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Energy Dispersive X-ray Fluorescence Analysis of Mine Waters from the Migori Gold Mining Belt in Southern Nyanza, Kenya

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Abstract Analyses of water samples from Mikei, Osiri, Masara and Macalder (Makalda) gold mines of the Migori gold mining belt of Southwestern Kenya were done to determine the level of heavy metals using the Energy Dispersive X-ray Fluorescence technique. The concentrations of the heavy metals were; copper (29.34 ± 5.01–14,975.59 ± 616.14 μg/L); zinc (33.69 ± 4.29–683.15 ± 32.93 μg/L); arsenic (958.16 ± 60.14–18,047.52 ± 175.00 μg/L) and lead (19.51 ± 5.5–214.53 ± 6.29 μg/L). High levels of arsenic and lead were noted. These heavy metals are not only dangerous to the lives of miners and the local inhabitants; they are also a threat to aquatic life since these waters finally find their way into Lake Victoria.

Keywords ED-XRF · Heavy metals · Gold mining · Mine water

A number of studies conducted in gold mining areas e.g., in the Witwatersrand have produced increasing evidence that mines frequently contaminate adjacent environment with heavy metals, salts and radionuclides, (Bowell et al. 1995). Heavy metals are of particular interest for a number of reasons; firstly they show a tendency to accumulate in the sediments and the soils, have a long persistence time and are non biodegradable. Secondly, they are ubiquitous in sediments and soil arising from both natural and anthropogenic sources with pathways including inheritance from the parent rocks, application of water as well as local and long range atmospheric and fluvial deposits of emissions from dust and mining (Deb et al. 2008). While in commercial mining there are some measures of environmental control, in artisanal mining there are no control measures and the mining environment is littered with tailings, overburdens and open pits.

Trace amounts of metals can be found in minerals constituting mineralized rocks. The size reduction process like crushing, during ore processing increases the surface area of the reaction of rock/mineral particles thereby accelerating oxidation and/or chemical weathering and hence the release of metals (Getaneh and Alemayehu 2006). Many of the metals are essential at low concentrations for plants, animals and human health but at higher concentration they can be toxic. In some cases the concentration of metals in different environmental media can exceed the maximum tolerable concentration and can cause harm to life; a number of case histories have been documented and reported from different parts of the world (Getaneh and Alemayehu 2006).

Due to the presence of gold and copper, we expected many heavy metals to be associated with the artisanal gold mining activities in the Migori gold mining belt as reported elsewhere in the world (Getaneh and Alemayehu 2006; Ogola et al. 2002; Serfor-Armah et al. 2006; Veiga and Hinton 2002; Weast 1968). This study was therefore meant to assess accumulation of heavy metals in the mine waters in the Migori gold mining belt and make relevant

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recommendations to the miners, the local populace and government authorities.

Materials and Methods

Eleven water samples were collected from Osiri, Macalder (Makalda), Mikei and Masara gold mines for heavy metal analysis. Ten of the eleven water samples were collected from panning ponds dug in the ground near the crushing sites, one each from Masara, Osiri A and Macalder. Three and four water samples, respectively were collected from Osiri B and Mikei, the eleventh sample was collected from one of the freshly dug mines at Mikei. At each sampling point, the bottles were rinsed at least three times with the water before taking the sample by immersing the bottle to about 10 cm below the water surface. The samples were tightly sealed and brought to the Nuclear Institute of Science and Technology, University of Nairobi for analysis.

One hundred mL of each water sample was preconcentrated by adding Nitric acid, where the pH went below 3.5; ammonium solution was added to adjust it upwards. Two mL of 1% ammonium-1-pyrolidonedithiocabomate (APDC) solution was then added to the preconcentrate before stirring for about 30 min, this was followed by suction filtration over a 0.45 μm nuclear pore filter paper (47 mm in diameter) and left to dry.

Although there are many X-ray fluorescence techniques, the energy dispersive X-ray fluorescence (ED-XRF) technique was preferred for this analysis because it offers non destructive and reliable multi-elemental analysis capability. This technique also requires little sampling and sample preparation. The ED-XRF spectrometer used in this study consisted of a X-ray generator as the excitation source operated at 35 V and 20 mA; Canberra Si (Li) detector, an ORTEC spectroscopy shaping amplifier model 571, ORTEC high voltage supply bias model 475, ORTEC liquid nitrogen monitor and a Canberra multichannel analyzer (S-100) interfaced with a 486 channel personal computer. Each filter was run for 500 s and the spectra collected by the Canberra detector with energy resolution of 195 eV for (Mn-K_α) X-rays at 5.9 keV. The characteristic X-ray spectra obtained from the samples was evaluated by non-linear least squares fitting using the AXIL-QXA software. Figure 1 shows a typical ED-XRF water spectrum obtained from the analysis.

Result and Discussion

The levels and detection limits of chromium, manganese, Iron, cobalt, copper, zinc, arsenic and lead are reported in Tables 1 and 2, respectively, where copper, iron and magnesium were registered in all the samples collected. Concentration of copper ranged from 29.3 ± 5.0–14,975.6 ± 616.1 μg/L. The average levels of copper at Mikei and Osiri B were 81.504 and 31.377 μg/L, respectively. Iron level ranged from 261.7 ± 29.7–77,903.1 ± 3,203.1 μg/L. Zinc level at Osiri A was the lowest, 33.7 ± 4.3 μg/L, while the highest level of 683.2 ± 32.9 μg/L was registered at Macalder panning pool. Average level of zinc of 183.2 ± 13.2 and 44.9 ± 6.5 μg/L were registered at Mikei and Osiri B, respectively. Absence of gold and mercury were noted in all the mine waters. For mercury, this could be due to its high density that makes it settle at the bottom of the pond with the sediments.

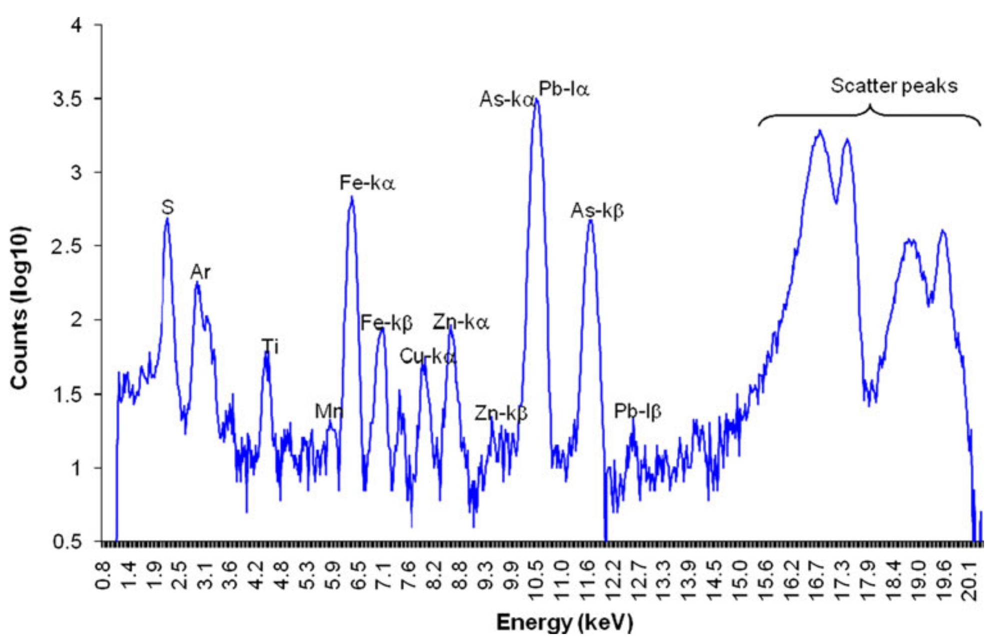

Fig. 1 Typical ED-XRF spectrum of a water sample

Table 1 Elemental concentration in water sample from Osiri, Mikei, Macalder and Masara (μg/L)

Element	Mas 1	Mac 2	Mik 1	Mik 2	Mik 3	Mik 4	Mik 5	Osi-A	Osi-B1	Osi-B2	Osi-B3
Ti	<30	112.9 ± 5.1	46.5 ± 11.3	207.5 ± 24.9	<30	84.3 ± 11.7	185.6 ± 13.8	23.9 ± 6.9	<30	<30	<30
Cr	144.9 ± 25.2	<25	22.4 ± 7.5	69.4 ± 12.5	39.2 ± 8.5	30.2 ± 9.9	48.1 ± 11.3	<25	<25	<25	<25
Mn	339.8 ± 5.7	35.0 ± 8.5	<15	158.0 ± 15.9	78.2 ± 8.3	46.7 ± 9.0	132.6 ± 15.1	34.5 ± 7.3	<15	<15	29.0 ± 8.2
Fe	77,903.1 ± 203.1	1,174.8 ± 66.9	1,153.7 ± 97.4	11,710.9 ± 492.1	3,101.0 ± 148.0	1,834.6 ± 89.2	11,775.3 ± 494.0	849.6 ± 2.7	520. ± 40.6	261.6 ± 29.7	360.5 ± 32.7
Co	1,014.1 ± 72.7	<10	<10	62.8 ± 6.7	37.5 ± 8.6	27.9 ± 8.6	51.9 ± 12.0	<10	<10	<10	<10
Cu	14,975.6 ± 616.1	45.3 ± 6.7	93.0 ± 9.5	113.6 ± 7.7	70.9 ± 7.6	67.4 ± 5.9	62.7 ± 5.6	34.0 ± 4.6	29.3 ± 5.0	30.1 ± 4.2	34.7 ± 7.0
Zn	444.2 ± 21.8	683.2 ± 32.9	169.8 ± 21.7	291.3 ± 16.1	102.5 ± 6.9	113.8 ± 7.7	238.3 ± 13.9	33.7 ± 4.3	56.5 ± 4.3	34.1 ± 6.9	44.0 ± 8.4
As	<20	58.2 ± 15.6	<20	958.2 ± 60.1	1,184.4 ± 78.8	18,047.5 ± 746.0	4,058.9 ± 175.0	<20	<20	<20	<20
Pb	88.1 ± 9.6	24.1 ± 4.8	<10	200.9 ± 13.1	214.5 ± 16.3	19.5 ± 5.5	<10	<10	<10	<10	<10

Mas Masara, *Mac* Macalder, *Mik* Mikei, *Osi* Osiri

Table 2 Detection limits in water samples (μg/L)

Element	Detection limit
Ti	30
Cr	25
Mn	15
Fe	12
Co	10
Cu	8
Zn	7
As	20
Pb	10

Arsenic was detected in Macalder and Mikei samples, the highest level of 18,047.5 ± 175.0 μg/L was registered at Mikei, and this confirms the study by Odumo et al. (2011) that found the level of arsenic to be higher in sediments at Mikei. This level is high compared to results from Adola region of Ethiopia where its average was found to be 92.8 μg/L (Deb et al. 2008). However, the concentration is lower than 72 mg/L registered at the Iron Duke mine in Zimbabwe (Williams and Smith 2000). Even though the miners don't drink these waters directly, they use them to clean their hands before eating at the mines. Cows, goats and sheep also in many occasions especially during dry periods drink these waters. The situation is worsened when this contaminated water find its way into the nearby rivers leading to direct domestic use by the locals since the rivers are their only source of water. The high level of arsenic can be dangerous to the miners and their livestock since it is toxic to both animals and human beings. However, the high level of arsenic should also be exploited if the concentration is economically viable since pure arsenic metal is used to produce crystalline gallium arsenide which is a semiconductor used in computing and electronic industries. It can also be used in agriculture, livestock and general industries (Winde and Sandham 2004).

Lead was also registered at higher levels from Mikei, this poses a threat to the lives of the miners since lead is a carcinogen. Other heavy metals like cobalt, manganese and titanium detected in some of the mines at low concentrations.

From this study, the concentration arsenic, copper, zinc and lead in the Migori gold mine waters is high and the miners should therefore be made aware of the consequences of their exposure to them. The miners should be educated on the possible ways of protecting themselves from the exposure to these heavy metals. Proper procedure of disposal of the mine wasters should be followed to avoid further contamination of the environment. It is also suggested that a further study be carried out to verify the results of this study using other methods. Though contamination of the rivers in the area had been done, the concentration of these metals should be investigated downstream.

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