

Redox speciation of chromium using sorption-based systems

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The difference in toxicity is one of the main reasons for the recent development of analytical procedures for differentiating chromium (Cr) species. Non-chromatographic speciation procedures using sorption-based systems offer very convenient tools and can be used as fast, cheap alternatives to chromatography. The methods based on sorbent extraction have proved to be the most attractive, due to their high separation and preconcentration efficiency.

This review presents procedures based on sorption principles for use in Cr-speciation analysis. They are discussed and compared in terms of selectivity and efficiency. This review covers the state of the art since 2005.

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1. Introduction

Chromium (Cr) occurs in the environment mainly in two different oxidation states, Cr(III) and Cr(VI). Due to its wide use in electroplating, leather tanning, metal finishing and textile industry, it is present in air, soil and aquatic systems. Cr can also enter drinking-water-supply systems from the corrosion inhibitors used in water pipes and containers.

Cr(III) exists in natural waters in hydrolyzed $\text{Cr}(\text{H}_2\text{O})_4\text{OH}^{2+}$ form and complexes, and is even adsorbed on colloidal matter. It is an essential micronutrient in the body and combines with various enzymes to transform sugar, protein and fat [1,2].

Cr(VI) is found as CrO_4^{2-} , HCrO_4^- or $\text{Cr}_2\text{O}_7^{2-}$, depending on pH. While Cr(III) may be considered an essential trace element for the proper functioning of living organisms, Cr(VI) is considered to be toxic and carcinogenic because of its ability to oxidize other species and its adverse impact on lung, liver and kidney [3]. Moreover, in air, Cr particulates play a role in the oxidation of sulfur dioxide and formation of acidic aerosols involved in global acid rain [4].

Under certain conditions, Cr(III) may be oxidized to Cr(VI) in natural environments [5,6]. The oxidation of Cr(III) by manganese oxides could be inhibited by the

reduction of MnO_2 to Mn(II) by dissolved organic matter [7,8].

Because of the dangerous effects of hexavalent Cr and its high mobility in the environment, several directives have been adopted by the European Commission to limit the release of Cr(VI) into the environment and to protect workers exposed to this metal [9]. The US EPA has set the concentration of 0.1 mg/L of total Cr for drinking water as a “maximum contaminant level goal”. The World Health Organization states that the guideline values of 0.05 mg/L for Cr(VI) are thought to be too high compared with its high risk of carcinogenicity. Thus, the development of speciation analysis with high sensitivity and sufficient selectivity is a challenge for analytical chemists in addition to the measurement of total Cr content.

Spectrometry techniques, including atomic absorption spectrometry (AAS), inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS), are the most commonly used for trace Cr determination. However, in practice for complex matrices, quantification is frequently very difficult due to the presence of interfering effects, comprising spectroscopic and non-spectroscopic interferences. Moreover, in some cases, the concentration of an analyte might be too low to be directly analyzed. The most effective way to avoid

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these problems is to perform appropriate sample pretreatment aimed at lowering the limits of detection (LODs), by removal of interferences as well as increasing the concentration of analyte. Various techniques for Cr separation and preconcentration have been proposed, including ion exchange, adsorption, coprecipitation and liquid–liquid extraction (LLE). The methods that are based on sorbent extraction have proved to be the most attractive due to their high separation and preconcentration efficiency. The broad range of choice for sorbent materials along with various chelating reagents and eluents make this technique very attractive for sample pretreatment. Moreover, they are very useful for non-chromatographic separation of Cr(III) or Cr(VI) species.

The aim of this review is to present the procedures based on sorption principles, which have been used for Cr-speciation analysis. They are discussed and compared in terms of selectivity and efficiency. The current analytical methods for total Cr determination are also presented to show their advantages and limitations. This review attempts to cover the state of the art since 2005. Earlier developments were presented in the previous reviews [10–12].

2. Chromium determination

UV-VIS spectrophotometry and atomic spectrometry techniques – mainly flame and electrothermal AAS (ETAAS) [13,14], and ICP-OES [15] and ICP-MS [16,17] – are extensively employed in Cr determination. Chemiluminescence [18,19] and electrochemical detection [20,21] are used less frequently.

The most commonly used chromogenic reagent for spectrophotometric determination is diphenylcarbazide (DPC), which is selective for Cr(VI) (vs. Cr(III)) with an LOD of 0.12 mg/L [22]. Because the DPC method suffers from the presence of interfering compounds, particularly Cu(II), Mo(VI), Fe(III), V(V) and Hg(II), which can react with DPC giving positive interferences, Themelis et al. [23] proposed the new assay based on the reaction of Cr(VI) with chromotropic acid in acidic medium in the presence of NaF as a masking agent for iron. The LOD for this assay was 1 µg/L.

FAAS presents a low-cost, operational facility and high sample throughput with significant precision and accuracy. Although the nitrous oxide-acetylene flame is mostly recommended for Cr determination, Sahuguilu et al. [24] found that fuel-rich air-acetylene flame with addition of 8-hydroxyquinoline a better choice to avoid interferences from the other metals with an LOD of 40 µg/L.

ETAAS is characterized by higher sensitivity, suitable selectivity and low requirements in terms of sample volume. However, chemical modification to enhance matrix elimination is often necessary. This is performed by creating conditions for matrix volatilization at lowest

temperatures or thermal stabilization of the analyte, which allows the use of highest temperatures during pyrolysis for efficient matrix elimination without analyte loss. In the past decade, different substances have been proposed as chemical modifiers for the determination of Cr {e.g., zirconium [25], magnesium [26], palladium [14,26,27], ruthenium and iridium [9] salts}. LODs were in the range 0.13–0.72 µg/L [14]. Direct solid sampling using ETAAS has been used as a good alternative to conventional methods of analysis where there are problems of sample digestion [25,26].

ICP-OES offers the great advantages of multi-element detection, but does not have LODs compatible with direct Cr determination in natural samples [15]. For this reason, analyte preconcentration is required in order to determine lower levels. However, ICP-OES exhibits tolerance for high contents of salt components greater than ETAAS and ICP-MS. One of the advantages of ICP-OES is the wide range of linearity, with over five orders of magnitude without changing experimental parameters.

ICP-MS detection achieves low LODs, but molecular ion interferences caused by the presence of carbon, nitrogen or chlorine species can disturb the measurement of the two most abundant Cr isotopes, ⁵²Cr and ⁵³Cr, during the detection process [16,17]. To reduce such interferences, several approaches have been explored. One is the use of a high-resolution ICP-MS instrument and collision/reaction cell [28,16]. However, the cost of the instrument is high and collision/reaction cell ICP-MS is not a routine analytical technique. Another approach is the use of mathematical correction [29]. Spectroscopic and matrix interferences can be minimized or eliminated by suitable sample pretreatment. Sun et al. [30] applied an on-line membrane desalter-ICP-MS system, while Wu et al. [31] proposed sol-gel zirconium coatings formed on the inner walls of a fused-silica capillary. Various extraction techniques have been also used to solve this problem [32–34].

3. Sample preparation

The general recommendation for total Cr determination and Cr(III) content in water samples includes filtration at site using a 0.45-µm filter, acidification with HNO₃ to pH <2 and storage at 4°C. For Cr(VI) determination, field preservation of samples using NaOH to pH >8 is recommended, as it can increase sample-storage times to 30 days [35].

Determination of Cr in groundwater samples containing iron may pose analytical problems due to sorption and fixation of Cr species onto Fe(III) hydroxides [36,37]. Parks et al. [36] reported that Cr species trapped inside iron hydroxides may not be soluble by HNO₃ digestion and hydroxylamine digestion is required to release this fraction. Kumar and Riyazuddin [37] confirmed these observations, but found that the NH₂OH procedure was

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