

Multivariate optimization of solid-phase extraction applied to iron determination in finished waters

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Abstract

In this work, Amberlite XAD-4 resin functionalized with salicylic acid was synthesized, characterized and applied as a new packing material for an on-line system to iron determination in aqueous samples. The detection method is based on the sorption of Fe(III) ions in a minicolumn containing the synthesized resin, followed by a desorption step using an acid solution and measurement of iron by vis-spectrophotometry (CAS method). The optimization of the solid-phase extraction system was performed using factorial design and Doehlert matrix considering six variables: sample percolation rate (0.5–9 ml min⁻¹), sample metal concentration (20–200 µg l⁻¹), flow-through sample volume (0–5 ml) (all three directly linked to the extraction step), elution flow-rate (0.5–9 ml min⁻¹), concentration and volume of eluent (HCl 0.1–0.5 M) (all three directly linked to the elution step). The aim of this study was to obtain a set of operating ranges for the six variables tested in order to obtain – by means of a mathematical function allowing maximisation of each response (desirability function) – at least 90% of iron recovery rates. Using the experimental conditions defined in the optimization, the method allowed iron determination with achieved detection limit of 2.3 µg l⁻¹ and precision (assessed as the relative standard deviation) of 9.3–2.8% for iron solutions of 10.0–150 µg l⁻¹. Real samples (coming from a water treatment unit) were used successfully when evaluating potentialities of the developed SPE procedure coupled to a spectrophotometric determination.

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1. Introduction

Occurrence of iron in potable waters originates from its natural abundance in the Earth's crust (4th element with 5.05% by weight) and it can be found in freshwaters at levels ranging from 0.5 to 50 mg l⁻¹. But iron may also be present in drinking-water as a result of iron coagulants (ferric chloride) used during raw water treatment to remove colloidal or suspended particles or to eliminate organic

matter. At the outlet of these units, maximum tolerable level of this cation has been fixed to 200 µg l⁻¹ by European Legislation (EC, 1998). This value originates mainly from aesthetic reasons (taste and coloration of water), from steel corrosion prevention during water distribution (Shi et al., 2004) or from safety reasons. Whereas iron is vital for almost all living organisms, participating in a wide variety of biologic processes, including oxygen transport, DNA synthesis, and electron transport (Gurzeau et al., 2003), and although iron deficiency is the most common nutritional deficiency worldwide (Swanson, 2003), health effects of iron excess have recently received increased attention: excess intake of iron is purported to play a role in the

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etiology of several chronic diseases, including diabetes (Salonen et al., 1998), cancer (Stevens et al., 1988) and cardiovascular disease (Salonen et al., 1992).

In order to optimise coagulation process in drinking-water plants and to minimise iron levels in finished water, monitoring of this metal content during and after raw water treatment is therefore needed. Up to now, the coagulant quantities are generally determined by the empiric Jar-Test technique (El Samrani et al., 2004), that induces problems to excess (or insufficient) reagent, particularly during a period of fast variation in water quality. Moreover, an European Directive has recently introduced the principle of self-monitoring, i.e. that producers must constantly ensure that the water distributed to consumers meets the minimum requirements set out. In response to any failure to meet a standard for drinking-water quality, the water company must establish the cause and the nature of the failure (EC, 2000).

These more and more stringent regulations have induced during last years many advances in the automation of analytical procedures, and in the development of coupled method associating solid-phase extraction (SPE) or solid-phase microextraction (SPME) – to reach required low levels of Metallic Trace Elements – with, in most cases, spectrophotometric methods (Yang et al., 2002; Legnerova et al., 2003; Luo and Bi, 2003; Dias et al., 2006). These last ones are actually the easiest detection method able to be automated and miniaturized, and have thus direct application for on-site and/or on-line micropollutant determination (Economou, 2005; Pons et al., 2005a; Pons et al., 2005b). Commonly used SPE sorbents consist of specific functional groups immobilized on a solid support, improving the efficiency of metal by providing better contact area with the samples (Garg et al., 1999). Sorbents may be in the form of extraction disks (Ree et al., 1979; Thurman and Snively, 2000; Boussetta et al., 2006) or in the form of resins (Léon-Gonzalez and Perez-Arribas, 2000; Tewari and Singh, 2001).

Most papers dealing with extraction step of metallic ions consider optimization strategies based in a single variable approach (SVA). Unfortunately, a SVA approach is not always suited when many parameters are involved, and can even lead to erroneous conclusions about the importance of certain factors on the extraction process, due to the fact that interactions between factors are not being considered.

A multivariate approach (MVA) to the optimization of the SPE process enables the simultaneous study of various factors, allowing thus to find the best compromise between potential conflicting criteria, and to find it in a faster and more cost-effective manner.

In this paper, SPE has been considered with its three or four successive steps, each one being influenced by several parameters:

- The solid sorbent should be conditioned with an appropriate solvent in order to enable the wetting of the packing material and the solvation of the functional groups. This step is essential when working with com-

mercial resins because of presence of impurities; moreover, this step enables removing of air present in the column and fills the empty volume with solvent.

- The percolation of the sample through the solid sorbent is a crucial step and stakes many parameters to be studied: sample volume, sample flow-rate, pH, absorption capacity of the resin. All these parameters will contribute to the sorbent extraction yield.
- The third step of washing is often considered as optional but may allow to remove water in the final extract and eliminate matrix component of no interest with some organic solvent; this step is not necessary if the chosen sorbent is so selective that analytes of no interest have not been retained during the step of percolation.
- The final step consists in the elution of the analytes of interest with an appropriate solvent; according to nature of sorbent used during percolation, the solvent used should be specific of targeted analytes, in order to ensure selective, or should be strong enough to disrupt interactions with the sorbent. The parameters to be studied are type, concentration and volume of eluent, eluent flow-rate and amount of targeted analytes retained on the sorbent. As can be easily concluded, the elution yield is strongly correlated to the extraction yield.

To determine the whole parameters affecting adsorption, extraction and elution of iron onto an extracting support, only a multivariate approach (MVA) allows one to obtain a global optimum with a minimum of experiments. To our knowledge, this statistical method – using a six-dimensional hypersphere – has never been applied to extraction and elution processes. Parameters affecting extraction and elution steps are sample percolation rate, sample metal concentration, flow-through sample volume (all three directly linked to the extraction step), elution flow-rate, concentration and volume of eluent (all three directly linked to the elution step). These parameters have been optimized as a function of a minimum extraction yield (at least 90%) of the targeted analyte, by means of an empirical mathematical model. To estimate the coefficients of the developed model, an uniform shell Doehlert design, consisted in a set of 45 distinct experiments, has been applied; these experiments consisted in GF-AAS determination of iron amounts in eluates after percolation of samples through modified support. Once parameters optimized, this extraction–elution procedure has then been coupled to a on-line spectrophotometric determination of Fe(III) ions. The method thus developed allowed the determination of Fe³⁺, in the range 0–200 µg l⁻¹, at the outlet of a potable water treatment unit, thanks to a MSFIA system.

2. Experimental

2.1. Reagents

All solutions were prepared with ultra-high quality deionised water (Millipore, resistivity >18 MΩ cm). All

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