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Determination of Some Trace Heavy Metals (Pb, Cr, Cd, Mn and Zn) Levels in Iron Ores from Mines in Wollega (Ethiopia) Using Atomic Absorption Spectrometric Technique

Milkessa Fanta and Yadav OP*

Chemistry Department, Haramaya University, Dire Dawa, Ethiopia

Abstract

Concentrations of some trace heavy metals (Pb, Mn, Cr, Zn and Cd) in iron ore minerals collected from Walage, Najo and Bikilal areas in Wollega (Ethiopia) have been determined using atomic absorption spectrometric technique. The method developed was validated by recovery test. Whereas, the order of trace metals in iron ores from Nejo and Wolage was: Pb>Mn>Cr>Zn>Cd, such order of metal levels in iron ore collected from Bikilal was: Pb>Cr>Mn>Zn>Cd. However, Cd concentration in studied iron ores were below its detection limit (0.04 mg/L). The reported data on the levels of trace heavy metals in the studied iron ores may be useful in optimizing the operational parameters as trace elemental composition in an iron ore significantly influences its reduction to metallic iron in smelting operation. Also, a pre-knowledge of heavy metals' levels in iron ores is important since their presence, even in traces, affects the properties such as: ductility, brittleness, resistance to corrosion and machining qualities of the end product.

Keywords: Trace; Metals; Chromium; Absorption; Spectrometric

Introduction

Minerals are naturally occurring inorganic substances with relatively definite chemical composition and well-defined physical properties. As with the passage of time, minerals may have been contaminated with extraneous substances, therefore, it is not possible to obtain absolutely pure minerals [1]. Iron has been known since prehistoric time. It was first smelted by Asian Hittites in 3000 years BC and until the fall of their empire, around 1200 BC, the process of smelting remained undisclosed. Subsequently, the knowledge about smelting spread world over thus beginning the "Iron Age" [2]. Even though the materials of great current interests include more exotic polymers, ceramics, composites and bioengineered substances yet the Iron Age is still with us [3]. Iron is the major component of two classes of siderite namely iron meteorites (a mixture of iron and nickel) and stony meteorites. Iron, the main constituent of the Earth's core, is vast and important both in human civilization as well as living system [4,5].

Iron, a flexible silvery metal found in a combined form in a variety of minerals, is the most abundant of heavy elements in the Earth's crust and is used on a larger scale than any of other metals. Metallic iron obtained by refining of its ores has diverse applications ranging from tools to cars and massive structures [6]. Due to an easy interchange of several atoms, one mineral may degrade into another. The inclusion of even trace amounts of some elements can have profound effects on the behavioral characteristics of a batch of iron on the operation of a smelter, good or catastrophically bad. The excess of carbon and other impurities are removed in subsequent steps before getting pure iron or other materials are often added to the iron and carbon mixture to produce steel with desired properties. For instance, Nickel and manganese incorporated in steel increases its tensile strength and chemical stability and added Vanadium increases the hardness while reducing the effects of metal fatigue. While preparing stainless steel, chromium (11%) is added that increases its hardness and melting temperature and produces hard oxide at the metal surface thus preventing corrosion of the product.

Analysis of trace elements in different minerals can provide important information on the geology of the mines and mineral localities [7]. A knowledge of trace elements' level in iron minerals is, particularly, of significance as these are involved in the production of iron and steel, a material of priority for infrastructural development. Trace elemental composition in iron ore also influences its reduction to metallic iron in smelting operations [8]. Therefore, trace elemental analysis in these materials and the certification of their contents in reference materials becomes important.

Kaczorek et al. [9] studied the content and binding forms of heavy metals, aluminium and phosphorus in bog iron ores from Poland. They observed a distinct relationship between the content of Fe and the quantity of other metals. Stephen and Oladele [10] determined baseline concentration levels of some heavy metals in the top soil around the iron ore deposit at Itakpe North Central Nigeria. They observed a decreasing gradient in the heavy metals concentrations from top soil (0-15 cm) to depth 110 cm. Ameh [11] has reported the distribution of heavy metals in soil around Itakpe Iron-ore Mining Area. Zhang et al. [12] have developed an online X-ray Fluorescence (XRF) analysis technique for determining heavy metals in pulverized coal on a conveyor belt. Stafilov and Zendelovska [1] developed flame and Zeeman electrothermal atomic absorption spectrometric (ETAAS) method for determining Pb, Co, Ni, Cr, Zn and Mn in iron minerals siderite ($FeCO_3$), hematite (Fe_2O_3), pyrite and marcasite (FeS_2) originated from different mines in the Republic of Macedonia. They eliminated the interference of Fe in the analysis of other metals by extracting the former using isoamyl acetate in hydrochloride acid solution.

We report, here, work on the quantitative evaluation of some trace

***Corresponding author:** Yadav OP, Chemistry Department, Haramaya University, Post Box: 138, Dire Dawa, Ethiopia, Tel: 9180596026; E-mail: yadavop02@yahoo.com

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elements: Pb, Cr, Cd, Mn and Zn in some iron ores collected from mines in Wollega, Oromia regional state, Ethiopia.

Materials and Methods

Description of the study area

Iron ore samples were collected from mines at Walage (9°41'N; 36°58'E), Nejo (9°41'N; 36°58'E) and Bikilal (9°15'N; 35°51' E) in Wollega (Ethiopia).

Chemicals and reagents

Lead nitrate [$Pb(NO_3)_2$, MW:331.2 $g.mol^{-1}$]; cadmium chloride [$CdCl_2$, MW:183.32 $g.mol^{-1}$]; potassium chromate [K_2CrO_4, 194.19 $g.mol^{-1}$]; manganese nitrate [$Mn(NO_3)_2$, 178.96 $g.mol^{-1}$] and Zinc nitrate [$Zn(NO_3)_2$, MW: 189.36 g.mol-^{1}] procured from **FLUKA** were of analytical grade.

Metal	Wavelength (nm)	Slit width (nm)	Lamp current (mA)	Detection limit (mg/kg)
Pb	283.3	1.0	5	0.100
Cd	326.1	0.5	4	0.040
Cr	357.9	0.2	7	0.050
Mn	279.5	0.2	5	0.001
Zn	213.9	1	5	0.005

Table 1: Optimized radiation wavelength, slit width and lamp current used in the FAAS measurements and detection limits for analyzed trace metals in studied iron ore samples.

Metal analyzed	Concentration of working standards (mg/L)	Correlation coefficient (R^2)	Regression equation
Pb	0, 5, 10, 15, 20, 25	0.992	y=0.001x+0.000
Cr	0, 1, 3, 5, 7, 9	0.999	y=0.010x+0.001
Cd	0, 1, 2, 3, 4, 5	0.992	y=0.1232x+0.019
Mn	0, 1, 5, 10, 15, 20,	0.997	y=0.009x+0.015
Zn	0, 0.1, 0.5, 1,0, 1.5, 2,0	0.995	y=0.454x+0.001

Table 2: Concentrations of working standard solutions, correlation coefficients and regression equations of the calibration curves for the studied metals.

Metal	Walage	Najo	Bikilal	Siderite@	Hematite-1@/ Hematite-2@	Marcasite@	Pyrite@
Pb	1359 ± 129	1426 ± 71	2369 ± 46	-	18.25/97.60	12.55	25.70
Cr	211 ± 12	217 ± 27	748 ± 44	7.98	16.41	0.90	11.60
Cd	< 0.040	< 0.040	< 0.040	-	-	-	-
Mn	428 ± 100	1174 ± 2	184 ± 15	-	98.0/1860	9.65×10^4	470
Zn	42 ± 1	44 ± 1	147 ± 80	1330	1.187×10^4/128	4.384×10^4	39.0

Table 3: Concentrations (mg/kg) of some trace metals in iron ores collected from Walage, Najo and Bikilal minerals areas in Wollega (Ethiopia) and their comparison with literature reported values for some common iron ores, from Ref [1].

Metal	Observed concentration in ore sample (mg/L)	Amount of metal added (mg/L)	Observed concentration in spiked sample (mg/L)	% Recovery
Pb	13.59	5.00	18.46	97.4
Cr	2.11	1.50	3.63	101.3
Cd	ND	-	-	-
Mn	4.28	10.00	14.03	97.5
Zn	0.42	0.20	0.63	105

Table 4: Percent recovery of studied trace metals for the analyzed Walage iron ore sample.

Methods

Digestion of samples: The collected iron ore samples were dried, overnight, at 105°C in an oven, homogenized and sieved (<2 mm). One gram dried ore sample and 10 mL 1:1 HNO_3 were mixed in a 250 mL round bottom flask and refluxed for 15 minutes and then allowed to cool down to room temperature. Five mL concentrated HNO_3 was added to the reaction mixture and further refluxed for 30 minutes. Three mL 30% H_2O_2 was then added and heating continued until effervescence subsided, cooled and centrifuged the product for 15 minutes at 3,000 rpm. The clear supernatant liquid was made to 100 mL using deionized water. The digestion of a reagent blank was also carried out, similarly, in parallel with each iron ore sample [13,14].

Calibration of the instrument: For calibrating FAAS, plot of standard concentration of metal versus absorbance was drawn for each studied metal and the correlation coefficient (R^2) and regression equations of the calibration curves were recorded.

Elemental quantitative analysis: Concentration of each metal in the studied iron ore samples were determined using flame atomic absorption spectrophotometer (FAAS) (Buck Scientific Model: 210VGP AAS, USA) equipped with deuterium back ground corrector, hollow cathode lamp and standard air-acetylene flame system. Radiation wavelength, lamp current and slit width, used in the FAAS were optimized for each metal. After calibrating the instrument, the reagent blanks and samples were aspirated into FAAS consecutively and minimum of three readings were taken for each sample as well as reagent blank solution and the mean value of the concentration signal was used in the subsequent calculations. Metal contents of samples were determined using their respective pre-constructed standard calibration curves.

Validation of the optimized procedure: Spiking method was adopted for validating the optimized procedure for quantitative elemental analysis. One gram dried ore sample was mixed with a known amount of metal, as its salt solution. The spiked samples, in triplicate, were then digested and total metal concentration determined using FAAS as described for non-spiked iron ore samples. Percent recovery (R) was calculated [15] using the relation (1):

$$R=[(C_s-C)/S].100 \quad (1)$$

Where, C_s=metal concentration of the spiked sample; C=metal concentration of non-spiked sample; S=concentration equivalent of analyte added to the sample.

Method detection limit: Method detection limit (MDL) is defined as the minimum concentration of analyte that can be measured and reported with 99% confidence that the analyte concentration is greater than zero, but it may not necessarily be quantified as an exact value [16]. The method detection limits were taken as three times reagent blank standard deviation.

Results and Discussion

Optimization of FAAS operating condition

Optimized operational radiation wavelength, slit width and lamp current used in the FAAS measurements and detection limit for each analyzed trace metal in studied iron ore samples are summarized in Table 1.

Calibration of the instrument

Concentrations of working standard solutions, correlation

coefficients (R^2) and regression equations for the calibration curves for studied trace metals are summarized in Table 2.

Quantitative evaluation of trace heavy metals

Concentrations of trace heavy metals (Pb, Cr, Cd, Mn and Zn) in iron ores from Walage, Najo and Bikilal minerals areas in Wollega (Ethiopia) determined using FAAS are recorded in Table 3.

Bilkilal iron ore was found to be richest in trace metal contents (except for manganese which was highest in Nejo ore) followed by Najo and Walage. Among the studied heavy metals, lead had the highest concentration in iron ores collected from three areas, followed by manganese, chromium and zinc. However, cadmium was found below the detection limit (0.040 mg/kg). The trace metals contents in the studied ores were: **Lead:** Bikilal>Nejo>Walage; **Chromium:** Bikilal>Nejo>Walage; **Maganese:** Nejo>Walage>Bikilal and **Zinc:** Bikilal>Nejo>Walage. Our observed trace metal concentrations in studied ores are also compared in Table 3 with the earlier reported values in literature (Stafilov and Zendelovska [1] for Siderite, Hematites, Maecasite and Pyrite ores. The levels of Pb and Cr in iron ores in the present study are much higher compared to those in Hematite, Marcasite and Pyrite ores reported by Stafilov and Zendelovska [1]. However, reverse is true in case of Mn and Cr contents in the two studies.

The reported data on trace heavy metals concentrations in the studied iron ores would be useful in optimizing the operational parameters during the reduction of iron oxide to metallic iron in the smelting process. A pre-knowledge of trace metals levels in iron ores is also of significance since their presence, even at very low concentrations, affects the physical properties of the end product.

Validation of the optimized procedure

In the present study, validity of the analytical procedure was verified by spiking method. Typically, percent recovery of each added trace metal for analyzed Walage iron ore sample is presented in Table 4. The observed high percent recovery values of metals verify the validity of the adopted analytical procedure.

Conclusion

Levels of trace metals: Pb, Cr, Mn, Zn and Cd in iron ores collected from Nejo, Wolage and Bikilal in wollega (Ethiopia) have been measured using flame atomic absorption spectrometry. The digestion method used for trace metals analysis in iron ores was validated by recovery experiment. Each analyzed iron ore was found to have different trace metal contents with their highest trace metals levels in Bikilal iron (except for manganese which was highest in Nejo ore) followed by Nejo and walage ores. Whereas, lead has the highest concentration in the studied ores followed by manganese, chromium, zinc, cadmium was found below its detection limit. The reported trace metals levels in the studied iron ores may be useful in optimizing the operational parameters during iron oxide reduction to metallic iron in the smelting process and also the presence of heavy metals, even in traces, can affect the physical characteristics of the end products.

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