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《**Original**》

A Study on the Radiometric Method for the Determination of Uranium and Thorium in Ores

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Abstract

The radio-equilibrium conditions of uranium and thorium in the Okcheon black shales and monazites have been studied. As the results, a radiometric method based on the measurements of gamma ray activity has been suggested for the simple analysis of many samples in the process of the prospecting and the grading of uranium and thorium minerals.

요 약

옥천계 흑혈암(black shale) 및 모나자이트에 함유된 우라늄 및 토륨의 방사화 평형조건에 관하여 연구하였다. 이 연구의 결과로 감마선 계측에 의한 이들 원소의 분석법을 제시할 수 있었으며 많은 수의 광물 시료분석이 손쉽게 되었다.

1. Introduction

While wet chemical and delayed neutron counting techniques provide an information on the accurate concentrations of uranium and thorium, the method based on gamma or beta activity is a general idea for the analysis of radioactive minerals[1-6]. This method is particularly helpful in the situations where accuracies of ±10% are quite satisfactory and rapidity and simplicity are significant factors in sites far removed from the reactor and without the facilities for chemical analysis.

This work presents an effort on standardizing radiometric methods based on the measurements of gamma activity for the analysis of many samples in the process of the prospecting and the grading of uranium and thorium minerals.

2. Principle

In ore samples, as one meets with in the course of normal work of this nature, the existence of radioactive equilibrium (R.E.) in the ^{232}Th family can be assumed, since the longest lived daughter of ^{232}Th is ^{228}Ra with a half-life of 6.7 yrs., so that R.E. is established in about 60 yrs. The only apparent contradiction to this statement would be cases where thoron (^{220}Rn) is lost from samples. This loss is generally accepted

to be insignificant[7] in view of the very short half-life ($t_{\frac{1}{2}}$=54 sec.) of this nuclide.

On the other hand, in the ^{238}U family, there are several long-lived daughter products such as ^{234}U ($t_{\frac{1}{2}}$=248,000 yr), ^{230}Th ($t_{\frac{1}{2}}$=75,000 yr), ^{226}Ra ($t_{\frac{1}{2}}$=1622 yr) and ^{222}Rn ($t_{\frac{1}{2}}$=3.8 d), the gaseous precursor of ^{210}pb ($t_{\frac{1}{2}}$=22 yr), which are likely to be lost in the geological history of the sample[8] or which may not have reached equilibrium abundance in a recent ore deposit. Similarly, ^{231}Pa ($t_{\frac{1}{2}}$=32,500 yr) is key isotope of the ^{235}U series[8] which controls the equilibrium condition in this series. In the absence of any evidence to show that significant variations in the ^{238}U to ^{235}U ratios occur in nature[9], the contribution of r-activity of the ^{235}U series to the total activity is less than 4%. It should also be mentioned that contribution made by ^{40}K to total r-activities of normal samples is negligible unless these are essentially potassium minerals containing only trace concentrations of uranium and thorium.

2-1. Gamma-ray Spectrometric Method

On comparing the γ-ray spectra of uranium oxides with ores containing uranium and thorium, the experimental observations are notified as follows[1].

(a) The major γ-activity in such uranium samples having daughter product deficiency as uranium oxide and recent surface deposits on granites is in the 50~100 KeV regoin which arises from the decay of ^{234}Th and hence an intensity measurement in this energy band can be correlated to the uranium content of the sample.

(b) In the case of a uranium ore in R.E., there are several additional peaks of high intensity in the 0.35, 0.61, 0.76, 1.12 and 1.76 MeV regions which are due to RaB (^{214}Pb) and RaC (^{214}Bi), the daughter products of ^{226}Ra.

(c) In the case of samples which contain thorium also, there are more additioal peaks in the 0.23, 0.91 and 2.61 MeV regions arising from the decay of ThB (^{212}pb), MsTh Ⅱ (^{228}Ac) and ThC (^{208}Tl). Hence the thorium content of a sample can be determined by measuring the intensity of the 2.61 MeV γ-ray, taking due care to operate a r-ray spectrometer at such an appropriate gain that the low intensity 2.45 MeV γ-ray of the uranium family is as well separated as possible.

3. Experimental

3-1. Standards and Samples

The uranium standard was a low-grade uranium ore (S4) supplied by IAEA, containing 0.375%U_3O_8.

The thorium standard was a monazite supplied by the New Brunswick Laboratory (N.B.L), containing 9.7% ThO_2 and 0.4% U_3O_8.

For pure U_3O_8 out of R.E., a sample of uranium dioxide, 99.9% pure, supplied by Tokosawa, Chem. Co., Japan, was ignited in air for about three hours to convert it to U_3O_8. The oxide was diluted with country rock of negligible radioactivity to give a 16% U_3O_8 standard.

Black shale sample of the Ocheon group were supplied by Korean Institute of Mining Geology and ground to pass 200 mesh.

Each sample was pressed to about 1 ton per cm^2 to form a uniform tablet of 7 cm dia.×2 cm high using a sintering apparatus. The sintered sample was mounted on a 3′ ×3″ NaI (Tl) crystal which was housed in a cave ($0.9\times0.9\times0.9m^3$) and conneced to a 400 channel analyzer (Hitach model 402)

3-2. Evaluation of the Constants for the Simultaneous Determination of Uranium and Thorium

Samples containing both uranium and thorium in R.E. can be analysed for the individual components by measuring intensities at two energy bands and setting up a set of simultaneous equations. The constants in such equations can be determined from the measured intensities atthe given two energy bands as follows.

The γ-activities of a sample at two energy bands E_1 and E_2 are related to the concentrations of uranium and thorium by the following relationships:

$$A_{E1}=K_{UE1}\times C_u+K_{ThE1}\times C_{Th}$$

and $$A_{E2}=K_{UE2}\times C_u+K_{ThE2}\times C_{Th},$$

where A_{E1} and A_{E2} are the observed activities per gram of the sample at the energy bands E_1 and E_2, respectively. K_{UE1} is the specific activity in the energy band E_1 per 1% U_3O_8 of a standard uranium ore in R.E. and K_{UE2} is the corresponding activity in the energy band E_2. Similarly K_{ThE1} and K_{ThE2} are the specific activities per 1% ThO_2 of a standard thorium ore in the energy bands E_1 and E_2, respectively. Cu and C_{Th} are the concentrations of uranium and thorium expressed as percentage in the sample.

An IAEA reference sample, S_4, was used for the evaluation of K_{UE1} and K_{UE2}. However, for the evaluation of K_{ThE1} and K_{TEE2}, the activites of the N.B.L. monazite were measured and corrected in order to eliminate the effects of the 0.4% U_3O_8 contents as follows.

The spectrum of the N.B.L. monazite was stored in the memory of the analyser and the monazite was removed. The IAEA uranium reference was positioned and with the analyser counting in the negative mode, the uranium spectrum was stripped for a time interval proportional to the calculated U_3O_8 content of the monazite. At the end of this period, the IAEA uranium was removed and the background subtraction was continued. The net spectrum obtained finally, which is due to the ThO_2 content of the N.B.L. monazite, was used for the calculation of K_{ThE1} and K_{ThE2}.

4. Results and Discussion

4-1. Determination of ThO_2 by the Measurements of γ-ray under 2.6 MeV Region

Because R.E. is assumed in the ^{232}Th family, it has some advantages to measure the γ-ray of the highest energy, i.e., 2.61 MeV. For the measurement of the 2.61 MeV γ-ray with the minimum interference from the tail of the 2.4 MeV γ-ray of uranium family, the base line of the analyser was adjusted so as to cut off the response from all radiations below 1 MeV. The analyser was operated at an appropriate gain so that 2.6 photon is centered around 200th channel. Thorium content of a sample was thus determined by measuring

Table 1. Determination of ThO_2 from Intensity Measurements of 2.6 Mev γ-ray Region

Sample	Sample wt(gm)	Act/min	Act/gr/min	ThO_2 Content(%)
N.B.L. Monazite	45.20	1.04×10^4	231	(9.7)
Koksung	44.65	5.64×10^3	126	5.34
Ipchang	42.47	5.26×10^3	124	5.20
Dukryung	46.21	5.46×10^3	118	4.96
Black Shales of Ockcheon	35.47	~17	~0.48	≤0.020

Table 2. Eqiuilibrium Condition of Okcheon Black Shales

Sample	Series No.	Activity (0.05~0.1 Mev)	Activity (0.61 Mev)	Activ ty ratio
Okcheon black shales	96	3.20×10^4	1.06×10^4	3.02
	139	6.40×10^4	1.82×10^4	3.52
	169	4.90×10^3	1.38×10^3	3.55
	170	1.65×10^4	4.80×10^3	3.44
	182	1.92×10^4	6.67×10^3	2.88
	183	2.25×10^4	6.89×10^3	3.27
	187	2.63×10^4	6.94×10^3	3.79
	Average	—	—	3.35 ± 0.29
IAEA reference Uranium	S4	1.30×10^4	1.54×10^4	0.841

the intensity of the 2.61 MeV γ-ray and comparing this with the corresponding value of the N.B.L. standard monazite. The analytical results of ThO_2 thus obtained are given in **Table 1.**

4-2. The Equilibrum Condition of the Okcheon Black Shale

For the investigation of the Okcheon black shales, activity measurements were made in the normal way so that even low energy radiations were counted. Erom the γ-ray spectra of some typical Okcheon black shales and the IAEA reference uranium samples (S4), the ratios of the γ-ray intensities between two energy bands, i.e., 50~100 KeV vs. 0.6 MeV regions, were calculated and are given in **Table 2.**

Considering the errors in these measurements the variation of the ratios among Okcheon black shales is not significant. Thus, a mean value 3.35 is taken for all Okcheon black shales. Because this value is much larger than that of IAEA reference sample which is assumed R.E., Okcheon black shales can be classified as uranium samples having daughter product deficiency[10].

From the above consideration, it is concluded that such a reference sample as the S4 of IAEA can not be used as a standard for the radiometric analysis of uranium in Okcheon black shales with the exception of measuring γ-ray activity at 0.050~0.10 MeV region.

The thorium contribution to the total activity in the black shales is so small and variations of the activity ratios given in Table 2 are not so significant that once the uranium content in a certain black shale has been determined the sample can be used as a reference standard for the radiometric analysis of other black shales, measuring total γ-ray or some activities at any γ-ray energy bands for the analysis.

It should also be noted that the thorium contribution to the total activity is so small that the adoption of the method for the simultaneous determination of uranium and thorium was not necessary on the analysis of of black shales, i.e., either measurements of total γ-ray or some activities at any γ-ray energy bands were necessary for the analysis of uranium in black shales. This contrasts with the analysis of monazite where the thorium contribution is significant.

The analytical data obtained by this radiometric method are compared with the accurate data obtained by delayed-neutron counting method[11] in **Table 3.** For the radiometric method, the black shale, those

Table 3. Analytical Results of U_3O_8 (ppm) and the Comparison with Other's

Sample	Series No.	Analytical results for the γ-ray energies used				Results by delayed-neutron counting
		0.05~0.01 Mev	0.61 Mev	1.1 Mev	total γ-ray counting	
Okcheon black shales	96	333	320	340	350	327
	139	621	630	550	590	588
	169	36	34	30	41	35.3
	170	140	160	155	130	158
	182	200	230	190	195	203
	183	175	170	180	190	176
	187*	231	231	231	231	231

* The sample has been used as the standard uranium.

uranium content had been accurately determined, was used as a uranium standard. The results in Table 3 show about 15% deviations between two methods. This discrepancy would be acceptable for the analysis of such many samples as in the process of the prospecting and the grading of uranium minerals.

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