

Short communication

Electrothermal atomic absorption spectrometric determination of total and hexavalent chromium in atmospheric aerosols

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Abstract

A method was developed which allow separate determination of Cr(VI) and total Cr from the same minute sample of atmospheric aerosols. Cr(VI) was leached with 0.1 M Na₂CO₃ and the total Cr concentrations were determined after acid digestion. The method was validated by the analysis of certified reference materials, CRM 545, Mess-3 and Pacs-2 with good agreement between certified and found values. Cr concentrations in air samples taken around the chromium smelter show concentrations that exceed the maximum allowed levels in 8 h with higher values closer to the smelter. The limit of detection (LOD) of the method for Cr(VI) determination in air samples was found to be 0.2 ng m⁻³, i.e. lower than offered by the commonly preferred spectrophotometric and colorimetric techniques.

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1. Introduction

The increasing number of industrialization activities has impacts on air quality around the world. The effects of industrial emissions on human health have been associated with air pollution [1]. Though atmospheric aerosol particles originate from both natural and anthropogenic sources, the latter are likely to exceed natural ones on a local scale due to the existence of important point sources as in many cities and industrialized areas [2].

Mining activities, specifically smelter processes, release metals into the air as fine particulate matter. Metals introduced into the atmosphere may be carried to the land surface by precipitation and dry fallout. In the process of chromium metal production, compounds of Cr(VI) are detected in soils and airborne particles as a result of both aerial transport and deposition of dust produced in the chromate processes.

Under normal conditions, chromium is not expected to create any unusual health hazard. However, if the product is subjected to burning, grinding or machining, then the metal particulate matter or elemental oxides from the products may be released.

Chromium's nutritional role has not been thoroughly delineated, but it appears that Cr(III) potentiates some metabolic activities in the human digestive system. It is known to prevent adverse effects in the metabolism of glucose and lipids [3–7]. In contrast, hexavalent chromium is primarily man-made and can diffuse as CrO₄²⁻ through cell membranes and oxidize biological molecules with toxic results [8].

Cr(VI) compounds have been shown to be a human respiratory carcinogen in epidemiological studies [9–12] when exposed to relatively high levels in the workplace. The occupational exposure to a toxicant is normally assessed against a threshold limit value, which is often expressed as a time weighted average (TLV-TWA), according to the ACGIH [13]. Permissible exposure limits for different chromium substances over an 8 h period are summarized in Table 1.

A variety of spectrophotometric and colorimetric techniques have been devised for the determination of Cr(VI) [18,19]. The most prevalent colorimetric method uses the selective reaction of Cr(VI) with 1,5-diphenylcarbazone complex. This spectrophotometric method suffers from the presence interfering compounds, which may be solubilized during the extraction of Cr(VI). These include compounds that reduce Cr(VI) under the acidic condition of the standard DPC method and species that absorb at the analytical wavelength of interest of DPC–Cr

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Table 1
Permissible exposure limits for different chromium substances over an 8 h period

Exposure limit (mg m ⁻³)	Regulatory body
0.05	ACGIH [13]
0.1 (as CrO ₃)	OSHA [14]
0.5 µg m ⁻³	OSHA [15]
0.001	NIOSH [14]
0.05	UK HSC [14]
0.05	DOL, DME [16,17]

colored complex [20]. The technique also suffers from poor sensitivity and high detection limitation. In spite of a tremendous number of publications connected with Cr(VI) speciation in different environmental samples [21,22], there is a notable lack of information pertaining to the speciation of Cr(VI) in air samples.

The method that has been successfully applied for the leaching of Cr(VI) from soil [23] was tested for the extraction of Cr(VI) in atmospheric aerosols followed by the determination with electrothermal atomic absorption spectrometry (ETAAS). The paper outlines a procedure for the leaching of Cr(VI) with Na₂CO₃. The developed method was applied to determine the levels of Cr(VI) in air particulate around the chromium smelter.

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 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. Polytetrafluoroethylene (PTFE) Membrane Filters from Millipore, FGLP 04700 with 0.2 µm of pore size and MF-Millipore Membrane Filters, PHWP 04700 with 0.3 µm of pore size were used for the collection of samples.

2.2. Reagents and standard solutions

Standard stock solutions containing 1000 mg l⁻¹ Cr(VI) as K₂CrO₄ (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 HClO₄ (Merck), HF (Merck) and HCl (Merck) were used during the digestion of the residue for the total chromium determination in atmospheric aerosols. 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 [Cr(VI) in atmospheric dust, BCR, Brussels] were used as quality control samples for the evaluation of analytical results of total and Cr(VI) determinations.

2.3. Sampling of airborne dust

Sampling of airborne dust were carried out at different sites around the chromium smelter simultaneously using portable Airmetrics Minivol samplers, which were positioned at a height of 2 m above the ground level. Air samples were collected on pre-weighed 47 mm diameter filters. Samplers were calibrated to an airflow rate of 5 L min⁻¹. Samples were collected over a period of 8 h using a size-selective PM₁₀ inlet of 10 µm aerodynamic diameter. Filters were weighed before and after sampling to 0.01 mg precision. Filters were stored in plastic petri dishes. All equipment was stored in plastic bags in a dust free environment.

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

The filters were removed from the petrislides with forceps and placed in a 100 mL beaker with the dust loaded side facing downwards. Exactly 5.00 mL of 0.1 M Na₂CO₃ solution was added to the filter. The beaker with the filter was boiled on a hotplate for about 10 min, with occasional swirling and careful observation not to boil it to dryness as that could result in conversion of Cr(VI) to Cr(III) due to excess heat [24]. After the treatment, the solution was transferred to 10 mL plastic tube and diluted with deionized water to a 5 mL mark. Before analysis, a 1.0 mL aliquot was filtered through 0.45 µm filter and placed in the sampling cups of the ETAAS autosampler.

2.3.2. Determination of total Cr

After the determination of Cr(VI), the remaining solution was evaporated to dryness in a sintered Pt crucible and the residue was treated with a mixture of 2 mL conc. HClO₄ and 1 mL conc. HF and finally dissolved in 0.5 mL conc. HCl. The final volume of the solution was adjusted to 10 mL with deionized water. Certified reference materials were also prepared in the same way.

3. Results and discussion

3.1. Temperature programme for the determination of Cr

The temperature program used by Panichev et al. [23] in the determination of Cr(VI) in soil samples was used for all analysis. The program is summarized in Table 2. Atomic profiles of Cr(VI) in aqueous standard solutions and air samples treated with Na₂CO₃ have same shape and appearance time indicating that the pyrolysis temperature has removed the majority of the

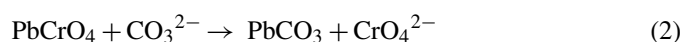
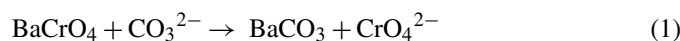
Table 2
Temperature program for the determination of Cr

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

matrix prior atomization and any residual amount of Na_2CO_3 had no influence on the release of Cr during atomization.

3.2. Extraction of Cr(VI)

For extraction of Cr(VI), all samples were treated with Na_2CO_3 solution in order to transform the insoluble Cr(VI) compounds to soluble forms according to the equations:



The procedure removes all common metals, including Cr(III) as insoluble carbonates, oxides, hydroxides, and basic carbonates, and also improves sample recovery and maintains the valence stability of Cr(VI) species [25]. After filtration, the solution contains only CrO_4^{2-} anions that were originally present in the sample in the form of insoluble salts of Cr(VI), like BaCrO_4 or PbCrO_4 (Eqs. (1) and (2)), as their soluble sodium salts.

3.3. Validation of the methods for the determination of total Cr and Cr(VI)

Standard reference materials were analyzed to evaluate the validity of the applied methods in the determination of total Cr and Cr(VI) in the collected samples. A summary of such analysis is shown in Table 3. Results of chromium determinations in CRMs are in good agreement with certified values and therefore the applied method was validated.

3.4. Results of Cr(VI) determination in air sample collected in filters

The limits of detection of Cr(VI) determination in air samples was established using a blank solution of Na_2CO_3 . The value of LOD, calculated according to the equation: $\text{LOD} = X_{\text{bl}} + 3s_{\text{bl}}$ ($n = 25$), where X_{bl} is the average blank concentration and s_{bl} is the standard deviation of the blank determination was found to be 1.4 ng of Cr(VI) or 0.2 ng m^{-3} as the concentration of Cr(VI) in air for a $10 \mu\text{L}$ of sample solution. The developed method therefore offers very low detection limit as compared with the commonly used spectrophotometric methods [18,19].

The results of the determination of Cr(VI) from all sites are summarized in Fig. 1. The results show that Cr(VI) is always present in relatively small concentrations with reference to the total Cr concentration. The higher levels of Cr(VI) in some samples are attributed to the marked increase in wind episode during sampling.

Table 3
Results of total chromium and Cr(VI) determinations in certified reference materials

CRM	Certified value ($\mu\text{g g}^{-1}$)	Measured value ($\mu\text{g g}^{-1}$)	Analyte
Mess-3	135 ± 5	132 ± 6	Cr
Pacs-2	90.7 ± 4.6	92.2 ± 3.4	Cr
CRM 545	39.5 ± 1.3	38.8 ± 1.2	Cr(VI)

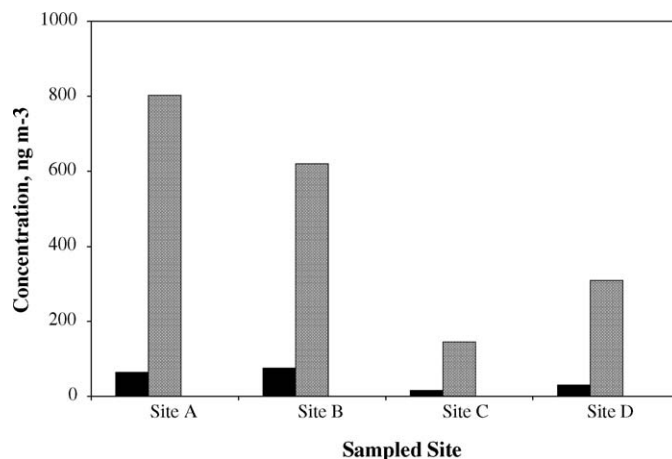


Fig. 1. Comparison of the concentration of Cr in different sites around the ferrochrome smelter: (■) Cr(VI); (▨) total Cr.

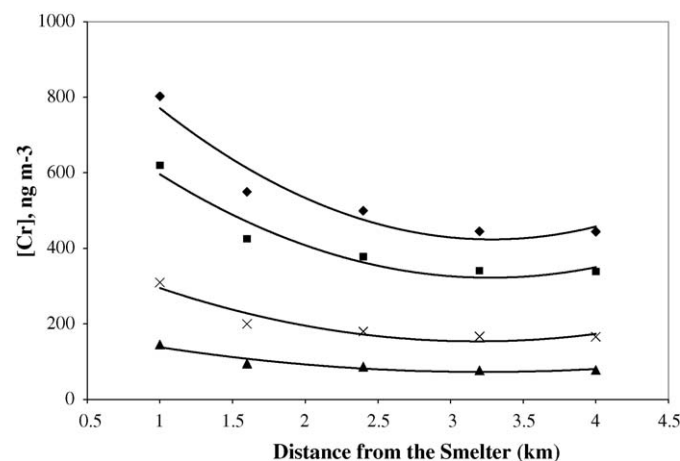


Fig. 2. Levels of Cr as a function of distance from the smelter: (◆) Site A; (■) Site B; (▲) Site C; (×) Site D.

The total content of chromium in air samples were compared with the maximum permissible exposure per 8 h [14]. Fig. 1 shows that out of four sites evaluated, Cr concentration exceeded the maximum acceptable level in two of the sites i.e. Sites A and B. The higher contamination in these sites may be influenced by winds that mostly blow in that direction with reference to the chromium smelter. The concentration of total amount of Cr varied between 145 and 800 ng m^{-3} . The results shown in Fig. 2 indicate that areas closer to the chromium smelter are more contaminated than those that are further away.

4. Conclusions

The determination of total Cr and Cr(VI) can be easily carried in small collected air sample. This is achieved by determining Cr(VI) first, followed by the determination of total Cr. The proposed method can reliably be used as its results were confirmed with good agreement between measured and certified values of the analytes in the reference materials. The higher values of Cr obtained around the chromium smelter illustrate more realistically the potential hazardous environment that may be created

by Cr(VI) emissions in the area as the values are higher than acceptable limits. The contamination of the area with Cr is more concentrated closer to the smelter (the source of pollution).

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