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The application of tree bark as bio-indicator for the assessment of Cr(VI) in air pollution

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Abstract

The impact of a chromium smelter on pollution was evaluated by determining Cr(VI) in topsoil, grass and tree bark by electhrothermal atomic absorption spectrometry (ETAAS). It was found that bark reflected the levels of air pollution better than soil and grass due to its high accumulative ability of Cr(VI). The tree bark was contaminated with Cr(VI) by a factor of 9 than in soil. It is therefore suggested that the bark be used as an indicator of air pollution for long-term exposure. The concentration of Cr(VI) in the bark was always a fraction of the total concentration of Cr and ranges between 1.6 and 3%. The method used in the preparation of samples was validated by the analysis of certified reference materials.

Keywords: Tree bark; Bio-indicator; Air pollution; Electhrothermal atomic absorption spectrometry

1. Introduction

The significant contribution of air pollution to the diminished health status of the exposed human populations has been a cause of increasing public concern throughout the world. A wide array of air pollutants including particulates, liquids, and gases are being emitted both from natural and anthropogenic sources. The controlling of air pollutants is a very complex problem as source of emission has to be identified, analytical methods to monitor pollutants have to be evaluated, risks involved have to be assessed, critical emissions have to be controlled, and economical aspects have to be integrated [1,2].

Biological indicators are normally used as a complementary system to monitor the effects of air pollutants and to provide reliable indications on the quality and the characteristics of the environment. Lichens and tree barks are the most widely used bio-indicators of air pollution because of their ability to detect numerous pollutants [3,4]. They overcome some of the shortcomings that are associated with direct measurements of pollution that depicts the impact of environmental pollution on organisms, and can potentially detect the long-term exposure of a site to environmentally harmful chemicals.

Most soils have the ability to immobilize the introduced metal species as a result of sorption properties that depend on the organic fraction, the pH, water content, temperature of the soil, and the properties of the particular metal ion [5,6]. All these play a significant role in giving the soil the ability to absorb, exchange, oxidise or reduce, catalyse, and precipitate chemicals and metal ions in particular.

Intracellular uptake of metal ions is a passive process of ion exchange that is determined by the character of the ligands in the plant cell wall, whereas intracellular uptake is limited by the nature of the metal ion, cell membrane permeability, and the concentration of extracellular ligands with affinity for cations [7]. Tree barks are appropriate natural bio-indicators for the assessment of long-term air pollution. The bark is exposed to air pollutants either directly from the atmosphere or from steam flow. Kuik and Wolterbeek proposed the use of tree bark samples as bio-monitors of heavy metal pollution in The Netherlands [8]. Tree barks used were recommended for larger scale surveys because of their greater availability and furthermore, bark sampling does not have an effect of the health of trees [9].

A biological monitoring survey of airborne metals was also carried out in a large area of the Kruger National Park, South Africa, to check the influence of copper pollution from the Phalaborwa copper smelter and mine on vegetation and animals [10]. Their results indicated that applications of bio-indicators such

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as barks were important for monitoring atmospheric deposition of metal.

Hexavalent chromium, Cr(VI), is such a potent carcinogenic and toxic agent for the respiratory tract that continuous monitoring is necessary. Although the mechanisms of Cr(VI) biological interaction are uncertain, its toxicity may be related to the ease with which it passes through cell membranes and its subsequent intracellular reduction to reactive intermediates. A number of studies have associated long-term exposure to Cr(VI) with both chronic health effects and increased mortality [11,12]. Furthermore, Cr(VI) activation is suspected of resulting in the chromium binding to DNA, thus altering its conformation [13].

The aim of the present study was to test the tree bark as a bio-indicator for Cr(VI) contamination of the environment and compare the results obtained to that of plants and soil.

2. Experimental

2.1. Apparatus

A Perkin-Elmer AAnalyst-600 atomic absorption spectrometer with Zeeman-effect background correction equipped with Cr hollow cathode lamp operating at 25 mA was used for all measurements. The wavelength and spectral band pass were set at 357.9 nm and 0.7 nm, respectively. Transversely heated graphite tubes (THGA) with integrated L'vov platforms (Perkin-Elmer, part N B050-4033) were used as atomizers with Argon as the sheath gas throughout.

2.2. Reagents and standard solutions

Standard stock solutions containing 1000 mg l^{-1} Cr(VI) as K_2CrO_4 (Merck) was used for the preparation of working standards for chromium. Ultra-pure water (resistivity, 18.2 MΩ cm), obtained from a Milli-Q water purification system (Millipore Corp., USA), was used for all dilutions and sample preparation. Ultra-pure $HClO_4$ (Merck), HF (Merck) and HCl (Merck) were used during the digestion for the total chromium determination. Hydrophilic PVDF 0.45 μm filters (Millipore Millex, USA) were used for the filtration of all solutions. Certified reference materials: PACS-2, MESS-3 (marine sediments for trace metals obtained from the National Research Council of Canada) and CRM 545 [atmospheric dust that contains only Cr(VI), Brussels] were used as quality control samples for the evaluation of analytical results of total and Cr(VI) determinations.

2.3. Collection of tree bark samples

Samples of bark were collected from free-standing trees around the chromium smelter in the North West Province of South Africa on September 2003. Outer rough, peeling of approximately 100 g was removed manually from *Acacia karroo Hayne*, commonly known as sweet thorn tree at 1.5–1.8 m above ground. Soil and grass (*Chloris gayana*) were taken from the same area to compare the level of the analytes to that in bark samples. The soil samples analyzed represented 20 cm of the upper soil layer and were collected into plastic bags.

Other similar types of sample matrices were collected in an uncontaminated area 100 km away for the purposes of checking the contamination factor with reference to the control site. The samples were carefully washed with deionized water, air-dried and homogenized by grinding in a IKA A11 milling system to a grain size less than 200 μm.

2.3.1. Sample preparation for the determination of Cr(VI)

Approximately 0.25 g of dry ground bark, soil or grass sample was weighed and transferred into a 100 ml glass beaker. Twenty-five millilitre of 0.1 M Na_2CO_3 was added and the content of the beaker was boiled on a hot-plate for ten minutes [14,15]. After cooling, the sample was filtered through Whatman no. 1 filter paper and diluted to a final volume of 25.0 ml with deionized water. Before the determination of Cr(VI) the solution was filtered through Hydrophilic Millipore PVDF 0.45 μm filter to remove Cr(III) species that may be trapped in the colloidal suspension.

2.3.2. Sample preparation for the determination of total Cr

For the determination of total concentration of Cr in the respective samples, 10 ml of concentrated HF and 2 ml of concentrated $HClO_4$ were added to 0.25 g of the sample in a platinum crucible. The mixture was heated till evaporation of the excess acid. To eliminate the remaining organic matrix, 2 ml of $HClO_4$ was added and heated to dryness. The residue was dissolved in 5 ml of 6 M HCl and diluted to 50.0 ml with deionized water.

3. Results and discussions

3.1. Temperature programme for the determination of Cr

The analysis of the samples were carried out to evaluate Cr(VI) and total Cr concentrations using electrothermal atomic absorption spectrometry (ETAAS) as a method of detection on a Perkin-Elmer AAnalyst-600 atomic absorption spectrometer, using recommended temperature program summarized in Table 1 [15]. The pyrolysis temperature used enhances the complete removal of the matrix prior atomization thereby preventing any influence of the matrix during atomization.

3.2. Analytical determination

The leaching of Cr(VI) in solid samples is easily achieved by treating the solid sample with 0.1 M Na_2CO_3 [15]. The insoluble Cr(VI) compounds are transformed into soluble form

Table 1
Temperature program for the determination of Cr

Step	Temperature (°C)	Ramp (s)	Hold (s)	Ar (ml min^{-1})
1	110	1	10	250
2	250	5	20	250
3	1400	5	30	250
4	2450	0	5	0
5	2450	1	3	250

Table 2
The results of the determination of Cr(VI) and total Cr in CRM ($\mu g\,g^{-1}$)

CRM	Total Cr		Cr(VI)	
	Certified	Found[a]	Certified	Found[a]
CRM 281, rye grass	1.68 ± 0.41	1.78 ± 0.25	–	–
CRM 545, atmospheric dust	–	–	39.5 ± 1.3	38.9 ± 1.2
PACS-2, marine sediments	90.7 ± 4.6	92.1 ± 3.8	–	–
MESS-3, marine sediments	135 ± 5	133 ± 6	–	–

[a] Average of six determinations at 95% level of confidence: mean $\pm\, t_{0.05} \times (s/\sqrt{n})$.

in an alkaline media forming Na_2CrO_4 while Cr(III) species form insoluble hydroxides or carbonates [16]. Therefore, by the treatment of solid samples with 0.1 M Na_2CO_3, Cr(III) and Cr(III) species are separated. Any Cr(III) species that remained in the colloidal suspension were removed from solution before analysis by filtering the resultant solution through hydrophilic Millipore PVDF 0.45 μm filter.

Though quality control of the analytical results seemed unnecessary as the analysis was carried using the well established method [10,14], certified reference materials (CRM), viz. MESS-3, PACS-2, CRM 281 and CRM 545 were analyzed to verify the method.

A summary of the determination of Cr(VI) and total Cr in CRM is presented in Table 2. The results of the analysis show good agreement between found and certified values thereby validating the whole analytical procedure.

3.3. Results of Cr(VI) determination in bark samples

Table 3 is a summary of the comparison of the levels of Cr(VI) and total Cr in bark with that of other sample matrix from the same area. The results show that the bark has high Cr(VI) levels as compared with soil and grass. The contamination factor of Cr(VI) in grass is approximately 74 times less than that on the tree bark. Furthermore, Fig. 1 which is a plot of the concentration of Cr(VI) in soil and bark against distance from the smelter, shows that that the deposition and accumulation of chromium decreases with increasing distance from the main source of emission.

Table 3
Results of Cr(VI) and total Cr determination in a sample of potential bio-indicators around chromium smelter for the assessment of air pollution

Sample	[Cr(VI)][a] ($\mu g\,g^{-1}$)	[Cr][a] ($\mu g\,g^{-1}$)
Soil	4.8 ± 0.3	5270 ± 272
Uncontaminated soil	0.25 ± 0.03	320 ± 25
CF	19	17
Grass	3.5 ± 0.4	132 ± 10
Uncontaminated grass	0.19 ± 0.02	5 ± 0.02
CF	4	26
Bark	44.2 ± 1.6	1400 ± 122
Uncontaminated bark	0.2 ± 0.04	4.8 ± 0.41
CF	221	29

CF, contamination factor.
[a] Average of six determinations at 95% level of confidence: mean $\pm\, t_{0.05} \times (s/\sqrt{n})$.

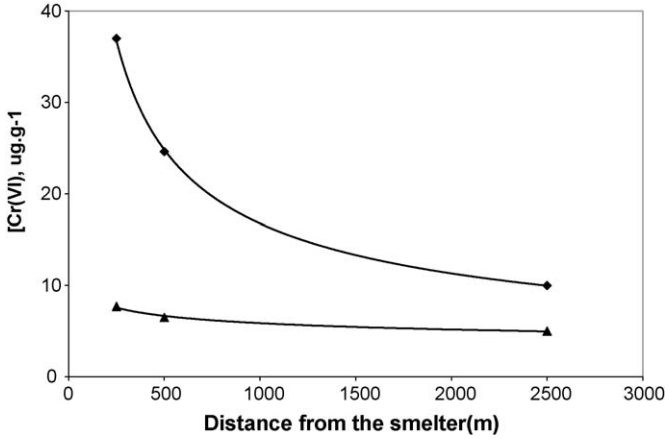

Fig. 1. Cr(VI) concentration in samples versus distance from the smelter: (♦), tree bark; (▲), Soil.

The levels of Cr(VI) in soil and bark samples is very high in the vicinity of the chrome smelter. The higher concentration of Cr(VI) in the bark is due to the high accumulation ability of the bark over the long period of time due to its large surface area. These concentrations represent the integrated value of Cr(VI) concentrations near the chrome smelter. This can also be associated with the observation made by Panichev and McCrindle [10], where the oxidation potential in bark was found to be higher than in soil. In contrast, grass accumulates chromium by much less factor than soil and bark samples.

The absorbance-time signals of total Cr and Cr(VI) in a bark sample (Fig. 2) indicates that the concentration of Cr(VI) in the bark samples is always a fraction of the total concentration of Cr and was in the range between 1.6 and 3%. Fig. 3 shows that even though bark has higher levels of Cr(VI) than soil, the total

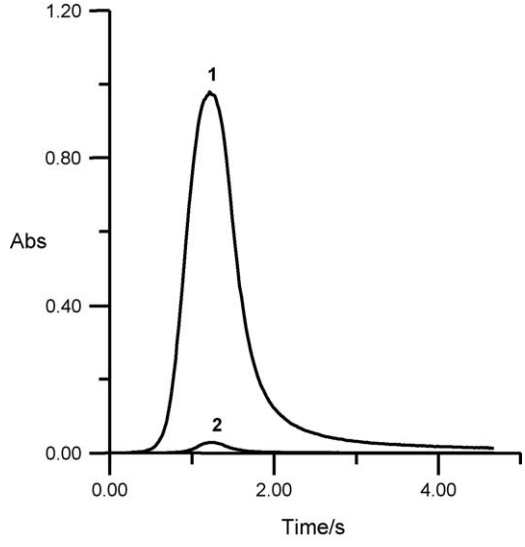

Fig. 2. Absorbance-time signals of total Cr and Cr(VI) in a bark sample: (1) total Cr; (2) Cr(VI).

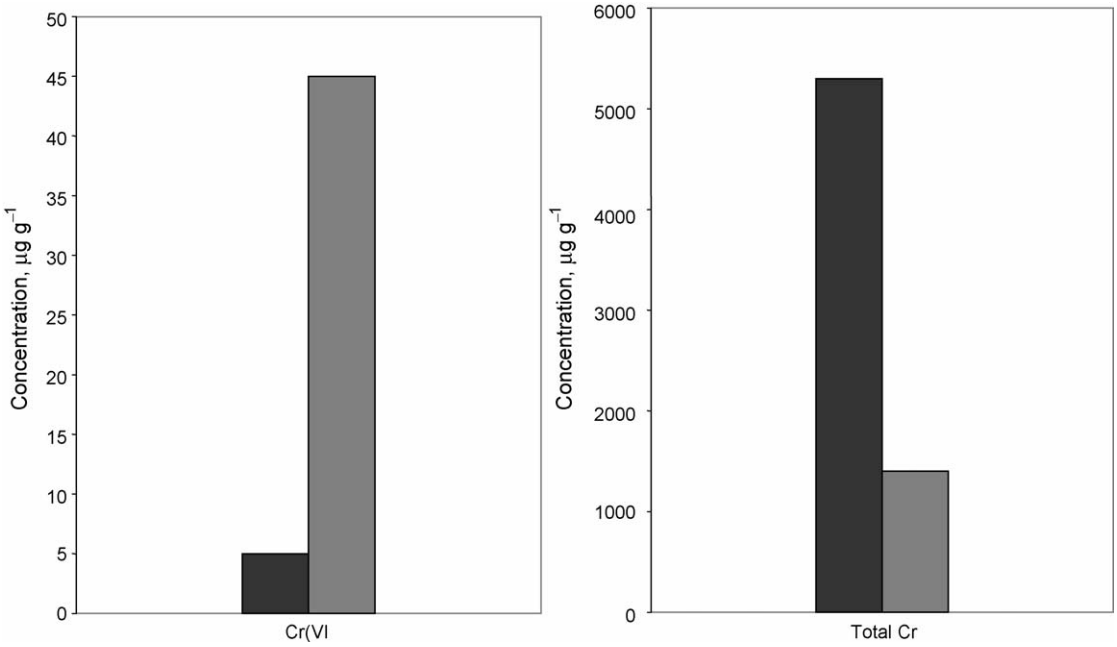

Fig. 3. Comparison of the ratio of Cr(VI) and total Cr in soil and bark: (■), Soil; (■), tree bark.

Cr concentration in soil is much higher than in the bark because soil has other sources of Cr like rocks, water, etc.

Generally, the results of the investigation indicate that the area around the chromium smelter in South Africa is polluted with Cr(VI). This is confirmed by the high level of this pollutant in bark samples. Soil show low levels of Cr(VI) may be because the pollutant is highly mobile due to its high oxidation state [15,17] such that during rainy seasons, it can easily be transported from one place to the other due to the action of CO_2 with the soil–water system. The positive results of the investigation was that the level of Cr(VI) in grass was found to be rather low such that plants has low accumulative ability of this pollutant. Therefore, it seems unlikely that animals including humans can have symptoms of Cr poisoning by consuming plants.

In contrast, the bark has high accumulation ability of Cr and the main source is suspected of being airborne and atmospheric dust from the smelter. Therefore, the hazard posed by Cr(VI) comes from air pollution or from direct deposition of dust on plants, followed by ingestion together with grass by animals.

The bark content reflects chromium species accumulated for long period of time. Therefore, they are more reliable than measurements of chromium from air samples collected once by filters. This is because trees are always there on the field all the time of the year and continue accumulating dust particles for years, and therefore can be used as good bio-indicators for environmental pollution. The higher levels of Cr(VI) in the bark samples may be the indicator which show that people, animals and plants in the area were exposed to this pollutant for longer period of time.

4. Conclusions

The results of the investigation showed that the tree bark can be used to asses the impact of Cr(VI) as a pollutant in the specific geographical area. This is because the bark has high accumulating ability of chromium from both atmospheric aerosols and dust. Therefore, Cr(VI) should be monitored in atmospheric aerosols released from the chromium smelter and efforts should be made to reduce this pollutant if it is above the maximum acceptable levels as this is the main way of exposure.

Grass consumption by animals is not expected pose any problems as their rate of accumulating Cr(VI) seemed to be limited to low levels of this pollutant.

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