ANALYSIS OF ZIRCONIUM MINERAL SAMPLES (PRODUCED IN BINH THUAN PROVINCE) BY XRF MACHINE, PREPARED PRESSED POWDER

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TÓM TẮT

PHÂN TÍCH MẪU KHOÁNG SẢN ZIRCON (SẢN XUẤT TẠI BÌNH THUẬN) BẰNG MÁY XRF, PHƯƠNG PHÁP ÉP BÁNH

Bình Thuận có bờ biển dài hơn 192 km, là nơi có trữ lượng cát đỏ rất lớn, chứa khoảng 557,5 triệu tấn khoáng sản Titan - Zircon, chiếm trên 92% tổng sản lượng khoáng sản Titan - Zircon của cả nước (557,5 / 664 triệu tấn). Nghiên cứu và ứng dụng này đề cập đến phương pháp phân tích mẫu khoáng sản zircon bằng máy XRF Epsilon 4 - một máy quang phổ huỳnh quang tia X phân tán năng lượng hiệu suất cao - có khả năng phân tích các chỉ tiêu ZrO_2, SiO_2, TiO_2, Fe_2O_3, Al_2O_3, MgO, CaO, Na_2O, K_2O, Cr_2O_3, P_2O_5, HfO_2 trong mẫu khoáng sản Zircon (được sản xuất tại Bình Thuận), cho kết quả có độ chính xác cao chỉ trong 22 phút phân tích, độ tuyến tính (R^2=0.99) và độ chụm (độ lặp lại, độ tái lập) phù hợp với phương pháp phân tích.

***Keywords**: Zircon minerals, XRF Epsilon 4, Titan-Zircon, Zirconium in Binh Thuan.*

1. INTRODUCTION

Binh Thuan has total reserves forecasted for Titanium - Zirconium mineral nearly 92% of the Vietnam's reserves (about 557,5 million tons). Zirconium mineral used in ultra-strong ceramics. It is used to make crucibles that will withstand heat-shock, furnace linings, foundry bricks, abrasives and by the glass and ceramics industries. It is so strong that even scissors and knives can be made from it. It is also used in cosmetics, antiperspirants, food packaging and to make microwave filters [1].

Zirconium is a natural semi-precious gemstone found in a variety of colours. The most desirable have a golden hue.

This study and application refers to the method of analyzing zircon mineral samples by XRF Epsilon 4 - a high-performance energy-dispersive X-ray fluorescence spectrometer - capable of analyzing ZrO_2, SiO_2, TiO_2, Fe_2O_3, Al_2O_3, MgO, CaO, Na_2O, K_2O, Cr_2O_3, P_2O_5, HfO_2 in Zircon mineral samples (produced in Binh Thuan). Giving highly accurate results in just 22 minutes of analysis, linearity (R^2=0.99) and precision (reproducibility, reproducibility) are consistent with the analytical method.

2. EXPERIMENTAL

2.1. Materials and equipment

- Materials:

Zirconium mineral from Binh Thuan (Song Binh Mineral Joint Stock Company, Binh Thuan province, Vietnam), adhesive aid compound: H_3BO_3 from Merck (Germany),

- Equipments:

Vibratopry disc Mill RS 200 from Retsch (made in Germany), Atlas™ Autotouch 40T Hydraulic Press from Specac (made in England).

Measurements were performed using an Epsilon 4 EDXRF spectrometer, equipped with a 10W, 50 kV silver anode X-ray tube, 6 filters, a helium purge facility, a high-resolution silicon drift detector, a spinner and a 10-position removable sample changer [3].

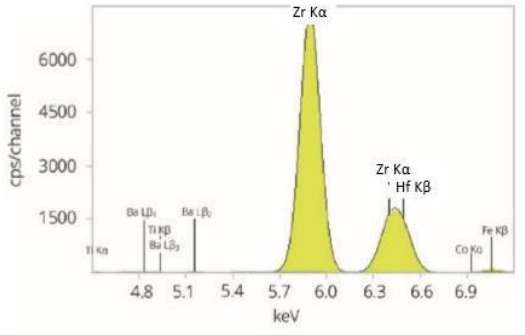

Fig.1. The spectrum of a standard obtained with 5-12 kV, showing the excellent resolution and the high sensitivity of the detector

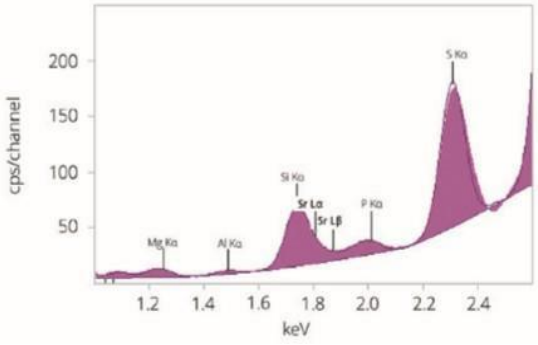

Fig.2. The spectrum of a standard obtained with 20-50 kV and Al thick filter.

2.2 Sample preparation

40 mm diameter pellets were prepared by mixing 16 g zirconium mineral sample material (manufactured from Binh Thuan, was milled to a particle size 75 µm) in 3.5 g of adhesive compound H_3BO_3 and pressed at 30 tons for 60 s by Atlas Autotouch 40T Hydraulic Press. The pellet samples were put in standard sample holders and loaded into the Epsilon 4 EDXRF.

2.3. Measurement procedure

Zirconium ore standards containing ZrO_2, SiO_2, TiO_2, Fe_2O_3, Al_2O_3, MgO, CaO, Na_2O, K_2O,Cr_2O_3, P_2O_5, HfO_2 were used to set up the calibration. The details of conditions are given in Table 1. For P a ROI (region of interest) was used to obtain the intensities. For other elements the intensities were obtained using deconvolution.

The total measurement time was 22 minutes per sample.All measurements were carried out in helium atmosphere. Figures 1 and 2 show the spectra obtained for the elements in a standard.

The calibration plots shown in Figures 3 and 4 demonstrate the strong correlation between the given concentrations and the measured intensities. The accuracies of the method calibrations are illustrated by the consistently low RMS values (Table 2).

Table 1. Measurement conditions

Elements	Oxit	kV	µA	Measurement time (s)	Medium	Filter
Al, Mg, Na, Si	Al_2O_3, MgO, Na_2O, SiO_2	5	60	60	Helium	none
Ca, K, Ti	CaO, K_2O, TiO_2	12	25	90	Air	Al thin (Al-50)
Cr, Fe	Cr_2O_3, Fe_2O_3	20	15	60	Air	Al thick (Al-200)
P	P_2O_5	9	30	60	Helium	Ti
Zr, Hf	ZrO_2, HfO_2	50	6	90	Air	Ag

2.4. Accurate calibration results

The calibration plots shown in Figures 3 and 4 demonstrate the strong correlation between the given concentrations and the measured intensities. The accuracies of the method calibrations are illustrated by the consistently low RMS values (Table 2).

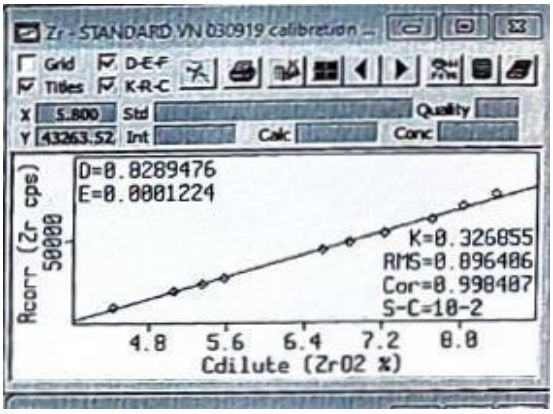

Fig.3. Calibration graph of Zr

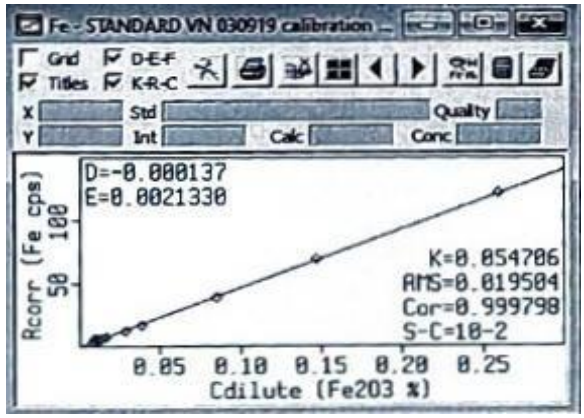

Fig.4. Calibration graph of Fe

The excellent calibration accuracies can be partially ascribed to the fact that the in-house standards used have a similar origin and mineralogy. This reduces the influence of so-called mineralogical effects that are commonly seen in pressed powder calibrations of certified reference materials that may have diverse mineralogies. The LLD values presented in Table 2 are calculated using the application measurement time.

Table 2. The RMS values of the calibration

Compound	Concentration range (wt%)	RMS (wt%)	LLD (wt%)
ZrO_2	50.0 - 66.0	0.505	0.001
HfO_2	0.50 - 1.50	-	-
SiO_2	30.0 - 40.0	0.825	0.007
TiO_2	0.01 - 1.00	-	-
Fe_2O_3	0.01 - 1.00	-	-
Al_2O_3	0.01 - 2.50	0.302	0.007
MgO	0.01 - 1.00	0.215	0.025
CaO	0.01 - 1.00	0.262	0.004
Na_2O	0.01 - 1.00	-	-
K_2O	0.01 - 1.00	-	-
Cr_2O_3	0.01 - 0.50	-	-
P_2O_5	0.01 - 1.00	0.085	0.040

3. RESULT AND DISCUSSION

An indication of the measurement precision was obtained by analysing a sample repeatedly (n=20). The averages and the standard deviations (1 sigma) are presented in Table 3.

Table 3. Results of the repeatability test

Compound	Average concentration (wt%)	Standard deviation (wt%)
ZrO_2	55.1	0.5
HfO_2	0.823	0.2
SiO_2	30.43	0.4
TiO_2	0.512	0.03
Fe_2O_3	0.534	0.03
Al_2O_3	1.742	0.18
MgO	0.436	0.06
CaO	0.621	0.04
Na_2O	0.531	0.04
K_2O	0.613	0.04
Cr_2O_3	0.475	0.04
P_2O_5	0.493	0.04

Sample preparation and sample grinding: Clean the mill with 70° alcohol, wipe it with a clean paper towel, and let it dry. Take 100g of zircon ore sample and put it in the mill. The crushed sample is poured out, mixed well, divided into 8 small parts. Take about 20 grams of sample into a porcelain cup to prepare for the next stage.

Pressing pellet preparation process:

Weigh exactly 3.50 grams of boric acid H_3BO_4 binder into a 50mL porcelain crucible, add 16.00 grams of the sample into the ceramic crucible and mix well. Put the above mixture in the agate mortar, grind until the mixture is homogeneous. Press the cake with the program of 30 tons, holding time 1 minute.

Analysis Procedure by XRF:

Start the computer, XRF machine, open the valve, check the helium pressure. Start the Epsilon

software. Power on the Epsilon 4, unlock the HT to let the XRF run gain after 30 minutes of sample analysis. Normally, when the XRF machine is in operation, XRF analysis is performed immediately. Insert the pressure pellet into the measuring chamber from position 01 to 10. Go to "Measure" ► select "Measure Application" ► select the Calibration established to run the samples: Zircon.

4. CONCLUSION

The data presented here clearly demonstrates the suitability of the Epsilon 4 EDXRF spectrometer for the quantitative analysis of ZrO_2, SiO_2, TiO_2, Fe_2O_3, Al_2O_3, MgO, CaO, Na_2O, K_2O, Cr_2O_3 and P_2O_5 in zirconium mineral samples. Accurate and precise results can be obtained in just 22 minutes. Giving highly accuracy analysis, linearity (R^2=0.99) and precision (reproducibility, reproducibility) are consistent with the analytical method.

This process provided a simple and effective method of analysis zirconium mineral in Binh Thuan. This research is also the basis for futher developments in mineral industry research in Viet Nam.

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