

Determination of Rare Earths and Other Trace Elements in Ore Samples of Mongolia by WDXRF and INAA

N. Baljinnyam¹, B. Davaasuren¹, N. Norov², M.V. Frontasyeva³, S.S. Pavlov³

¹Central Geological Laboratory, Ulaanbaatar, Mongolia

²Nuclear Research Center, NUM, Ulaanbaatar, Mongolia

³Frank Laboratory of Neutron Physics, JINR, Dubna, Russia

Wavelength dispersive X-ray fluorescence (WDXRF) and Instrumental Neutron Activation Analyses (INAA) were used to determine the REE and other trace elements in rare earth ore samples from province Dornogovi, Lugiin gol. Seven rare-earth elements (REE) namely La, Ce, Sm, Eu, Tb, Dy, and Yb, as well as other trace elements (Zn, As, Rb, Sr, Au, Ba, Br, Ta, Hf, Th and U) have been determined by WDXRF at Central Geological Laboratory of Mongolia, Ulaanbaatar. For comparison, the same elements were determined by INAA using by epithermal neutron activation analyses at the IBR-2 reactor, FLNP JINR, Dubna. It is demonstrated that the WDXRF have satisfactorily agreed with INAA results within the limits of the uncertainty. It is shown that the values of the relative discrepancies between the WDXRF and the INAA results are in the range of 1.5-30.0 %.

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I. INTRODUCTION

Nowadays we are witnessing an ever growing use of rare earth metals (REM) for industrial purposes. Apart from their classic utilization in the manufacturing of explosives, glass and ceramics, they have now become important in the electronics industry, the production of semi- and superconductors, microwave techniques and the fabrication of luminescent materials. Therefore, the demand for quick and accurate quantitative analysis methods is continuously growing.

Mongolia has about 17% of the world reserves of rare earths, with approximately 60 deposits situated in six provinces (Altay, Umnugobi, North Mongolian Hentii, Hangay, Southeast Mongolian, and South Mongolian) [1]. Four deposits are of particular importance, especially that of Mushgia Khudag in the province of Umnugobi, which reportedly has reserves comparable to those of Bayan-Obo in China's Inner Mongolia, or 200 million tons of rare earth oxide ore. The Lugiin-gol vein-carbonatite rare-earth deposit is located in Dorongovi Aimag. The deposit occurs within the endo- and exo-contact zones of the early Jurassic nepheline and pseudoleucitesyenite Lugiin-gol massif, which lie in on the eastern flank of the South-Gobi alkaline rock belt.

Many of the existing classical methods for the determination of REEs have been superseded by physical techniques, including spectroscopic techniques. Atomic absorption and plasma emission spectrometry have recently been used for the simultaneous determination of lanthanides at lower concentrations. In recent years nuclear analytical methods such as WDXRF and INAA have become

one of the most promising and attractive analytical methods. The methods have been widely applied to study geological, biological and environmental materials [2, 3].

However, apart from plasma spectrometry, these methods were not satisfactory. For concentrations greater than 1 mg.g⁻¹, X-ray fluorescence (XRF) spectrometry is probably still the most versatile technique.

In this work the concentrations of REE and other trace elements have been determined in the rare earth ore samples by WDXRF. For comparison, the same elements were determined by INAA using by epithermal neutron activation analyses at the IBR_2 reactor, FLNP JINR, Dubna.

II. MATERIALS AND METHODS

A. Sampling and sample preparation

We were collected ore samples from rare-earth deposit Lugiin-gol where located in province Dornogovi. Three rare earth ore samples (S1, S2, S3) carried out a setting for X-ray fluorescent analysis of Central Geological Laboratory of Mongolia. The samples we have pulverized test portion is mixed with proper flux and fused at high temperature, prepared glass beads.

B. X-ray analysis:

The XRF analysis determines the abundance of elements in a material, which has been used for the chemical analyses of rocks, minerals, sediments, soils, steels, and water. The characteristics and operating conditions of the equipment WDXRF are described in Table 1.

TABLE 1. X-Ray Fluorescence Spectrometer with Wave Dispersive (WDXRF) parameters

Model Number	PW4400
Brand	PANalytical
Detector	MCA Flow, Sealed Xe, MCA Scint
Conditions	Automatic analysis for Qualitative/Quantitative from Na to U.
Used Atmosphere	water
X-ray tube	Rh with 4kV and 160mA
Collimator (μm)	150, 300, 700

Low dilution fused glass bead for the analysis was prepared by the following manner: a sample powder (1.0 g) was mixed with a 5 flux ($\text{LiBO}_2 + \text{LiBO}_2$) and kept in a platinum crucible. The crucible was set in a high-frequency melting furnace (FUSION MASHINE POENIX 6000), and fused at 1100°C for 15 min.

Power voltage and current condition to the X-ray anode are 4kV and 160mA, respectively.

Glass bead samples we were measured for 45 min. and done processing of spectrum using the Super Q program equipped with the spectrometry.

C. INAA Analysis:

Ore samples were dried during 24 hours in oven 105°C . After drying samples were powdered in an agate mortar and homogenized. Samples of about 0.3 g were heat-sealed in polyethylene foil bags and packed in aluminum cups for short and long irradiation, respectively, and stored until irradiation at the IBR-2 reactor.

The concentration of elements in the ore samples was determined by a multi-elemental instrumental neutron activation analysis using fast, thermal and epithermal neutrons (ENAA) at the IBR-2 reactor, FLNP JINR, Dubna. Thermal NAA takes advantage of the high intensity of neutrons available from the thermalization of fission neutrons and the large thermal neutron cross sections for most isotopes. Epithermal NAA (ENAA) is a useful extension of INAA in that it chances the activation of a number of trace elements relative to the major matrix elements. Epithermal is taken to be neutrons with energies from the Cd «cut-off» of 0.55 eV up to approximately 1 MeV. In general, the activation cross sections of the matrix elements of environmental samples are inversely proportional to the neutron energy. The trace elements also follow

this general trend but many of them have large activation cross section at specific energies in the epithermal energy region [4].

Epithermal neutron activation analysis (ENAA) has certain advantages over conventional instrumental activation analysis for many trace elements in terms of improvement in precision and lowering of detection limits, reduction of high matrix activity.

The analytical procedures and the basic characteristics of the employed pneumatic system are described in detail elsewhere [5].

Two types of irradiation were carried out. One is a short irradiation for 3–5 min to determine short-lived isotopes (Al, Ca, Cl, I, Mg, Mn, and V). After a decay-period of 5–7 min the irradiated samples were measured twice, first for 3-5 min and then for 10–15 min. A long-irradiation of 4–5 days was used to analyze for long-lived radionuclides. After irradiation the samples were re-packed and measured twice: first after 4–5 days for 40–50 min to determine As, Br, K, La, Na, Mo, Sm, U, and W and after 20 days for 2,5–3 hours to determine Ba, Ce, Co, Cr, Cs, Fe, Hf, Ni, Rb, Sb, Sc, Sr, Ta, Tb, Th, Yb, and Zn. The gamma spectra of induced activity were measured with aHPGe detector with a resolution of 1.9 keV for the ^{60}Co 1332 keV line.

The processing of the data and determination of the concentrations of elements were performed using certified reference materials and flux comparators with the help of software developed in FLNP, JINR [6].

In order to measure the precision of measurement, the specific gamma-ray peaks of each interesting radionuclide have been chosen carefully. The half-lives and gamma ray energies of isotopes selected for counting are listed in Table 2.

TABLE 2. Nuclear properties of the rare earth nuclides

Stable isotopes	Abundance (%)	Activation product	Half life	Gamma energy, keV	Cross-section, barn
La-139	99.9	La-140	40.2 h	1596	8.9
Ce-140	88.5	Ce-141	32.5d	145	0.6
Pr-141	100	Pr-142	19.13 h	1575.3	-
Nd-146	17.2	Nd-147	11 h	531	2
Eu-151	47.8	Eu-152	13.3 y	1408	2800
Sm-152	26.7	Sm-153	47 h	103	210
Gd-158	24.8	Gd-159	18.5 h	363.5	<180
Dy-164	28.2	Dy-165	2.33 h	94.7	-
Ho-165	100	Ho-166	26.9 h	80.6	64
Tm-169	100	Tm-170	130 d	84.3	125
Yb-168	31.6	Yb-169	32 d	198	11
Tb-159	100	Tb-150	72.1 d	86.8	-
Lu-166	2.6	Lu-167	161 d	208	2100
Er-170	14.9	Er-171	7.5 h	308.3	9

III. RESULTS AND DISCUSSION

We have been determined five rare-earth elements (REE) namely La, Ce, Pr, Sm, and Y in some trace elements in three ore samples (S1, S2, S3) by WDXRF at Central Geological Laboratory of Mongolia, Ulaanbaatar and twelve rare-earth elements (REE) namely La, Ce, Nd, Sm, Eu, Gd, Tb,

Dy, Er, Tm, Yb and Lu in three ore samples (S1, S2, S3) by INAA at the IBR-2M reactor, FLNP, JINR, Dubna.

The results of study show that comparison of the WDXRF results have satisfactorily agreed with the INAA for REE elements. (Table 3).

TABLE 3. Comparison for REE analysis of the samples by WDXRF and INAA (ppm)

Element	Sample 1		Sample 2		Sample 3	
	WDXRF $\pm\Delta C$	INAA (%)	WDXRF $\pm\Delta C$	INAA (%)	WDXRF $\pm\Delta C$	INAA (%)
La	16300 \pm 100	13100(5.0)	19900 \pm 110	15500(5.0)	433 \pm 30	312(5.0)
Ce	26000 \pm 290	20300(30)	25800 \pm 50	21300(5.5)	1000 \pm 8	688(5.4)
Pr	2770 \pm 28	-	2450 \pm 30	-	120 \pm 10	-
Sm	700 \pm 10	630(2.2)	496 \pm 62	395(3.3)	118 \pm 5	76.7(3.3)
Nd	5140 \pm 90	5430(30)	5980 \pm 30	5570(30)	454 \pm 23	496(30)
Gd	415 \pm 78	545(30)	276 \pm 10	287(30)	120 \pm 20	225(30)
Eu	178 \pm 15	102(31)	91.8 \pm 8.5	46.5(31)	9.0 \pm 1.5	76(31)
Tb	34.7 \pm 5.3	28(30)	37 \pm 8	13(30)	25.6 \pm 5	25(30)
Dy	202 \pm 30	201(40)	-	284(30)	175 \pm 30	223(30)
Y	946 \pm 35	-	159 \pm 15	-	1106 \pm 50	-
Yb	59.52 \pm 5	68(30)	18.4 \pm 2	18,6(30)	130 \pm 25	131(30)
Hf	-	2.08(8.0)	-	1.24(10)	398 \pm 30	326(5.9)

Value of bold italic – determined by ICP-MS

The content of trace elements such as Sr, Ba, Zn, and As measured by WDXRF were underestimated in comparison with the data obtained by INAA.

The results in Table 4 show that concentration of some trace elements in study samples by WDXRF and INAA.

TABLE 4. The concentration of some trace elements in study samples by WDXRF and INAA.

Element	Sample 1		Sample 2		Sample 3	
	WDXRF $\pm\Delta$ C	INAA (%)	WDXRF $\pm\Delta$ C	INAA (%)	WDXRF $\pm\Delta$ C	INAA (%)
Zn	600 \pm 40	1050 (3.51)	380 \pm 21	258(4.2)	434 \pm 28	464(3.3)
As	155 \pm 25	82,1(2.0)	212 \pm 23	146 (2.0)	33.7 \pm 3.7	25.5(2.2)
Sr	22400 \pm 10	22900(6.7)	5102 \pm 40	5420 (6.5)	128 \pm 12	106(14)
Rb	43 \pm 10	33.9 (17)	65.7 \pm 65	63(17)	541 \pm 50	528(17)
Mo	26.7 \pm 15	37.1(30)	45.6 \pm 35	50 (30)	9.8 \pm 12	7.64(32)
Ba	870 \pm 50	763(5.3)	290 \pm 10	260(6.0)	93 \pm 10	73(15)
W	-	4.43(30)	15.8 \pm 18	9.15(30)	80 \pm 13	1.97(30)
Th	217 \pm 40	143(2.7)	687 \pm 45	348(2.5)	200 \pm 10	101(2.5)
U	-	134(3.3)	45.2 \pm 50	29.5(3.4)	50 \pm 10	37(3.5)

To investigate the behavior of REE in ore samples, their REE concentrations are normalized to chondrite value. The chondrite values used are recommended by HOSHIN et al [7]. The chondrite normalized 10 REE patterns for rare earth ores are given in Fig 1. It is shown that the REE patterns of all ore samples are similar. The results of the REE patterns are very useful for studying geological structure, the formation of REE in the earth's crust and environmental pollution.

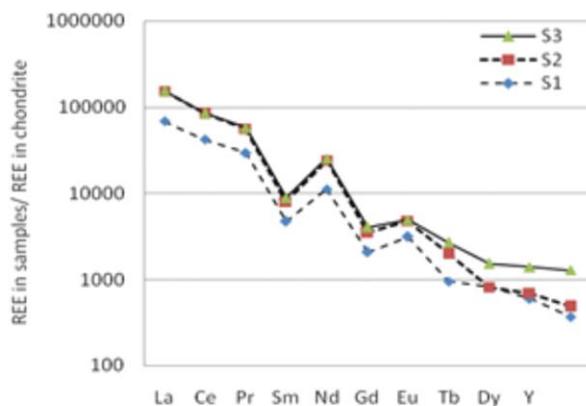


Fig 1. Chondrite normalized REE patterns for studied samples

IV. CONCLUSION

Comparing the results obtained for elemental analysis in rare earth ore, it can be noted that both methods present satisfactory results comparatively. According to the quantitative analysis of REEs in the rare earth ore samples there is an acceptable agreement between the WDXRF and INAA measured values.

In the analysis of rare earth ores with high content of trace elements needed to use standard samples, similar in elemental composition to the matrix of the studied objects.

To improve the results of the INAA techniques it is necessary the use of CRM for REE and the results can be considered very satisfactory, since relative deviation around 30% can be considered accurate when using CRM. Finally, for our further investigations we can use the WDXRF with ICP-MS method. In spite of the good comparability of the WDXRF results with INAA, this one is more suitable method than the INAA for the determination of the REE concentration in ore. INAA is a time consuming and expensive method, and requires a nuclear reactor and long cooling times prior to the concentration measurements.

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