Factorial design for optimising chromium determination in tanning wastewater

V. Gómez *, A. Pasamontes, M.P. Callao

Department of Analytical and Organic Chemistry, Rovira i Virgili University, Marcel·lí Domingo s/n, Campus Sescelades 43007 Tarragona, Spain

Abstract

A totally automatized procedure for determining chromium by sequential injection analysis (SIA) linked to multivariate curve resolution with alternating least squares (MCR-ALS) is proposed. With this system Cr(III) is oxidised to chromate (Cr(VI)) and this form is then converted to dichromate in order to obtain second order data. The experimental design method was used to establish the best conditions. The identification of the most influential factors was validated using ANOVA tests. We used this method to successfully analyse total chromium in several aqueous tannery samples from various steps of a tanning process. The results from this method and those from the atomic absorbance spectroscopy (AAS) method are comparable. Sample frequency was 30 samples h^{-1}.
© 2006 Elsevier B.V. All rights reserved.

Keywords: Chromium; Tanning samples; Sequential injection analysis; Second order data; Experimental design

1. Introduction

Tanning agents bring about permanent stabilization of the skin matrix against biodegradation. This industry has gained a negative image in society with respect to its pollution potential and therefore is facing a severe challenge. The unit processes that cause tanners the most difficulty with regard to perceived environmental impact are unhairing and chrome tanning [1]. Basic chromium sulphate (BCS) is a tanning agent, which is employed by 90% of the tanning industry. Chromium content in wastewater tanning samples ranges between 0.5 and 30 g/L depending on the treatment [2]. Chromium in its trivalent form is an essential trace element when present at the micro level [3], whereas the same when present in excess is proven to be a potential soil, surface water, groundwater, and air contaminant under specific conditions [4]. Considering the large amounts applied and the low biodegradability of such chemicals, tannery wastewater treatment represents a serious environmental and technological problem [5]. For economic reasons, and also to ensure compliance with environmental regulations, it is interesting to determine the chromium content at the various stages of the tanning processes.

The reference method for determining chromic oxide [6] usually takes up to several hours. Several alternatives [7–9] have been reported for the determination of total chromium in final effluent from a leather tannery, but these process are slow and laborious and require large volumes of reagents. Some methods based on spectroscopy and multivariate calibration [10] are promising alternatives to the reference method. However, multivariate calibration is costly to implement and must be valid over time.

In this paper we propose to determine chromium using sequential injection analysis (SIA) and chemometric tools of second order data treatment. SIA was developed by Ruzicka and co-workers in 1990 [11–13]. These systems are versatile and efficient for automatization and miniaturization, the frequency of analysis can be high and the consumption of samples and reagents is low. Thanks to these advantages, SIA has been used in a wide range of applications, for example in environmental, food, pharmaceutical and bioprocessing fields.

The basic configuration of a SIA system is shown in Fig. 1. The valve selects the carrier, the sample and reagent volumes to be sequentially aspirated towards the holding coil. The flow is

---

* Corresponding author. Tel.: +34 977 558122; fax: +34 977 558446.
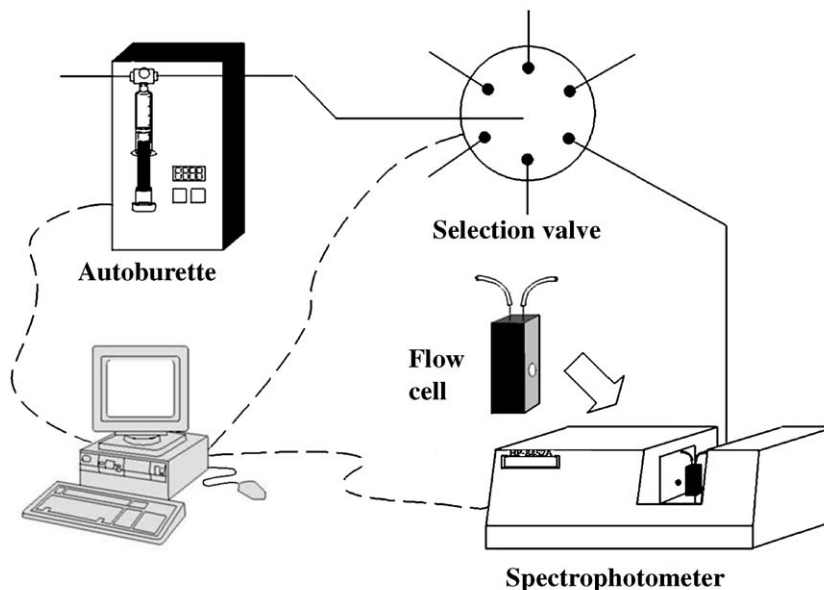*E-mail address:* veronica.gomez@urv.net (V. Gómez).

Fig. 1. Scheme of a sequential injection analyser. Dotted lines are computer connections.

then reversed and the valve is switched to direct the processed sample towards the detector. During this process, the sample and reagents are mixed by interdiffusion. By the time they reach the detector, the sample and the reagents will have reacted either partially or totally. If they have reacted partially, the signal that reaches the detector depends on the measurement times (t_1, t_2, t_3, etc.). If the detector used is a UV–visible diode–array detector (or any other multivariate detector) that obtains
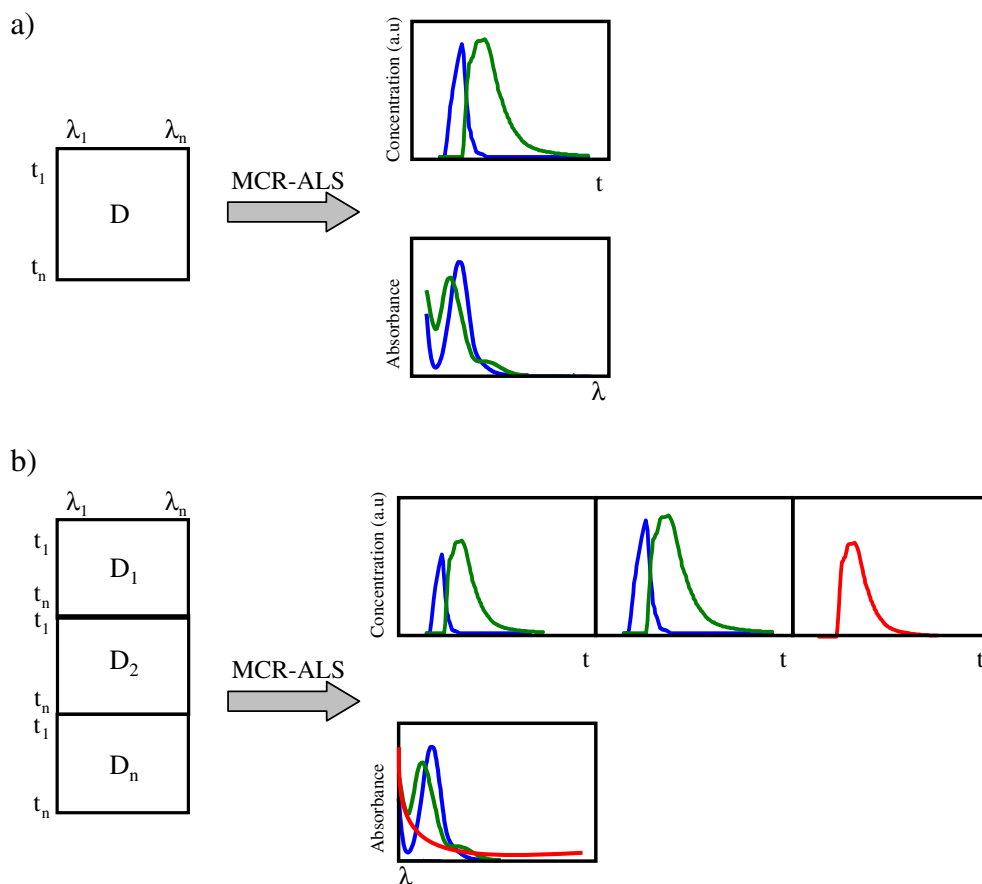

Fig. 2. MCR-ALS procedure working with a single matrix of data (a) or with an augmented matrix (b) maintaining the order of the columns.