

Determination of Cr(III), Cr(VI) and total chromium in atmospheric aerosol samples

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Abstract. This study addresses the optimization and validation of an analytical method based on the ultrasound-assisted extraction of soluble Cr from atmospheric particulate matter (PM) and subsequent determination of Cr(III) and Cr(VI) by catalytic adsorptive stripping voltammetry (CA_{ASV}) by using diethylenetriamino pentaacetic acid (DTPA) as complexing agent in the presence of nitrate. We evaluated the influence of various filter materials and of extracting conditions and validated the method on both reference material and real PM₁₀ samples. The accuracy of total extractable Cr determination was checked by parallel ICP-OES measurements. The determination of total chromium was performed by ED-XRF. Results of field campaigns carried out in two industrial areas (North Italy and Tunis) and at a peri-urban site near Rome are reported. At the peri-urban site, the total Cr concentration in PM₁₀ ranged from 2 to 5 ng/m³, with a soluble fraction of 5-13%, and Cr(VI) concentration was always below the detection limits (50 pg/m³). In the industrial area of Northern Italy, total Cr concentration ranged between 6 and 11 ng/m³, the soluble fraction was about 11-28% and detectable amounts of Cr(VI) were found, with a Cr(VI)/Cr(III) ratio ranging from 0.5 to 2.5. A further increase of Cr(VI) concentration was evidenced at the industrial site of Tunis, where the total Cr concentration ranged from 6 to 26 ng/m³, with a soluble fraction accounting for about 8-44% and a Cr(VI)/Cr(III) ranging from 1.6 to 3.6. The results of size-segregated samples, collected in Northern Italy by a 10-stage cascade impactor, indicate a relevant fine fraction of Cr(VI), with Cr(VI)/Cr(III) ratios increasing with the decrease of particle size.

Key words: particulate matter, chromium speciation, catalytic stripping voltammetry, size distribution.

Introduction

The growing interest in the environmental diffusion of chromium and the development of an analytical method for chromium determination originates from the widespread industrial use of this element and by its toxic effects on human health.

Chromium is generally released to the environment as airborne particulate matter (PM) and deposited by dry and wet deposition into terrestrial and aquatic ecosystem (Mukherjee, 1998). The range of airborne chromium levels in Europe is 0–3 ng/m³ in remote areas, 4–70 ng/m³ in urban areas and 5–200 ng/m³ in industrial areas (Lahmann et al., 1986).

Sources of chromium are mostly anthropogenic (60±70%); the remaining amount is released from natural

sources (Seigneur et al., 1995). Main anthropogenic sources include metallurgical industries, refractory brick production, electroplating, combustion of fuels, waste incineration and production of Cr-containing chemicals, mainly chromates and dichromates, pigments, Cr trioxide and Cr salts. Natural sources include volcanic eruptions and erosion of soils and rocks (Kotas and Stasicka, 2000). Most of the anthropogenic sources produces particles in the finest fraction of PM (aerodynamic diameter below 1 µm) [EPA, 2000, Nriagu et al., 1988], which is characterized by long residence time in the atmosphere and therefore subjected to long-range transport (Nriagu et al., 1988).

It is known that the effects of chromium on human health may be influenced by its oxidation state: Cr(III) is essential for the metabolism of lipids, glucose and

proteins and is generally present as insoluble species; Cr(VI) is carcinogenic, toxic for humans and animals, absent in nature and its chemical species are characterized by higher solubility.

The relative impact of the several sources of Cr is, instead, still largely unknown and the source apportionment of this element, as well as the assessment of its health effects, requires further investigations.

Materials and Methods

PM₁₀ samples were collected by means of Hydra Dual Samplers, operating at the flow rate of 2.3 m³ h⁻¹ (FAI-Instruments, Fonte Nuova, Italy) and equipped with three different 47 mm filter materials: Quartz (Pall Co., MI-USA), Teflon (Pall Co., MI-USA) and Cellulose (Whatman, UK).

Rotating MOUDI (Model 110, MSP Co., Minneapolis, USA) was used to collect size-resolved aerosol samples. Aerodynamic cut sizes of the impactor are 0.18, 0.32, 0.56, 1.0, 1.8, 3.2, 5.6, 10 and 18 μm. Sampling flow rate was 30 L min⁻¹.

The determination of active chromium (Cr(III)+Cr(VI)) was carried out by using a Metrohm Model 747 VA electrode stand with a multimode electrode (MME) operating in the hanging mercury-drop electrode (HMDE) mode. An Ag/AgCl, 3M KCl reference electrode and platinum wire auxiliary electrode were used.

The determination of the two species was carried out in two steps. The first step involves the addition of the chelating agent (DPTA) and the immediate analysis of the solution for determining the total soluble amount Cr_{SOL} = Cr(III) + Cr(VI). During this step, Cr(III) forms a stable complex with DTPA, Cr(III)-H₂DTPA. The complex is adsorbed and reduced on the HMDE surface to form Cr(II)-H₂DTPA, giving a peak current. In the presence of nitrate, this complex is re-oxidized to Cr(III)-H₂DTPA. Cr(VI) is adsorbed on the mercury drop, reduced at Cr(III) and then reacts with DTPA, as described.

The second step involves the addition of DPTA into a second aliquot of the sample; in this case the analysis is carried out after one hour. During this period, the Cr(III)-H₂DTPA converts into a non-active electrochemical form, Cr(III)-DTPA, allowing the determination of Cr(VI) only. Cr(III) is then determined by difference (Boussemart et al., 1995, Li and Xue, 2001).

For calibration of the system, we used standard solutions of Cr(III) for the first step and of Cr(VI) for the second step. Results of the first step (total extracted chromium: Cr_{SOL}) were corrected by the equation:

$$Cr'_{SOL} = Cr_{SOL} - 1/3Cr(VI)$$

that was experimentally obtained in order to compensate for the analytical artifact due to the

different diffusion rate of Cr(III)-H₂DTPA and Cr(VI) (Dominguez and Arcos, 2002).

The determination of the total soluble Cr was also carried out by inductively coupled plasma optical emission spectroscopy (ICP-OES, Simultaneous Vista MPX, VARIAN, Australia), while the total chromium concentration was measured by energy-dispersive X-Ray (ED-XRF, Spectro Xlab-2000 spectrometer, Spectro Analytical Inst. GmbH, Kleve, Germany).

Results and Discussion

The first phase of the validation study addressed the stability of chromium species towards redox interconversion. Three different sampling membranes (cellulose impregnated with NaHCO₃ 0.12M, Teflon and Quartz) were tested in order to evaluate the possible redox reactions occurring between the Cr species and the filter material (Kotas and Stasicka, 2000, Hazelwood et al., 2004). In addition, two different extracting solutions were considered: water and carbonate/bicarbonate buffer solution 0.06 M. These two solutions are of interest because the toxicity of Cr(VI) depends on its solubility (U.S. Agency for Toxic Substances and Disease Registry, 2000, International Agency for Research on Cancer (IARC), 1990) and in some Countries the occupational exposure limit for soluble Cr(VI) (extractable by water) is different from the limit for insoluble Cr(VI) (extractable by alkaline solution) (American Conference of Governmental Industrial Hygienists (ACGIH), 2008). The analysis were performed by both ICP-OES and CAAdSV after different time periods: immediately after the extraction by ultrasonic bath, after 3 days and after 10 days.

In the case of Cr(VI), high recoveries were obtained when using all types of filter and both extracting solutions. In the case of Cr(III), however, the recovery from quartz membrane, when using water solution, ranged from 84% (immediately) to 72% (after 10 days), as a result of a probable adsorption process. When using alkaline solution, instead, no significant loss of Cr(III) was observed. Alkaline solutions on quartz, however, may induce solubilization of the filter material (Swietlik et al., 2010). Teflon and cellulose filters, instead, showed good performance in all cases. As Teflon filters show lower chromium blank levels, these filters were selected for subsequent experiments. Analytical detection limits (LOD) were 1.8 ng/filter for Cr(III) and 2.6 ng/filter for Cr(VI).

Matrix effects were investigated by adding 1-5 mg of NIST1648 Reference Material to the standard Cr(III) and Cr(VI) solutions. In all cases, the interconversion of Cr(III) to Cr(VI), which was reported by some Authors (Tirez et al., 2011, Krystek and Ritsema, 2007), was below the measurement uncertainty (about 8%, N=20).

To evaluate the effect of variations in the extraction time, we used 48-h real PM₁₀ parallel samples collected at an industrial site in Northern Italy. The extracted amounts of Cr(III) and Cr(VI) reached a plateau after 20

minutes in the case of both extracting solutions. However, the extracted amounts were higher in the case of the alkaline solution, that was selected for subsequent experiments, carried out in the field.

The method was applied to 24-h PM₁₀ samples collected at a peri-urban site in the vicinity of Rome (site A), at an industrial site in Northern Italy (site B) and at a second industrial site, located in the outskirts of the city of Tunis (site C). The concentration of soluble Cr(III) and Cr(VI) determined by CAdSV were compared with the values determined by ICP-OES and with the concentration of total Cr determined on the same Teflon membrane by X-ray fluorescence (ED-XRF).

At site A, the concentration of total Cr was quite low (2 - 5 ng/m³). In these samples the concentration of Cr(VI) was below the detection limit, while extractable Cr(III) concentration was in the range 0.12 - 0.35 ng/m³. At site B (Figure 1, higher panel), where the concentration of total Cr was higher (6-11 ng/m³), it was possible to determine also Cr(VI) concentration, which was of the same order of magnitude than Cr(III) (Cr(VI)/Cr(III) ratio between 0.5 and 2.5).

The sum of the concentrations of the two species was between 0.7 and 2.7 ng/m³. At site C (Figure 1, lower panel), total Cr concentration was much higher; see, for example, the remarkable values reached on June 18th (> 25 ng/m³). Anyway, the sum of Cr(III) and Cr(VI) was in the range 2.3 - 4.3 ng/m³, not so far from the values recorded at sites A and B. The remarkable difference between the total Cr values recorded at site C (Tunis) with respect to site B (northern Italy) has to be ascribed to insoluble species, probably mostly associated to desert dust. However, it is worth noting that at site C, Cr(VI) concentration is much higher than at the other two sites, with a Cr(VI)/Cr(III) ratio between 1.6 and 3.6. In all cases, the comparison between the total soluble Cr determined by CAdSV and by ICP yielded satisfactory results.

The method was also applied to size-segregated PM samples, collected at site B and analyzed by both CAdSV and ICP-OES. The size distribution of extractable chromium shows that Cr(VI) is mainly in the fine fraction, with a maximum in the range 0.56-1.0 μm. Cr(III), instead, shows a bi-modal distribution and a relevant coarse fraction, with maxima in the ranges 1.0-1.8 and 5.6-10 μm. Also in this case, a good agreement between the sum of the two extractable Cr species determined by CAdSV and the total extractable Cr determined by ICP-OES is observed (Figure 2).

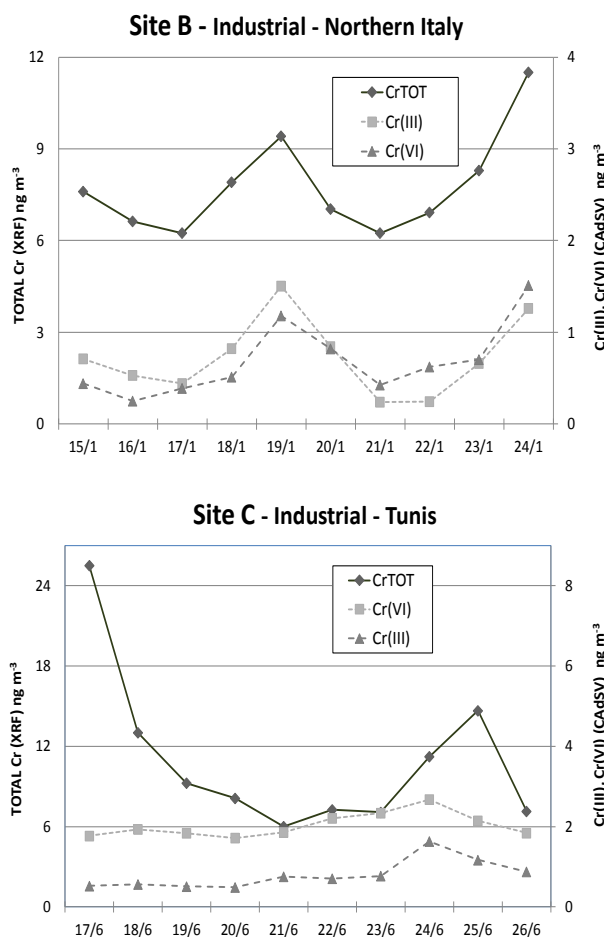


Fig. 1. XRF determination of total Cr and determination of Cr(III) and Cr(VI) during a short monitoring campaign at an industrial sites in Northern Italy (site B) and in Tunis (site C).

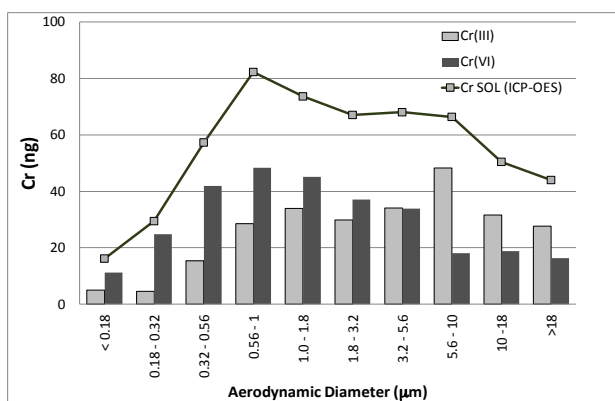


Fig. 2. Size distribution of soluble Cr and of Cr(III) and Cr(VI) at an industrial sites in Northern Italy (site B).

Conclusions

The proposed method for the redox speciation of extractable chromium in atmospheric particulate matter proved to be robust and reliable. It is based on PM collection on Teflon membrane filters, US-assisted extraction in alkaline solution and analysis by catalytic adsorptive stripping voltammetry (CAdSV) with (DTPA) as complexing agent in the presence of nitrate.

The application of the method to real PM samples in different locations showed that relevant concentrations of Cr(VI) can be measured at industrial sites, while in rural areas Cr(VI) is often below the detection limits.

In agreement with its prevalent industrial origin, Cr(VI) is mostly in the fine fraction of PM, while Cr(III), of both anthropogenic and natural origin, shows a bimodal distribution with a relevant coarse contribute.

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