ANALYSIS OF MONAZITE SAMPLES

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ABSTRACT : *The "monazit" analytical program has been set up for routine work of Rare Earth Elements analysis in the monazite and xenotime minerals' samples. Total relative error of the analysis is very low, less than 2.50%, and the reproducibility of counting statistic and stability of the instrument were very excellent. The precision and accuracy of the analytical program are very good with the maximum percentage relative are 5.22% and 1.61%, respectively. The mineral compositions of the 30 monazite samples have been also calculated using their chemical constituents, and the results were compared to the grain counting microscopic analysis.*

1. INTRODUCTION

The Rare Earth Elements (REE) and yttrium are essential constituents in more than 100 minerals, however, only a few minerals occur in sufficient concentration to qualify as an ore. Monazite, bastnasite and xenotime are the most important rare earth bearing ore minerals. Monazite and xenotime are produced as byproduct of tin ore (cassiterite) processing, at Banka tin mine. The REE usually called lanthanide is a homogenous group of metallic elements occupying the area from lanthanum to lutetium in group III of the Periodic Table of the elements. Other elements that have similar chemical properties and are also grouped into the same family are yttrium (Y, atomic number 39), thorium (Th, atomic number 90) and Scandium (Sc, atomic number 21).

The REE have been classified into two subgroups [1], namely the light and the heavy subgroups. The light cerium subgroup, consist of: lanthanum (57), cerium (58), praseodymium (59), neodymium (60), promethium (61), samarium (62) and europium (63). Promethium, a fission product of uranium, has no known naturally occurring stable isotopes. The heavy or yttrium subgroup, is comprising of gadolinium (64), terbium (65), dysprosium (66), holmium (67), erbium (68), thulium (69) ytterbium (70), lutetium (71) as well as yttrium (39). Despite its low atomic weight, yttrium is categorized with the heavy rare earth because its occurrence, ionic radius, and behavioral properties are closer to those of the heavier rare earth elements than to the lighter subgroup.

1.1. Rare earth uses and typical analysis of monazites

The industrial uses of REE are diversified in several areas: metallurgy, glass, ceramics, illuminations, electronics, chemical, magnets, nuclear and miscellaneous uses. The application of REE has been tabulated by Vijayan et.al.[2,4]
Monazite is the principal source of thorium and the rare earth elements but its composition and the distribution of its component elements may vary within very wide limits. Table 1, shows typical chemical analysis of monazite from the western and eastern coast line of

Australia, black monazite from Taiwan and reference standard monazite that has been prepared by Seatrad Centre from Malaysia.[2,3] The model analysis of Seatrad Centre reference sample is shown in the Table 2.

1.3. Objective

The aims of this activity are:

- To study and prepare a standard analytical method of rare earth elements containing minerals (monazite and xenotime), by using X-ray fluorescence spectrometry technique, which can be used for routine work.
- To develop a method of quantitative mineralogical analysis of monazite sample by using its chemical formula and it's elemental content so that the calculated concentration can be used for routine work.
- To compare the mineral composition of the monazite samples that has been analyzed by microscopic grain counting method with the chemical formula calculation.

2. EXPERIMENT

2.1. Standard Calibration

It has been known that the XRF technique is a comparative method. Therefore, the accuracy and precision of the analysis depend upon the quality of the standard calibration. The "monazit" program uses 30 standards when plotting the calibration curve by mixing the monazite and xenotime of Seatrad Centre reference sample. To get the series of appropriate REE concentration and to wider the area of the calibration, ultra pure chemical reagent of RE spex-mix 1031-2 ex LABSPEC and gold label of CeO_2, Pr_6O_{11}, Nd_2O_3, Eu_2O_3, Tb_4O_7, Ho_2O_3, Tm_2O_3, Lu_2O_3, ThO_2 and U_3O_8 FROM Aldrich chemical Company were added to these reference samples above.

2.2. Error of Analysis

In the analysis with the XRF technique, a random error could happen in association with each reading of the intensity (count-rate) and defined as precision of the measurement (Table3).

This error comprises of three major sources:

- Counting statistic, which is dependent only on time of the exposed X-ray radiation
- Instrumental error (generator, X-ray tube stability)
- Sample preparation error.

2.3. Precision and accuracy

The precision of an analysis is the degree of agreement among the replicate determinations made under SAME conditions as nearly as possible. Quantitatively, it is the difference between the individual analysis and the mean values of a large number (in this experiment 10 times) of independent replicate analysis, usually expressed in percentage. The greater or better the precision, the smaller is its numerical value.(Table 4).

The accuracy of an analysis is the degree of agreement of the analysis result with the "true", accepted or most reliable known value. Quantitatively the accuracy is the difference between the individual analysis result and the "true" value, usually expressed in percentage. Numerically, the greater or better the accuracy, the smaller is its numerical value.

2.4. Analytical Results

Thirty monazite samples which had been prepared by PPBT Mentok of PT Timah, were analyzed by using a created analytical program "monazite".

2.5. Mineralogical Analysis

On the basis of chemical formula of monazite, its mineral content was calculated as following formula:

Method 1: (La, Ce, Nd, Th) PO_4
Method 2: ($Ce_{1.714}$ $La_{1.305}$ $Th_{0.430}$ $Nd_{0.350}$ $Pr_{0.110}$) $(PO_4)_4$
Method 3: (La, Ce, Nd) PO_4.

3. DISCUSSION

3.1. Chemical composition

The concentrations of REE constituents in the 30 analyzed monazite samples are much lower than the Australian monazite (Table 1). This might be due to the fact that monazite produced is contaminated with xenotime (Y, Er) (PO_4).

The Y_2O_3 and Er_2O_3 content, in the analyzed samples are still very high. The concentration of Y_2O_3 and Er_2O_3 in the sample are (2.297-8.858%) and (0.24-1.12%) respectively, while the Australian monazite has (0.03-0.60%) for Y_2O_3 and no available data is available for Er_2O_3.

Figure 1 shows the diffractograms of sample codes VII and XXX with the monazite content 70.35% and 35.58%, respectively. In the diffractogram XXX, the xenotime has very intense peak compared to monazite peak, while the diffractogram VII has monazite peak height, nearly twice of the XXX difractogram.

3.2. Mineralogical composition

The grain counting analysis is assumed as the most reliable one for monazite content in the analyzed samples. The difference of the third chemical calculation method compared to the respective grain counting result, is less than 10 % for the method 3.

The accuracy of chemical calculation methods could be increased by using a series of standards as reference samples. In the experiment the analyzed samples were compared directly to the Seatrad Center's reference sample, therefore, the analytical accuracy depends on the quality of the reference sample.

4. CONCLUSION

(1) Sample preparation plays an important role in XRF technique to achieve high precision and accuracy of the analysis. The fusion method of the preparation of beads shows that the total relative error is less than 2.50%, counting statistic error is less than 0.15% and the instrumental error < 0.1%. The error during preparation of the sample such as weighing, ignition, fusion etc. is less than 2.0%.

(2) The "monazit" analytical program has been set up and the program shows an excellent precision and accuracy of the analysis. This program can be used for routine work monazite analysis.

(3) The mineral composition of monazite sample can be calculated using its chemical composition and the experiment shows that 70% of the analyzed sample have relative error less than 10%.

(4) It is recommended to apply the chemical calculation method for mineralogical monazite analysis from a series of reference standards to observe the accuracy of the created analytical program.

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Table 1. Typical analysis of monazite

% Oxides	Capel W. Australia	Cudgen (N.S.W.)	Black monazite (Taiwan)	SC Standard
La_2O_3	16.20	15.60	25.41	11.98
CeO_2	26.70	27.50	23.18	26.07
Pr_6O_{11}	2.60	3.50	1.27	2.90
Nd_2O_3	11.00	11.80	7.95	11.84
Sm_2O_3	1.30	2.70	-	1.90
Eu_2O_3	0.02	0.03	-	<0.10
Gd_2O_3	0.30	1.60	-	1.37
Tb_4O_7	-	-	-	0.06
Dy_2O_3	0.20	0.40	-	0.62
Ho_2O_3	trace	0.05	-	0.04
Er_2O_3	-	-	-	0.20
Tm_2O_3	-	-	-	0.05
Yb_2O_3	-	-	-	0.07
Lu_2O_3	-	-	-	0.04
P_2O_5	27.00	28.90	20.55	22.99
Y_2O_3	0.60	0.03	1.07	2.07
ThO_2	6.80	7.30	trace	7.47

Table 2. Model analysis of monazite reference sample

Mineral	% Weight
Monazite	89.00
Zircon	4.50
Ilmenite	4.00
Tourmaline	1.50
Iron hydroxide	0.50
Nb/Ta rutile	0.50
Cassiterite	Trace

Table 3. The relative analytical error of the experiment (%)

Source of error	Yttrium (Y)	Cerium (Ce)	Neodymium (Nd)	Thorium (Th)
Total error	1.508	1.743	2.490	1.545
Counting statistic	0.142	0.099	0.356	0.086
Instrumental	0.030	0.084	0.130	0.095
Sample preparation	1.501	1.737	2.461	1.540

Table 4. Precision and accuracy of the analysis monazite using "monazit" program

Oxides	Mean (%)	Limit Minimum	Limit Maximum	Precision (%)	True Value (%)	Accuracy (%)
La_2O_3	12.096	11.659	12.268	3.61 - 1.42	11.98	0.97
CeO_2	26.030	25.095	26.403	3.59 - 1.43	26.07	0.15
Pr_6O_{11}	2.873	2.723	1.945	5.22 - 3.22	2.90	0.93
Gd_2O_3	1.35	1.31	1.40	3.18 - 3.47	1.37	1.46
Dy_2O_3	0.61	0.59	0.62	2.96 - 1.98	0.62	1.61
Y_2O_3	2.074	1.969	2.121	5.06 - 2.26	2.07	0.19
ThO_2	7.46	7.25	7.62	2.80 - 2.15	7.47	0.13

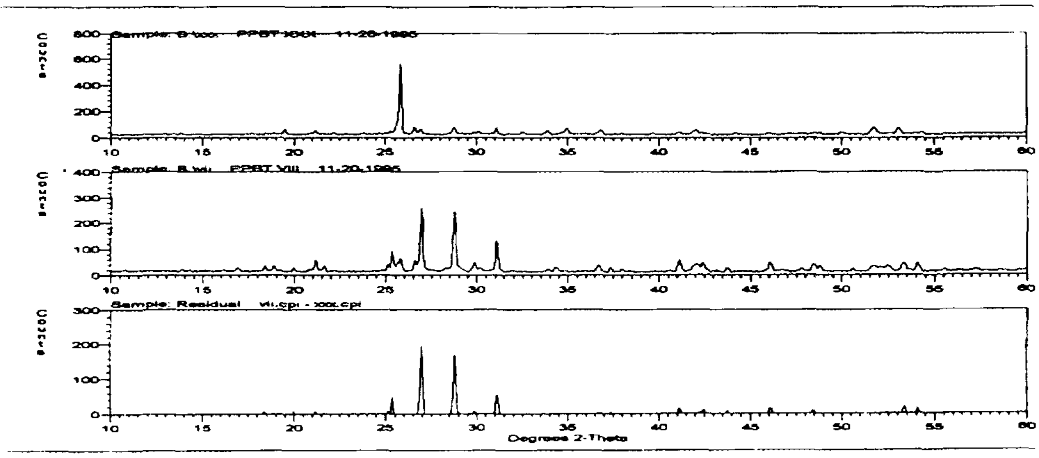

Figure 1: Diffractogram of sample codes VII and XXX

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