

The Importance of Chromium Speciation in Environmental Relevant Matrices



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Abstract

Chromium (Cr) is released to the environment by industrial activities such as metallurgy, power generation, leather tanning, and pigments. It typically occurs in its trivalent (Cr(III) or Cr³⁺) or hexavalent (Cr(VI) or Cr⁶⁺) form, with the first being an essential trace element and the latter being highly toxic, carcinogenic, mutagenic, and teratogenic even at trace concentrations. Therefore, chromium's effects on living organisms grossly depend on its chemical form/species rather than its total concentration. For this reason, research has focus on Cr speciation in different environmental relevant matrices and particularly in water and foodstuffs. To this end, Online (usually HPLC/ICP-MS) and offline (e.g., ET-AAS, F-AAS, ICP-MS, and X-ray spectroscopy) analysis is employed, however the latter often requires a preconcentration/extraction step. During the past few years, simpler and/or more robust techniques based on electrochemical sensing, microfluidic paper-based analytical devices, polymer dots, solid-phase extraction, and colorimetric sensors have been also proposed or modified to improve Cr sensing and speciation.

Keywords: Chromium speciation; Environmental contamination or pollution; Cloud point microextraction; Dispersive micro-solid phase extraction (DMSPE); Analytical chemistry

Introduction

Chromium (Cr), from the Greek word 'χρῶμα' (color), is a naturally occurring element that is encountered in its trivalent (Cr(III) or Cr³⁺) or hexavalent (Cr(VI) or Cr⁶⁺) form, which are its most stable valence states [1]. Other forms, such as Cr(II), Cr(IV), and Cr(V) are very unstable and they result from the oxidation and reduction reactions of Cr(III) and Cr(VI), respectively [2]. Owing to its unique properties, Cr(III) is widely used in electroplating, alloys, dyes, pigments, leather, anti-corrosion, and other industrial applications [3]. As such, large quantities of Cr have found their way into different environmental compartments, particularly after the industrial revolution [4]. In trace concentrations Cr(III) is considered an essential nutrient [5], since it helps regulate carbohydrate, lipid, and protein metabolism [6]. However, in higher concentrations Cr(III) is considered an important environmental contaminant and has been linked with reproductive toxicity, embryotoxicity, dermatitis, carcinogenicity, and increase risks of diabetes and cardiovascular disease, along with DNA, protein, and lipid damage [3].

The main problem lies with Cr(VI) occurrence in the environment, since even at trace concentrations Cr(VI) is a highly toxic, carcinogenic, mutagenic, and teratogenic [6]. Therefore, even though the estimation of the total Cr concentration is relatively simple to be determined [7], it does not provide insight since the effects of Cr contamination to living organisms are mainly linked to its species rather than its total concentration [2]. Cr is typically absorbed by living organisms either through inhalation (e.g., during coal combustion for power generation Cr(VI) can be generated and released to the atmosphere [4]) or the digestive tract (according to the World Health Organization (WHO) Cr(VI) concentration in drinking water should be 0.05 mg L⁻¹ or below [8]) [1]. In terms of Cr speciation, foodstuffs such as plants, fish, boiled wheat, mushrooms, beer, and particularly meat, dairy products, bread, and tea which are considered as the main sources of Cr in human diet, have been examined [9]. Biological samples, including urine, whole blood, serum, plasma along with tissues, saliva and joint effusion have also been examined in terms

of Cr species [1]. Cr speciation is achieved either using online (HPLC/ICP-MS) or offline (ET-AAS, F-AAS, ICP-MS) techniques, with research making large strides during the past few years in introducing new or optimising existing techniques.

Recent Advances in Cr Speciation

Spectrometry analysis

Cr is typically measured, at trace levels, using inductively coupled plasma mass spectrometry (ICP-MS) or optical emission spectrometry (ICP-OES), atomic absorption spectrometry (AAS), and spectrophotometry [8]. For trace elements analysis ICP-MS is considered as one of the most powerful technique, owing to fast and reliable ultra-trace (sub-ppb) analysis and its multi-element capabilities [2,10]. However, it cannot distinguish between different element species [11] and therefore for online analysis ICP-MS is usually coupled with HPLC [2]. For offline analysis AAS, ICP-MS or OES, and spectrophotometry are typically used, however a preconcentration/extraction step is required for speciation analysis [12]. In foodstuffs Cr speciation is achieved through selective extraction, using alkaline media such as a mixture of NaOH/Na₂CO₃ or NaOH/NH₄NO₃, prior to determination by different online or offline analytical techniques [9]. This is also the case for Cr speciation in biological samples, however different extraction media are used coupled with offline analysis [1].

For Cr(III) and Cr(VI) speciation in water a simple and rapid approach, based on electro dialytic ion pre-concentration for the rapid transfer of chromium ions into respective acceptors and coupled to ICP-MS has been proposed [13]. A custom-built HPLC/ICP-MS system, using a metal-free HPLC-DAD system and a sector-field ICP-MS detection (ICFsMS) with desolvating injection and optimization of sample handling, was proposed to improve ICP-MS sensitivity, dynamic range, mass resolution, and address the problems of interferences. This system was tested for Cr speciation in protein and pigments and results at ultra-trace levels were obtained [14].

X-ray techniques

For non-invasive analysis of the Cr(VI)/Cr ratio in different types of plastics the X-ray emission spectroscopy (XES) and synchrotron-based X-ray absorption fine structure (XAFS) appears to be promising [15]. Cr speciation in water can be also achieved using resonant inelastic X-ray scattering under total reflection geometry (TRIXS) combined with principal component analysis and linear discriminant analysis, with the added benefit of manganese determination [16]. Finally, speciation by means of total reflection X-ray fluorescence (TXRF), after membrane immobilization with special ligands, has also been proposed [5].

Microextraction, solid phase extraction, and adsorption

For Cr speciation in water ultrasound assisted microextraction coupled with AAS [17] or graphite furnace AAS (GFAAS) [18] has been proposed. Cloud point extraction (CPE) in the presence of

unmodified silver nanoparticles [19] or when using graphene oxide [20] has also be used for ultratrace Cr speciation in aqueous samples. Dispersive micro-solid phase extraction (DMSPE), using an aluminium oxide supported on graphene oxide (Al₂O₃/GO) nanocomposite, is also promising [21]. A new extractant was synthesized and used as adsorbent (solid phase extraction) in combination with HPLC/ICP-MS for Cr speciation in wastewater [22]. For offline analysis of water with ICP-MS carboxyl-functionalized [11] and amine- and carboxyl-bifunctionalized hybrid columns [23], along with carboxyl-group functionalized mesoporous silica (CFMS) [10] have been proposed. These adsorbents can assist the extraction of Cr(III), which can be then selectively collected by chelation. Microfluidic paper-based analytical devices (μ PADs) [24] and polymer dots (PDs) [12] have been also examined for Cr speciation in water. For rapid detection of Cr(VI) in food and water samples, sandwich structured (triadic silica gel-supported) copper sulfide (CuS) nanocomposites were used as the solid phase extraction adsorbent for Cr(VI), followed by FAAS analysis [25].

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Electroanalysis and Sensors

Gold nanoparticle-decorated titania nanotube arrays have been used for Cr(VI) electrochemical sensing in tap and lake water, leading to a 23-fold improvement of peak current compared to polycrystalline gold electrodes, thus achieving the detection limit suggested by WHO [26]. A few years later, an activated glassy carbon electrode (GCE) was proposed for the electrochemical determination of Cr(III) and Cr(VI) in different samples (e.g., drugs and/or biological samples), with the added benefit of signal amplification compared to conventional glassy carbon electrodes, however more research is needed on identifying the mechanisms that govern the different activation methods [27]. A dual channel structured ion imprinted fluorescent sensor was also proposed for the simultaneous determination of both Cr(III) and Cr(VI) in river water, without the need for Cr(VI) reduction or Cr(III) oxidation, while its sensitivity in Cr(VI) detection was on par or higher than previously reported fluorescent sensors (results were verified using ICP-MS) [28]. An indirect photoelectrochemical sensing platform for Cr(VI) determination in water, based on Cr(VI) inhibition by quercetin oxidation at a titanium dioxide modified glassy carbon electrode in the presence of solar irradiation, was examined and verified using GFAAS [26]. Similarly, for Cr(VI) sensing in water, graphite printed macroelectrodes, based on the electrochemical reduction of Cr(VI), achieved limit of detection (LoD) as low as 0.19 $\mu\text{g L}^{-1}$ (ppb), with the added benefits of portability and low cost [29].

Other techniques

For portable Cr(III) determination in water a miniaturized immune-barometer sensor (IBS) was proposed for cost effective and environmentally friendly Cr(III) analysis and tested in tap and river water (LoD 0.35 ppb) [3]. This sensor was able to detect pressure changes induced when gold core platinum shell nanoparticles decompose H_2O_2 to generate O_2 in a sealed chamber. Furthermore, a colourimetric lab-on-a-disc sensor gave a 4 ppb LoD for Cr(VI) in water [30], thus enabling on-site measurements.

Conclusion

The effects of Cr contamination to living organisms are mainly linked to its chemical species rather than its total concentration. Even at trace levels Cr(VI) is highly toxic, carcinogenic, mutagenic, and teratogenic and therefore research has focus on Cr speciation rather than in identifying its total concentration in environmental relevant matrices. Online analysis using HPLC/ICP-MS is typically used for Cr speciation, while preconcentration/extraction followed by offline analysis (e.g., AAS and ICP-MS) is also used. Future research should focus on introducing simple, fast, cost-effective, and sensitive techniques for Cr speciation, focusing on on-site (portable) applications. Chromium speciation in environmental relevant matrices is a prerequisite to safeguard human health and the environment. However, its speciation remains challenging, particularly in real environmental matrices. Many analytical techniques have been developed or improved in recent years, with particular emphasis on optimizing the limit of detection, portability (on-site determination), speed, cost, and avoidance of interferences.

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