

Determination Rydberg Constant using X-ray Fluorescence Spectroscopy

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Abstract: X-ray fluorescence is a non-destructive compositional analysis technique, which allows the measurement in field, requiring minimum to no sample preparation. This mini-review presents the physical principles and examples of applications of XRF for the analysis in this study X-ray Fluorescence Spectroscopy (XRF). Technique is widely used for the determination of both major and trace elements in three iron oxides (Hematite, Magnetite and Kagnatite) such as Fe, Mn, Cu, As, Pb, and Rb, at low and different concentration. Moseley's Law was conducted to determine the concept's strength, and the value of the Rydberg constant R_∞ for each sample (Hematite, Magnetite and Kagnatite) was determined to be $2.233 \times 10^{-18} \text{ J}$, $2.144559 \times 10^{-18} \text{ J}$ and $2.329451 \times 10^{-18} \text{ J}$ respectively.

Keywords: Rydberg constant R_∞ , X-ray fluorescence spectroscopy (XRF)

1. Introduction

X-Ray Fluorescence Spectroscopy (XRF), is an elemental qualification technique with broad application in science and industry [1]. It's an analytical method to determine the elements composition of samples as liquid, solid powder and thin film due to ability to provide reliable qualitative and quantitative information about the composition of materials. The methods are fast and non-destructive and usually require minimum of sample preparation. The applications are very broad and include the metal, oil, polymer, plastic and food industries along with mining geology, petrology, mineralogy, archaeology agriculture], forensics and art conservation [2] when atoms in a material sample are excited by the primary X-radiation, electrons from the innermost shells are released; the resultant vacancies are then filled by electrons from the outer shells. Consequently, energy is released in the form of the photon which is equal to the difference of the energy of the involved orbitals see Fig 1. This emitted radiation and energy is unique to the material involved and can be used to identify different elements and their concentrations in a sample [3]. This is read by the detector and the data plotted as intensity (counts/s) as a function of energy (KeV) [4].

This observed intensity for given atoms represents the amount of that particular atoms present in the sample. Therefore, XRF provides qualitative and quantitative data for involved atoms of the elements in the sample. In other words, qualitative approach provides information of involved elements in the sample by identifying atoms associated with the observed characteristics lines of the corresponding atom [5].

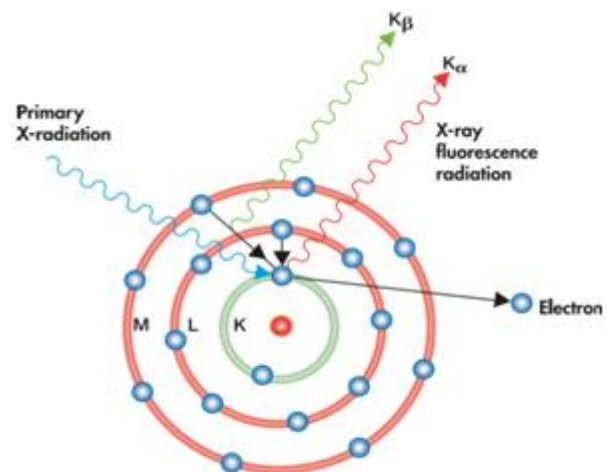


Figure 1: Schematic of X-ray Fluorescence in an Atom

2. Theory

Moseley, who was studying K_α X-ray spectra at the same time as Bohr, used this expression, but modified Z to $Z-1$ to fit to his experimental data. Thus, Moseley's relationship [3] was,

$$E = \frac{3R_\infty(Z-1)^2}{4} E_{K\alpha} \dots\dots\dots (1)$$

E = the Energy in J ,

R_∞ = the Rydberg constant (m^{-1}),

Z = the atomic number.

$$R_\infty = \frac{4}{3} \text{Slope} \dots\dots\dots (2)$$

Where the slope is equal the rate of energy in joule divided by $(Z - 1)^2$. The above equation is usually referred to as Moseley's law

3. Experimental part

3.1 Sample Preparation

Three samples of iron oxide: (Hematite, Magnetite and Akaganeite), prepared through the chemical methods. Firstly, the Hematite (Fe_2O_3), was obtained using 40 grams of ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) was dissolved in 500 ml of twice distilled water in polyethylene flask. Then, 300 ml of one molar (1M) potassium hydroxide (KOH), was added to the flask followed by 50 ml of one molar (1M) NaHCO_3 . The mixtures were heated to 90°C , till formation of red brown precipitates of Ferrihydrite. The flask and the content were allowed to stand for 48 hours. During this time the red brown suspension of Ferrihydrite was transformed to Hematite with pH of 8 to 8.5 [6]. Secondly, the Magnetite (Fe_3O_4), sample can be obtained, using Fe^{11} Sulphate in air at 500°C through equations [6].

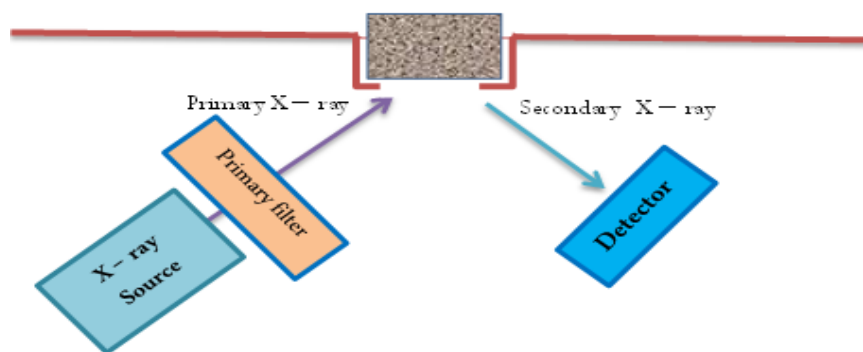
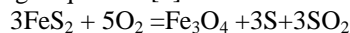


Figure 2: XRF Set up

3.3 Experimental procedure

EDXRF spectrometer was used to quantify the elemental compositions in three samples (Hematite, Magnetite and Kagnatite). The atoms in the samples material are excited directly with $\text{Cd}109$ radioactive source as source excitation for a life time of 100s, and fluorescence coming from the sample were detected using Si (Li) with Full Width at Half Maximum intensity (FWHM) equal 190 eV at 5.96 KeV. The detector receives all excited lines of all the specimen elements at once. For each incident x-ray photon, the detector generates a pulse of electric current having height proportional to its photon energy. The detector output is amplified and subjected to electronic pulse-height analysis to separate the pulses arising from the several detected wavelengths on the basis of their heights and thereby on the basis of the photon energies of the incident x-ray lines. By appropriate setting of the operating parameters, the pulses of each line of interest can be measured individually.

4. Result and discussion

The statistical data obtained for each three samples analyzed beginning after samples convert to bulk types and analysis three times and major and trace elements listed in parts per million. The XRF results are presented for each sample. In Hematite sample, the values of some trace elements, such as Fe, Mn, Cu, Rd and Rb were collected and this mentioned in the literatures (8, 9). The average percentage elemental

Thirdly, Akaganeite (FeOOH), 0.1 molar (0.1M) of FeCl_3 solutions was held in to 2 liters in closed vessel at 70°C for 48h. During this time the pH of the system drops from 1.7 to 1.2 and compact yellow precipitate of Akaganeite was formed [7].

3.2 Equipment

Energy Dispersive X-ray Fluorescence spectrometer {EDXRF} was used in shown in Fig.2 EDXRF provides one of the simplest, most accurate and most economic analytical methods for the determination of the chemical composition of many types of materials. And provides detection limits at the sub-ppm level; it can also measure concentrations of up to 100% easily and simultaneously. EDXRF spectrometer contains the x-ray tube or radioactive material primary filter (to filter out unwanted x-ray peaks), sample chamber, detector, detector electronics.

composition of include: Fe(214746ppm), Mn (275.29ppm), Cu (100 ppm), Rd(24.14ppm), and Rb(15.96 ppm). Recording of the X-ray fluorescence spectra (K_α -lines) of different elements and determination of the corresponding X-ray energies see Fig.3 and table (1). The energy values have been plotted in Figure 4 against $(Z-1)^2$, yielding a linear relationship.

The slope of the curve is 0.01674395 keV. By using Moseley's Law (1), we obtain the value for the Rydberg constant equals 2.233×10^{-18} joule and this agreed with the results of other research.

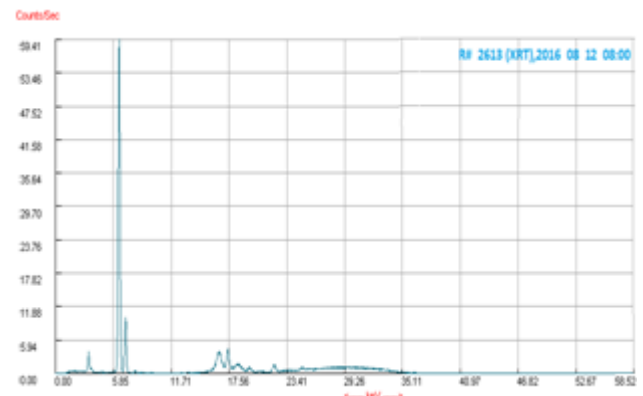


Figure 3: XRF spectrum of Hematite sample

Table 1: Trace Element Concentrations in Hematite Sample

Element	% Content/ ppm	% Error/ ppm	Energy gap (Kev)	Atomic Number (z)	(Z-1) ²	Energy (J) × 10 ⁻¹⁶
Mn	275.29	275	5.85	25	576	8.94
Fe	21474622	1991.51	6.4	26	625	10.25
Cu	100	70	8.2	144	784	13.14
Rb	24.14	5.6	14.8	37	1296	23.71

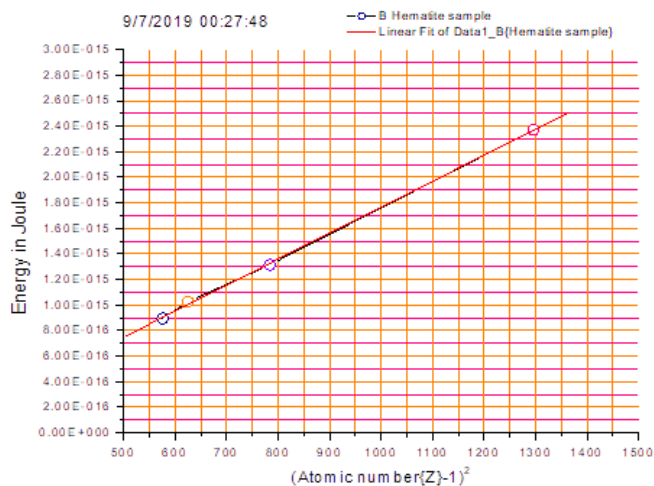


Figure 4: Graph of the energy (J) gap values of Hematite sample versus $(Z - 1)^2$ as shown in the table 1

Secondly in Fig.5 spectrum XRF of magnetite show, major and trace elements in sample that were listed in Table.2 in parts per million the values of some trace elements were collected and the average percentage elemental composition of include: Fe (21474622 ppm), Mn (275.29 ppm), Cu (100 ppm) and Rb(24.14ppm). The energy values have been plotted in Fig.6 against $(Z - 1)^2$, yielding a linear relationship, the slope of the curve equal 0.017696keV. Using Moseley's Law (1), we obtain from the slope the following value for the Rydberg constant $R = 2.144559 \times 10^{-18}$ J this agrees sufficiently well with the value in the literature [10].



Figure 5: XRF spectrum of Magnetite sample

Table 2: Trace Element Concentrations in Magnetite Sample

element	% Content/ ppm	% error /ppm	Energy gap (Kev)	Atomic number	(Z - 1) ²	Energy gap(J) × 10 ⁻¹⁶
Mn	275	275	6.0	25	576	9.61
Fe	21474622	1991.51	6.9	26	625	11.06
Cu	100	70	8.6	29	784	13.78
Rb	24.14	5.6	15.8	37	1296	25.31

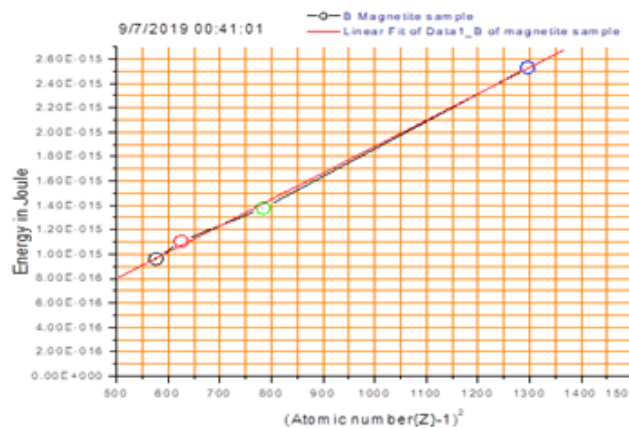


Figure 6: Graph of the gap values of magnetite sample versus $(Z - 1)^2$ as shown in the table 2

In Akaganeite sample spectrum XRF figure.7 show ,most of elements found in sample that were recorded in Table .3 in parts per million and the average percentage elemental structure contain: Fe (1,524,175.42 ppm), Mn (5,967.3), Cu (601.38 ppm) and As(102.21). The energy values have been plotted against $(Z - 1)^2$ noted in Fig.8; yielding a linear relationship. The slope of the curve is 0.0174708825keV. By using Moseley's Law (1), we obtain from the slope the following value for the Rydberg constant 2.329451×10^{-18} J according to reference [11].

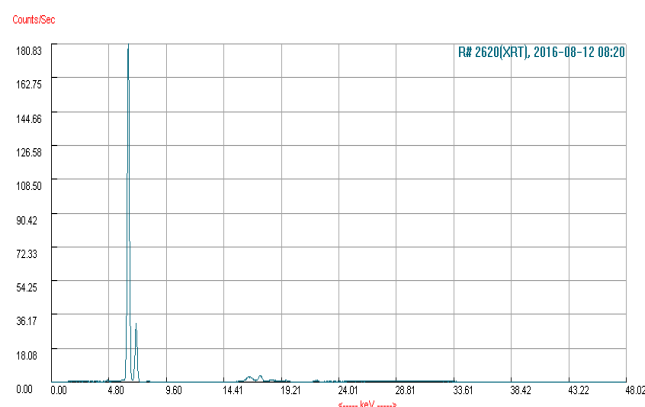


Figure 7: XRF spectrum of Akaganeite sample

Table 3: The analysis data of XRF of Akaganeite

Element	% Content/ ppm	%Error/ ppm	Energy gap (Kev)	Atomic Number	(Z-1) ²	Energy gap(J) × 10 ⁻¹⁶
Mn	5,967.3	275	6.50	25	576	10.41 × 10 ⁻¹⁶
Fe	1,524,175.42	1991.51	7.00	26	625	11.22 × 10 ⁻¹⁶
Cu	610.38	70	8.6	29	784	13.78 × 10 ⁻¹⁶
As	102.21	5.6	10.62	33	1024	16.98 × 10 ⁻¹⁶

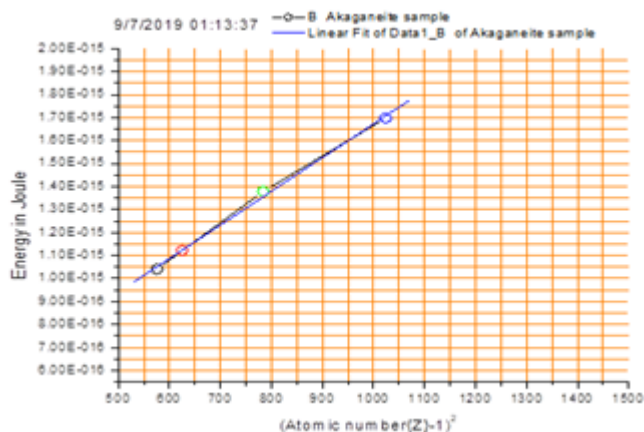


Figure 8: Graph of the gap values of Akaganeite sample versus $(Z - 1)^2$ as shown in the table 3

5. Conclusions

X-ray fluorescence spectroscopy it's a powerful tool method for estimation elemental concentration in three iron oxide samples (Hematite, Magnetite and kagnatite). Alsois reliable method for determination the value of the Rydberg constant, small sample preparation, high-stability and precision, Speed of analysis and Wide dynamic range

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Reading No	Time	Type	Duration	Units	Rb	Rb Error	Pb	Pb Error	As	As Error	Cu	Cu Error	Fe	Fe Error	Mn	Mn Error
2613	#####	BULK	101.16	ppm	21.32	5.47	26.8	14.62	-5.25	11.03	83.95	70.4	214746.2	1991.51	386.33	286.11
2614	#####	BULK	104.19	ppm	23.61	5.58	18.43	13.4	12.29	11.74	139.31	72.15	214087.7	1959.46	141.55	270.7
2615	#####	BULK	104.97	ppm	27.42	5.77	2.66	11.01	17.6	10.63	77.41	67.45	214016.3	1929.79	298	271.81
2616	#####	BULK	100.51	ppm	14.19	8.85	53.86	26.72	-28.57	22.21	129.46	154	2157950	9631.34	1626.35	1266.38
2617	#####	BULK	15.21	ppm	-11.3	23.17	-30.56	59.44	-36.13	51.63	-59.37	673.77	2154942	33019.85	2993.37	4448.13
2618	#####	BULK	116.48	ppm	-1.64	5.45	-3.44	12.3	-1.92	14.56	187.42	121.44	1889880	7578.72	2211.59	1014.98
2619	#####	BULK	102.07	ppm	-0.35	6.29	7.34	16.79	-8.79	16.96	192.9	138.84	1871727	8340.38	2490.16	1122.26
2620	#####	BULK	102.03	ppm	8.05	9.24	112.62	39.08	103.9	41.69	705.15	210.81	1743512	9347.5	5264.61	1357.94
2621	#####	BULK	96.62	ppm	8.71	9.36	86.45	37.5	69.31	37.95	548.29	211.77	1259682	8210.84	5344.53	1250.03
2622	#####	BULK	101.21	ppm	12.52	10.41	64.96	35.6	133.42	43.02	577.72	225.42	1569332	9374.8	7292.76	1438.92
2623	#####	BULK	103.56	ppm	4.52	7.33	38.88	24.74	-25.33	19.64	208.91	156.75	1559528	8033.46	-3051.09	925.98
2624	#####	BULK	101.96	ppm	4.74	7.19	10.56	18.33	-9.26	17.09	152.62	141.85	1568616	7760.45	-3636.95	872.79
2625	#####	BULK	105.03	ppm	-0.99	5.94	29.04	21.15	3.93	20.27	231.38	141.45	1552348	7553.39	-2576.12	882.72