

Research on chromium and arsenic speciation in atmospheric particulate matter: short review

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Abstract. Atmospheric particulate matter (PM) plays an important role in the distribution of elements in the environment. The PM-bound elements penetrates into the other elements of the environment, in two basic forms - those dissolved in the atmospheric precipitation and those permanently bound to PM particles. Those forms differs greatly in their mobility, thus posing a potential threat to living organisms. They can also be an immediate threat, while being inhaled. Chromium (Cr) and arsenic (As) belong to the group of elements whose certain chemical states exhibit toxic properties, that is Cr(VI) and As(III). Thus, recognition of the actual threat posed by Cr and As in the environment, including those present in PM, is possible only through the in depth speciation analysis. Research on the Cr and As speciation in PM, more than the analogous studies of their presence in other compartments of the environment, have been undertaken quite rarely. Hence the knowledge on the speciation of PM-bound As and Cr is still limited. The state of knowledge in the field of PM-bound Cr and As is presented in the paper. The issues related to the characterization and occurrence of Cr and As species in PM, the share of Cr and As species mass in different PM size fractions, and in PM of different origin is also summarized. The analytical techniques used in the speciation analysis of PM-bound Cr and As are also discussed. In the existing literature there is no data on the physical characteristics of Cr and As (bound to a different PM size fractions), and thus it still lack of data needed for a comprehensive assessment of the actual environmental and health threat posed by airborne Cr and As.

1 Introduction

Chromium (Cr) and arsenic (As) are two elements widely common in environment. They occur in different chemical forms, which in case of As are more differentiated. The circulation of chromium and arsenic in the environment mostly involve their biologically active forms, present in an ionic forms, and by definition bioavailable for living organisms. The impact of chromium and arsenic on human's health depends mostly on their oxidation state. It is documented that Cr(III) takes a part in the processes of the formation and transformation of lipids, glucose and proteins, while Cr(VI) form is a known human

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carcinogen, characterized by a high toxicity [1]. After inhalation Cr(VI) migrate easily into respiratory track, where it cross the cell membranes and is further transported into the bloodstream. Similarly to Cr, also the toxicity of As is related to the different chemical forms and oxidation states in which it can be found. It is recognized, that the inorganic arsenic species are more toxic than the organic ones (except trivalent organoarsenicals), and that As(III) is more toxic than As(V). At the cellular level, As(III) interacts with proteins and enzymes, causing oxidative stress and ablation of DNA by its methylation [2].

Considering the fact of As and Cr toxicity it can be stated that understanding their speciation is more important, than knowing its total contents in the exact elements of the environment [3]. All over the world the quantitative assessment of As and Cr species in all elements of the environment such as water, soil, sediments, wastes, plants, particulate matter etc. is a huge challenge. While looking into scientific literature it appears that particulate matter is probably the least recognized among above mentioned.

Atmospheric particulate matter (PM), also referred as aerosol, represents mixture of solid, liquid, semi-volatile and volatile compounds. PM is very complex, regarding particle size and composition, as it may contain metals, metalloids, inorganic ions, organic compounds, black carbon and biogenic material (e.g. algae, pollen, bacteria or fungi) [4]. Airborne chromium (i.e. PM-bound Cr) exists in two valence states Cr(III) and Cr(VI). Similarly arsenic exist in PM in two valence states As(III) and As(V), in inorganic and/or organometalloid forms. Five different species of As have been detected in PM so far: the two inorganic species arsenite (As(III)) and arsenate (As(V)) and the organoarsenic methylated forms of As(V), that is methylarsonate (MA), dimethylarsinate (DMA) and trimethylarsine oxide (TMAO) [5].

The occurrence of different oxidation states of PM-bound As and Cr is dependent on their origin. It has been estimated that approximately two thirds of the Cr and As emissions to the atmosphere is related to anthropogenic sources. The main industrial Cr sources are: ferrochrome metallurgy, brick manufacturing, plating, fuels combustion, waste incineration, the production of Cr-containing chemicals, mainly chromates and dichromates, pigments, Cr trioxide and Cr salts. Arsenic sources include mainly metal smelting, fossil fuels combustion and pesticide use, therefore 60% of the global anthropogenically-generated atmospheric arsenic is attributable to copper smelting and coal combustion. Natural sources of Cr and As emission include volcanic eruptions and erosion of soils and rocks. As can also be released from low temperature volatilization of organoarsenic compounds, forest fires and sea spray [6-8].

The prevailing compounds of considered elements in PM are inorganic compounds of As(V) and Cr(III). Cr(VI) contribute from 3 to 8% of the total chromium emission into atmosphere and it's lifetime is relatively short 0.7-4.8 days [6,9]. The compounds of Cr and As in PM as well as the shares of its particular species are shaped by emission sources. X-ray analysis of PM collected in industrial area showed that arsenic is present as: $\text{Ca}_3\text{Sr}_2(\text{AsO}_4)2.5(\text{PO}_4)0.5(\text{OH})$, As_2O_3 and As_2O_5 [10] and chromium is present in the chemical forms: Cr_2O_3 , Cr-Fe spinel, $\text{Cr}(\text{OH})_3$, $\text{Cr}(\text{NO}_3)_3$, $\text{Cr}_2(\text{SO}_4)_3$, and CrCl_3 . Most of them are not soluble in water in contrary to Cr(VI) compounds, which are water-soluble unless existing as PbCrO_4 , BaCrO_4 and ZnCrO_4 (emitted during utilization of chromate pigments and dyes). Soluble Cr(VI) is reported to be dominant in mobile and fuel combustion emission [11].

The source of PM emission also affects the mass shares of particles in specific size ranges (size fractions) and in the total PM mass. While most mining operations generate coarse PM, high temperature processes, such as smelting and coal combustion, are typically associated with fine PM. Coarse PM (particles with aerodynamic diameter $\geq 2.5 \mu\text{m}$) are produced usually by mechanical processes such as crushing and grinding of ore and may be resuspended via wind erosion and mechanical disturbance. Fine PM (particles with

aerodynamic diameter $\leq 2.5 \mu\text{m}$) are produced during smelting and combustion through the condensation of high temperature vapors, diffusion and coagulation [12]. It is known that PM generated by anthropogenic sources consists mostly of fine particles, with the domination of particles below $1 \mu\text{m}$ [13, 14]. Generally, it can be stated, that fine particles, mainly due to the chemical composition, are characterized by much greater surface area than coarse one. Many studies confirm connection between the size of the surface area, and the ability of PM particles to cumulate metals and metalloids. In the Polish urban areas, approximately 70-90% of total PM-bound metal mass is bound to submicron particles (PM₁) [15-17].

The aim of the paper is to synthesize the state of knowledge on the presence of chromium and arsenic species in atmospheric particulate matter available in the national literature including such information as: (i) characterization and occurrence of Cr and As species in PM, (ii) the mass share of Cr and As species in different PM size fractions and in PM of different origin, (iii) the analytical techniques used in the speciation analysis of PM-bound Cr and As.

2 Application of Chromium and Arsenic Speciation Analyses in PM Samples

Among PM-bound elements in urban air, Cr and As are those, which can affect human health. The negative health effect, after exposure by inhalation of PM-bound Cr and As, depends mainly on their oxidation states, solubility of their compounds and their mass distribution respect to inhaled particles [1, 12]. It is established that the smaller is the PM diameter, the higher its capacity to penetrate into the respiratory track: particles with aerodynamic diameter equal to $10 \mu\text{m}$ can reach the larynx, $2.5 \mu\text{m}$ the bronchi, and $1 \mu\text{m}$ the alveoli [18]. For this reason interest in species-selective analysis especially of fine PM samples has increased in recent decades.

Research on Cr and As and their species show that the concentrations of their species in PM are spatially dependent and are mainly shaped by local emission. Higher concentration of PM-bound Cr and As and their species (Cr(VI) and As(V)) were determined in the regions where local emission is mainly industrial, in comparison to areas, where the influence of industry is not prevailing, or where the area is located far from the direct impact of the industrial source emission [19-24]. For example, in urban areas, close to chromium emission sources in particular, Cr(VI) concentration can achieve values, e.g. 20 ng/m^3 close to a foundry [19] and $20\text{-}70 \text{ ng/m}^3$ around a ferrochrome smelter [20]. Talebi [21] reported $5.4\text{-}8.2 \text{ ng/m}^3$ ambient concentration of PM-bound Cr(VI) in Isfahan (Iran), where two large iron and steel factories were located nearby. The PM₁₀-bound Cr(VI) concentrations in Belgium were 5.2 ng/m^3 close to stainless steel factory and 1.2 ng/m^3 in location further away [22]. Świetlik et al. [23] determined Cr species in PM (TSP) collected in 4 locations characterized by domestic and vehicular emission and in one with an industrial emission (co-fired plants and metalworking plants) in Radom (Poland). The PM from industrial zone turned out to be almost fivefold richer in Cr(III). The level of Cr(VI) in air over the whole city was similar and the mean concentration of PM-bound Cr(VI) was 6.0 ng/m^3 . In non-polluted areas mean concentration of Cr(VI) was lower than 0.5 ng/m^3 [24].

While examining the influence of industry on PM-bound As levels Oliveira et al. [25] found that close to the cooper smelter the contents of As species in TSP were 1.2 ng m^{-3} As(III) and 10.4 ng m^{-3} As(V). In Taiwan in China the average concentrations of TSP-bound arsenic species at industrial area (thermal power plant) were 1.06 ng/m^3 and 2.49 ng/m^3 for As(III) and As(V), respectively; while in residential area they were 0.83 ng/m^3

for As(III) and 1.96 ng/m^3 for As(V) [26]. More examples of As species concentration from various mining operations are presented in review paper by Martin et al. [12].

Most of studies on Cr and As speciation in PM has been performed on total PM samples (so called total suspended particles, TSP) or either PM_{10} and $\text{PM}_{2.5}$. Speciation of PM-bound Cr and As in size-segregated samples has been studied only to a little extent. Inorganic arsenic species were determined for example in $\text{PM}_{2.5-10}$ and $\text{PM}_{2.5}$ in Tapada and Sines in Portugal [27], in PM_{10} and $\text{PM}_{2.5}$ in Huelva in Spain [28], in Antwerp in Belgium [10] in $\text{PM}_{2.5}$ and PM_1 in Zabrze, Poland [29]. These studies indicate the presence of As(V) as the dominating specie in the PM samples, followed by As(III); only Tirez and co-workers [10] showed that the dominant specie in $\text{PM}_{2.5}$ was As(III).

Chromium species was determined in $\text{PM}_{2.5-10}$ and $\text{PM}_{2.5}$ in Wielgegund, Southern Africa [30], in PM_{10} and $\text{PM}_{2.5}$ in New Jersey, USA [31, 11], and in $\text{PM}_{2.5}$ and PM_1 in Zabrze, Poland [29]. In Africa the majority of Cr(VI) was found in $\text{PM}_{2.5}$ [30]. This observation was explained by the nature of PM-bound Cr(VI) - emitted by pyrometallurgical plants in the studied region and the atmospheric lifetimes of different PM size fractions. Yu et al. and Huang et al. [11, 31] found that at the MERI site (~700 m from New Jersey Turnpike) concentrations of PM_{10} -bound Cr(VI) were higher than concentrations of $\text{PM}_{2.5}$ -bound Cr(VI) both in summer and in winter. Widziewicz et al. [29] noticed higher concentrations of $\text{PM}_{2.5}$ -bound Cr(VI) than PM_1 -bound Cr(VI) only in summer. Generally, the higher concentration of Cr(VI) and higher ratio Cr(VI)/Cr(III) were observed in summer season compared to the winter season. Authors explained their findings by the fact, that the airborne Cr(III) can be oxidized to Cr(VI) by reactions with reactive oxygen species (ROS), characterized by strong oxidative capacity. Photoreactions are expected to be more intensive in the summer, also as a result of the presence of manganese in the ambient air [6]. Multiple linear regression analysis confirmed that the ambient concentrations of Cr(VI) were significantly affected by meteorological factors (i.e. temperature and humidity) and reactive gases particles (i.e. O_3 , Fe and Mn) [31]. The mass distribution of Cr(VI) in respect to the particle size (8 PM fraction) was determined at the William site (~50 m from New Jersey Turnpike) [31]. Authors found that greater mass of Cr(VI) was allocated in the size range below $2.5 \mu\text{m}$ and the maximum of mass size distribution of Cr(VI) were found around the particle size of $2.5 \mu\text{m}$. The results of Cr species masses distribution among 10 PM fractions from an industrial site in Northern Italy indicated that both mass concentration of Cr(VI) and Cr(VI)/Cr(III) ratio increase with the decrease in particle size [32]. The mass size distribution of Cr(VI) was unimodal and their maximum was in the range $0.56\text{-}1.0 \mu\text{m}$. Mass size distribution of Cr(III), instead, was a bimodal with maxima in the ranges $1.0\text{-}1.8$ and $5.6\text{-}10 \mu\text{m}$ [32]. The mass size distribution of Cr(III) is consistent with the distribution of total chromium in size-fractionated PM (13 PM fractions) collected in Zabrze (Poland) during winter [16, 17]. In Zabrze, Cr were accumulated mostly in fine particles and had bimodal mass size distribution with maxima in the ranges $1\text{-}1.6$ and $6.8\text{-}10 \mu\text{m}$. Arsenic was accumulated mostly in submicron particles and had tetramodal distribution with maxima in the ranges $0.108\text{-}0.17$; $0.4\text{-}0.65$; $2.5\text{-}4.4$ and $6.8\text{-}10 \mu\text{m}$. As speciation in size-segregated PM samples has not been found in literature. Therefore it seems reasonable to undertake further research on chromium and arsenic speciation in size-segregated PM.

3 Sample preparation and analytical techniques for PM-bound Cr and As speciation

Speciation of PM-bound Cr and As as an analytical process involves a few step, that are typically sampling, sample storage, sample pretreatment (extraction), separation of species

and detection. Each of these steps of the procedural chain can influence the accuracy of determination of every specie of particular element, and each has to be optimized with respect to the other.

According to regulations referring to sampling of atmospheric air, PM can be collected on filters made of glass or quartz fiber filters, and cellulose or polycarbonate or PTFE (Teflon) membranes. The filters/membranes differ among each other for instance by flow resistant and so called "blank values" for determined element. Usually blank filters are initially prepared in order to minimize the analyte background ("blank values" in clean filters/membranes), i.e. minimize of positive artifacts in chemical analysis. The selection of the material of the filters is an important matter, because both filters and PM (deposited on filters) have to be digested or extracted with a suitable solution for posterior analysis of PM-bound Cr and As present. The desired extraction method must be therefore compatible with the analytical detection methods used and ideally require a small amount of PM sample. Since nineteen's a few methods using the alkaline digestion, for Cr(VI) determination in solid matrices, including atmospheric PM have been developed [32]. Among mentioned, standard methods dedicated for PM (ASTM, NIOSH and OSHA) differ on sample pretreatment level - filter material (PVC, quartz, Teflon), except ASTM, and/or extraction conditions (NaOH, Na₂CO₃, NaHCO₃) but all are followed by Ion Chromatography and UV detection after DPC derivatization (Table 1). US EPA 3060A alkaline digestion method for determination of Cr(VI) in solid matrices was also used for PM samples [23, 29, 30]; its modified version was used by Huang et al. [11]. Chromium in extracts has been analyzed also by such techniques as: catalytic cathodic stripping voltammetry with adsorption of Cr(III)-DTPA complexes (CCSV-DTPA), graphite furnace atomic absorption spectroscopy (GF-AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) (Table 1).

Over the past few years, two review papers have been published on the methodology used to determine the inorganic and organic species of arsenic in PM samples [34, 35]. Therefore in the presented work the authors focused only on the latest publications (Table1). As shown in Table 1 PM samples for arsenic species determinations were prepared by acid extraction/digestion with using solution such as: HNO₃, H₃PO₄, NH₂OH·HCl, ascorbic acid or with citrate buffer. The latest trends in detection element species concern the so-called hyphenated techniques [36]. Determination of As species in PM has been performed with a very sensitive HPLC methodology coupled with hydride generation and atomic fluorescence spectrometry (HPLC-HG-AFS) or with inductively coupled plasma mass spectrometry (HPLC-ICP-MS).

The environmental conditions in which the extraction of analytical species is carried out are conducive to its transformation. Especially Cr(VI) is very reactive, and inter-conversion between Cr species can easily occur during sampling and sample processing. So very important in the speciation analyses is the optimization of the extraction procedure (time and conditions of ambient air), followed by compatible detection method, in order to minimize changes of analytes oxidation state. Because there is no CRM for Cr and As species in PM, accuracy of the method (including possible determined element species interconversion) can be evaluated mainly by recovery of known concentration of proper species standards added to PM sample. In case of Cr recovery of Cr (VI) both by external standard method from soil CRM and by speciated isotope-dilution mass spectrometry (SIDMS) method (EPA Method 680) from isotope Cr (VI) and Cr (III) enriched PM sample were studied [33, 38, 39]. SIDMS method occurred to be useful in correction of possible Cr species interconversion for determination of their soluble forms [11, 39].

Table 1. Comparison of methodologies in speciation of PM-bound Cr and As

Location	PM fraction Cr/As species (chemical analysis) Cr/As species (calculations)	Sample extraction/digestion	Technique of chemical analysis(*)	Type of location	References
Radom (Poland)	TSP Cr(VI) and Cr _{total} Cr(III) = Cr _{total} - Cr(VI)	Quartz EPA 3060A: Na ₂ CO ₃ +NaOH	CCSV-DTPA	Five sites with different municipal structure	Świadlik et al. (2011)
Wielgungud (Southern Africa)	PM _{2.5-10} /PM _{2.5} Cr(VI)	Teflon Na ₂ CO ₃ +NaOH	IC-UV	Industrial – pyrometallurgical smelter, coal-fired power station	Venter et al. (2016)
Belgium	PM ₁₀ Cr(VI)	Cellulose NaHCO ₃	IC-UV	Industrial-stainless steel factory	Tirez et al. (2011)
Katowice (Poland)	PM _{2.5} /PM ₁ Cr(VI) and Cr _{total} Cr(III)=Cr _{total} - Cr(VI)	Quartz EPA 3060A: Na ₂ CO ₃ +NaOH	GF-AAS	Urban traffic site	Widziawicz et al. (2016)
Tunis (North Italy)	PM ₁₀ PM _{0.18} -PM ₁₈ Cr(VI) and Cr (III)	Cellulose, teflon, quartz Na ₂ CO ₃ +NaHCO ₃	CASV-DTPA ICP-OES	Industrial, peri-urban site	Catrambone et al. (2013)
New Jersey (USA)	PM _{2.5} PM _{0.18-18} Cr(VI) soluble	Cellulose filter cleaned with HNO ₃ , pretreated with NaHCO ₃ Extraction in 4% HNO ₃	IC-ICP-MS	Urban traffic site	Yu et al. (2014)
New Jersey (USA)	PM ₁₀ Cr(VI) PM ₁₀ Cr(VI) soluble	Teflon Na ₂ CO ₃ +NaOH Cellulose filter cleaned with HNO ₃ , pretreated with NaHCO ₃ , samples extracted in 4% HNO ₃	IC-ICP-MS IC-UV	Urban traffic site, suburban	Huang et al. (2014)
Huelva (Spain)	PM ₁₀ /PM _{2.5} As(V) and As(III)	Quartz NH ₂ OH·HCl	HPLC-HG-AFS	Industrial-copper smelter	Sanchez-Rodas et al. (2012)
Antwerp (Belgium)	PM ₁₀ /PM _{2.5} As(V) and As(III)	Cellulose Ascorbic acid+ H ₃ PO ₄	HPLC- ICP-MS	Industrial –metallurgical plant	Tirez et al. (2015)
Katowice (Poland)	PM _{2.5} /PM ₁ As(III)and As _{total} As(V)=As _{total} - As(III)	Quartz Citric acid+sodium citrate	HG-AAS	Urban traffic site	Widziawicz et al. (2016)
Juan (China)	PM _{2.5} As(V) and As(III)	Glass fiber membrane 1% HNO ₃	HPLC- ICP-MS	Industrial - coal-fired power station	Yin et al. (2017)

(*) Abbreviations: IC-UV Ion Chromatography-UV detection; GF-AAS Graphite Furnace Atomic Absorption Spectroscopy; HG-AAS Hydride Generation Atomic Absorption Spectrometry; CCSV-DTPA Catalytic Cathodic Stripping Voltammetry with adsorption of DTPA complexes; ICP-OES Inductively Coupled Plasma Optical Emission Spectrometry; IC-ICP-MS Ion Chromatography-Inductively Coupled Plasma-Mass Spectrometry; HPLC-ICP-MS High Performance; HPLC-ICP-MS High Performance; Liquid Chromatography-Inductively Coupled Plasma-Mass Spectrometry; HPLC-HG-AFS High Performance Liquid Chromatography-Hydride Generation-Atomic Fluorescence Spectrometry

4 Overall summary and conclusions

Chemical speciation of toxic elements, such chromium and arsenic, in an environmental samples gives a crucial information on their amounts present in different oxidation form, that are characterized by different toxicity, availability, and reactivity. The share of toxic forms of airborne As and Cr in their total PM-bound mass is of great importance in environmental and human health effects. Most interesting seems to be the information on the contents of toxic forms of Cr and As in fine particulate matter, characterized by long residence time in atmosphere and free migration to the respiratory tract.

Till now the most research works on Cr and As speciation concern their presence in PM_{2.5}, PM_{2.5-10} or PM₁₀₋₄₀. There is a scarce research on chromium and arsenic speciation in ultrafine PM fraction and on the mass size distribution of their species in PM. Published results of research on mass size distribution of Cr in atmospheric air (two studies) indicate that their toxic specie - Cr(VI) tend to cumulate in fine PM_{2.5}. Published results on As species in coarse and fine fraction (collected during the same research campaign) indicated that toxic As(III) was rather tend to cumulate in finer one.

It can be stated that in the present state of knowledge there is not enough data on PM-bound Cr and As distribution within size-fractionated particles for a comprehensive assessment of the actual threat posed by atmospheric Cr and As. In connection with the above, it is still a challenge to describe the nature of Cr and As species distribution of in the function of the PM aerodynamic diameter in relation to all factors shaping the distribution.

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