of the titanium complex. The absorbance increased with increasing H2O2 up to 0.6% (v/v) and then reached a plateau. It could be understood that the low H2O2 concentration (i.e., < 0.6%) was not enough to react with Ti ions to form the complex and thus, making low absorbance records. Therefore, the concentration of H2O2 of 0.6% was selected for further experiments.

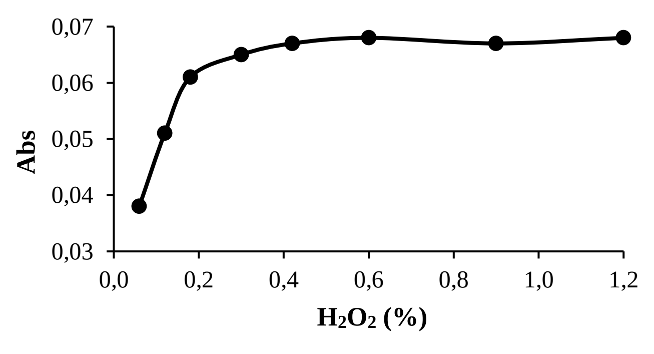

Figure 2. *The influence of H_2O_2 on the Ti complex.*

3.1.2. Effects of Fe^{3+} concentration

Fe^{3+} ions up to 50 mg/L seemed not to cause any effect on the absorption of the titanium complex (Figure 3). It could be explained that H_3PO_4 effectively eliminated the color effect of Fe^{3+} ions due to forming colorless complexes with Fe^{3+} ions [12] - [13]. It is known that Fe^{3+} ions do not make a complex with H_2O_2.

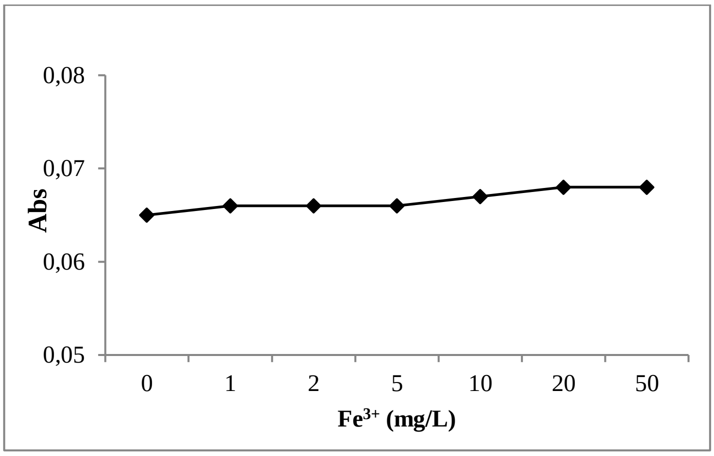

Figure 3. *Effects of Fe^{3+} on Ti complex.*

3.1.3. Method validation for Ti determination

The sample solutions after digesting by microwave (see sample preparation in Figure 1) were used to evaluate the efficiency of the methods i.e., using the calibration curve and the standard addition methods. The linearity, LOD, and LOQ of the method are summarized in Table 2. The plot between the absorbance and Titanium concentration of 0.5–10 mg/L achieved good linearity with a coefficient correlation (R^2) of 0.9995. The LOD and LOQ were estimated to be 0.27 and 0.91 mg/L, respectively.

Table 2. *Parameters showing the efficiency of UV-vis for Ti determination.*

Parameters	**Salicylate**
LOD - LOQ (mg/L)	0.27 - 0.91
Linear range (mg/L)	0.5 - 10.0
Regression equation	$y = (0.0133 \pm 0.0006)x - (0.0002 \pm 0.0001)$
R^2	0.9995

Ti concentration in the samples was not different between both methods, relatively uniform (Table 3). The relative standard deviation of the results ranged from 0.1 to 0.4%.

Table 3. *The Titan concentration in solution using a calibration curve and standard addition methods.*

Sample	**CL1-1-3**	**CL 1-6-3**	**VL 39-2**	**VL 14-2**	**NC1**	**NC3**	**NC6**
Calibration curve method (mg/L)	9.81	9.53	0.23	11.41	3.04	2.29	6.43
Standard addition method (mg/L)	10.02	9.72	0.30	12.26	3.97	3.01	7.23

3.2. Analysis of Fe, Mn, Ca, Mg, Na, K contents

The calibration curves show that the elements analyzed by the FAAS were high linearities ($R^2 > 0.999$) (Figure 4). The regression equation obtained for Fe, Na, K, Ca, Mg and Mn were $y = 0.0718x + 0.0029$; $y = 0.0953x + 0.0093$; $y = 0.079x + 0.0056$; $y = 0.0178x + 0.0058$; $y = 1.1228x + 0.0066$ và $y = 0.1971x – 0.0034$, respectively. Four representative samples, including NC1, NC6, VL14-2 and CL1-6-3 were used to evaluate the analytical methods. The results obtained from the calibration curve and standard addition method were shown in Table 4. Except for Na in the sample VL 14-2, the results show that Na, K had no significant difference analyzed by both methods. This phenomenon could be attributed that K and Na exist in free form in an aqueous solution and less heat-stable compounds are formed during acetylene/air flame atomization.

For Mg, except for VL 14-2 and NC1, the results presented the same ranges of Mg concentration in VL 1-6-3 and NC6 between the two methods. The deviation in sample VL 14-2 was also observed in the case of Na, this may be due to errors in the experimental process. Ca also had similar properties to Mg, atomization process and influencing factors when analyzed by the FAAS method. Therefore, we can use the calibration curve method to determine both of these elements. The Fe contents showed a big deviation between the calibration curve and the standard addition method. This phenomenon could be attributed that the rock sample containing a large amount of Si, which induces a negative effect on the absorbance of the iron complex. Besides, iron can exist in many forms of stable complex such as FeF_6^{3-} (i.e., difficult to atomize)

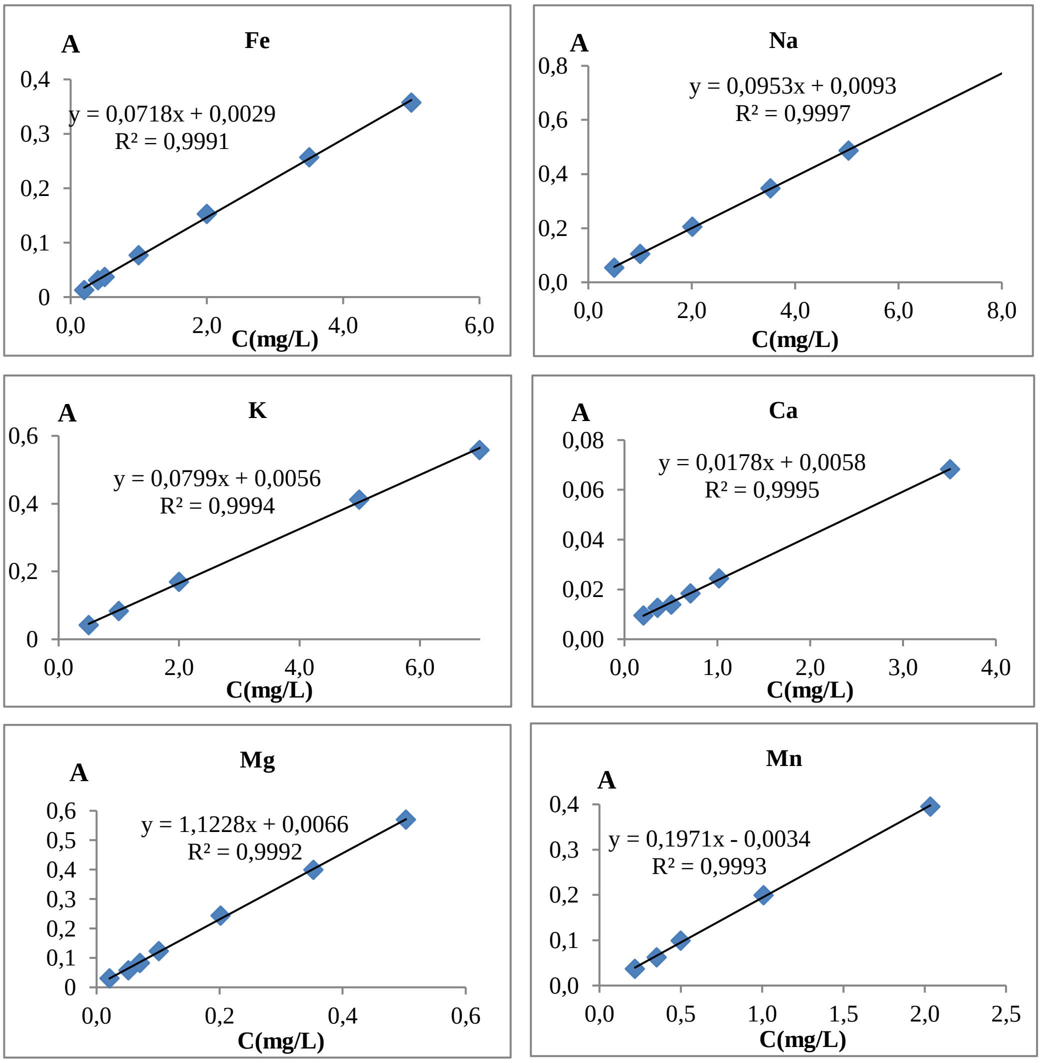

Figure 4. *Calibration curve of metals using FAAS*

Table 4: *The content of elements in samples prepared by microwave.*

	Content (mg/L)					
	Calibration curve method	**Standard addition method**	**The relative standard deviation of element concentration (%)**	**Calibration curve**	**Standard addition method**	**The relative standard deviation of element concentration (%)**
Samples	**VL 14-2**			**VL 1-6-3**		
Fe	154.59	76.61	47.70	113.16	100.97	8.05
Na	11.57	18.67	33.20	15.05	16.95	8.40
K	41.54	62.31	28.28	51.94	59.18	9.21
Mg	20.69	22.972	7.39	16.97	15.43	6.72
Samples	**NC1**			**NC6**		
Fe	47.70	59.26	15.28	98.19	105.15	4.84
Na	49.16	53.41	5.86	59.11	61.61	2.93
K	79.47	78.76	0.63	88.94	104.85	11.61
Mg	3.29	1.26	63.10	15.02	13.14	9.64

3.3. The content of elements in the rock

The composition of elements in the seven rock samples was determined and shown in Table 5. The composition of elements was different between the two sample subjects. In the same rock sample or geological drill sample, the content of the elements was close. The geological drill sample had a lower total content of elements than the rock sample, which was completely consistent with the sensory state and properties of the sample. The geological drill sample contains more organic components, so the inorganic ions content is lower than the rock sample. It can be found that the content of elements is consistent with the reports on the main chemical composition of the rock.

Table 5: Average *content (%) of elements in rock.*

Elements *Samples*	**Fe**	**Na**	**K**	**Ca**	**Mg**	**Mn**	**Ti**
CL 1-1-3	3.62	0.31	1.38	0.08	0.45	0.10	0.24
VL 14-2	5.19	0.39	1.39	0.10	0.69	0.03	0.29
VL 39-2	4.05	0.63	1.71	0.09	0.59	0.08	0.00
CL 1-6-3	3.33	0.44	1.53	0.08	0.50	0.08	0.24
NC1	2.38	2.46	3.97	0.12	0.16	0.04	0.16
NC3	2.69	2.19	2.91	0.13	0.17	0.03	0.12
NC6	4.09	2.46	3.71	0.23	0.63	0.04	0.36

4. Conclusions

This study reports the simple and cost-effective methods for the analysis of element contents in different rock samples. It is helpful to make a preliminary assessment of the composition of rocks interactions among the components in rocks, promising a great advantage in geological exploration studies.

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