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Hexavalent chromium quantification in solution: Comparing direct UV–visible spectrometry with 1,5-diphenylcarbazide colorimetry

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ABSTRACT

Quantification of Cr(VI) in an aqueous solution is conducted by direct UV–visible spectrophotometry based on the yellow coloring of the chromate ion. Measurements show that absorption follows the Beer–Lambert law over a wide range of concentrations. At pH below the pK_a of 6.4 ($HCrO_4^-/CrO_4^{-2}$), the absorption maximum lies at 350 nm wavelength and the linear range spans from 0.5 to 100 mg Cr(VI)/L; above the pK_a (pH 6.4), the absorption maximum is 373 nm and linearity occurs in the range of 0.5–25 mg/L. The wide range of validity of the Beer–Lambert law is advantageous for the measurement of concentrated samples. The standard method of analysis of aqueous Cr(VI) is by colorimetry with the 1,5-diphenylcarbazide (DPC)–Cr(VI) complex. This method, although very sensitive, bears a narrow range of linearity from 0 to 0.8 mg Cr(VI)/L. It is shown that when analyzing Cr(VI) solutions with concentrations in the range of 30–500 mg/L, the DPC method gives inaccurate results and relative standard deviations of 20–50%. This is due to high dilution factors. On the contrary, the direct method performs with high accuracy. Relative standard deviation is only 0.5% at 500 mg Cr(VI)/L. The direct method is fast, reliable, and nondestructive for the sample. The direct method is recommended for the quantification of Cr(VI) at concentrations greater than 1 mg/L.

RESUME

Mots clés:
Chrome hexavalent
Cr(VI)
Spectrométrie UV–vis directe
1,5-diphenylcarbazide

Le dosage du Cr(VI) en solution aqueuse est effectué par spectrométrie UV–visible directe, grâce à la couleur jaune de l'ion chromate. Les mesures montrent que la loi de Beer–Lambert est respectée sur un large intervalle de concentrations. A pH inférieur à 6,4 (pK_a $HCrO_4^-/CrO_4^{-2}$), l'absorption maximale se situe à la longueur d'onde 350 nm et la game linéaire d'étalonnage s'étend de 0,5 à 100 mg Cr(VI)/L; au dessus du pK_a, l'absorption maximale se situe à 373 nm, la game de linéarité couvre l'intervalle 0,5–25 mg/L. Au contraire, la méthode standard d'analyse du Cr(VI) en solution, méthode colorimétrique au 1,5 diphénylcarbazide (DPC), présente une fenêtre de mesure très étroite, de 0 à 0,8 mg Cr(VI)/L. On montre que la méthode DPC appliquée à des échantillons de concentrations 30–500 mg/L, donne des résultats avec une incertitude importante et des écarts types de 20–50% autour de la moyenne. Les fortes déviations sont attribuées aux forts facteurs de dilution nécessaires. Pour la même game de concentrations, la méthode

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directe donne des résultats avec une très faible incertitude. Pour un échantillon de 500 mg Cr(VI)/L, l'écart type est de seulement 0,5%. La méthode directe est rapide, fiable, et elle permet de préserver l'échantillon. La méthode directe est conseillée pour le dosage du Cr(VI) à concentrations supérieures à 1 mg/L.

1. Introduction

Hexavalent chromium (Cr(VI)) is a widely occurring pollutant in soils, groundwaters, and waste materials, especially in chromite ore processing residue (COPR) and foundry slags. Chromium in the hexavalent oxidation state is toxic and carcinogenic. As sodium dichromate, Cr(VI) is a base compound used in the chemical industry for the production of pigments, wood treatment, and tannery products, as well as corrosion inhibitors. For the production of sodium dichromate from chromite ore (main mineral phase, $FeCr_2O_4$), a relatively inefficient metallurgical technique is still widely used, which has given rise to a legacy of COPR material worldwide. This is a major contributor of Cr(VI) to the environment [5,6,13]. To quantify Cr(VI) in solution, most practitioners use the colorimetric method with the 1,5-diphenylcarbazide (DPC) complex, the standard method of Cr(VI) determination [1,9,14]. The color complex is very strong, leading to a high sensitivity of the method. This explains why the DPC method applies only to a fairly small concentration range, roughly from 0 to 0.8 mg/L Cr(VI). For concentrations greater than 0.8 mg/L, the samples need to be diluted. The DPC method is commonly used with sample dilution being a general practice. In our studies on COPR remediation [11,17], we are confronted with concentrations exceeding thousand times (>800 mg/L) the concentration limit for the DPC method, leading to very high dilution factors of the samples (up to 2500×). We question to what extend these very high dilutions may decrease the accuracy of the quantification data. Another practical way to measure Cr(VI) in solution is the method of "direct UV–vis spectrometry", based on the natural color of the chromate ion in solution. Absorbing linearly over a wide range, this method may avoid excessive dilution of the samples. In addition, this direct method is fast and reliable in contrast to the DPC method that needs lengthy preparation of reagents and produces a color complex of limited stability. Few articles are available on measurement of Cr(VI) by direct UV–vis spectrometry. Hug and colleagues [3,4,8] used direct UV–vis spectrometry in kinetic studies where fast redox reactions between Fe(II) and Cr(VI) were investigated. Chromium VI shows charge transfer absorption bands, which differ in acid and alkaline conditions, thus allowing in situ studies of Cr(VI) acid–base speciation. According to their work, protonated Cr(VI) ($HCrO_4^-$) has a maximum absorption at 349 nm, whereas chromate (CrO_4^{2-}) peaks at 373 nm. Hug and colleagues showed that $HCrO_4^-$, CrO_4^{2-}, and Fe(III)–oxalate complexes have characteristic but overlapping spectra. They used a spectral fitting technique to quantitatively evaluate the different species in their system. In studies by Kim and Om [10] and Levitskaia et al. [12], standard solutions were scanned in the range of 300–700 nm. Levitskaia et al. retained the length of 372 nm as the length of maximum absorption, whereas Kim and Om defined the maximum absorption at 363 nm. Precise observation of the absorption curve in Fig. 1 of Kim and Om's work, however, shows that peak absorbance is actually much closer to 350 nm. Kim and Om studied the interference of various ions on Cr(VI) absorption. Common ions such as Na^+, K^+, NO_3^-, and Cl^- did not affect results up to 1 g/L, SO_4^{2-} and CO_3^{2-} did not interfere up to 200 mg/L, whereas Al^{3+} and Mg^{2+} had an influence at concentrations greater than 100 and 15 mg/L, respectively. Fournier-Salaün and Salaün [7] used direct UV–vis spectrometry at 371 nm in a method of continuous chromium VI quantification of samples with varying pH values. The method uses molar absorption coefficients of acid and alkaline chromium species and applies a mass balance equation to link total absorption values to species-specific, pH-dependent concentrations. The authors reached good correspondence between initially added and modeled total Cr(VI) concentrations with deviations less than 6.5%. This study was limited to synthetic samples.

Levitskaia et al. used a liquid waveguide capillary cell to quantify very low Cr(VI) concentrations from 7.3×10^{-5} to 0.1 mg/L by using direct spectrophotometry at 372 nm. They conducted measurements on polluted groundwater samples and confirmed that solution ions including complexing cations did not impair the Cr(VI) analysis. The influence of pH on absorption intensities was treated as in Fournier-Salaün and Salaün for pH values close to the pK_a ($HCrO_4^-/CrO_4^{2-}$).

Although previous studies showed that the charge transfer absorption bands of Cr(VI) can be used to define linear calibrations and allow direct quantification of Cr(VI) in solutions, we will focus in this work on the comparison between direct and DPC methods. Emphasis will be on the quantification of high chromium concentrations as encountered in effluents or leachates of chromium processing industries and production residues. The two analytical methods having different calibration ranges, the effect of sample dilution on measurement accuracy will be investigated. Also, to deal with the pH dependency of the charge transfer absorption bands, a simple method is proposed that distinguishes two broad pH domains with specific absorption bands. The overall goal of the study is to propose an accurate, easy to use, direct Cr(VI) quantification method and to define the concentration ranges most adequate for best use of either this or the DPC method.

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