Egyptian Journal of Chemistry

http://ejchem.journals.ekb.eg/

Determination of Zirconium and Hafnium in Egyptian Monazite by ICP-OES

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Abstract

The determination of Zirconium and Hafnium in presence of each other in geological sample by using Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) technique had established, the physical parameters of the instrument were adjusted and the suitable zirconium and hafnium lines were selected to give the most accurate determination, the sensitivity of each line was tested by a solution of 20 ppm zirconium mixed with 1 ppm hafnium to obtain the most sensitive lines which were 339.198 nm for zirconium and 239.336 nm for hafnium. The interference effect was studied which prove the interference effect of the major elements of monazite as Uranium, Thorium, Rare earth elements, Iron and Aluminium on the determination of the elements under studying. The sample used in this work was a mineral of monazite from black beach sand which was upgraded of about 97% purity; the sample was leached by concentrated sulfuric acid (H_2SO_4) at 250 ^{0}C to separate zircon which contains zirconium and hafnium as a residue which dried, weighed and fused by sodium hydroxide for complete decomposition and measured by ICP-OES (Nuclear Materials Authority, Egypt) on the selected lines.

Introduction

Zirconiumis obtained from heavy zircon available in the beach sands [1,2], widely used as a basic raw material in nuclear field as a metallic fuel alloys in nuclear reactors because of its strong resistance to corrosion and low thermal neutron capture cross-section [3,4,5], beside its important use in steel industry [6]. While hafnium is used in the control rods of nuclear reactors because it is a good absorber of neutrons, most zirconium ores include about 5% hafnium [7].The behavior of zirconium and hafnium in the environment is very similar, most zirconium and hafnium bearing minerals have limited solubility and reactivity. Zirconium and hafnium are likely not essential for human health and generally have low toxicity to human [8]. Zircon ($ZrSiO_4$) is considered the major source of zirconium which is very stable and requires extremely drastic conditions to be decomposed [9]. Because of the lanthanide contraction effect, both the atomic radii of zirconium and hafnium (1.45 and 1.44 A respectively) and the radii of their ions (0.74 and 0.75 A respectively) zirconium and hafnium are virtually identical. So, the chemical and geochemical behaviour of them is extremely similar [10].Despite of zirconium occurs widely over the earth's crust but by trace amount of concentration. Zircon ($ZrSiO_4$) is the most common mineral for zirconium which form primarily as accessory mineral in igneous rocks. Because of the chemical similarity of zirconium and hafnium, hafnium is found in nature in all zirconium minerals in the range of fractions of a percent of the zirconium content and the separation of the two elements is extremely difficult [10]. The main deposits of ore worldwide are heavy-mineral sands produced by the weathering and erosion of rocks, the zircon concentration and other heavy minerals are economically important. In coastal deposits, heavy minerals enrichment occurs by winds, waves and currents. Zircon makes up a relatively small percentage of the economic heavy minerals in most deposits and is produced as a by product of heavy-mineral sand [8].In recent years, Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) [11], Inductively Coupled Plasma Mass Spectrometry (ICP-MS) [12] and Flow- Injection Inductively Coupled Plasma Mass Spectrometry (FI-ICP-MS) [13] have emerged as widely used techniques for

trace element determinations, especially for REEs and have been applied to their determination in geological materials like rocks, ores, minerals, and concentrates [14]. The goal of the present work is a study for the determination of a trace amount of zirconium and hafnium in the presence of each other in the Egyptian beach black sand monazite which was selected and physically separated [15]. In Egypt, the essential source of thorium ores and REEs is the Egyptian black sand beach deposits due to the presence of monazite [16] which includes zircon as a byproduct of the recovery of thorium and REEs.

Experimental

Instrumentation

Inductively coupled plasma Optical Emission spectrometry (ICP-OES), Teledyne Leeman Labs. (U.S.A.) was used for the determination of the target elements. Ultra-pure water, Human Lab. Instrument Co., fed with deionized water (aquatron).Heater with stirring, IKA C-MAG HS 10, Germany. Environmental Scanning Electron Microscope (ESEM), XL 30, Philips, Germany.

Reagents and materials

All chemical reagents are of ultra-pure grade, sulfuric acid of 97.99% (Adwic, Egypt), sodium hydroxide of 99.00% (India) and all standard solutions of used elements (Zr, Hf, U, Th, Fe, Ca, Na, K, Pb, Ti and individual REEs) are of 1000 ppm concentration spikes in 4% nitric acid for ICP use, Canada.

Analytical Procedure

15 g of Egyptian monazite of grade 97% was leached with 50 ml concentrated sulphuric acid, heated at 150-160°C for 10 hours. After cooling, the sample was added to 250 ml iced water with stirring for three hours, the sample was filtered using ash less filter paper.0.05 g of the dried residue was alkali fused by sodium hydroxide and analyzed by ICP-OES under the optimum conditions to determine zirconium and hafnium.

Results and Discussion

As an extension of our study [17-18], the target of this study is zirconium and hafnium determination in

presence of each other despite the presence of hafnium in infinitesimal concentration after the separation of zircon from monazite as a residue. For this purpose, several steps will be done as follows:

Spectral lines selection and physical parameters optimization

The first step in this study is the selection of three or four spectral lines at least for each element and test the sensitivity of each line by a solution of 20 ppm zirconium mixed with 1 ppm hafnium to obtain the most sensitive lines which were 339.198, 343.053 and All chemical reagents are of ultra-pure grade, sulfuric acid of 97.99% (Adwic, Egypt), sodium hydroxide of 99.00% (India) and all standard solutions of used elements (Zr, Hf, 343.823 nm for zirconium and 277.336 and 239.336 nm for hafnium. Then, the physical parameters of the ICP-OES were optimized by using the same standard solution (table 1).

Table 1: The optimum operating conditions of ICP – OES in present work

Parameter	Plasma conditions
RF power current	1500 Watt
Coolant gas	18 L/min.
Nebulizer gas flow	34 L/min.
Sample uptake rate	1.4 ml/min.
Sample uptake time	20 sec.
Replicates	3

Construction of the calibration curves

The calibration curves of zirconium and hafnium were constructed by using a series of mixed standard solutions of zirconium and hafnium in the range from (10 ppm Zr and 0.2 ppm Hf) to (50 ppm Zr and 1 ppm Hf) and select calibration curves with the best linearity and relative standard deviation for determination (figure 1).
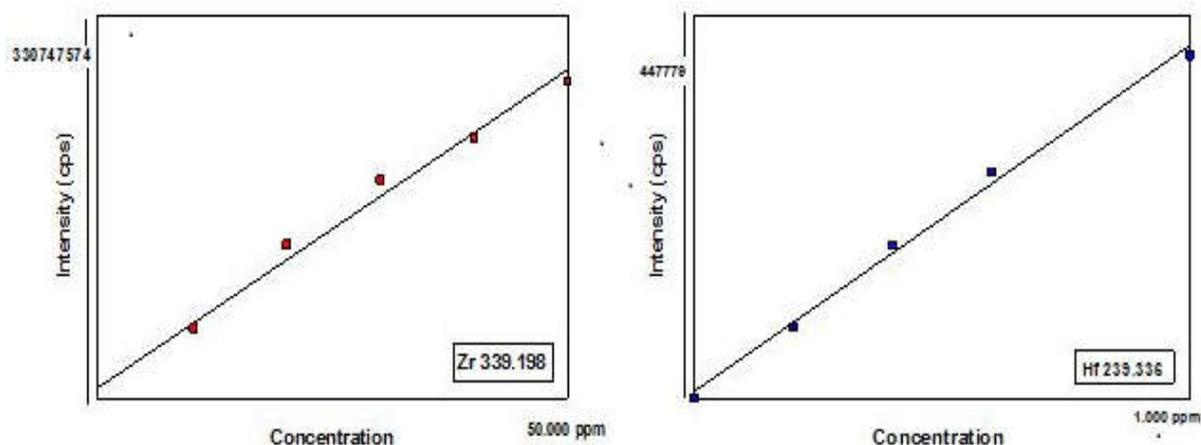
Fig. 1: The selected calibration curves of Zirconium and Hafnium

The interference effects

ICP-OES is a very suitable technique for measuring the trace level of element concentration but the spectral interference caused by matrix effect is the most common problem in the analysis of geological materials especially when the interfering element concentration is too high relative to the analyzed element. In this study, the interference is caused by the existence of zirconium and hafnium together which affect the determination of hafnium and also by the existence of other elements in monazite. Tables 2 and 3 show the complete analysis of monazite under studyat Mineral Laboratories, Canada.From tables (2 and 3), the interference of U, Th, REEs, Fe, Ca, Mg, Na, K, Ti and Pb which are relatively of high concentration were studied (table 3), which shows high interference effect of U, Th, REEs, Fe, Al and Mg on the lines of Zr and Hf, while the presence of Na, K and Ti affect only on Zr lines.On the other hand, both Zr and Hf lines are not effected with Ca and Pb. For this reason, a standard solution of 25 ppm zirconium and 0.5 ppm hafnium was used separately and with each interfering element (table 4).

Table 2: Complete analysis of monazite 97% (Mineral Laboratories, Canada) [Conc. (ppm)]

Element	Conc.(ppm)	Element	Conc.(ppm)
Zr	579.6	Er	748.3
Hf	15.5	Yb	357.9
U	3039.2	Tm	70.7
Th	>4000	Lu	25.1
Y	>2000	Ba	73.0
Ce	>2000	Cr	116.0
Gd	>2000	Sr	70.0
Pr	>2000	Pb	2064.6
Nd	>2000	Mn	57.0
Sm	>2000	Zn	202.1
Eu	561.8	Ni	95.4
Tb	1153.1	Cu	58.2
Dy	>2000	Co	3.8
La	>2000	Ho	503.2

Table 3: Complete analysis of monazite 97% (Mineral Laboratories, Canada) [Conc. (%)]

Element	Fe	Ca	Mg	Ti	Al	Na	K
Conc. (%)	2.65	1.03	0.13	0.142	<0.01	0.343	0.01

Table 4: The interference effect on Zr and Hf lines

Conc. of interfering element added to Zr& Hf	Zr (339.198 nm)	Zr (343.053 nm)	Zr (343.823 nm)	Hf (227.336 nm)	Hf (239.336 nm)
Zr &Hf	25.11	24.43	22.12	0.488	0.494
With 600 ppm Fe	20.50	19.23	20.35	0.40	0.377
600 ppm Al	19.60	19.42	19.33	0.34	0.39
40 ppm K	21.95	20.58	21.32	0.48	0.49
100 ppm U	20.06	20.85	20.44	n.d.[*]	0.40
100 ppm Pb	24.96	24.00	23.10	1.37	0.50
360 ppm Ca	24.89	24.80	25.10	0.50	0.51
140 ppm Th	22.13	21.04	22.00	0.20	0.40
185 ppm REEs	15.90	12.38	14.86	n.d.	0.42
40 ppm Mg	19.07	18,34	18.88	0.38	0.39
50 ppm Ti	14.88	15.40	16.38	0.50	0.51
120 ppm Na	29.76	27.71	89.14	0.50	0.52

* n.d.: Not detected.

Applications:

The sample used in this work was monazite (purity~ 97%), Egyptian monazite mineral was physically upgraded from black beach sand of Abou-Khashaba near Rosetta and extending from Rosetta to Rafah through 400km by (NMA) of Egypt. Monazite is primarily composed of rare earth phosphates especially those of low atomic numbers (cerium group) along with numerous minor constituents among thorium and uranium are of major interest (figure 2).The range of hardnessis from 5.0 to 5.5 (Moh's Scale) and its specific gravity from 4.9 to 5.3 g/cm^3.
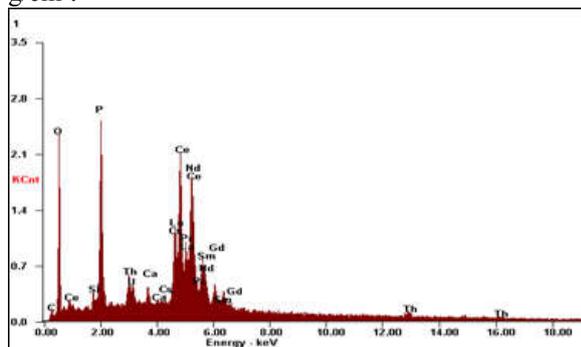
Fig. 2: EDAX of Egyptian monazite

To get rid of the interfering elements, sulfuric acid leaching was used. Monazite reacts with H_2SO_4 to give rare earth, thorium and uranium sulphate according to the following equations:

$$2REPO_4 + 3H_2SO_4 \rightarrow RE_2 (SO_4)_3 + 2H_3PO_4$$

$$Th_3 (PO_4)_4 + 6H_2SO_4 \rightarrow 3Th (SO_4)_2 + 4H_3PO_4$$

$$2U_3O_8 + O_2 + 6H_2SO_4 \rightarrow 6UO_2SO_4 + 6H_2O$$
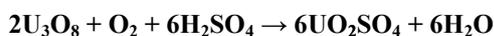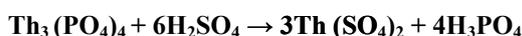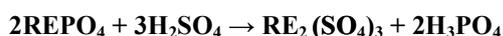
Sulfuric acid can diffuse deeply to react with monazite; after decomposition, REEs, Th and U are all dissolved into the leachate [17]. So, 10 g of the monazite sample (97%) was leached with concentrated H_2SO_4 (97.99%) at 160 °C for about 10 hours to dissolve all componentsexcept zircon which is acid resistance mineral. After cooling, the sample was added to 250 ml iced water with stirring for 3-4 hours. It was filtered using ash less filter paper to obtain the residue which contain zircon, the residue was dried, weighed and scanned (figure 3).
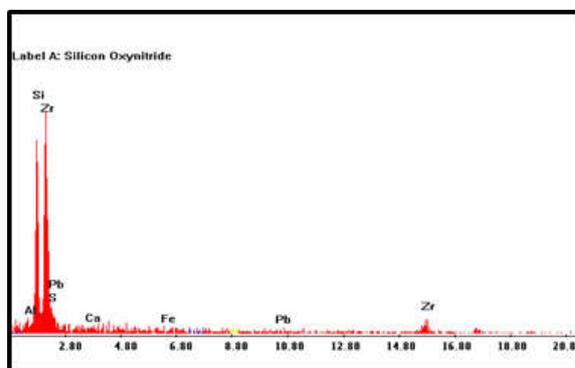
Fig. 3: Scanning of the residue after leaching

The weight of residue after drying was 0.5 g which is mainly composed of Si, Zr (included Hf) and some traces of Al, Ca, Fe and Pb (figure 2). 0.05 g of dried residue was digested by alkali fusion using 0.5 g NaOH to obtain a solution of final volume50 ml which analyzed by ICP-OES (Nuclear Materials Authority, Egypt). The analytical data from the present work is compared with that from Mineral Laboratories (Canada) and the statistical parameters

which confirm the validity of the method are calculated (table 5). A comparison between the obtained RSD% from the present work and other previous work for the determination of Zr and Hf in some geological samples is tabulated in table 6.

Table 5: The measured concentration of Zr and Hf (ppm) in a sample of Egyptian monazite by ICP-OES

Element	Wavelength (nm)	Measured conc.(ppm) (NMA)	Expected conc.(ppm) (Canada)	Accuracy%	RSD%	Uncertainty %
Zr	339.198	566.6	579.60	97.757%	0.03%	0.10%
Hf	239.336	18.00	15.50	83.871%	1.47%	0.15%

Table 6: Comparison between RSD% of the present work by ICP-OES for Zr &Hf determination in Egyptian monazite and some previous work for certified standard references by ICP-MS

Element	RSD% of present work by ICP-OES	RSD% for JB-1 by ICP-MS[18]	RSD% for JB-2 by ICP-MS[19]	RSD% for JB-3 by ICP-MS[20]
Zr	0.03%	2%	2.8%	0.8%
Hf	1.47%	2%	4.0%	0.5%

JB-1, JB-2 and JB-3 are certified standard references.

Conclusion

For the determination of zirconium and hafnium in presence of each other in some geological sample as monazite mineral obtained from black beach sand, ICP-OES was used.After acid leaching for monazite, zircon was obtained as a residue which contains Zr,Hf and traces of some elements which did not affect the determination because of the selection of the most sensitive and selective lines for determination. The results of analysis of the applied sample were compared by that obtained from Mineral Laboratories by ICP-MS (Canada), which have acceptable Accuracy, RSD and Uncertainty. From this study, ICP technique is recommended for the determination of zirconium and hafnium in presence of each other even if their concentrations were very low.

Conflicts of interest

No conflicts of interest.

Formatting of funding sources

Acknowledgement:

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