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Elemental Analysis of Six Mines in Erzincan Region Using Wavelength-Dispersive X-Ray Fluorescence Spectrometry

N. EKINCI[1], E. KAVAZ[1,*], E. CINAN[1] and C. SEVINDIK[2]

[1]Department of Physics, Science Faculty, Atatürk University, 25240 Erzurum, Turkey
[2]Department of Geography, Art Faculty, Atatürk University, 25240 Erzurum, Turkey

*Corresponding author: Fax: +90 442 2360948; Tel: +90 442 2314083; E-mail: esrakvz@gmail.com

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This investigation concentrated on mines in the eastern Erzincan region of Anatolia, Turkey. Wavelength-dispersive X-ray fluorescence spectrometry was used to determine elemental concentrations of the ores taken from six different mines. The presence of C, O, Mg, Al, Si, P, Cl, K, Ca, Ti, V, Cr, Mn, Zn, As, Sr and Ba elements in ores were found. The relative errors for results have been given ± 7 %.

Keywords: Wavelength-dispersive X-ray fluorescence, Ore.

INTRODUCTION

Turkey has traditionally been a source of economic minerals and ores and is an important part of its economy and the world's economy. The demand for these resources is magnified in the 21st century by the explosion of high-tech electronic devices.

Several techniques for mineral analysis are employed globally, but wavelength dispersive X-ray fluorescence analysis (WDXRF) is the most accepted analytical method. Its desirable characteristics are the accuracy and precision for elemental concentrations from 100 % down to the trace level. Many mines and service laboratories use this instrument for its ease of operation, discrimination and quality and control of the exploration process. In geological surveys, the precision of analytical flexibility makes WDXRF an indispensable tool for geological research.

Recently, many researchers have focused on the elemental analysis of various materials by using WDXRF. A study of South African chromite ore, a material of great interest in the ceramic industry [1]. In another investigation from Egypt, the applicability of thermal neutron activation analysis for the determination of gold and other rare elements was found useful [2]. Because of the increasing demand in industry and agriculture, WDXRF is appropriate to use to locate deposits of phosphate ores [3]. Another article has reviewed the analysis of chromite values from various types of ores [4]. A method for the determination of germanium in coal ash by WDXRF spectrometry has been developed [5]. In the mining industry, the quality and extent of an ore body is usually determined by routine assays *via* drill cores and chip samples. Wavelength dispersive X-ray fluorescence spectrometry can give both the elemental composition and the mineralogical classification critical for the exploration of an ore body [6].

Turkey has a geography of diverse mineral deposits. This study focuses on eastern Erzincan province and the concentration of elements found in its ore bodies. The locations of collected samples are given in Fig. 1.

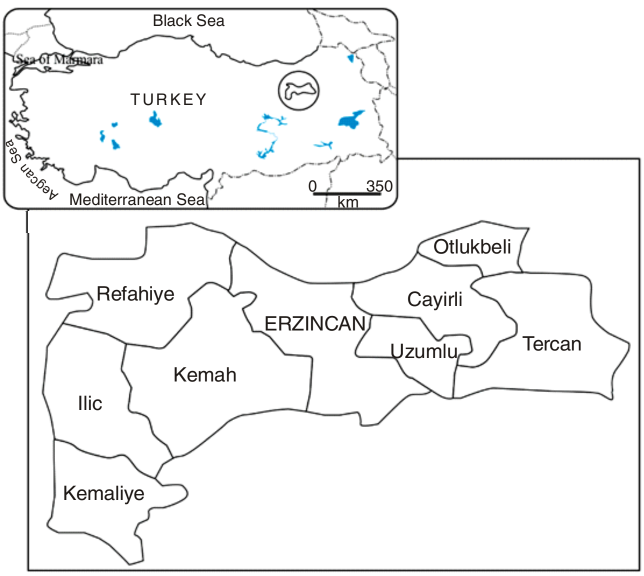

Fig. 1. Province of Erzincan collected S1, S2, S3, S4, S5, S6 samples

EXPERIMENTAL

The analysis of elements present in ores was carried out by WDXRF. A schematic of the WDXRF system is given in Fig. 2.

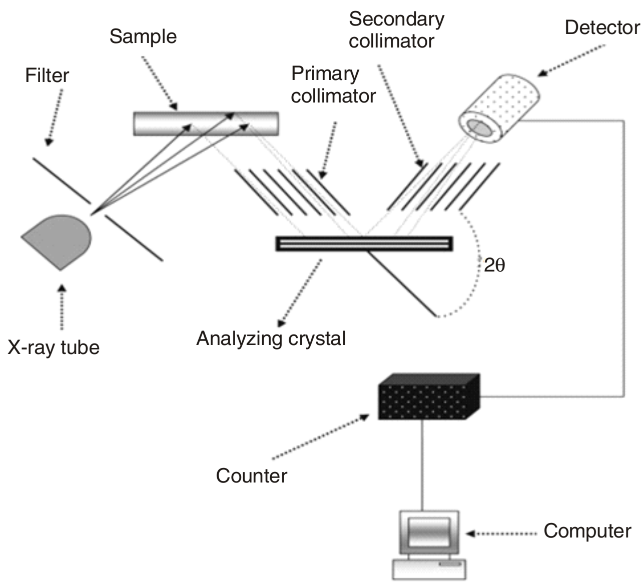

Fig. 2. Experimental system

A Rigaku wavelength-dispersive X-ray fluorescence spectrometer (ZSX-100e) with the established instrumental conditions, such as voltage (kV), current (mA), collimators, filters, attenuator, analyze crystal, detector, 12 positions and fixed counting time for Rh anode tube was used.

Ore from 6 mines within the Erzincan province were targeted collecting 3 samples from each mine. The procedure is to dry the samples in porcelain crucibles at 300 °C for 1-2 h. After drying, these materials are grounded and sieved to a mesh size of 200 μm. Then, a 10 ton hydraulic press compresses the sample powder into a thin 0.5 to 0.6 g pellet about 12 mm in diameter. The advantage of making these pellets is that interelement enhancement effects in the sample are minimized. It is well known that the measurement of thin samples in WDXRF analysis presents several advantages over the methods using thick targets. In former case, the absorption and enhancement effects are less significant and can be easily corrected or neglected. For thick samples, the increase of background by multiple scattering within the sample material causes absorption and enhancement effects that dominate over the gain in characteristic line intensity resulting from the increase in sample thickness. Each sample is then radiated for about 3 h.

RESULTS AND DISCUSSION

Qualitative Analysis Chart acquired by A Rigaku wavelength-dispersive X-ray fluorescence spectrometer (ZSX-100e) for S2 sample is presented in Fig. 3.

The mean concentrations with relative error (7 %) obtained for six ore samples using WDXRF are shown in Table-1.

The following elements were found to be present in the samples: C, O, Mg, Al, Si, P, Cl, K, Ca, Ti, V, Cr, Mn, Zn, As, Sr and Ba. Further, x and y coordinates of the samples are given.

For six mine samples, Mg concentrations ranged from 0.167 ± 0.012 to 20.539 ± 1.438 with sample 4 (S4) having the highest Mg value. Magnesium and its alloys, is a desirable metal with many applications in electronic devices. Its characteristics of low density, good mechanical and electrical properties, make it desired material in the aerospace industry.

Concentration of aluminium varied from 0.483 ± 0.034 to 5.824 ± 0.408. Sample, S6 has the highest value of aluminium. Its alloys are vital to the aerospace industry and are important in other areas of transportation and structural materials.

The silicon concentration varied from 0.638 ± 0.045 to 22.588 ± 1.581. Sample, S1 has the highest value of silicon. Most silicon is used commercially without much post-mining processing. These include direct industrial building-use of clays, silica and stone. Silica is commonly used in used in ceramic brick. Elemental silicon also has a large impact on

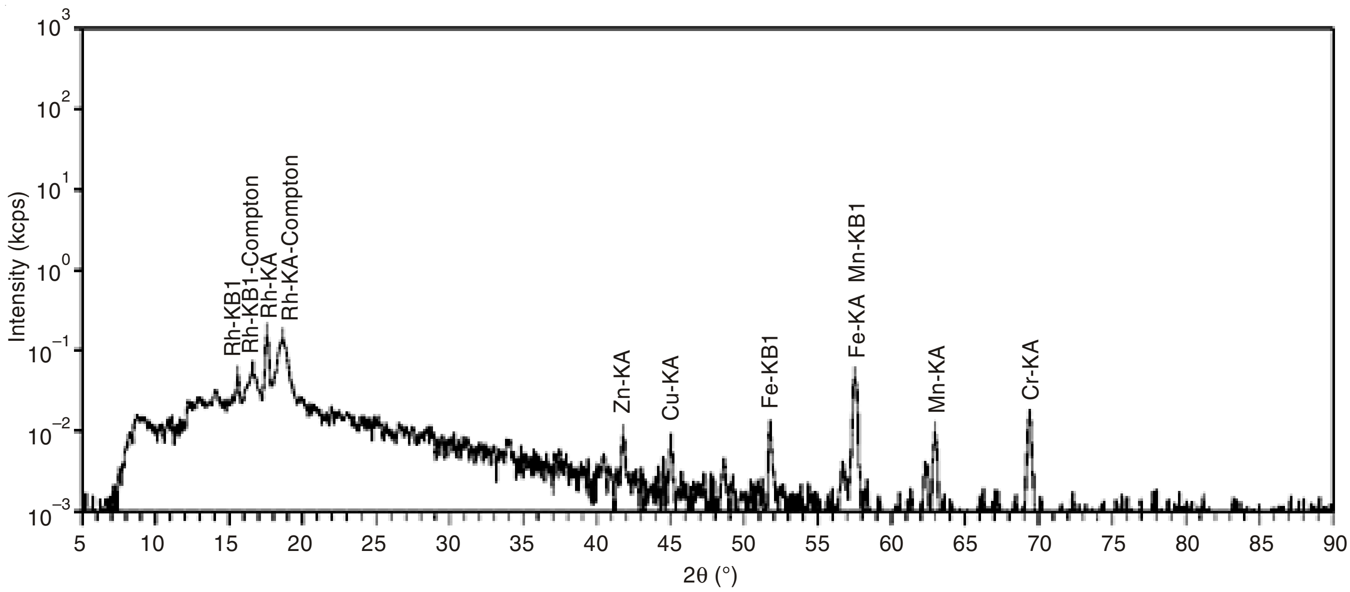

Fig. 3. XRD obtained from sample 2

TABLE-1
MEAN CONCENTRATIONS (%) OF SIX ORES AMPLES WITH RELATIVE ERROR 7 % USING WDXRF

Element	Concentration (%)					
	S1 X = 490245 Y = 4408618	S2 X = 462431 Y = 4367207	S3 X = 477534 Y = 4416987	S4 X = 479581 Y = 4417375	S5 X = 500524 Y = 406647	S6 X = 475421 Y = 4419966
C	0.835 ± 0.584	3.031 ± 0.212	1.029 ± 0.072	0.997 ± 0.069	1.077 ± 0.075	0.835 ± 0.058
O	49.632 ± 0.347	42.335 ± 2.963	44.670 ± 3.127	45.045 ± 3.153	44.389 ± 3.107	46.235 ± 3.236
Mg	0.234 ± 0.016	0.167 ± 0.012	16.215 ± 1.135	20.539 ± 1.438	19.283 ± 1.349	16.326 ± 1.143
Al	0.593 ± 0.041	0.483 ± 0.034	2.935 ± 0.205	5.094 ± 0.356	3.125 ± 0.219	5.824 ± 0.408
Si	22.588 ± 1.581	0.638 ± 0.045	13.603 ± 0.952	17.343 ± 1.214	15.146 ± 1.060	9.650 ± 0.676
P	0.034 ± 0.002	0.009 ± 0.001	0.008 ± 0.001	–	0.011 ± 0.001	–
Cl	–	–	0.107 ± 0.008	0.147 ± 0.010	–	0.093 ± 0.007
K	0.078 ± 0.005	0.017 ± 0.001	–	0.018 ± 0.001	0.018 ± 0.001	0.034 ± 0.002
Ca	4.861 ± 0.340	52.927 ± 3.705	3.829 ± 0.268	0.244 ± 0.017	0.209 ± 0.015	0.040 ± 0.003
Ti	–	–	0.047 ± 0.003	0.051 ± 0.004	–	0.052 ± 0.004
V	–	–	0.023 ± 0.002	0.036 ± 0.003	0.043 ± 0.003	0.047 ± 0.003
Cr	–	0.133 ± 0.009	14.164 ± 0.991	7.619 ± 0.533	13.586 ± 0.951	17.581 ± 1.231
Mn	20.967 ± 1.468	0.059 ± 0.004	–	–	–	–
Zn		0.010 ± 0.001	0.016 ± 0.001	0.009 ± 0.001	0.007 ± 0.001	0.011 ± 0.001
As	0.031 ± 0.002	–	–	–	–	–
Sr	0.018 ± 0.001	–	–	–	–	9.650 ± 0.676
Cu	0.016 ± 0.001	0.009 ± 0.001	–	–	–	–
S	0.024 ± 0.002	0.011 ± 0.001	0.019 ± 0.001	0.034 ± 0.002	0.029 ± 0.002	0.020 ± 0.001
Ni	–	–	0.039 ± 0.003	0.077 ± 0.005	0.074 ± 0.005	0.039 ± 0.003
Fe	–	0.172 ± 0.012	3.294 ± 0.231	2.745 ± 0.192	3.002 ± 0.210	3.211 ± 0.225
Ba	0.091 ± 0.006	–	–	–	–	–

the computer chip industry. Although most free silicon is used in the steel refining, aluminum-casting and fine chemical industries, the relatively small portion of highly purified silicon that is used in semiconductor electronics is perhaps even more critical. Because of wide use of silicon in integrated circuits, the basis of most computers, a great deal of modern technology depends on it.

Calcium concentration ranged from 0.040 ± 0.003 to 52.927 ± 3.705. Sample, S2 has the highest value of calcium. Calcium has a higher electrical resistivity, because of its lower density, than copper or aluminum. However, its use in terrestrial applications is usually limited by its high reactivity with air.

Chromium ranged from 0.133 ± 0.009 to 17.581 ± 1.231. Sample, S6 has the highest value of chromium. Chromium was regarded with great interest because of its high corrosion resistance and hardness. A major development was the discovery that steel could be made highly resistant to corrosion and discolouration by adding chromium to form stainless steel. This application, along with chrome plating (electroplating with chromium), are currently the highest demand use of the metal.

Manganese was observed in two samples. Their values are 0.058 ± 0.004 and 20.967 ± 1.468. Sample, S1 has the highest value of manganese. Manganese is found as a free element in nature (often in combination with iron) and as a component of many minerals. Manganese is a metal with important industrial metal alloy uses, particularly in stainless steels. Depending on their oxidation state, manganese ions have various colours and are used industrially as pigments.

Phosphorus was found in four samples. Their values ranged from 0.008 ± 0.001 to 0.034 ± 0.002. Sample, S1 has the highest value of phosphorus. Phosphorus is never found as a free element on earth. The vast majority of phosphorus compounds are consumed as fertilizers. Other applications include the role of organophosphorus compounds in detergents, pesticides, nerve agents and matches. Phosphorus is one of the six essential elements for biochemical reactions.

Chlorine was observed in three samples. Their values ranged from 0.093 ± 0.007 to 0.147 ± 0.010. Sample, S4 has the highest value of chlorine. Chlorine is a component of various compounds, including table salt. It is the most abundant halogen. Principal applications of chlorine are in the production of a wide range of industrial and consumer products. For example, it is used in making plastics, solvents for dry cleaning and metal degreasing, textiles, agrochemicals, pharmaceuticals, insecticides, dyestuffs, household cleaning products and others.

Potassium concentration ranged from 0.017 ± 0.001 to 0.078 ± 0.005. Sample, S1 has the highest value of potassium. Potassium ions are another essential element for living systems. Commercially, Potassium is in great demand as a fertilizer in agriculture.

Titanium was found in three samples. Their values ranged from 0.047 ± 0.003 to 0.052 ± 0.004. Sample, S6 has the highest value of titanium. Titanium is used in steel as an alloying element to reduce grain size and as a deoxidizer and in stainless steel to reduce carbon content. Titanium is often alloyed with aluminum, vanadium, copper, iron, manganese, molybdenum and with other metals. Applications for titanium mill products can be found in industrial, aerospace, recreational and emerging markets.

Vanadium concentration ranged from 0.023 ± 0.002 to 0.047 ± 0.003. Sample, S6 has the highest value of vanadium. It is mainly used to produce specialty steel alloys such as high speed tool steels. Several vanadium alloys show superconducting behaviour. Vanadium-gallium tape is used in superconducting magnets.

Zinc concentration ranged from 0.007 ± 0.001 to 0.016 ± 0.001. Sample, S3 has the highest value of zinc. Zinc is an essential mineral of exceptional biological and public health importance. Zinc deficiency affects about two billion people in the developing world and is associated with many diseases. In children, it causes growth retardation, delayed sexual maturation, infection susceptibility and diarrhea. Consumption of excess zinc can cause ataxia, lethargy and copper deficiency.

Arsenic was found only in sample S1. Its value is 0.0031 ± 0.002. It exists in various allotropes, although only the grey form has important use in industry. The main use of metallic arsenic is for strengthening alloys of copper and especially leads (for example, in car batteries). Arsenic is a common n-type dopant in semiconductor electronic devices and the optoelectronic compound gallium arsenide is the most common semiconductor in use after doped silicon. Arsenic and its compounds, especially the trioxide, are used in the production of pesticides (treated wood products), herbicides and insecticides. These applications are declining. However, arsenic is notoriously poisonous to multicellular life.

Strontium was found only in two samples. Its value is 0.018 ± 0.001 in S1 and its value is 9.650 ± 0.676 in S6. Strontium is used in scientific studies of neurotransmitter release in neurons.

Copper concentration was found in two samples. Sample, S1 has the highest value of copper. Its value in S1 is 0.016 ± 0.001. Also, its value in S2 is 0.009 ± 0.001. Copper is a ductile metal with very high thermal and electrical conductivity. It is used as a conductor of heat and electricity, a building material and a constituent of various metal alloys. The major applications of copper are in electrical wires, roofing, plumbing and industrial machinery. Copper is mostly used as a metal, but when a higher hardness is required it is combined with other elements to make an alloy such as brass and bronze. A small part of copper supply is used in production of compounds for nutritional supplements and fungicides in agriculture.

Sulfur concentration ranged from 0.011 ± 0.001 to 0.034 ± 0.002. Sample, S4 has the highest value of sulfur. Sulfur is an abundant, multivalent non-metal. The element's commercial uses are primarily in fertilizers, because of the relatively high requirement of plants for it and in the manufacture of sulfuric acid, a primary industrial chemical. Other well-known uses for the element are in matches, insecticides and fungicides. Sulfur is an essential element for all life and is widely used in biochemical processes.

Nickel concentration ranged from 0.039 ± 0.003 to 0.077 ± 0.005. Sample, S4 has the highest value of nickel. Nickel is a silvery-white lustrous metal with a slight golden tinge. Nickel belongs to the transition metals. The metal is chiefly valuable in the modern world for the alloys it forms; about 60 % of world production is used in nickel-steels (particularly stainless steel). Nickel is used in many specific and recognizable industrial and consumer products, including stainless steel, alnico magnets, coinage, rechargeable batteries, electric guitar strings, microphone capsules and special alloys. It is also used for plating and as a green tint in glass.

Iron concentration ranged from 0.172 ± 0.012 to 3.294 ± 0.231. Sample, S3 has the highest value of iron. Iron is the most common element (by mass) forming the planet Earth as a whole, forming much of Earth's outer and inner core. Iron is the most widely used of all the metals, accounting for 95 % of worldwide metal production. Its low cost and high strength make it indispensable in engineering applications such as the construction of machinery and machine tools, automobiles, the hulls of large ships and structural components for buildings.

Finally, barium was found only in S1 sample (0.091 ± 0.006). Barium is never found in nature as a free element, due to its high chemical reactivity. Barium has few industrial applications, but the metal has been historically used to scavenge air in vacuum tubes. Barium ion is a component of the YBCO (high-temperature superconductors) and electroceramics.

Conclusion

In this study, quantitative and qualitative analysis of ores were taken from six mines of Erzincan region. Through analysis using wavelength dispersive X-ray fluorescence spectrometer, the elements of: C, O, Mg, Al, Si, P, Cl, K, Ca, Ti, V, Cr, Mn, Zn, As, Sr and Ba were detected in the ore samples. The wavelength dispersive X-ray fluorescence spectrometer (WDXRF) provides superior analytical performance for most demanding tasks regarding accuracy, precision, speed and reliability in industrial and scientific research.

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