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Chromium speciation using sequential injection analysis and multivariate curve resolution

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Abstract

In this paper we develop a suitable method for the speciation of chromium in tanning and environmental water samples.

We use sequential injection analysis (SIA) with a diode array detector linked to chemometric tools such as multivariate curve resolution-alternating least squares (MCR-ALS) to determine Cr(III) and Cr(VI) species. Although Cr(III) is an absorbent species, its sensitivity is much lower than that of Cr(VI). To increase its sensitivity, therefore, it was complexed with EDTA.

This method involves generating a pH gradient in the system reactor that converts dichromate into chromate in such a way that, when the sample reaches the detector, selective areas are observed and a data matrix is obtained. Applying MCR enables Cr(III) and Cr(VI) to be successfully determined simultaneously in tanning and environmental wastewater samples.

Keywords: Chromium speciation; Sequential injection analysis; Multivariate curve resolution; Tanning and environmental samples

1. Introduction

Chromium (Cr) is found in several chemical forms with oxidation numbers that range from zero (free metal) to six (chromate and dichromate). Only the trivalent (III) and the hexavalent (VI) forms are stable enough to be found in the environment [1]. Because of the different toxicities of Cr(III) and Cr(VI) (the former, an essential micronutrient [2] and the latter, a high toxic element [3]), it is important to determine them separately as well as to determine the total chromium content [4]. This difference in toxicity is one of the main reasons for the enormous recent development of analytical methods for differentiating the various forms of Cr in the medium of interest [5–13].

Several possibilities for the speciation of Cr(III) and Cr(VI) in aqueous solutions exist. One is to complex and selectively extract both Cr(III) and Cr(VI) before instrumental analysis [14–20]. The other is to analyse one of the two species and the total chromium and then calculate the concentration of the other species by subtraction [21–24]. Recent studies [25–27] have proposed retaining both species of chromium on different sorbents and then eluting them specifically.

In this study we propose an analytical method for the simultaneous speciation of chromium in a single process using sequential injection analysis (SIA) with a UV–visible detector array and second-order data treatment.

SIA, developed by Ruzicka and Marshall in 1990 [28] has great potential for on-line measurements. It is a simple technique and sample manipulations can be easily automated. It is also highly versatile, both in terms of instrumental configuration and in terms of the type of data it can provide, which ranges from zero-order data (a scalar) to second-order data (a matrix) [29]. If second-order data have been obtained by a suitable treatment, with multivariate curve resolution-alternating least squares (MCR-ALS) it is possible to resolve the various species present in a sample and conduct the joint analysis in the presence of interferents without having to apply physical separation steps for both species [30,31]. In a previous paper [32] we proposed a method based on the same instrumental configuration and data treatment to determine total chromium. In the present paper we determine both species of chromium (Cr(III) and Cr(VI)) simultaneously in a single step. The advantages of this method are clear since many fields of applica-

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tion, for example, the environment, require speciation in many cases.

Though Cr(III) is an absorbent species in the UV–visible region, its sensitivity is low. Cr(III) has a strong tendency to form hexacoordinate octahedral complexes with ligands such as water, ammonia, urea, ethylendiamine (EDTA) [15,33,34] and other organic ligands containing oxygen, nitrogen or sulphur [35]. A previous complexation of Cr(III) with EDTA is therefore proposed in order to increase its sensitivity. Most complexation kinetics are slow [36], so several studies have been conducted to speed up the reaction [37,38]. In this paper we determine the best experimental conditions for this step. To do so, we consider these conditions to be compatible with the subsequent process, which will be conducted in the SIA system. We also developed the SIA experimental conditions that provide the optimal responses (e.g. spectra correlation, model fit and error quantification).

Using second-order calibrations, we determined the concentrations of Cr(III) and Cr(VI), as well as several figures of merit in wastewater samples from the leather-tanning process. This process only uses Cr(III) at concentrations in the order of those in this study. However, because of the storage and subsequent treatment of the samples, we thought this strategy could be used to check for the appearance in the samples of any Cr(VI), which is a toxic species. We also applied this method to analyse industrial wastewater. Although these samples did not contain chromium at the levels studied, they were of interest because we were able to test whether the method is applicable to other types of samples.

2. Experimental

2.1. Procedure

The procedure used is illustrated in Fig. 1. In a first step, the Cr(III) is complexed with EDTA to increase its sensitivity.

The second step involves the sequential aspiration of NaOH and sample and their subsequent expulsion towards the detector, which generates a pH gradient such that Cr(VI) evolves from $Cr_2O_7^{2-}$ to CrO_4^{2-} [32] in the following order: first $Cr_2O_7^{2-}$, then a mixture of $Cr_2O_7^{2-}$ and CrO_4^{2-}, and finally CrO_4^{2-}. The Cr(III)–EDTA species is present throughout the time the sample passes through the detector. The results correspond to a data matrix $\boldsymbol{D}(m \times n)$, where m are the times and n are the wavelengths at which the signal is recorded.

In the third step, the data are treated using MCR-ALS [39]. The aim of the MCR-ALS method is the bilinear decomposition of the experimental data set $\boldsymbol{D}$ in order to obtain matrices $\boldsymbol{C}$ and $\boldsymbol{S}^{\mathrm{T}}$ (which have a real chemical significance), according to Eq. (1):

$$\boldsymbol{D} = \boldsymbol{C}\boldsymbol{S}^{\mathrm{T}} + \boldsymbol{E} \tag{1}$$

where matrix $\boldsymbol{C}(m \times p)$ has column vectors corresponding to the profiles of concentration of the p pure components that are present in matrix $\boldsymbol{D}$. The row vectors of matrix $\boldsymbol{S}^{\mathrm{T}}(p \times n)$ correspond to the spectra of the c pure components, and $\boldsymbol{E}$ is the matrix of the residuals.

Specifically, MCR-ALS is an iterative method that, at each cycle, calculates new matrices $\boldsymbol{C}$ and $\boldsymbol{S}^{\mathrm{T}}$. In this process, a set of constraints [40] is introduced. These constraints derive from chemical knowledge of the system, so that the value of $\boldsymbol{E}$ is minimum. For example, the concentration profiles or spectra could not be negative, so the non-negative constraint was applied. In practical applications of MCR-ALS, it is common to use augmented matrices. These matrices are formed by arranging individual matrices and keeping one order in common. Working with augmented matrices can also solve the rotational ambiguity problem and break rank deficiency [41–43].

In Fig. 1 (step 3), the vectors of matrices $\boldsymbol{C}$ and $\boldsymbol{S}^{\mathrm{T}}$ are graphically superimposed. This figure for the concentration profile shows information about three augmented matrices whose columns have been kept in common: a sample containing Cr(III) and Cr(VI), a standard of Cr(III) and a standard of Cr(VI) in which the two species in evolution appear ($Cr_2O_7^{2-}$ and CrO_4^{2-}).

To evaluate the quality of the resolution process, we considered the following parameters:

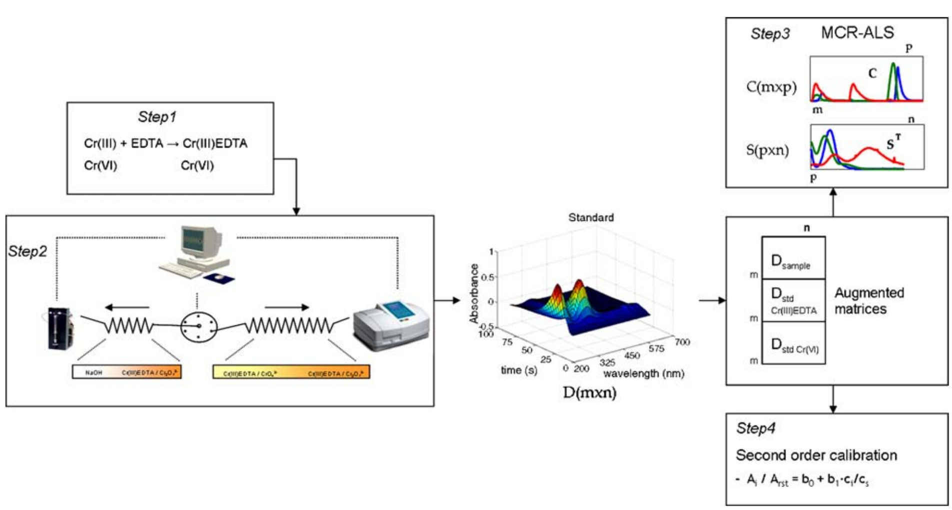

Fig. 1. Scheme of the proposed process for the speciation of Cr(III) and Cr(VI).