Elemental Analysis of Hematite by Instrumental Neutron Activation Analysis

A. El-Taher [1]and W.R. Alharbi[2]

[1]Physics Department, Faculty of Science, Al-Azher University, Assuit 71452, Egypt
[2]Physics Department, Faculty science for Girls, king Abdulaziz University, Jeddah, Saudi Arabia
walhrbi@kau.edu.sa

Abstract: Instrumental neutron activation analysis (INAA) have been used to achieve accurate knowledge about the elemental analysis of hematite. The samples were prepared for irradiation by thermal neutrons using the irradiation facilities of the TRIGA Mainz research reactor. The gamma-ray spectra were obtained by using a hyper pure germanium detector. The value of iron concentration in our hematite samples of 57.7 % is in fair agreement with the results reported by other workers. From the economical point of view the hematite field is suitable for iron production due to its high iron content. Altogether, 32 elements were detected both qualitatively and quantitatively. In addition X-ray fluorescence XRF is used to detect other elements such as F, P, Si, W, Cu, Mo, Ni, Pb, Sr not determined by INAA. In brief, the presence of any elements in higher or lower levels is contingent on the occurrence of its bearing minerals, nature of parent sediments and depositional environments of these sediments.
[El-Taher A. and W.R. Alharbi. **Elemental Analysis of Hematite by Instrumental Neutron Activation Analysis**. *Life Sci J* 2012;9(4):5457-5461 (ISSN:1097-8135). http://www.lifesciencesite.com. 808

Keywords: Elemental Analysis, Hematite, Neutron Activation Analysis, TrRIGA Mainz

1. Introduction

A number of techniques such as calorimetric, atomic absorption and emission spectroscopy, X-ray fluorescence and mass spectrometry have been used by geologists for multi-elemental and trace analysis of mineral, meteorites, lunar rocks and other earth related materials. For any analytical method there are several desirable characteristics, above all, sensitivity, accuracy, cheapness, speed contamination by reagent blanks and possibilities of automation, which need to be considered. Relative merits of the above listed methods to some extent do suffer from one drawback or the other. Compared to these, instrumental neutron activation analysis (INAA) using HPGe γ-spectrometry offers a combination of high sensitivity, good accuracy and absence of contamination and extremely well-suited for large number of elements. Here we report on the determination of major, minor and trace elements in hematite by non-destructive activation analysis involving neutron irradiation of the samples and standard reference materials followed by γ-spectrometry. Iron is the most abundant element in the core of the earth and one of the most abundant in the earth's crust. Regarding its biological activity, iron is also the most versatile of all elements (Merian, 1991 ; Raoof et al., 1990; Erdlmann, & Retri ., 1986). In the present work instrumental neutron activation analysis was used to achieve accurate knowledge about the elemental analysis and iron content in hematite deposits.

2. Experimental procedure

Samples preparation and irradiation:

Five hematite samples have been collected for investigation. The samples were crushed to small pieces using a mechanical crusher. The crushed samples are dried at 105 ^{0}C to constant weight. The dried samples were grounded to form fine powder. Then, the powdered samples were sieved using a standard set of sieves of having diameters in the range of less than 125 μm and greater than 63 μm. Every powdered sample was shacked using an electric shaker. For X-ray fluorescence 8 g from the powdered sample and 1.6 g from wax material are pressed under 300 N/cm^{2} to give a disc with 4-cm diameter. These discs are then measured by XRF.

For neutron activation analysis, polyethylene capsules filled with 100 mg of powder samples are irradiated together with the standard reference materials by thermal neutrons using irradiation facilities at the TRIGA Mainz research reactor. Three different cycles of irradiation are applied (KCh-Report, TRIGA Mainz, 1989). Two short activations followed by one gamma measurement (Kz1 and Kz2) and one long time activations followed by three gamma measurements (Lz1, Lz2 and Lz3). Tables 1 and 2 summarizes the irradiation cycles, measuring conditions and the nuclear data for the elements determined (El Abd, 2008; "El-Taher ., 2010 a-c).

Instrumentation:

All γ-measurements were performed with a HPGe (efficiency 29%, resolution 1.7 keV at 1332 keV ^{60}Co and 0.686 keV at 122 keV ^{57}Co) with standard amplifier and ADC-converter. The detector is shielded in a chamber of 2 layers of lead (10 cm

thick), copper (0.3 mm thick) and finally cadmium (1mm thick) with dimensions 30x30x30 cm to prevent back scattering of gamma-rays. The measurements were performed and spectra analysed with the Intergamma software. The element contents were determined relative to certified reference materials (WSE, PMS) produced by the Open University Milton Keynes, U.K as geostandards. They were irradiated and measured under the same conditions. The electronic dead time in all measurements was less than 10 % and was corrected by Intergamma Software.

Table (1): Irradiation cycles of the elements determined.

Activation cycle	Thermal neutron flux (cm^{-2} s^{-1})	Irradiation time	Decay time	Measuring time	Elements Determined
Kz1	$1.7x10^{12}$	1 min	5 min	4 min	Mg, Al, Ca, Ti, V
Kz2	$1.7x10^{12}$	5 min	1 h	15 min	Na,K,Mn, Ba, Eu
Lz1	$0.7x10^{12}$	6 h	2 d	1 h	Na, K,Ga, As, La, Sm, U
Lz2	$0.7x10^{12}$	6 h	14 d	8 h	Sc,Cr,Fe,Co,Zn,Rb,Zr,Sn,Ba, Ce,Nd, Eu, Yb, Lu, Hf,Ta,Th
Lz3	$0.7x10^{12}$	6 h	28 d	8 h	Sc, Cr, Fe, Co, Zn, Nb, Sn,Ba Cs, Ce, Eu, Yb, Lu, Hf, Ta, Th

Table (2): The nuclear data for the detected elements (Erdtmann, 1976 & Kinsey,1996).

Element	Activation product	Energy keV	$T_{1/2}$	Kz1	Kz2	Lz1	Lz2	Lz3	Detection Limits (μg/g)
Al	^{28}Al	1179	2.2m	*					35
As	^{76}As	559	26.3h		*	*			0.3
Ba	^{131}Ba	496	11.8d				*	*	16.4
Ca	^{49}Ca	3984	8.7m	*					10
Ce	^{141}Ce	145	32.5d				*	*	0.3
Co	^{60}Co	1332	5.3y				*	*	0.2
Cr	^{51}Cr	320	27.7d				*	*	0.5
Cs	^{134}Cs	604	2y					*	0.07
Eu	^{152}Eu	1408	13.3y				*	*	0.09
Fe	^{59}Fe	1099	44.5d				*	*	75
Ga	^{72}Ga	834	14.1h			*			0.6
Hf	^{181}Hf	428	42.4d				*	*	0.06
K	^{42}K	1524	12.4h		*	*			90
La	^{140}La	1596	40.3h			*			0.4
Lu	^{177}Lu	208.4	161d				*	*	0.01
Mg	^{27}Mg	1014	9.5m	*	*				1.7
Mn	^{56}Mn	846	2.6h		*				0.01
Na	^{24}Na	1369	15h		*	*			1.2
Nb	^{95}Nb	765	35d					*	2.2
Nd	^{147}Nd	531	11d				*	*	3.8
Rb	^{86}Rb	1077	18.7				*	*	2.6
Sc	^{46}Sc	889	38.8d				*	*	0.007
Sm	^{153}Sm	103	46.3h		*	*			0.03
Sn	^{117}Sn	158	13.6d				*	*	9.6
Ta	^{182}Ta	1221	115d				*	*	0.11
Th	^{233}Pa	312	27d				*	*	0.2

Ti	^{51}Ti	320	5.8m	*					0.4
U	^{239}NP	106	2.4d			*			0.3
V	^{52}V	1434	3.4m	*					0.003
Yb	^{169}Yb	198	32d				*	*	0.05
Zn	^{65}Zen	115	244d				*	*	3.2
Zr	^{95}Zr	756	64d				*		19

3. Results and Discussion

The elemental constituents of the samples under investigation in the present work were determined by means of the activities induced by (n,γ) reactions. The gamma rays emitted were identified according to the energies of the well resolved gamma ray lines taking into consideration that some of the product isotopes could exhibit more than one gamma-ray line. Thirty-two elements were identified in hematite samples. The average concentration values are expressed in units of ppm for all elements except for Al, Na, K, Mn, Mg, Ca, Fe and Ti in units of g/kg.

The statistical counting errors are,
< 2 % for Na, Mn, Sc, Co, Zr, Hf, Al, Sm,
2-5 % for V, Eu, La, Cr, Fe, Sn, Ce, Yb, Lu, Th,
5-10 % for Ta, Cs, Zn, As, K,
10-20 % for Mg, Ti, Ca, Ga, Rb, Nb,
20-30 % for Ba, U.

From the results we can conclude that the elemental contents of hematite samples were,
< 10 ppm for Lu, Ta, Th, U, Yb, Cs,
10-50 ppm for As, Ce, Co, Eu, Ga, Hf, Nb, Rb, Sc, Sm,
50-100 ppm for La, Zn, Zr,
>100 ppm for Ba, Cr, V,
> 1 % for Al, Ca, Fe, K, Mg, Mn, Na, Ti.

Table (3) shows the elemental analysis of hematite samples determined by both INAA and XRF techniques. There are also some elements which can only determined by XRF such as F, P, Si, Cu, Mo, Ni, Pb, Sr and W. The average contents of these elements are 1.8, 0.5, 21.5, 53, 5, 46, 31, 255 and 36 ppm, respectively except for the contents of the elements F, P, S and Si in units of g/kg.

X-Ray Fluorescence (XRF) analysis of hematite

Though XRF is one of the most important techniques for the analysis of metals and trace elements, it is also independent of the chemical form of the element as INAA. X-rays emitted from an ionized atom have energies characteristic of the element involved; and the intensity of an X-ray is proportional to the concentration of an element and the strength of the ionizing source. Thus, X-ray fluorescence XRF analysis is based on the generation of characteristic X-rays from a sample irradiated by an energetic beam and hence, capable of measuring the concentrations of different elements in the sample (Eberhardt, 1989).

Determination of iron concentration in hematite

The constituents of the iron were determined by means of activities induced by (n,γ) reactions. The ^{59}Fe ($t_{1/2}$ = 45d) γ-peak at 1099 keV was used for the Fe determination. Quantitative analysis was carried out for each Fe isotope by comparing the activities from the favourable peak in the gamma spectra of the samples with those of the standard reference materials. In this analysis we used the ^{59}Fe peak, since this peak has less interferences than lower-energy peaks due to the Compton effect. Table (4) lists the concentration values with their accuracy for iron in the five samples obtained by both, NAA and XRF techniques. The value of iron concentration in hematite samples of 57.7 % is in fair agreement with the results reported by (Sroor et al., 2001).

Rare Earth Elements

Rare earth elements are becoming more and more technologically significant due to their widespread utility as fine chemicals in modern industry. The main areas of application of the REE are in solid state lasers and superconducting materials. Activation analysis plays a preponderant part in REE determination. The accuracy and the limit of detection of the REE data using INAA depends strongly on the type of material analysed. Polyethylene capsules filled with 100 mg of hematite and standard reference materials were irradiated for 6 hours in the rotary specimen rack of the Mainz TRIGA research reactor by a thermal neutron flux of $7x10^{11}$ n/cm^2.s. After the irradiation, two measurements were performed for each sample. The elements La and Sm were measured 2 days after the end of irradiation. A second measurement after 14 days cooling time allowed the determination of the elements Ce, Nd, Eu, Yb and Lu. Table 3 shows the concentration values of REE in hematite samples. The results obtained indicate the viability of using the INAA for the determination of the elements La, Ce, Nd, Sm, Eu, Yb and Lu (El-Taher et al, 2003; El-Taher, 2007 and El-Taher , 2010 d).

Determination of uranium and thorium content

Instrumental neutron activation analysis techniques have been used to determine the elemental concentrations of uranium and hematite samples. They also allow to overcome many of the limitations encountered in other methods. For INAA, the samples were irradiated for 6 hours in the rotary specimen rack of the TRIGA Mainz research reactor. After two days of cooling time the samples were counted for 1 hour for ^{238}U. For the thorium case, the samples were counted 8 hours after 14 and 28 days cooling time. The activation converts ^{238}U and ^{232}Th into ^{239}Np and ^{233}Pa, respectively (El-Taher et al., 2004 and El-Taher , 2010 e). The average concentration values for uranium and thorium presented in our study are listed in Table 3.

Table (3): The average values of the elements determined in hematite in by INAA and XRF.

Element and Units	Activation product	Energy keV	T ½	INAA	XRF
Al %	^{28}Al	1179	2.24m	12.1	8.8
Ca %	^{49}Ca	3084	8.72m	6.7	6.1
Fe %	^{59}Fe	1099	44.5d	58.1	54.4
K %	^{42}K	1524	12.4h	1	0.9
Mg %	^{27}Mg	1014	9.46m	4	1.1
Mn %	^{56}Mn	847	2.58h	3.3	0.3
Na %	^{24}Na	1369	14.5h	0.8	0.2
Ti %	^{51}Ti	320	5.8m	1.3	1.1
As ppm	^{76}As	559	26.3h	16	13
Ba ppm	^{131}Ba	496	11.5d	440	348
Ce ppm	^{141}Ce	145	32.5d	43	+
Co ppm	^{60}Co	1332	5.3y	47	47
Cr ppm	^{51}Cr	320	27.7d	173	201
Cs ppm	^{134}Cs	604	2y	0.4	+
Eu ppm	^{152}Eu	1408	13.3y	17	+
Ga ppm	^{72}Ga	834	14.1h	14	+
Hf ppm	^{181}Hf	482	42.4d	15	+
La ppm	^{140}La	1596	40.3h	52	+
Lu ppm	^{177}Lu	208	161d	1	+
Nb ppm	^{95}Nb	765	35d	24	+
Nd ppm	^{147}Nd	531	11d	62	+
Rb ppm	^{86}Rb	1077	18.7d	26	+
Sc ppm	^{46}Sc	889	38.8d	15	+
Sm ppm	^{153}Sm	103	46.2h	13	+
Sn ppm	^{117}Sn	159	13.6d	12	2
Ta ppm	^{182}Ta	1221	115d	2	+
Th ^{a} ppm	^{233}Pa	312	27d	8	+
U ^{a} ppm	^{239}Np	106	2.35d	3	+
V ppm	^{52}V	1434	3.4m	**314**	**313**
Yb ppm	^{169}Yb	198	32d	**7**	**+**
Zn ppm	^{65}Zn	115	244d	**97**	**67**
Zr ppm	^{95}Zr	756	64d	**220**	**+**

Table (4): Concentration of iron Hematite by INAA and XRF

Sample number	INAA* * 2 weeks decay time	Error %	INAA** ** 4 weeks decay time	Error %	XRF
1	58.1	2.3	57.4	2.5	54.4
2	57.7	2.3	57.2	2.5	54.2
3	57.5	2.5	56.8	2.5	53.9
4	57.3	2.5	56.3	2.5	53.4
5	57.7	2.5	56.5	2.5	53.6
Average %	57.7		56.8		53.9

Conclusion

In conclusion, the applied technique (INAA) is quite successful in obtaining an accurate concentration of elemental constituents of hematite samples. Also, it can be concluded that, from the economical point of view the hematite field is suitable for iron production due to its high iron content. It is hoped that the data presented here will be useful to those dealing with geochemistry of hematite and related fields.

Acknowledgement

The authors, wishes to thank Dr. N. Trautmann and the staff of the TRIGA Mainz research reactor for assistance during the progress of the work.

Corresponding author
W.R. Alharbi
Physics Department, Faculty science for Girls, king Abdulaziz University, Jeddah, Saudi Arabia
walhrbi@kau.edu.sa

References

Eberhardt, H, 1989. "Röntgenflureszenz analyse". Springer Verlag, Berlin.

El Abd, A., 2008 "Determination of iron and nickel in geological samples by activation analysis with reactor fast neutrons" , presented at the 3 rd Environmental Physics Conference, Aswan, Egypt, Feb 19-23.

El-Taher, A.., Nossair, A,, Azzam, A.H. ratz, K.L and Abdel Halim, A.S. 2004. Determination of traces of uranium and thorium in some Egyptian environmental matrices by instrumental neutron activation analysis" Environmental protection Engineering, Vol 30, pp 19-30.

El-Taher, A., Kratz, K.L., Nossair, A., Azzam, A.H., 2003 Determination of gold in two Egyptian gold ores using instrumental neutron activation analysis. J. Radiation Physics and Chemistry, 68,751 - 755.

El-Taher, A., 2007 Rare earth elements in Egyptian granite by instrumental neutron activation analysis. J. Appl. Radiat. Isot., 65, 458-464.

El-Taher, A., 2010 a Elemental Analysis of two Egyptian Phosphate rock mines by Instrumental Neutron Activation Analysis and Atomic Absorption Spectrometry. J Appl. Radiat & Isot. 68 511-515.

El-Taher, A., 2010 b Determination of Chromium and Trace Elements in El-Rubshi Chromite from Eastern Desert Egypt by Neutron Activation Analysis.Appl. Radiat & Isot. 68, 1864-1868.

El-Taher, A., 2010 c Elemental Content of Feldspar from Eastern Desert, Egypt, determined by INAA and XRF. Appl. Radiat & Isot. 68, 1185-1188.

El-Taher, A., 2010 d Rare Earth Elements Content in Geological Samples from Gabal Gattar Eastern Desert-Egypt Determined by INAA. Appl. Radiat & Isot. 68, 1859-1863.

El-Taher, A., 2010 e INAA and DNAA for uranium determination in geologica samples from Egypt. Appl. Radiat & Isot. 68, 1189-1192.

Erdtmann, G. 1976 "Neutron Activation Tables". Verlag Chemie, Weinheim,

Erdlmann, G. And Retri, H, 1986. Nuclear Activation Analysis Fundamentals and Techniques, Copyright by John Wiley and Sons, Inc.

KCh-Report, 1989 Tables for Neutron Activation, TRIGA Mark II Mainz Research Reactor.

Kinsey, R., 1996. PC NU Dat. Electronic Nuclear Data Services. Version 1.0.

Merian, E, 1991 "Metals and their compounds in the environment". VCH, Weinheim, New York.

Raoof, M A., Naeem, A., Zaghloul, R., Abdel Fatah, A and Obied, M.A., 1990 Multielement neutron activation analysis of an iron ore. Journal of radioanalytical and nuclear chemistry 60, 273-279.

Sroor, A, Abdel-Baset, N, Abdel-Haleem, A.S,., and Hassan, A.M, 2001 "Elemental analysis of two Egyptian iron ores and produced industrial iron samples by neutron activation analysis". Appl. Radiation and Isotopes, 54, 559-562.

12/2/2012