

The oxidation of Cr(III) to Cr(VI) in the environment by atmospheric oxygen during the bush fires

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Abstract

The presence of Cr(VI) in soils and plants of remote unpolluted areas can be explained by partial oxidation of Cr(III) with atmospheric oxygen during seasonable bush fires, which are rather frequent event in South Africa. Experiments with thermal treatment of a veld grass, *Hyperthelia dissoluta*, in muffle furnace at high temperature, followed by electrothermal atomic absorption spectrometry (ETAAS) determination of chromium, show a remarkable increase in Cr(VI) concentration from initial 2.5 to 23.2% after the treatment of grass ash at 500 °C and to 58.1% at 900 °C. Before ETAAS determination, the two chromium species of interest were separated by the treatment of samples with 0.1 M Na₂CO₃. Thermodynamic calculations confirm the possibility of Cr(III) to Cr(VI) oxidation with atmospheric oxygen at high temperature in alkaline media, which is typical for vegetation ash. Analysis of field samples show that percent of Cr(VI), in respect to the total amount of chromium increased from initial 2.5% in grass to 9.3% in ash of grass. Without oxidation the percent of Cr(VI) in grass and ash of grass should be a constant value. After the fire Cr(VI) concentration in top soil (0–3 cm) increased from 0.3 ± 0.05 to $1.8 \pm 0.5 \mu\text{g g}^{-1}$ and the total Cr from 26 ± 9 to $69 \pm 14 \mu\text{g g}^{-1}$. The reason for the appearance of additional amount of Cr on top soil can be explained by condensation of chromium species from flame and shouldering ash on a soil surface. The results of studies demonstrate that Cr(VI) is formed by Cr(III) oxidation with atmospheric oxygen at high temperature during bush fires.

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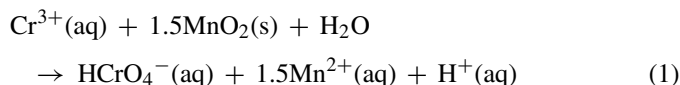
Keywords: Chromium; Oxidation; Hexavalent chromium; Atmospheric oxygen; Grass burning; Electrothermal atomic absorption spectrometry

1. Introduction

The interest in chromium speciation originates from drastically different biochemical properties of Cr(III) and Cr(VI) compounds. While Cr(III) is a trace element essential for the proper functioning of living organisms, Cr(VI) has toxic effects on biological systems and has been classified by the International Agency for Research on Cancer (IARC) as a Group 1 human carcinogen [1]. Hexavalent chromium compounds are more soluble in the environment than sparingly soluble Cr(III) species [2]. Their high mobility under natural environmental conditions can be explained by the leaching of CrO₄²⁻ ions from sparingly soluble chromates, like CaCrO₄, BaCrO₄ or PbCrO₄ in soil–water system saturated with CO₂ [3].

The presence of Cr(VI) species in the environment is not surprising in places near chromium smelters, because Cr(VI)

is formed during ferrochrome production [4]. The phenomenon of Cr(VI) existence in soils of remote non-industrial areas has always been linked to presence of MnO₂ in unpolluted soils whereby Cr(III) is oxidized to Cr(VI) compounds [5]:

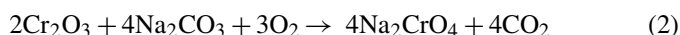


This reaction occurs on solid/aqueous interface and is strongly dependent on the presence of water and thus the interconversion of chromium oxidation states is dominated by water chemistry [6,7]. These conditions are not typical for South Africa, where the climate is semi-arid [8].

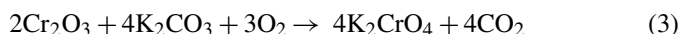
It is quite probable that some amount of Cr(VI) is formed during seasonable grass fires by Cr(III) oxidation at high temperature with atmospheric oxygen. Cr(III) is consumed by plants mostly as oxalate or citric acid complexes in relatively high concentrations [9]. The oxidation of Cr(III) is thermodynamically feasible [10] especially in alkaline media in presence of CaCO₃,

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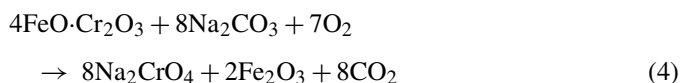
Na₂CO₃ or K₂CO₃, which are the major components of vegetation ash formed at 600–900 °C [11,12]. In burning grass, the oxidation of Cr(III) can be explained by one of the following reactions:



or



These reactions are similar to alkaline chromite ore roasting, where the mixture of chromite ore with soda-ash is heated at ~1200 °C to produce soluble sodium chromate [4,10]:



The other example of Cr(III) oxidation with atmospheric oxygen at high temperature is Cr(VI) formation in cement [13].

From this discussions follows that the conditions for Cr(III) oxidation into Cr(VI) have been naturally created, but could be realized only at high temperature. The aim of this study is to verify the possibility of Cr(III) to Cr(VI) oxidation in burning grass by atmospheric oxygen during seasonable bush fires in South Africa.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer atomic absorption spectrometer Model Analyst 600 with Zeeman-effect background correction was used for all measurements. The spectrometer was equipped with an AS-800 autosampler and the system was controlled by means of AAWinlab software running under Microsoft Windows program. A chromium hollow cathode lamp (Perkin-Elmer), operating at 25 mA, was employed, using the Cr 357.9 nm resonance line with spectral bandpass of 0.7 nm. The tubes of transversely heated graphite atomizer (THGA) with integrated L'vov platforms (Perkin-Elmer, part N BO50-4033) were used for Cr atomization. Argon (Afrox, South Africa) was used as the sheath gas throughout. A compact mill system IKA A11 (IKA—Werke, Germany) was used for the grinding of air-dried plant samples. Microwave Model Mars 5 (CEM Corp., USA) was used for the wet-acid digestion of samples.

2.2. Materials and reagents

Standard solution containing 1000 mg L⁻¹ Cr(III) as Cr(NO₃)₃ (Merck) was used for preparation of working standards for chromium determination in the range of 2.5–50 µg L⁻¹ by appropriate dilution. Ultra-pure water with a resistivity 18.2 MΩ cm⁻¹, obtained with Milli-Q water purification system (Millipore Corp., USA), were used for all dilutions and sample preparations. Hydrophilic PVDF 0.45 µm filters (Millipore Millex, USA) were applied for filtration of all samples before ETAAS determination of chromium. K₂CO₃ of analytical grade (Rochelle Chemicals, South Africa) was used to test

efficiency of Cr(III) oxidation at high temperature in a muffle furnace.

Certified reference materials: BCR CRM 281 (trace elements in rye grass), PACS-2 and MESS-3 (trace elements in marine sediments) were used for evaluation of analytical results of total Cr determination and BCR CRM 545 (Cr(VI) in atmospheric dust) for Cr(VI) determination.

2.3. Sampling site and samples collection

Samples of veld grass, *Hyperthelia dissoluta*, which is used by local population for thatching [14], its ash, top soil (0–3 cm) and soil at 20 cm depth were collected before and after veld fires in Suikerbosrand Mountains, Gauteng Province, Republic of South Africa. Suikerbosrand Mountains located about 60 km south of Johannesburg. The site chosen for this study is not affected by industrial pollution. All samples were collected at the end of dry season in September 2006.

2.4. Sample preparation

2.4.1. Sample preparation for total Cr determination

Samples of grass, its ash and soil for the total chromium content were prepared in microwave according to the standard digestion method of US EPA [15]. Approximately, 0.2500 ± 0.0004 g of the dried grass, soil or grass ash was placed into 100 mL tetrafluoromethoxyl (TFM) vessel with 5.0 mL of concentrated HNO₃ (65%) and 3 mL concentrated HCl (36%) before undergoing microwave digestion. For grass samples, 3 mL of concentrated H₂O₂ (30%) were added instead of HCl. Samples were digested in a microwave oven for 5 min at 700 W (to reach 180 °C) and 10 min at 500 W (to keep 180 °C). After cooling, samples were transferred into calibrated polypropylene tubes and diluted to 25.0 mL with deionized water.

2.4.2. Sample preparation for Cr(VI) determination

The leaching of Cr(VI) from soil, grass and ash samples was carried out with 0.1 M Na₂CO₃ according to the procedure, which was described in our previous articles [3,16]. For this purpose, approximately 0.2500 ± 0.0004 g of dry plant, ash or soil sample was weighed in a 100 mL glass beaker and 25.0 mL of 0.1 M Na₂CO₃ was added. After boiling on a hot plate for 15 min, samples were transferred to polypropylene tubes without filtration and diluted to 25.0 mL with deionized water. All samples, before analysis were filtrated through a 0.45 µm PVDF filter and placed in the sampling cups of the AS-800 autosampler for Cr(VI) determination.

3. Results and discussion

3.1. Analytical results of chromium determination

Because the absorption signals of chromium, obtained after atomization of the same amount of Cr(III) and Cr(VI) from the corresponding standard solutions do not differ in their appearance time nor in values of integrated absorbance [3], the calibration has been performed with Cr(III) standard solutions.

Table 1
Results of total chromium and Cr(VI) determination in CRMs

CRMs	Cr species	Certified value ($\mu\text{g g}^{-1}$)	Found value ($\mu\text{g g}^{-1}$)
CRM 281	Total Cr	2.14 ± 0.12	2.27 ± 0.19
MESS-3	Total Cr	105.0 ± 4.2	107.3 ± 6.3
PACS-2	Total Cr	90.7 ± 4.6	90.8 ± 4.8
CRM 545	Cr(VI)	40.2 ± 0.6^a	38.8 ± 1.2^b

^a Certified value in $\mu\text{g mg}^{-1}$.

^b Found value in $\mu\text{g mg}^{-1}$.

The calibration graph is linear up to $50 \mu\text{g L}^{-1}$ and is described by the following equation: $Y = 0.0065X - 0.0043$, where X is the analyte concentration ($\mu\text{g L}^{-1}$) and Y is the integrated absorbance, with correlation coefficient $R^2 = 0.9987$. The limit of detection (LOD) of Cr(VI), using solutions of $0.1 \text{ M Na}_2\text{CO}_3$ as blanks (3s criteria, $n = 11$) was found to be $0.24 \mu\text{g L}^{-1}$. Therefore, for plants and soil samples, assuming that the leaching of Cr(VI) was carried out from 0.25 g of soil or plant material with 25.0 mL of $0.1 \text{ M Na}_2\text{CO}_3$, the LOD of Cr(VI) determination is $0.024 \mu\text{g g}^{-1}$. Results of chromium determination in CRMs show a good correspondence between found and certified values of total Cr and Cr(VI) species (Table 1).

3.2. Thermodynamical data for Cr(III) oxidation with atmospheric oxygen

Thermodynamical data for calculations of standard Gibbs free energy change ($\Delta_r G^\circ$) were taken from Lange's Handbook of Chemistry [17]. The calculated values of Gibbs free energy change ($\Delta_r G^\circ$) at standard conditions and their changes with temperature for reactions (2) and (3) of Cr(III) oxidation with atmospheric oxygen in presence of Na_2CO_3 and K_2CO_3 are given in Table 2. Since $\Delta_r G^\circ$ is negative for both reactions, Cr(III) can be oxidized to Cr(VI) in burning plants. More negative $\Delta_r G^\circ$ value for Cr(III) oxidation in presence of K_2CO_3 means greater reaction efficiency. Because the amount of chromium, Na_2CO_3 and K_2CO_3 which were formed in ash of different plants may be different, the results of ($\Delta_r G^\circ$) calculations presented in Table 2 should be considered as approximate values for calculation of Cr(VI) output after the burning of grass. It is known that the average content of alkali and alkaline earth elements in dried plant matter fluctuate around average 1.9% for

Table 2
Free energy change for Cr(III) oxidation calculated per mole of Na_2CrO_4 or K_2CrO_4

Temperature ($^\circ\text{C}$)	$\Delta_r G^\circ$ (kJ mol^{-1})	
	Na_2CrO_4	K_2CrO_4
25	-58.3	-99.2
500	-84.8	-129.0
600	-90.8	-135.4
700	-97.0	-141.7
800	-103.0	-148.1
900	-107.4	-154.3

Table 3
Results of Cr(VI) and total Cr determination in grass, *Hyperthelia dissolute*

Sample	Cr(VI) ($\mu\text{g g}^{-1}$)	Total Cr ($\mu\text{g g}^{-1}$)	Cr(VI)/Cr total (%)
1	0.30	11.0	2.7
2	0.34	11.8	2.9
3	0.35	15.4	2.3
4	0.26	12.5	2.1
5	0.27	14.4	1.9
6	0.28	9.7	2.9
Mean	0.30 ± 0.05	12.5 ± 2.2	2.5 ± 0.5

potassium, 0.15% for sodium, 1.0% for calcium and 0.2% for magnesium [18].

The change of Gibbs free energy with increasing temperature to more negative values indicates that high temperature favors Cr(III) transition into Cr(VI). The calculations were made on the assumption that $\Delta_r H^\circ$ and $\Delta_r S^\circ$ are constant in the $500\text{--}900 \text{ }^\circ\text{C}$ temperature range.

3.3. Results of Cr(VI) formation during thermal treatment of grass ash in a muffle furnace

The possibility of Cr(VI) formation was tested by the treatment of grass samples at high temperature in a muffle furnace. For this, a set of 30 grass samples ($0.2500 \pm 0.0004 \text{ g}$ each) were ashed in individual crucibles at $200 \text{ }^\circ\text{C}$ for 4 h. Then, set of six samples of ash were additionally heated for 1 h at steadily increasing temperatures, ranging from 500 to $900 \text{ }^\circ\text{C}$. This range of temperatures was chosen because similar values were measured with a thermocouple in the burning fields [18]. After heating at specific temperature for 1 h, samples were used for Cr(VI) determination, confirmation of the total amount of Cr and Cr(VI) formed in ash after addition of K_2CO_3 .

The concentration of Cr(VI) in air-dried grass (Table 3), was found to be quite uniform ($0.30 \pm 0.05 \mu\text{g g}^{-1}$), as well as the total amount of chromium ($12.5 \pm 2.2 \mu\text{g g}^{-1}$). After thermal treatment of the grass in muffle furnace at different temperatures the concentration of Cr(VI) became much higher. Results presented in Fig. 1 shows that after the treatment of grass ash at $500 \text{ }^\circ\text{C}$, the concentration of Cr(VI) increased from initial "nat-

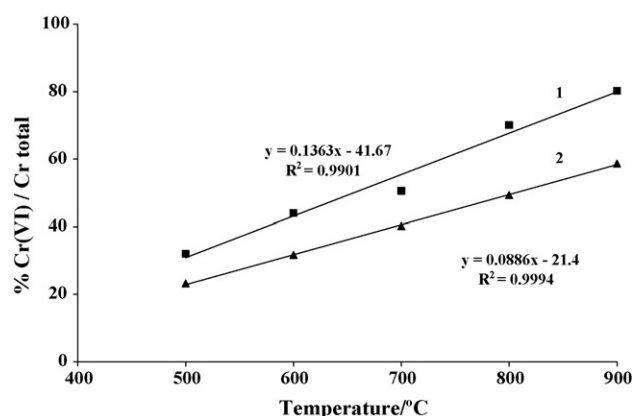


Fig. 1. Conversion of Cr(III) to Cr(VI) in grass ash at different temperatures with (1) and without (2) addition of K_2CO_3 .

Table 4
Results of Cr(VI) and total chromium determination in ash and soil samples

Samples	Cr(VI) ^a ($\mu\text{g g}^{-1}$)	Cr total ^a ($\mu\text{g g}^{-1}$)	Cr(VI)/Cr total (%)
Top soil, 0–3 cm unburned grass	0.21 \pm 0.08	26 \pm 9	0.80 \pm 0.4
Soil at 20 cm depth unburned grass	0.25 \pm 0.1	29 \pm 16	0.90 \pm 0.4
Top soil, 0–3 cm burned grass	1.8 \pm 0.5	69 \pm 14	2.7 \pm 1.0
Black ash	3.2 \pm 0.9	34 \pm 3	9.3 \pm 3.0

^a Average of four determinations at 95% level of confidence: mean \pm $t_{\alpha,n} \times (s/\sqrt{n})$.

ural” level of 2.5% in respect to the total amount of chromium, to 23.2%, and to 58.1% after heating at 900 °C.

The results of Cr(VI) formation with addition of 10.0 mg K_2CO_3 show that in accordance with thermodynamic calculations, efficiency of Cr(VI) formation increased in comparison with samples, to which K_2CO_3 was not added (Fig. 1).

3.4. Results of Cr(VI) determination in field ash samples

The grass ash that was formed after fires in the field, usually include pure white ash and black ash. The latter prevails. Pure white ash is a product of complete grass combustion. Black ash contains carbonized and partially burned stems and leaves, because fire was not sufficiently hot for their complete combustion. The presence of Cr(VI) in black ash samples has been confirmed by EPA recommended method 7196A of colored complex formation with 1,5-diphenylcarbazide [19], but its relatively poor detection limit of $30 \mu\text{g L}^{-1}$ [20] in comparison with ETAAS detection ($0.24 \mu\text{g L}^{-1}$) was not enough for Cr(VI) detection in all samples.

The results of Cr(VI) and total Cr determination by ETAAS (Table 4) show that the content of both chromium species in black ash (3.2 ± 0.9 and $34 \pm 3 \mu\text{g g}^{-1}$) were much higher than in grass itself ($0.3 \pm 0.05 \mu\text{g g}^{-1}$ versus $12.5 \pm 2.2 \mu\text{g g}^{-1}$). This result can be explained by “preconcentration” of both chromium species by “ashing”, because the main part of organic matter was destroyed during grass combustion. Without oxidation, the percent of Cr(VI) in ash should be the same as in non-burned grass. Higher percent of Cr(VI) in grass ash, $9.3 \pm 3.0\%$, in comparison with Cr(VI) concentration in non-burned grass, $2.5 \pm 0.5\%$ can only be linked to Cr(III) oxidation by atmospheric oxygen.

3.5. Results of Cr(VI) determination in soil samples

Before combustion of grass, the Cr(VI) concentration in top soil samples taken at 0–3 cm depth was found to be only $0.21 \pm 0.08 \mu\text{g g}^{-1}$ (Table 4). This value does not differ from Cr(VI) concentration, $0.25 \pm 0.10 \mu\text{g g}^{-1}$, in soil samples taken at 20 cm depth. The total amount of chromium in top soil sample, $26 \pm 9 \mu\text{g g}^{-1}$ were also not different from $29 \pm 16 \mu\text{g g}^{-1}$ in soil sample on 20 cm depth.

After grass was burned down, the Cr(VI) concentration in top soil increased to $1.8 \pm 0.5 \mu\text{g g}^{-1}$ and the total Cr to $69 \pm 14 \mu\text{g g}^{-1}$. The reason for the appearance of additional amount of Cr on top soil can be associated with condensation of chromium species from flame and smouldering ash on a cool soil surface. As a consequence of chemical changes in burning

grass some additional amount of Cr(VI) species settles on the top soil surface. The phenomena of top soil enrichment with Na, K, Mg and Ca after grass burning and its influence on soil properties had been reported previously [21]. Additional amounts of these elements will be consumed by new generation of plants as nutrients, but the consumption of Cr(VI) can contaminate plants with dangerous species.

4. Conclusions

Thermodynamic calculations and model experiments with yellow thatching grass, *H. dissoluta*, treated at high temperature in muffle furnace confirm the possibility of Cr(III) to Cr(VI) oxidation with atmospheric oxygen. It was found that the initial content of Cr(VI) in grass, 2.5%, in respect to the total amount of Cr, increased to 23% after 1 h of heating at 500 °C and to 58% at 900 °C.

In accordance with thermodynamic calculations, the efficiency of Cr(III) oxidation with atmospheric oxygen increased after addition of K_2CO_3 .

It was found that before fire, Cr(VI) in top soil ($0.8 \pm 0.4\%$) was not different from Cr(VI) concentration in soil at 20 cm depth ($0.9 \pm 0.4\%$), while after the fire Cr(VI) concentration in top soil increased to $2.7 \pm 1.0\%$. It appears to be that ashing enriches the surface of top soil with Cr(VI) species.

The percent of Cr(VI) in grass ash, in respect to the total amount of Cr was found to be $9.3 \pm 3.0\%$, in comparison with $2.5 \pm 0.5\%$ of Cr(VI) in non-burned grass. Such an increase of Cr(VI) can only be explained by Cr(III) oxidation.

The results of this studies demonstrate that Cr(VI) presence in soils of unpolluted remote areas of South Africa is connected with the oxidation of Cr(III) with atmospheric oxygen during bush fires.

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