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Speciation of chromium in soils near Sheba Leather Industry, Wukro Ethiopia

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ABSTRACT

A study on speciation of chromium in soils near Sheba Leather Industry was performed by Flame Atomic Absorption (FAAS) after selective extraction of Cr(VI) using the EPA 3060A method, and oxidizing the Cr(III) residue in the soils with HNO_3 and H_2O_2. The extraction method was evaluated using the spiking method with satisfactory results (recoveries > 95% and RSDs < 5%). The limit of detection (LOD) for Cr(VI) based on three times the standard deviations of the blank (for $n=5$) was 0.56 μg g^{-1}.

Statistical evaluation indicated that the comparison of the sum of the concentrations of chromium species to that of the total concentration of chromium do not show any difference at 95% level of confidence. Besides, no statistically significant difference at 95% confidence level was observed between the UV–vis spectrophotometry and FAAS results for Cr(VI). However, it is observed that selective extraction of Cr(VI) using EPA 3060A and subsequent determination by FAAS is simple and faster compared to the other method. Furthermore, for comparison and as control two soil samples collected from a distance of about 2 km from the main Industry and effluent stream. The results indicate that higher total chromium content was observed in soils collected from the target area. Nevertheless, the maximum concentrations of Cr(VI) found in soil samples collected around Sheba Leather Industry was 9.9 μg g^{-1} and are within the acceptable level of 10 μg g^{-1} in accordance with the WHO.

1. Introduction

Environmental pollution is currently drawing attention globally and is one of the issues that concern everyone all over the world. Though, it is caused due to human activities and natural phenomenon, the role of mankind in the release of toxic heavy metals from industries and factories is becoming a serious environmental issue. These is causing adverse health effects such as damage nerves, liver, kidney, bones, and also blocks functional groups of vital enzymes [1] to aquatic and terrestrial life systems.

Soils that are not affected by contamination or pollution by natural or anthropogenic source will contain small amount of chromium. The content will increase depending on the nature of the source. Generally, higher chromium content in soils is resulted from improper discharge of effluents or wastewater from metal smelting, electroplating, tanning, metallurgy and mining [2,3]. The tanning industry is one of such industries regarded as major source or cause of environmental pollution all over the world because tanning process use significant amounts of chromium salts [3].

Nevertheless, toxicological studies have shown that the extent of toxicity of some elements is dependent on the chemical form and oxidation state in which the metal is present. Hence, there is growing interest for information about speciation of elements. In the case of chromium it commonly occurs Cr(III) and Cr(VI) states and is essential to know their content in the sample separately because they differ in biological, geochemical and toxicological properties [3–5]. Therefore, the speciation of chromium is particularly important due to the toxicity of Cr(VI) and the bio-dependence of Cr(III) in plants, soils and sediments [6–8]. Due to this reason, different extracting methods have been developed by different researchers [6–8] to selectively extract Cr(VI) from solid samples which include:

(i) rapid leaching of Cr(VI) in soil with Na_3PO_4 [6],
(ii) selective extraction of chromium(VI) using a leaching procedure with sodium carbonate [7],
(iii) ultrasonic extraction in alkaline solutions with (0.05 M $(NH_4)_2SO_4$–0.05 M NH_3) [8], and
(iv) the most widely accepted method for the selective extraction of soluble, adsorbed and precipitated forms of Cr(VI) from soil

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involves digestion with an alkaline solution (0.28 M Na_2CO_3/ 0.5 M NaOH) at temperatures of 90–95 °C (US EPA method 3060A) [9].

There are also numerous techniques available to quantify the concentration of Cr(VI) in aqueous solutions. These include:

(i) adsorptive stripping voltammetry (ASV) [3],
(ii) electrothermal atomic absorption spectrometry (ETAAS) [6,10],
(iii) 1,5-diphenyl-carbazide spectrometry (DPC) [11],
(iv) inductively coupled plasma atomic emission spectrometry (ICP-AES), high performance size exclusion chromatography coupled to inductively coupled plasma mass spectrometry (HP-SEC–ICP-MS) [12], and
(v) flame atomic absorption spectrometry (FAAS) [13,16–18].

2. Experimental

2.1. Apparatus

A Varian AA240 FS (Fast Sequential), which is fully automated PC-controlled true double-beam Atomic Absorption Spectrometer, was used for the determination of total chromium. The spectrophotometric measurements were carried out on a double beam spectrophotometer, model UNICAM UV300, using a 1.0 cm quartz cell throughout the spectrophotometric determination of Cr(VI)-1,5-diphenylcarbazide complex.

The pH of the solutions were also measured with a Hatch Lange pH meter using a combined glass electrode calibrated with buffers of pH – 2, 4, 7 and 10. The extraction of soluble Cr(VI) was performed using a shaker, model KS 125 Basic, IKA Labortechnik.

2.2. Reagents and standard solutions

$K_2Cr_2O_7$ (Bahadurgarh, India), NaOH (Barcelona, Spain), K_2HPO_4 (FINKEM), Na_2CO_3 (Mumbai, India), KH_2PO_4 (NICE), $Mg(NO_3)_2 \cdot 6H_2O$ (Oslo, Norway), HNO_3 (69% BDH, England), 1,5-diphenylcarbazide (DPC) (Fischamend, Austria), acetone (NICE), H_2SO_4 (Guangda, China) and H_2O_2 (Runcorn, England) are the reagents of analytical grade, which were used in the study. Ultra pure distilled deionized water with conductivity 0.055 μS cm^{-1} was used throughout the study for dilution and preparation of solutions. Glassware were cleaned by soaking in 10% (v/v) nitric acid and rinsed with deionized water prior to use. 2.0 N NaOH and 5.0 N HNO_3 were used for pH adjustment.

2.3. Samples and sample analysis

2.3.1. Soil sampling

Five soil samples in the vicinity of the study area, from a depth of about 20.0 cm with 5 m difference between them were collected into plastic sample bags. For comparison purpose, two soil samples were also collected at a distance of about 2.0 km from the main Industry and effluent stream as controls. The soil samples were air dried and sieved using a 1.0 mm mesh.

2.3.2. Preparation of standard solutions for FAAS analysis

1000 mg L^{-1} Cr(VI) was prepared by dissolving 2.829 g of dried $K_2Cr_2O_7$ in 1 L volumetric flask and from the stock solution, a series of working standards of 5.0, 10.0, 20.0 and 40.0 mg L^{-1}. In all cases standard solutions were prepared freshly.

2.3.3. Preparation of standard solutions for spectrophotometric analysis

Series of standards 0.5, 1.0, 2.0 and 4.0 mg L^{-1} was prepared, using suitable volume of Cr(VI), 2.0 mL 0.5% 1,5-diphenylcarbazide and 1.0 mL of 0.1 M H_2SO_4 in 100.0 mL volumetric flask. It was allowed to stay for 5 to 10 min for complete color development. A suitable portion of each colored solution was transferred to a 1.0 cm absorption cell and absorbance of the colored Cr(VI)-1,5-diphenylcarbazide complex was measured at 540 nm against a reagent blank.

2.3.4. Preparation of extracting reagent

The digesting solution was prepared by dissolving 20.0 g NaOH and 30.0 g Na_2CO_3 in deionized water in a 1 L volumetric flask and diluted up to the mark. The pH of the extracting solution was 12.65. The phosphate buffer was prepared by dissolving 87.09 g K_2HPO_4 and 68.04 g KH_2PO_4 in 1 L volumetric flask and diluted the volume up to the mark.

2.3.5. Sample preparation for the determination of total chromium in the soils

2.5 g of soil was weighed and transferred into 250.0 mL flask. 1.0 mL of 2.0 N H_2SO_4 was added to dissolve the soil. 20.0 mL of HNO_3 and 3.0 mL H_2O_2 were also added and the solution was heated to almost dryness. An additional 3.0 mL concentrated HNO_3 and 1.0 mL H_2O_2 were added to ensure that organic substances were completely decomposed. The residue was dissolved with 1.0 mL of 2.0 N H_2SO_4 and 10.0 mL of deionized water. Then it was filtered using Whatman 540 filter paper and followed by 0.45 μm pore size. Finally, it was diluted up to the mark of 100.0 mL volumetric flask and the content of total chromium in the filtrate was determined using FAAS.

2.3.6. Sample preparation for the determination of water soluble Cr(VI) in soils

2.5 g of soil sample was weighed and transferred into 250.0 mL flask. 50.0 mL of deionized water was added and shaken for 24 h at 300.0 rev min^{-1}. Then it was filtered through 0.45 μm pore size, finally made up to the mark of 100.0 mL volumetric flask. The content of water soluble Cr(VI) was determined by FAAS and spectrophotometry.

2.3.7. Leaching of Cr(VI) using EPA 3060A

The procedure described by EPA 3060A was employed for selected soil samples (Soils 1, 3, 5 and 7). From each of these soil samples, 2.5 g was weighed and transferred to 250.0 mL beaker. 50.0 mL of the extracting solution (0.28 M NaOH and 0.5 M Na_2CO_3) and 1.0 mL of the buffer solution were added to the beaker. Besides, 1.067 g of $Mg(NO_3)_2 \cdot 6H_2O$ was added to prevent oxidation of Cr(III) to Cr(VI).

Each sample was stirred for 5 min before heating and covered with watch glass. The beaker was heated for 60 min at 90–95 °C by continuous stirring using magnetic stirrer and cooled by agitation. It was initially filtered using Whatman 540 filter paper and the residue was preserved for the determination of Cr(III). The filtrate was further filtered using 0.45 μm pore size and filled up to the mark of 100.0 mL volumetric flask. Finally, the content of Cr(VI) was determined using FAAS and UV–vis spectrophotometry. For the spectrophotometeric determination, 1.0 mL of the sample and 2.0 mL of DPC solution was taken into 10.0 mL graduated cylinder. The pH of the solution was adjusted from 1–2 by adding 3–5 drops of 5.0 N HNO_3 and was diluted up to the mark. The determination was performed on the day of extraction.

2.3.8. Sample preparation for the determination of Cr(III) in the soil residue

The Cr(III) precipitated in the soil residue was dissolved with 1.0 mL of 2.0 N H_2SO_4. 20.0 mL of concentrated HNO_3 and 3.0 mL H_2O_2 were also added, and the solution was heated to almost dryness. An additional 3.0 mL concentrated HNO_3 and 1.0 mL H_2O_2 of were added to ensure that organic substances were completely decomposed. The residue was dissolved with 1.0 mL of 2.0 N H_2SO_4 and 10.0 mL of deionized water. Then it was filtered using Whatman 540 filter paper and further filtered through 0.45 μm pore size and diluted up to the mark of 100.0 mL volumetric flask. The content of Cr(III) in the filtrate was determined using FAAS.

3. Results and discussion

3.1. Calibration graph for FAAS analysis

The calibration graph for the FAAS analysis of chromium was drawn by using standard solutions and the graph is described by the following equation: $Y = 0.047X + 0.007$, where X is the analyte concentration and Y is the integrated absorbance, with good correlation coefficient $R^2 = 0.9996$ ($n = 4$) (Table 1).

3.2. Calibration graph for spectrophotometeric analysis

The calibration graph for the spectrophotometric analysis of Cr(VI) was drawn by using standard solutions and the graph is described by the following equation: $Y = 0.549X + 0.076$, where X is the analyte concentration and Y is the integrated absorbance respectively, with good correlation coefficient $R^2 = 0.9962$ ($n = 4$) (Table 2).

Table 1
Operating parameters of FAAS instrument.

Number	Parameters	Setting
1	Lamp current	7.0 mA
2	Wavelength	357.9 nm
3	Slit width	0.2 nm
4	Flow rate of combustion-supporting gas (air)	13.5 L min^{-1}
5	Flow rate of combustion gas (acetylene)	2.5 L min^{-1}
6	Lamp optimization (gain)	38%
7	Fame type	Reducing

Table 2
Operating parameters of UV–vis spectrophotometer instrument.

Number	Parameter	Setting
1	Scan type	Intelliscan
2	Mode	Absorbance
3	Wavelength Start	400.0 nm
4	Wavelength stop	900.0 nm
5	Band width	1.5 nm
6	Speed	Normal
7	Data interval	1.0 nm
8	Peak table	Peaks
9	Graph height	2
10	Graph low	0
11	Smoothing	None
12	Lamp change	325.0 nm

Table 3
Total chromium content in soils.

Sample	Mean ± SD (μg g^{-1})	% Recovery
1	212.12 ± 5.8	90.47
2	63.05 ± 2.8	91.34
3	73.23 ± 3.0	90.45
4	47.94 ± 2.2	99.8
5	41.29 ± 1.9	92.28
6	11.51 ± 1.2	104.14
7	16.14 ± 1.4	101.05

Table 4
Total Cr(VI) determined by FAAS and UV–vis spectrophotometer.

Soil	FAAS results Mean ± SD (μg g^{-1})	% Recovery	Spectrophotometeric results Mean ± SD (μg g^{-1})	% Recovery
1	9.99 ± 0.4	104.31	8.32 ± 0.6	102.0
3	4.65 ± 0.2	98.53	3.66 ± 0.5	95.6
5	4.30 ± 0.2	97.04	3.27 ± 0.5	93.32
7	ND[a]	–	ND	–

[a] Not detected.

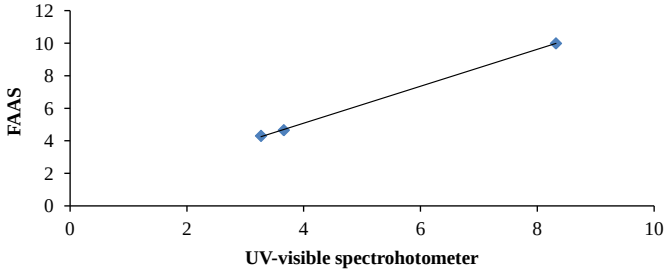

Fig. 1. Correlation of results obtained by FAAS and UV–vis spectrophotometer.

3.3. Determination of total chromium in the soils using FAAS

Total chromium content in soil samples was determined by FAAS after digesting with HNO_3 and H_2O_2. The results found are indicated below in Table 3. The pollution level of the soil near the leather industry was compared with two soil samples collected 2 km away from the main effluents stream. Higher values for chromium was found in the soils collected from the target area (soil samples 1–5) which were attributed to the improper disposal of chromium containing wastewater from the industry. This is compared to the results obtained for the control soil samples (6 and 7) which contain lower amount of chromium.

3.4. Determination of extracted Cr(VI) using FAAS and UV–vis spectrophotometer

The extraction method employed was in good agreement with the recoveries for three soil samples (Table 4) and this simplified the efforts that would be involved for evaluating the other parameters like pH, redox potential of the soil and temperature. To examine the reliability of the determination, comparative determination of Cr(VI) was carried out in the same soil extracts by FAAS and spectrophotometer. For the spectrophotometric analysis, the λ_{max} of Cr(VI)-1,5-diphenylcarbazide complex was set at 540 nm and determinations were performed at this wavelength against a reagent blank.

Results obtained (see Table 4) revealed that there is an indication for the availability of Cr(VI), as the maximum amount determined is being 9.99 μg g^{-1} in soil sample 1. Besides, soil sample 7 which was

Table 5
Summary of soil analytical results determined by FAAS.

Sample	Water soluble [Cr(VI)] ($\mu g\ g^{-1}$)	Total [Cr(VI)] by EPA 3060A ($\mu g\ g^{-1}$)	[Cr(III)] ($\mu g\ g^{-1}$)	{[Cr(VI)] +[Cr(III)]}[a] ($\mu g\ g^{-1}$)	{Total [Cr]}[b] ($\mu g\ g^{-1}$)
1	0.92 ± 0.08	9.99 ± 0.4	191.64 ± 5.2	201.63	212.12
3	0.52 ± 0.05	4.65 ± 0.2	64.14 ± 3.2	68.79	73.23
5	ND	4.30 ± 0.2	35.5 ± 2.3	39.86	41.29
7	ND	ND	15.08 ± 1.6	15.08	16.14

[a] The sum of Cr(VI) and Cr(III) in soils.
[b] Total chromium determined by an independent method.

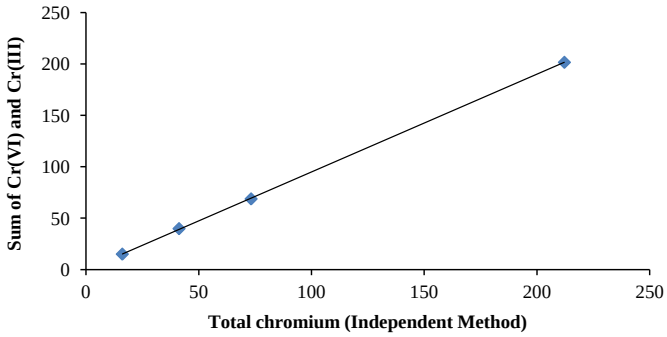

Fig. 2. Correlation of chromium results obtained by the sum of Cr(VI) and Cr(III); and by an independent method.

considered as a control has no detectable amount of Cr(VI) using both methods.

Fig. 1 shows the correlation between the two methods: FAAS and UV–vis spectrophotometry. The regression equation is given by: $Y = 1.134X + 0.544$ and its correlation coefficient is $R^2 = 0.9998$. The analytical method applied (FAAS) for the speciation analysis was compared with a standard method which involves spectrophotometry and statistical results showed that there is no significant difference between these two methods at 95% confidence level. In addition, the limit of detection (LOD) for Cr(VI) based on three times the standard deviations of the blank (for $n = 5$) was 0.56 $\mu g\ g^{-1}$. Comparable detection limit, RSDs and recoveries were obtained with the early reported results in aqueous solutions [16 – 18].

3.5. Summary of soil analytical results determined by FAAS

Table 5 shows, results obtained by FAAS and indicating chromium exists in the form of Cr(III) in these soil samples more predominantly. This may be associated with the formation of insoluble crystalline compounds in soils. Besides, it is indicated that insoluble Cr(VI) is the dominant species as it was reported earlier [14]. It is also indicated that the total amount of Cr(VI) in the soils under investigation was very small. This may be associated with clay nature of the soil under investigation. It was suggested that clay soil support the reduction of Cr(VI) as there exist a large surface area which in turn can increase the reaction rate between the reductants and Cr(VI) [15]. The concentrations of soluble Cr(VI) (see Table 5) were very small relative to the concentration of total Cr(VI) extracted using the EPA method 3060A. This may be associated with the formation of insoluble salts in the presence of Ba^{2+}, Pb^{2+} and other precipitate forming metals with Cr(VI) in the soil [6].

Fig. 2 shows the correlation between the sum of (Cr(VI) and Cr(III)) contents and total chromium determined by the total digestion method. The regression equation is given by: $Y = 0.95X - 0.121$ and its correlation coefficient is $R^2 = 0.9999$. The sum of the two forms of chromium, Cr(VI) and Cr(III), was compared with an independent method and the results show that there is no significant difference between them at 95% confidence level.

4. Conclusion

A speciation analysis of chromium in soils was done using FAAS after selective extraction of Cr(VI) using EPA 3060A. The extraction method was evaluated using the spiking method with satisfactory results (recoveries > 95% and RSDs < 5%). The limit of detection (LOD) for Cr(VI) based on three times the standard deviations of the blank (for $n = 5$) was 0.56 $\mu g\ g^{-1}$.

The new method was validated by statistical evaluation which indicated that the sum of concentrations of chromium species is the same as the total concentration of total chromium at 95% level of confidence.

Besides, the results for Cr(VI) concentration were compared with a standard method that involves Cr(VI) complexation with 1,5-diphenylcarbazide and quantification using a UV–vis spectrophotometer. Statistically, there is no significant difference between these two methods at 95% confidence level, suggesting both methods can be used for the determination of Cr(VI) in soil extracts. However, it was observed that selective extraction of Cr(VI) using EPA 3060A and subsequent determination by FAAS is simple and faster compared to the other method.

The soil samples collected from the site near the leather industry showed the presence of higher levels of chromium contamination, due, most probably to the release of untreated industrial effluent from the tannery.

The maximum concentration of Cr(VI) found in the soil samples collected near the main effluent stream was 9.99 $\mu g\ g^{-1}$, this just falls within the World Health Organization (WHO) guidelines acceptable level of 10 $\mu g\ g^{-1}$.

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