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DETERMINATION OF HEAVY METALS IN VARIOUS ROCK SAMPLES IN RIYADH, SAUDI ARABIA BY INDUCTIVELY COUPLED PLASMA MASS SPECTROMETRY (ICP-MS)

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ABSTRACT

Open acid digestion technique was investigated to obtain a simple, rapid, and safe method for the determination of metals in rock samples. The digests were subsequently analyzed for heavy metal content by inductively coupled plasma mass spectrometry (ICP-MS). The elements (Al, Na, Mn, Cr, Co, Fe, Mo, Zn, Sr, Pd and Cu), which are trace elements, were identified. The rock samples were collected from difference regions in Riyadh. The samples were digested by mixed of acids then analyzed by (ICP-MS). The results showed different concentration of heavy metals in rocks. The highly-concentrated elements, such as Fe, Na and Al were detected in the rock samples collected from industrial zones. Mo, Cd and Pd were present at low concentration in all samples. The proposed method was linear with correlation coefficient(r) values between (0.999-0.996) for all metals with relative standard deviation values (%RSD) in range (0.3 - 5.1).

KEYWORDS: Rock, Heavy metal, open digestion, ICP-MS.

INTRODUCTION

Rocks and stones are indispensable in our lives in general, and there are many useful uses in many areas of life for the existence of many of its main types such as rocks Igneous rocks, sedimentary rocks and metamorphic rocks, consisting of igneous rocks consist of rocks frost frozen and cooling. Result of one or more of the three processes: increase in temperature, lower pressure, and change in configuration. Fire rocks are associated with volcanic activity, while sedimentary rocks are formed by low temperature and high pressure. The rocks are formed from rocks that have been exposed to temperature and / or pressure. They are also used in arches of ports, construction, leaves, paint and others. Have physical properties collected by geologists to study the engineering behavior of rocks to assess their response to the impact of atmospheric conditions and temperatures and divided into physical properties (durability, hardness, porosity), mechanical properties (deformability, strength), hydraulic properties (permeability, storability) and thermal properties (thermal expansion, conductivity).[1-3]

Numerous artificial and natural metals exist in the environment and they have a significant influence on technical and industrial advancement. Most metals are not destroyed; indeed, they are accumulating at an accelerated pace, due to the ever-growing demands of modern society. A fine balance must be maintained between metals in the environment and human health. The toxicity of metals raises many concerns regarding their environmental distribution. Many metals are of concern because of their toxic properties and some metals are also essential for survival and health of animals and humans. Metals have been classified as essential, beneficial, or detrimental. Elements, such as zinc, copper, iron, iodine, chromium, molybdenum, selenium and cobalt are known as Trace elements and are deemed vital for human health. There is also a second group of elements thought to be beneficial to life (e.g., silicon, manganese, nickel, boron, and vanadium). Some of these elements may be essential to vegetative life and perhaps beneficial to human health but, generally, they are not yet accepted as essential for human health. Metals that are regarded as purely toxic metals such as lead, cadmium, and mercury which are not known to provide any essential or potentially beneficial health effect at any level of exposure.[4] Out of 106 identified elements, about 80 of them are called metals. These metallic elements can be divided into two groups: those that are essential for survival, such as iron and calcium, and those that are nonessential or toxic, such as cadmium and lead. These toxic metals, unlike some organic substances, are not metabolically degradable and their accumulation in living tissues can cause death or serious health threats. Pollution from man-made sources can easily create local conditions of elevated metal presence, which could lead to disastrous effects on animals and humans.[5]

In 1962[6] and 2001[7], traces of heavy elements were determined in rocks by X-ray fluorescence in a light matrix. Kvalheim[8], Saunderson[9] and Nilssonl[10] developed spectrochemical method to determination the major constituents of minerals and rocks. Furthermore, the geochemical sample contained trace-elements, which were identified in rocks using laser –ablation inductively coupled plasma mass spectrometer(LA-ICPMS).[11] In 1997[12] using ICP-MS to determination malty element in rocks. The trace elements in graitic rocks were determined by ICP-MS.[13]

Ultimately, the purpose of this study is to investigate geological samples collected from different locations within Riyadh in the Kingdom of Saudi Arabia to detect the heavy metals they contain using ICP- MS.

Experimental

Apparatus

The analytical determination of trace metals was carried out by ICP-MS (Inductively Coupled Plasma-Mass Spectrometer): NexION^{TM} 300 D (Perkin Elmer, USA). The table below highlights the operational conditions of the instruments used in this study is presented in Table 1.

Table 1: Instrument operating conditions for the determination of metallic species in Rock samples.

RF power	1600 W
Nebulizer gas flow	0.65 L/min
Lens Voltage	9.55 V
Analog Stage Voltage	-1745 V
Pulse Stage Voltage	950 V
Number of Replicates	3
Reading / Replicates	20
Scan Mode	Peak Hopping
Dwell Time	40 ms
Integration	1200ms

Sample Collection

Total nine Rock samples were collected from different place in Riyadh city in 2019. The samples were collected and kept in plastic bags at room temperature for further analysis. Samples 1-3 were collected from southwest of Riyadh, sample 4-5 were collected from south Riyadh which it is industrial zone, sample 6-9 were collected from north Riyadh.

General procedures

First, the sample rock was grinded to powder by amortar. The powdered samples (1.000 g) were each weighed into 150 ml PTFE beakers. The addition of 2 ml of HNO_3 (concentrated) to the beakers was followed by a swirl to ensure the powder was wet. Both beakers were capped and placed on a heater for 20 minutes at 90 °C approximately. Care was taken that the samples did not dry. Additionally, 2 ml of concentrated HNO_3, 3 ml of concentrated $HClO_4$ and 10 ml concentrated HFwere blended together to form a mixture, then added to the samples to be left overnight to enable the occurrence of a reaction. The day after, both beakers were set on a heater for 2 hours at about 90 °C. Subsequently, further boiling allowed the evaporation of most of the acid present after the removal of PTFE covers from the beakers. Essentially, appropriate measures were taken to prevent the samples from drying as that would make the process of their return into solution nearly impossible. Moreover, a consistency of higher viscosity was achieved as a result of adding 5 ml of concentrated HCl, which was soon heated with the samples. Furthermore, gentle heating resumed following the addition of 40 ml of 6.2 M (51.5% v/v) HCl until a clear solution was reached. A quantity of 150 ml of the solution was finally obtained. Following that, the addition of 5 mL of concentrated $HClO_4$ took place. The solutions were made to volume with deionized water.[14] The emission intensity of metal was measured by ICP- MS.

The ICP-MS calibration was carried out by external calibration. The calibration curves of twelve elements: Na, Al, Cr, Mn, Fe, Co, Cu, Zn, Sr, Mo, Cd and Pd obtained by the instrument using the blank and three working standards 0, 0.5, 1.0 and 2 mg/L, starting from a 1000 mg/L single standard solutions for ICP-MS (Aristar grade, BDH laboratory supplies, England for the elements).

High purity water obtained from Millipore Milli-Q water purification system was used throughout the work.

RESULT AND DISCUSSION

Calibration curves showed an excellent linearity for all elements with correlation coefficients (R) = (0.999-0.996). The relative standard deviation values (%RSD) were in the range (0.3-5.1).

The mean of heavy metals concentrations (Na, Al, Cr, Mn, Fe, Co, Cu, Zn, Sr, Mo, Cd and Pd) in Rock samples are presented in Table 2.

The Aluminum element in sample 4 recorded the highest value of all samples and elements. Concentrations of Iron were the highest values where Cadmium recorded the lowest values among rock samples followed by lead and molybdenum.

Samples 4 and 5 (north Riyadh) were the highest concentration of all metals under study; this may be due to the nature of the place where it was collected from industrial areas in the Riyadh region where there are different factories.

Samples 6-9 were collected from the same place in the north of Riyadh city. The concentrations of most metals were close together in Sample 7 and 8 except sodium metal which recorded a double value in the sample 7, this may be due to the different type of rock.

Samples 1-3 were different types although were collected from the same area southwest of Riyadh city. The concentration of metals was different value due to the different rock types.

It is generally recognized that the dissolution of solid samples is one of critical factors controlling accuracy in the analysis of environmental geological materials. Incomplete digestion of refractory mineral phases and the loss of volatile species during sample preparation are two constant problems facing the geoanalyst. The accessory minerals, such as chromite, zircon, etc., which occur at significant quantities in the rocks, pose problem. In the open acid dissolution, this problem was resolved by repeated evaporation with the addition of acid mixture.[14]

Table 2: Heavy metal concentration* (mg/kg) in Rock samples.

sample	**Na± %RSD**	**Al± %RSD**	**Cr± %RSD**	**Mn± %RSD**	**Fe± %RSD**	**Co± %RSD**	**Cu± %RSD**	**Zn± %RSD**	**Sr± %RSD**	**Mo± %RSD**	**Cd± %RSD**	**Pd± %RSD**
1	171.0± 5.1	28.0± 4.8	231.7± 1.2	21.7± 2.6	*424.0± 1.4*	0.5± 3.6	2.9± 2.0	64.2± 3.2	64.8± 1.5	1.1± 2.0	0.1± 1.4	0.9± 1.8
2	881.8± 2.3	495.0± 2.9	195.8± 2.1	20.3± 2.2	692.7± 2.6	1.1± 1.6	7.0± 4.6	46.5± 1.3	28.9± 2.9	1.3± 0.4	0.1± 1.1	0.7± 0.8
3	88.7± 5.8	46.0± 4.2	446.9± 3.2	8.9± 2.6	102.8± 4.7	0.6± 3.5	8.2± 1.4	52.5± 2.2	25.9± 1.8	0.7± 3.5	0.03± 1.2	0.5± 2.3
4	22977± 2.8	80169± 3.1	73.0± 1.7	136.9± 1.5	6649.1± 2.2	2.4± 1.7	146.3± 2.1	176.2± 1.2	5.6± 2.8	1.1± 3.0	0.05± 1.6	14.1± 1.1
5	18135± 4.8	73838± 5.0	80.7± 3.2	409.1± 0.3	17116.4± 0.6	0.4± 1.5	618.9± 2.0	489.5± 1.9	16.3± 1.7	2.0± 2.4	0.3± 2.1	32.2± 1.1
6	259.1± 1.6	108.7± 2.5	517.3± 5.5	23.1± 1.3	201.7± 1.7	0.7± 2.9	56.7± 4.6	85.7± 1.7	32.3± 3.3	0.8± 1.4	0.1± 3.4	1.5± 1.4
7	604.7± 2.0	45.4± 3.2	570.2± 2.1	17.3± 3.0	206.9± 0.9	0.7± 2.9	7.0± 5.0	61.5± 1.7	35.2± 2.6	0.8± 1.5	0.05± 5.1	0.5± 0.5
8	293.5± 2.4	33.1± 2.5	448.1± 2.2	17.5± 5.1	179.9± 2.9	0.7± 2.5	4.6± 3.5	64.7± 1.6	29.2± 1.7	0.8± 2.6	0.1± 1.5	0.6± 0.7
9	53.3± 5.1	28.9± 4.2	398.2± 2.8	105.6± 1.3	502.5± 2.2	2.5± 2.2	14.2± 2.8	66.2± 5.0	16.4± 0.4	5.3± 0.5	0.3± 2.0	2.2± 1.0

Mean three measurmenets*

CONCLUSION

In this study, nine geological samples(Rock) collected from different regions in Saudi Arabia (Riyadh) were digested to determination of heavymetals (Na, Al, Cr, Mn, Fe, Co, Cu, Zn, Sr, Mo, Cd and Pd) by ICP-MS. The obtained results show that Al metal concentration was higher in the rock samples while Cd metal was the lowest. The rocks which collected from industrial area, recorded the highest value of all metals.

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