QUANTITATIVE ANALYSIS OF URANIUM AND THORIUM IN LOCAL ZIRCON AND TIN SLAG BY THE EDXRF TECHNIQUE

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ABSTRACT

Considerable amount of uranium and thorium are found in our local zircon and the level is much higher than the maximum value adopted by Malaysia and many importing countries. Energy Dispersive X-ray Flourescence (EDXRF) proves to be a very valuable tool in the determination of these radioactive elements as it can perform the analysis simultaneously in shorter time. Quantitative analysis of this mineral involves the use of a fundamental parameter technique developed by National Bureau of Standard, USA and Geological Survey Canada (NBS-GSC FPT). The analysis for tin slag is more challenging as there is no reference standard of similar material. Thus the standard addition method was applied to correct the error from the matrix of the sample.

ABSTRAK

Kandungan uranium dan torium yang tinggi terdapat didalam zircon tempatan dan nilai ini adalah lebih tinggi daripada had maksimum yang diterimapakai oleh Malaysia dan banyak negara pengimport yang lain. EDXRF merupakan satu teknik yang bernilai didalam penentuan unsur radioaktif ini kerana ia dapat melakukan analisis secara spontan didalam masa yang lebih singkat. Analisis kuantitatif mineral ini dilakukan dengan menggunakan teknik yang dibangunkan oleh National Bureau of Standard, USA and Geological Survey Canada (NBS-GSC FPT). Analisis sangga timah adalah lebih rumit kerana tiada piawai rujukan bagi bahan yang sama. Jadi kaedah piawai tambahan telah digunakan bagi membetulkan ralat disebabkan oleh matriks sampel tersebut.

Keywords: EDXRF, zircon, tin slag, Nbs-Gsc fundamental parameter technique, standard addition

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INTRODUCTION

Malaysian zircons are obtained from *amang*, which also comprises of different heavy minerals. The characteristics of this mineral differ from one source area to another as the result of differences in their impurities content, shape and particle size (Dahan A.R., 1990). Traditionally zircon had been classified into the premium and standard grades. Iron and titanium impurities in the mineral play an important role in the determination of these grades. As shown in Table 1 below, the better quality premium grade zircon has lower impurity content than the standard grade.

Table 1: Minimum content of different zircon grades (Skillen A., 1992)

Zircon Grade	$ZrO_2 + HfO_2$	TiO_2	Fe_2O_3	$U_3O_8 + ThO_2$
Premium	66.0%	0.10%	0.05%	450ppm
Standard	65.0%	0.25%	0.15%	450ppm

The normal content of uranium and thorium in zircon may vary from a few ppm to 4000ppm even though higher content had also been reported. Very high uranium content in the range of 6.1 – 12.9% was detected from zircon within the Chernobyl area. Naturally occurring radioactive elements like uranium and thorium are distributed throughout the earth and oceans. The present of these elements in zircon may be due to the following sources (Hart et *al*., 1993):

a. Contamination with radioactive minerals which is also present in *amang* such as monazite and xenotime as free grains or inclusions
b. Adsorption of these radioactive elements on the surfaces of lattice defects or crystal and grain boundaries
c. Incorporation of thorium and uranium into the concentrated minerals by direct cation substitution at the time of formation in their original host rocks.

Recently more attention had been placed on the content of naturally occurring radioactive elements of uranium and thorium in zircon and other related minerals due to the greater awareness among the public on their radiological effect. Legislations and Acts had been proposed for the reduction in their level in imported zircon (Clark, 1993).

Malaysia was one of the biggest tin producers in the world and there were two tin smelting plants, one located at Prai on the mainland of Peninsular Malaysia and the other at Penang Island. Over the years these plants smelt tin ore (cassiterite) from both local as well as overseas suppliers and processed it into tin metal. The process besides producing the tin metal also produces a slag waste (Hasbi A., 1985). When the price and demand for tantalum superconductors were high, tin slag waste that contains high content of this element was recovered from the ground. Significant amount of uranium and thorium was found to be present in the slag. As the activities involving radioactive materials comes under the legislation of Act 304, companies and individuals carrying out these activities are require to possess a proper license issued by Atomic Energy Licensing Board (AELB). In carrying out their activites, the AELB needs to know accurate amount of uranium and thorium present in tin slag. Thus the objective of this study is to develop an accurate and reliable quantitative analysis for determining uranium and thorium in zircon and tin slag. EDXRF had been found to be suitable in analysis of uranium and thorium due to its fast analysis, simple sample preparation and reliable results (Antje Wittenberg and Ulrich Schwarz-Schampera, 2006, Natarajan *et al*., 2008, Sangita Dhara *et al*., 2009)

EXPERIMENTAL

The zircon samples are collected from different localities of tin mines and amang plans. Quantitative mineral estimation technique (QME) was performed to determine the mineral constituent of these samples. The procedure was done at the Malaysian Mining Corporation (MMC) Laboratory in Batu Caves, the test can also identify the present of radioactive minerals in the samples. Samples were first dried in oven and then grinded to particle size below 180 µm by Fritsch pulverisette ball and sieve mills. The tin slag sample was collected from Butterworth, Penang and the material was first ground to fineness of 2mm using Retsch BB100 jaw crusher. This was then followed by the ball and sieve mills as in the above treatment of zircon mineral.

Elemental composition in zircon was determined by the EDXRF technique (Baird model 3000) at Malaysian Nuclear Agency. For the quantitative analysis of zircon, the uranium and thorium content in these samples were measured by the NBS-GSC Fundamental Parameter Technique. The technique involves the use of three different zircon standard reference materials BCS 388, ASCRM-008 and SEATRAD-3 with fundamental parameter technique to help in improving the accuracy.

In determining uranium and thorium for the tin slag sample, standard addition method was used. This involved spiking of different concentrations of uranium into the milled tin slag sample and then dried overnight under infra red light. Different uranium concentrations were prepared by diluting 1000 ppm standard uranium stock solution with distilled water. Similar procedure was applied for thorium.

In the analysis for uranium and thorium the high voltage used was 50 kV while current used was 100 μA. Also 100 seconds counting time was used for the analysis and the background intensity was reduced by using a molybdenum filter. Spiked tin slag samples were then with the EDXRF instrument where the uranium and thorium Lα peaks were identified at 13.613 KeV and 12.966 KeV respectively. Areas under these peaks were determined by using the gross method.

RESULTS AND DISCUSSION

Zircon samples

Eight zircon samples were collected from tin mines as well as amang treatment plants. Some of these samples such as that found in Dengkil and Puchong are two different samples but from the same amang treatment plants. Zircon Puchong1 and Puchong2 are samples from the same locality (Puchong, Selangor) but collected at different times, which is also similar with that of Dengkil1 and Dengkil2 samples. Table 2 below shows the EDXRF analysis for the eight different zircon samples.

Naturally occurring radioactive elements, U and Th, have been focused due to the greater awareness of their radiological effect (Hart, 1993; Clark, 1993). Legislations and Acts had been proposed for the reduction in their level in imported zircon. As can be seen from the above tables, all the Malaysian zircon samples analysed seems to contain higher concentration of U and Th than the AELB permitted level of 500ppm. The range of combined uranium and thorium present in these samples are from 0.16% (1600 ppm) to 1.72% (17200 ppm). Samples that contain very high concentration of these radioactive elements are those that contain lower zirconium like Kemaman and Kampar. In these samples too, the thorium content is higher than that of uranium. For the high zirconium samples the uranium and thorium content is lower in the range of 0.16% to 0.24%. Also, these samples have higher uranium content than that of thorium.

Analysis of samples from same locality (Dengkil and Puchong) shows that their radioactive elementals content are different. These differences may be resulted from the source of the sample or their mineral processing procedure. The normal practice in the tin mining industry is that the *amang* produce from a particular tin mine is offer for bidding and the highest bidder will secure the mineral (Hasbi, 1985; Dahan, 1990). An *amang* treatment plant does not only treated *amang* from a particular area but also from other sources. The reason for the different results of Puchong1 and Puchong2 samples are that may be these minerals are being source from different locality.

Table 2: EDXRF results for different Malaysian zircon samples

Zircon samples	Concentration (%)	
	U_3O_8	ThO_2
Zircon Kemaman	0.14	0.32
Zircon Puchong1	0.16	0.06
Zircon Dengkil1	0.15	0.02
Zircon Lahat	0.18	0.06
Zircon Kampar	0.25	1.47
Zircon Puchong2	0.13	0.03
Zircon Dengkil2	0.16	0.08
Zircon Bidor	0.15	0.07

Table 3(a): Mineral content of different zircon sample by QME method

Mineral content (%)	Zircon Kemaman	Zircon Puchong1	Zircon Dengkil1	Zircon Lahat
Zircon	65.0	68.0	98.0	98.0
Ilmenite	27.0	25.0	-	-
Tourmaline	trace	1.0	trace	trace
Limonite	trace	trace	-	-
Xenotime	trace	trace	trace	trace
Monazite	1.0	1.0	trace	trace
Cassiterite	1.0	1.0	trace	-
Rutile	2.0	1.0	1.0	1.5
Anatase	trace	1.5	trace	-
Quartz	1.0	-	1.0	-
Pyrite	-	-	-	-

Table 3(b): Mineral content of different zircon sample by QME method

Mineral content (%)	Zircon Kampar	Zircon Puchong2	Zircon Dengkil2	Zircon Bidor
Zircon	78.0	97.0	98.0	95.0
Ilmenite	0.5	-	-	-
Tourmaline	trace	-	-	trace
Limonite	-	-	-	-
Xenotime	0.5	trace	-	trace
Monazite	16.0	trace	trace	1.5
Cassiterite	4.0	1.0	1.0	trace
Rutile	1.0	trace	trace	0.5
Anatase	trace	trace	-	-
Quartz	-	1.0	-	3.0
Pyrite	trace	-	-	trace

Another analysis done on the zircon samples is to determine its mineral content. This was done by using the Quantitative Mineral Estimation (QME) technique that uses the binocular microscope to identify and quantify the mineral fractions. Tables 3(a) & (b) below list the QME results for the different zircon samples.

The minimum quoted quantitative measurement by the QME technique is 0.5%, mineral fractions that is lower than this value is term as trace. In the production of zircon from amang at the local retreatment plants, three different grades of zircon are produced (Dahan, 1990). The first group comprise of samples that contain more than 95% zircon mineral and is termed as zircon concentrate. This group normally means as an export commodity and the retreatment process was done to satisfy the needs of the would-be importers. The second group contains a lower zircon concentration which is about 70-80% zircon minerals and is termed as crude zircon. A third zircon group is called partially upgraded concentrate with significant present of other minerals. The second and third groups are normally produced as an intermediate grade to the zircon concentrate. As a normal practice for the amang industry, the market force controls production of a specific mineral grade. Zircon concentrate will be produced in large quantities when ever price is high. At the time of low demand, the mineral is kept as crude zircon or partially upgraded concentrate (Hasbi, 1985).

The mineral zircon content in Dengkil1, Lahat, Puchong2, Dengkil2 and Bidor is more than 95% and can be categorized as zircon concentrate. The zircon Kampar can be classified as a crude zircon since the zircon concentration is 78%. This is due to the present of higher quantity of monazite in the zircon sample. It was reported that the monazite fraction in crude zircon may be in the range of 10-20% (Dahan, 1990). One of the drastic different in the radioactive elements present in the samples is that some of the zircons have higher thorium content than uranium while the majority has the opposite. The above QME results can be used to explain this different as the present of a thorium-rich mineral like monazite ($Ce,La,ThPO_4$) could lead to high thorium concentration in the sample. This can be seen for example in the elemental analysis of zircon Kampar shown previously which has higher thorium content than the other zircon samples. Zircons Kemaman and Puchong1 can be classified a partially upgraded zircon concentrate. Unlike crude zircon, the partially upgraded zircon concentrate contains most of its mineral impurity from ilmenite, the most abundant heavy mineral present in amang (Hasbi, 1985). The present of thorium in this sample is not that high due to small amount of monazite present in it.

Analysis of the radioactive elements in sample zircon Dengkil2 shows that it has a U_3O_8 content of 0.16% and ThO_2 content of 0.08% (Table 2). While QME analysis on the same sample shows that it only has a traceable amount of monazite present in the sample. The higher uranium concentration than thorium also tends to support the QME result on the content of monazite in the sampl as monazite may also resulted in a higher thorium than uranium content in the zircon (Tadza, 1990). A possible source for this radioactive element is the replacement of the U^{4+} and Th^{4+} with Zr^{4+}. This replacement may happen because both of these actinide elements have the same oxidation state. Furthermore the ionic radius of Zr^{4+} (1.09A) is quite close to U^{4+} (1.00A) and Th^{4+} (1.05A).

a. Tin slag sample

For the tin slag sample, as there is no availability of international reference standard, we determined the uranium and thorium by EDXRF in cooperated with the standard addition technique. The method is based on spiking known concentrations of the interested elements on the tin slag samples. Relationship between intensity measured from the uranium and thorium Lα peaks and spiked concentration will resulted into a linear graph that will intercept at the negative y-axis (Skoog &

West, 1980). The following equations relate the intensities before and after spiking of the added concentrations;

$$I_x = kC_x \quad (1)$$

And $I_t = k\,(C_s + C_x)$ (2)

Where:

C_x = initial concentration (ppm)

C_s = added concentration (ppm)

I_x and I_t = measured intensities before and after addition (cps)

Combining equations (1) and (2):

$$C_x = C_s \{ I_x / (I_t - I_x) \} \quad (3)$$

The initial element concentration can be determined by the intercept of $C_x = -C_s$ if the straight line is extrapolated at $I_t = 0$. Thus the value of uranium and thorium present initially can be established from the standard addition graphs. The standard addition graph for uranium (Figure 1) obtained is linear with a R^2 value of 0.9889. Initial uranium content of 60 ppm in the tin slag sample was obtained by extrapolating this linear line to the y-axis.

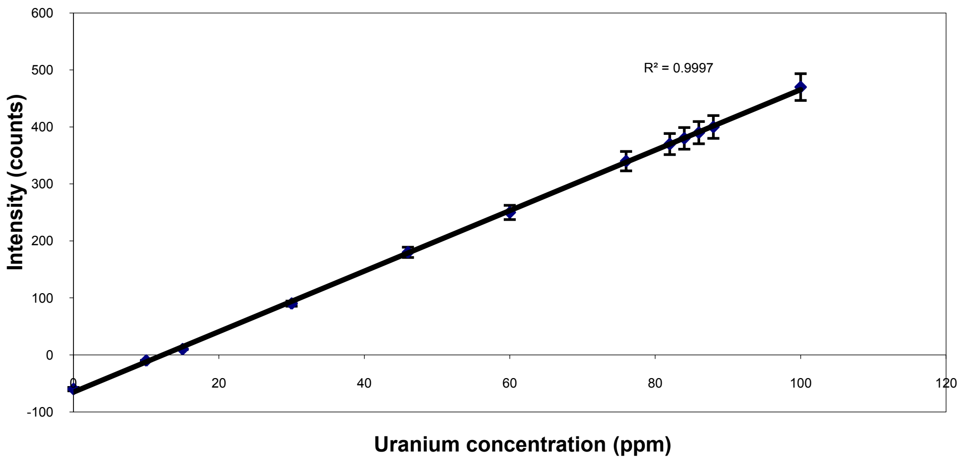

Figure 1: Standard addition for uranium in tin slag

Similar procedure as done in uranium analysis was carried out for the determination of thorium. The standard addition graph for thorium is as that shown in Figure 2. A linear graph was also obtained with the R^2 value of 0.9915.

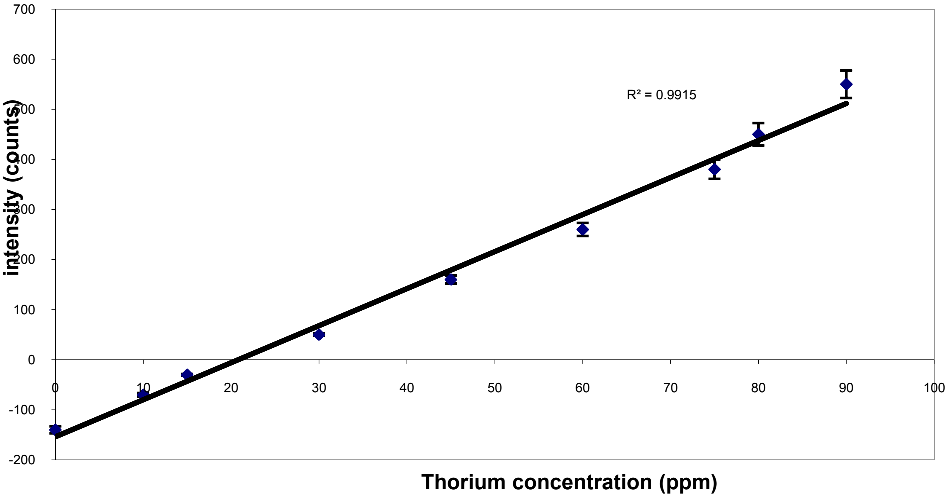

Figure 2: Standard addition for thorium in tin slag

CONCLUSION

EDXRF proves to be a valuable in the determination of uranium and thorium in zircon as well as tin slag samples due to its fast and simultaneous analysis also the minimum sample preparation required. It is possible to analyze these radioactive elements accurately by using the NBS-GSC Fundamental Parameter Technique. The absence of tin slag reference standards can be compensated by using the standard addition method.

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