Experimental design approach for the solid-phase extraction of residual aluminium coagulants in treated waters

P. Vanloot [a], J.-L. Boudenne [a,*], Laurent Vassalo [a], M. Sergent [b], B. Coulomb [a]

[a] *Université de Provence – CNRS, Laboratoire de Chimie et Environnement, FRE2704, 3 Place Victor Hugo, Case 29, 13331 Marseille Cedex 3, France*
[b] *Université Paul Cézanne – CNRS, Laboratoire de Méthodologie de la Recherche Expérimentale, UMR6171,*
Avenue Escadrille Normandie Niémen, 13397 Marseille Cedex 20, France

Abstract

Solid-phase extraction (SPE) of trace elements before their analysis has become a conventional pretreatment step of analytes because of their frequent low concentrations in numerous samples. Additionally, interfering compounds often accompagny analytes of interest, thus requiring a clean-up step. The preconcentration step and/or matrix removal can be efficiently improved by chemometric approaches allowing obtention of reliable results. Single variable approach is often used but is time and cost consuming, and may be the source of mistakes; multivariable approach allows to overcome these problems and increases the probability of global optimum finding.

In order to obtain a set of experimental conditions for the selective extraction of Al(III) in water samples, onto a modified organic support (salicylic acid grafted on XAD-4), a multicriteria approach (response surface methodology) has been applied. The extraction method was optimized by the aid of a factorial design and a uniform shell Doehlert design for six variables: sample percolation flow rate, trace metal amount, sample volume, concentration and volume of HCl used for elution of aluminium. Results demonstrate the synergic effects of four factors and allow us to define working ranges for each parameter tested. The designed SPE procedure was then sucessfully applied to synthetic and real samples, issued from a potable water treatment unit.
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Keywords: Aluminium; Solid phase extraction; Functionalized resin; Response surface methodology; Desirability indice

1. Introduction

Aluminium determination at low level is of particular interest in potable water units because this metallic ion is commonly used as reactant for coagulation–floculation in the treatment of raw waters 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 $200\,\mu g\,l^{-1}$ by European Legislation [1]. This cation is associated with various health problems in numerous studies, from gastrointestinal damage and phosphate deficiency to dialysis encephalopathy, renal oestrodistrophy and Alzheimer's disease [2,3]. In order to optimise coagulation process in drinking water plants and to minimise aluminium levels in finished water, monitoring of this metal contents during and after raw water treatment is there-fore needed. Up to now, the coagulant quantities are generally determined by the empiric Jar-test technique [4], that induces problems of excess (or insufficient) reagent, particularly during period of fast variation in water quality [5]. 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 [6]. 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 methods 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 [7–10].

These last ones are actually the easiest detection methods suitable for automation and miniaturization, and have thus direct application for on site and/or on-line micropollutant determina-

tion [11–13]. Commonly used SPE sorbents consist of specific functional groups immobilized on a solid support, improving the efficiency of metal extraction by providing better contact area with the samples [14]. Sorbents may be in the form of extraction disks [15–17] or in the form of resins [18,19]. Recently, our research group has developed a new sorbent intended for the selective determination of aluminum in water samples. This support is a modified commercial resin (Amberlite® XAD-4) onto which we have chemically bond a chelating function (salicylic acid). Its synthesis scheme has already been published in a previous paper [20].

In this paper, our purpose is to determine factors affecting the extraction–elution steps of aluminum onto this support, in order to spectrophotometrically detect this cation in future studies. Levels of aluminum at the outlet of potable water treatment unit are relatively low and lay down this extraction–preconcentration step. Factors influencing accuracy of the spectrophotometric method will be directly linked to the step of elution, and this last one will be strongly correlated to the factors linked to the sequestration step onto the support. This paper will at first determine the relative influence of three factors affecting the elution yield (elution rate, concentration and volume of hydrochloric acid) thanks to a new experimental design approach and to the use of a desirability function (95% of aluminum recovery during the elution step. Next, a desirability function will be applied to the global procedure (extraction + elution) and will allow us to determine optimal conditions to reach a minimum of 95% yield.

2. Experimental

2.1. Reagents

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

Amberlite XAD-4 resin was obtained from Acros Organics (Noisy-le-Grand, France). It was suspended under agitation in methanol for 24 h after which the washed resin was filtered off, rinsed with methanol and dried at 60 °C for 48 h before use.

All chemicals used in this work were of analytical grade and purchased from Acros Oragnics and used without further purification, except for thionyl chloride, which was purified before use by distillation under argon at atmospheric pressure (76 °C fraction) and was used immediately.

A commercial stock solutions of $1 \, g \, l^{-1}$ of Al^{3+} was purchased from Merck (Darmstadt, Germany). Further dilutions were prepared daily as required. Synthetic multielement samples were prepared as required from dilution of a stock solution used for ICP–AES calibration. This PlasmaTEST® solution, purchased from SCP Sciences (Canada) was constituted of 18 elements (As, Be, Ca, Cd, Co, Cr, Cu, Fe, Mg, Mo, Ni, Pb, Sb, Se, Ti, Tl, V, Zn) at $10 \, mg \, l^{-1}$ ($\pm 0.08 \, mg \, l^{-1}$). Before each extraction, samples were acidified to pH 2.5 with nitric acid. For on-line detection of Al(III) ions, a chromazurol-S (CAS) solution was used at a concentration of $1.5 \times 10^{-4} \, mol \, l^{-1}$, with cetyltrimethylammonium bromide at $4.5 \times 10^{-4} \, mol \, l^{-1}$. o-Phenanthroline ($4 \times 10^{-4} \, mol \, l^{-1}$) and hydroxylammonium hydrochloride ($1 \times 10^{-3} \, mol \, l^{-1}$) were added to mask interfering species (Fe^{3+} and Cu^{2+}). Acetate buffer was used to adjust colorimetric reagent solution pH at 5.1

2.2. Synthesis of SA-XAD resin

The sorbent SA-XAD was prepared by a procedure already described in a previous paper [20] and described briefly herein. Amberlite XAD-4 resin (5 g) was treated with 2.7 ml acetyl chloride and 5.62 g anhydrous aluminium chloride in 1,2-dichloroethane. The system was refluxed for 16 h at 40 °C. The solid was washed with hydrochloric acid, water and methanol before repeated treatments with KMnO$_4$ (2.5 g) and sodium hydroxide (5.75 g). The carboxylated resin was refluxed with thionyl chloride (30 ml) at 70 °C for 2.5 h and then stirred with 2-methylanisole (15 ml) and anhydrous aluminium chloride (3.6 g) during 12 h at 60 °C. Methyl groups were then oxidized into carboxylic groups by a mixture of sodium hydroxide (0.16 g) and KMnO$_4$ (3.76 g) in water at 60 °C. Finally, methoxy groups were converted into hydroxy groups by mixing previous resin with anhydrous aluminum chloride (5.76 g) and toluene (30 ml) at 60 °C for 8 h. The final resin (SA-XAD) was collected by filtration, washed with water and methanol, and dried under vacuum.

2.3. MSFIA aluminium determination: apparatus and procedure

The manifold used for aluminium extraction and determination is depicted Fig. 1. It is mainly composed of three modules: the new resin (40 mg) packaged into a methyl polymetacry-
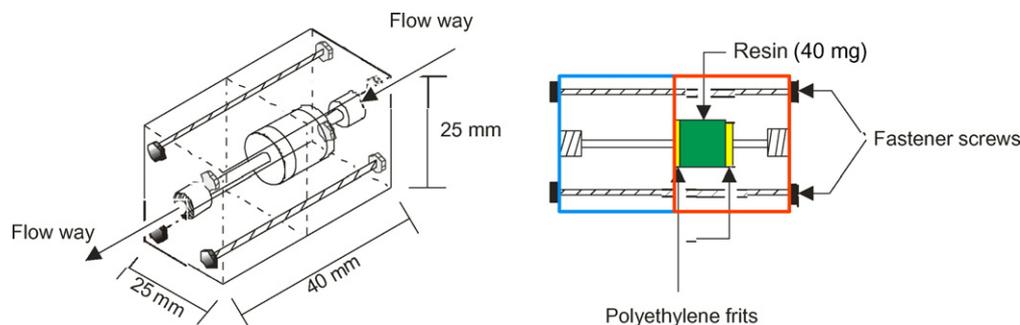
Fig. 1. Design of the microcolumn used for Al(III) solid-phase extraction.

late micro-column of 6 mm i.d. and 10 mm length, affording thus flow-through percolation of samples, an automatic multi-burette CRISON Microbur BU4S (Crison Instruments, Alella, Spain) equipped with three 5 ml syringes (Hamilton, Interchim, France), each of them being connected to a three-way selection valve CRISON 2045. The fourth selection valve of multibu-rette was only used for sampling. Tubings, 0.8 mm i.d., are made of Teflon. A Secomam S1000 UV–vis spectrophotome-ter (Secomam, Alès, France) was used to perform absorbance measurements. SPE system was adapted to a flow-through quartz suprasil cell (2 cm optical pathlength) of the UV–vis spectropho-tometer.

The whole modules of the MSFIA system (automatic burettes, valves, spectrophotometer) were connected to a com-puter via a RS-232C interface and controlled by the Autoanalysis Station 3.0 software (SCIware, Palma, Spain) [21].

The operation of the on-line aluminium extraction and deter-mination was as follows: during extraction step, sample was aspired in an holding coil, whereas the three other syringes were filled with water used as carrier, with hydrochloric acid (HCl) and with the reagent (R). Then the four modules pushed each of their liquids upwards: sample and water were percolated through the microcolumn that retained the metal, while HCl and reagent came back to their own tanks. Thus, Al(III) ions were retained on the SA-XAD sorbent and the remaining solution was discharged.

During the elution step, HCl and the spectrophotometric reagent are pushed together, the first one to the inlet of col-umn to elute Al^{3+}, the second one to the outlet of the column to be mixed with eluate in a mixing loop. Complexes thus formed were then determined by spectrophotometry at $\lambda = 546$ nm.

2.4. Metal analysis and resin characterization

Graphite furnace–atomic absorption spectrometry (GF–AAS) was used to determine recovery rates after the aluminium extraction–elution procedure. GF–AAS measure-ments are carried out on a Perkin-Elmer 1100B spectrometer equipped with an HGA700 graphite furnace. A Perkin-Elmer aluminium hollow-cathode lamp was operated at 25 mA. Argon flow was 300 ml min^{-1} except during atomisation. Pyrolytically-coated graphite furnace tubes were used.

Furnace settings were: drying at 160 °C, ramp for 20 s, hold for 35 s; cracking at 1200 °C for Al; no ramp; hold for 5 s; atom-ising at 2400 °C, no ramp and 2 s hold; and cleaning at 2800 °C, no ramp and 2 s hold.

Inductively coupled plasma–atomic emission spectrometry (ICP–AES) measurements were carried out with a Jobin YVON JY2000 Ultratrace spectrometer, equipped with a CMA spray chamber and a Meinhard TR50-C1 glass nebuliser, when con-sidering interfering cations. Determinations were performed with the following parameters: power 1000 W, pump speed 20 ml min^{-1}, plasma flow rate 12 l min^{-1}, coating gas flow rate 0.2 l min^{-1}, nebuliser flow rate 0.83 l min^{-1} and nebuliser pres-sure 3.1 bar.

Infrared (IR) spectra were recorded on a Nicolet Impact 410 Spectrometer (Montigny-le-Bretonneux, France). Samples were pressed into KBr pellets.

2.5. Experimental design

2.5.1. Experimental factors

Preliminary studies have shown that six parameters – noted as factors X afterwards – have to be considered during SPE optimization in order to obtain three experimental responses – noted as factors Y later on – that are extraction (Y_1), elution (Y_2) and aluminium recovery (Y_3) rates: flow-through sample volume (X_1), sample percolation rate (X_2), sample metal concentration (X_3), (all three directly linked to extraction step), eluent volume (X_4), elution flow-rate (X_5) and concentration of eluent (X_6), (all three directly linked to elution step). The domains of variation for each factor was determined based on knowledges of the sys-tem (mainly volume of syringes and piston speed available with CRISON Instruments) and acquired from initial experimental trials:

- X_1: 0.5–5 ml
- X_2: 0.5–9 ml min^{-1}
- X_3: 20–200 µg l^{-1}
- X_4: 0.2–5 ml
- X_5: 0.5–9 ml min^{-1}
- X_6: 0.1–0.5 mol l^{-1}

For calculation, the factors were transformed in coded fac-tors, varying from -1 to $+1$, and the experimental domain of the coded factors (X_i) is represented by a six-dimensional hyper-sphere (radius 1).

2.5.2. Experimental design methodology

The aim of this study was to determine the best conditions for extraction and elution, and for that, the value of extraction yields over the whole experimental domain is desired. To get this information, an empirical mathematical model was used, which establishes the relationship between the variation of the responses, η, and the variation of the factors X. This model is a quadratic model of the form:

$$\eta = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \cdots + \beta_k X_k + \beta_{11} X_1^2 + \beta_{22} X_2^2$$
$$+ \cdots + \beta_{kk} X_k^2 + \beta_{12} X_1 X_2 + \cdots + \beta_{k-1,k} X_{k-1} X_k$$

where η represents the variation of the responses; k is the number of factors; β_0 is the constant factor; β_i, β_{ii} and β_{ij} are coefficients of the linear, quadratic and cross-product terms, respectively.

To estimate the coefficients of this model, we need a set of experiments well spread in the domain, that is a design of exper-iments optimal for a second order polynomial model. Indeed, the quality of the coefficient estimation and the quality of the prevision only depend on the choice of the experimental points. Among the set of designs, we chose a uniform shell Doehlert design, which is an optimal design for the spherical domain defined by the factors [22]. For a studied response (η), the esti-mates (β_i, β_{ii}, β_{ij}) were calculated using a multilinear regression. Some experiments were replicated in order to estimate the vari-ance of the experimental results. Then, to minimize the effect of systemic errors, experiments were carried out in a random fash-ion. The calculations have been performed with the Nemrod-W
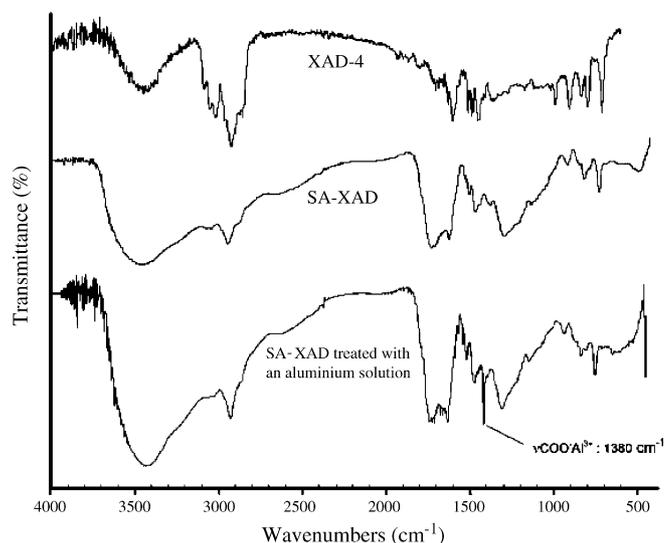
Fig. 2. FTIR spectra of Amberlite XAD-4, modified resin (SA-XAD) and treated with an aluminium solution.

software (LPRAI, Marseille, France), which was developed for building and processing designs of experiments [23].

The isoresponse curves and the desirability function [24] were used to determine the best compromise in the experimental domain.

Table 2 shows ANOVA results for aluminium recovery rate (Y_3). The F-ratio shown is used to determine the statistical significance of the extraction–elution process. The F-value is a ratio of two independent estimates of experimental error. Associated with this ratio is a P-value wich quantifies the probability of making an error by associating an effect with a given factor. The P-value also provides the exact level of significance of a hypothesis test. The R-square values indicate the percentage of variation of the response that is explained by the deliberate variation of the factors in the case of experiment [25].

3. Results and discussion

3.1. Resin characterization

Each step of the grafting procedure was characterized by FTIR (Fig. 2). FTIR spectra of original Amberlite XAD-4 revealed the presence of pendant ethylbenzene groups; 2955 and 2871 cm^{-1} valence vibrations of CH$_3$ were observed. The groups originate from the presence of ethylvinylbenzene in the commercial divinylbenzene used for preparation of the resin. Presence of pendant vinylbenzene groups was assessed as well by the valence vibration of the C–H bonds at 3083 cm^{-1} (vinylic CH$_2$) and 3017 cm^{-1} (vinylic CH) and of C=C vinylic bond at 1628 cm^{-1}. After the first acylation, those three vibration bands disappeared which showed that pendant vinylbenzene groups reacted with aluminum chloride and acetyl chloride. Addition of acetyl groups on the phenyl rings of poly(styrene-*co*-divinylbenzene) was evidenced by bands at 1266 and 1196 cm^{-1} (aryl ketones), 1359 cm^{-1} (deformation vibration of CO–CH$_3$) and 1685 cm^{-1} (vibration band of C=O fixed on a aromatic ring). Oxidation of these acetyl groups by KMnO$_4$ in basic

medium leads to a small modification of the C=O vibration band (1668 cm^{-1}) and an emergence of an O–H band at 2624 cm^{-1}. Grafting of 2-methylanisole was assessed by the FTIR bands: 1262 cm^{-1}, aryl ether and aryl ketone; 1122 cm^{-1}, C–O vibration band of ethoxy group; and 1025 cm^{-1}, deformation band of trisubstituted phenyl. Oxidation induced the presence of a valence vibration of the C=O bond of the carboxy group at 1720 cm^{-1} and of the C–O bond of this group at 1231 cm^{-1}. Deprotection of the methoxy group caused the disappearance of the aryl ether band at 1122 cm^{-1}.

The comparison of FTIR spectra for grafted complexed and uncomplexed resin shows a modification of intensity of the band previously assigned to carboxylic group. A band of medium intensity, in the region near 1380 cm^{-1} appeared. This band could be attributed to the formation of a carboxylate moiety resulting from complexation with aluminium. This phenomenon has been reported for several metallic complexes of salicylic acid [26].

3.2. Doehlert design

Two factors have been prefixed according to previous batch experiments [27].

Mass of sorbent used during extraction–elution optimization has been fixed to 40 mg which is a large excess when considering extraction capacity of the modified resin (4.4 ± 0.3 mg g^{-1} for Al^{3+}). pH aluminium extraction has been fixed to 2.5 according to chelating properties of modified resin towards Al^{3+}.

The six other factors affecting solid-phase extraction of aluminium have been optimized by use of a Doehlert design. This one was devoted to the extraction step optimization as a experimental design within six factors: flow-through sample volume (X_1), sample percolation rate (X_2), sample metal concentration (X_3), HCl volume (X_4), elution flow-rate (X_5) and concentration of eluent (X_6).

This design consists of a set of 43 distinct experiments and the central point of the experimental domain – represented by experiment #43 – was repeated three times to evaluate the repeatability of the measurements (Experiments 43, 44 and 45). Experiments required for this design are described in Table 1. This design includes the possibility of adding additional factors without any adverse effects on the quality of the design.

From these results, coefficients estimation were calculated using multilinear regression from NEMROD-W [24] for aluminium extraction yield Y_1 (Eq. (1)) – which depends only on factors X_1, X_2 and X_3 – for aluminium elution Y_2 (Eq. (2)) and aluminium recovery rates Y_3 (Eq. (3)):

$$Y_1 = 85.93 - 0.48X_1 - 8.55X_2 + 0.39X_3 + 2.82X_1^2$$
$$+ 3.15X_2^2 + 0.43X_3^2 - 1.96X_1X_2 - 3.23X_1X_3$$
$$- 1.23X_2X_3 \tag{1}$$

$$Y_2 = 90.967 - 2.771X_1 + 0.544X_2 - 0.980X_3 + 4.391X_4$$
$$- 13.410X_5 - 2.411X_6 - 1.167X_1^2 - 0.333X_2^2$$
$$- 1.425X_3^2 - 2.802X_4^2 - 6.540X_5^2 - 1.148X_6^2$$

Table 1
Doehlert design and experimental results

Experiment	X_1 (ml)	X_2 (ml min^{-1})	X_3 (µg l^{-1})	X_4 (ml)	X_5 (ml min^{-1})	X_6 (mol l^{-1})	Y_1 (%)	Y_2 (%)	Y_3 (%)
1	5.00	4.75	110.00	2.60	4.75	0.30	88.20	86.60	76.40
2	0.50	4.75	110.00	2.60	4.75	0.30	89.30	93.00	83.00
3	3.88	8.45	110.00	2.60	4.75	0.30	79.80	87.60	69.90
4	1.63	1.05	110.00	2.60	4.75	0.30	96.50	91.50	88.30
5	3.88	1.05	110.00	2.60	4.75	0.30	96.00	89.20	85.60
6	1.63	8.45	110.00	2.60	4.75	0.30	83.70	93.40	78.10
7	3.88	6.00	185.00	2.60	4.75	0.30	83.70	89.10	74.60
8	1.63	3.50	35.00	2.60	4.75	0.30	86.90	87.50	76.10
9	3.88	3.50	35.00	2.60	4.75	0.30	91.50	89.50	81.90
10	2.75	7.20	35.00	2.60	4.75	0.30	82.30	92.50	76.10
11	1.63	6.00	185.00	2.60	4.75	0.30	85.50	91.50	78.20
12	2.75	2.30	185.00	2.60	4.75	0.30	93.40	88.50	82.70
13	3.88	6.0	128.75	4.50	4.75	0.30	85.90	90.50	77.70
14	1.63	3.50	91.25	0.70	4.75	0.30	87.90	86.40	75.90
15	3.88	3.50	91.25	0.70	4.75	0.30	88.40	83.70	74.00
16	2.75	7.20	91.25	0.70	4.75	0.30	81.70	85.90	70.20
17	2.75	4.75	166.25	0.70	4.75	0.30	87.60	84.90	74.30
18	1.63	6.00	128.75	4.50	4.75	0.30	86.50	93.80	81.20
19	2.75	2.30	128.75	4.50	4.75	0.30	92.20	92.80	85.60
20	2.75	4.75	53.75	4.50	4.75	0.30	88.20	92.80	81.80
21	3.88	6.00	128.75	2.98	8.10	0.30	86.70	74.50	64.60
22	1.63	3.50	91.25	2.22	1.40	0.30	86.50	97.40	84.30
23	3.88	3.50	91.25	2.22	1.40	0.30	88.40	94.90	83.80
24	2.75	7.20	91.25	2.22	1.40	0.30	81.70	96.10	78.50
25	2.75	4.75	166.25	2.22	1.40	0.30	87.60	94.80	83.00
26	2.75	4.75	110.00	4.12	1.40	0.30	86.30	97.40	84.00
27	1.63	6.00	128.75	2.98	8.10	0.30	86.50	78.00	67.50
28	2.75	2.30	128.75	2.98	8.10	0.30	93.00	76.00	70.70
29	2.75	4.75	53.75	2.98	8.10	0.30	86.20	78.30	67.50
30	2.75	4.75	110.00	1.08	8.10	0.30	86.30	77.30	66.70
31	3.88	6.00	128.75	2.98	5.3	0.45	86.70	85.20	73.90
32	1.63	3.50	91.25	2.22	4.2	0.15	87.90	95.90	84.30
33	3.88	3.50	91.25	2.22	4.2	0.15	88.40	93.20	82.40
34	2.75	7.20	91.25	2.22	4.2	0.15	82.90	94.70	78.50
35	2.75	4.75	166.25	2.22	4.2	0.15	86.10	92.10	79.40
36	2.75	4.75	110.00	4.12	4.2	0.15	85.20	95.00	81.00
37	2.75	4.75	110.00	2.60	7.55	0.15	86.30	75.80	65.40
38	1.63	6.00	128.75	2.98	5.3	0.45	85.60	88.00	75.40
39	2.75	2.30	128.75	2.98	5.3	0.45	92.20	86.80	80.00
40	2.75	4.75	53.75	2.98	5.3	0.45	86.20	90.50	78.00
41	2.75	4.75	110.00	1.08	5.3	0.45	86.30	77.30	66.70
42	2.75	4.75	110.00	2.60	1.95	0.45	85.20	96.80	82.50
43	2.75	4.75	110.00	2.60	4.75	0.30	86.30	91.00	78.50
44	2.75	4.75	110.00	2.60	4.75	0.30	86.30	91.00	78.50
45	2.75	4.75	110.00	2.60	4.75	0.30	85.20	90.90	77.50

X_1: flow-through sample volume; X_2 = Sample percolation rate; X_3 = Sample metal concentration; X_4 = Volume of HCl; X_5 = HCl flow-rate; X_6 = [HCl]; Y_1 = Al^{3+} extraction rate; Y_2 = Al^{3+} elution rate; Y_3 = Al^{3+} recovery rates.

$$-2.021X_1X_2 - 1.980X_1X_3 - 1.261X_2X_3 + 0.870X_1X_4$$
$$-0.466X_2X_4 - 0.349X_3X_4 + 0.452X_1X_5 + 0.961X_2X_5$$
$$-0.917X_3X_5 - 2.915X_4X_5 + 0.971X_1X_6 + 0.321X_2X_6$$
$$-1.203X_3X_6 + 7.0559X_4X_6 + 2.581X_5X_6 \tag{2}$$

$$Y_3 = 78.167 - 2.436X_1 - 6.545X_2 - 0.044X_3 + 4.728X_4$$
$$-10.636X_5 - 1.582X_6 + 1.533X_1^2 + 2.567X_2^2 - 0.875X_3^2$$
$$-1.572X_4^2 - 5.453X_5^2 - 0.957X_6^2 - 3.175X_1X_2$$
$$-4.634X_1X_3 - 2.039X_2X_3 + 1.344X_1X_4 - 0.119X_2X_4$$

$$-2.466X_3X_4 + 0.581X_1X_5 + 1.617X_2X_5 - 1.592X_3X_5$$
$$-2.213X_4X_5 + 2.324X_1X_6 + 0.309X_2X_6$$
$$-0.169X_3X_6 + 7.239X_4X_6 + 2.812X_5X_6 \tag{3}$$

The experimental results and the predicted values could be compared – from three last columns in Table 1 – and they match properly (S.D. = 3.454 for Y_1, 2.316 for Y_2, 2.070 for Y_3).

The statistical significance of the ratio of mean square variation due to regression and mean square residual error was tested using analysis of variance. ANOVA is a statistical technique which subdivides the total variation in a set of data into component parts associated with specific sources of variation for the

Table 2
ANOVA of the regression for aluminium recovery rates (Y_3)

Source	Sum of square	Degrees of freedom	Mean square	F-ratio	P-value (significance)
Regression	1523.87	27	56.4398	13.1700	<0.01
Residual	72.8531	17	4.28548		
Lack of fit	72.1864	15	4.81243	14.4373	6.7
Pure error	0.6666	2	0.3333		
Total	1596.73	44			

purpose of testing hypotheses on the parameters of the model. Only results obtained for aluminium recovery rates (Y_3) are presented herein for clarity of purpose. According to the ANOVA (Table 2), the regression mean squares (56.4398) and the residual mean square (4.81243) allowed the calculation of the Fisher ratios (F-value) for assessing the statistical significance. The model F-value of 56.44 implies that most of the variation in the response can be explained by the regression equation. The associated P-value is used to judge whether F-ratio is large enough to indicate statistical significance. A P-value lesser than 0.01 (i.e. $\alpha = 0.01$ or 99% confidence) indicates that the model is considered to be statistically significant. The P-value for the regression obtained ($r^2 = 0.954$) was less than 0.01 and means consequently that at least one of the term in the regression equation has a significant correlation with the response variable. The ANOVA table also shows a term for residual error, which measures the amount of variation in the response data left unexplained by the model. The form of the model chosen to explain the relationship between the factors and the response is correct.

3.3. Response surface regression analysis

After validation, these equations were used to represent the responses in the whole domain and to determine, in a first time, what step of solid-phase extraction is most influencial on aluminium recovery rates.

In Fig. 3, Y_3 has been plotted versus aluminium extraction rate Y_1 and versus aluminium elution rate Y_2. This representation allows one to see at the first glance that the elution step is preponderant upon the extraction step.

In order to determine what parameters are significant during aluminium elution step, response surfaces have been represented graphically. Aluminium recovery rates (Y_3) were plotted versus levels of X_4, X_5 and X_6 (respectively, HCl volume, elution flow-rate and HCl concentration) with the three factors linked to the

elution step fixed. Flow-through sample volume (X_1) was fixed at 2.75 ml, sample percolation rate (X_2) was fixed at 4.75 ml min^{-1} and sample metal concentration (X_3) was fixed at 110 µg l^{-1}.

In the first contour plot (Fig. 4a), we see that for a Y_3 superior to 95%, HCl volume has to be at least equal to 1.77 ml with elution flow-rate below 3.9 ml min^{-1}; the second one (Fig. 4b) confirms this 95% yield is obtained when working with elution flow-rate below 3.9 ml min^{-1} and with HCl at a concentration below 0.40 mol l^{-1}.

These primary results show a preponderant effect of elution flow-rate upon aluminium recovery rate. In order to confirm preponderance of elution step and to assess the suitability of the micro-column used for Al^{3+} extraction in the range 0–200 µg l^{-1}, supplementary contour plots have been drawn (Fig. 5).

Y_3 has been plotted versus levels of elution flow-rate (X_5) and (i) flow-through sample volume (Fig. 5a), (ii) sample percolation rate (Fig. 5b) and (iii) sample metal concentration (Fig. 5c). These contour plots confirm when working below 3.9 ml min^{-1}, a 95% aluminium recovery rate may be reached whatever sample percolation rate (X_2) – in the range 0.45–9.05 ml min^{-1} – and whatever sample metal concentration (X_3) – in the range 20–200 µg l^{-1}.

3.4. Desirability function

The maximization of each response was not obtained at the same conditions. One way to overcome this difficulty was to define an acceptable range for response Y_3. The satisfactory zone was that part of domain for which the value of the response was acceptable. To determine this acceptable zone, we use a multicriteria optimization procedure based on desirability function. This varied from 0 to 1, according to the closeness of the response to its target value. For Y_3, we have chosen to reach a target value of 95% and the desirability D at this point was equal to 1. An
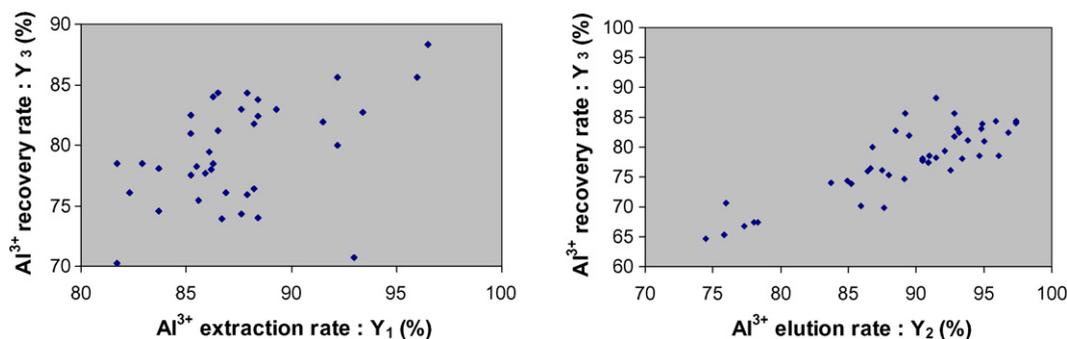
Fig. 3. Correlation between aluminium extraction rate Y_1, aluminium elution rate Y_2 and aluminium recovery rate Y_3.
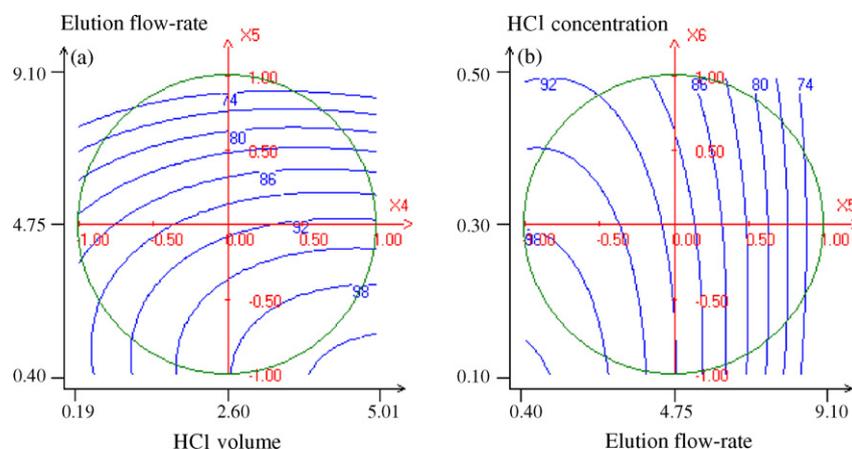
Fig. 4. Study of elution parameters (a) variation of the response-Y_3 in the plane: X_4 (HCl volume), X_5 (elution flow-rate) and fixed factors, flow-through sample volume = 2.75 ml, sample percolation rate = 4.75 ml min^{-1}, sample metal concentration = 110 μg l^{-1} and HCl concentration = 0.30 mol l^{-1}. (b) Variation of the response-Y_3 in the plane: X_5 (elution flow-rate), X_6 (HCl concentration) and fixed factors, flow-through sample volume = 2.75 ml, sample percolation rate = 4.75 ml min^{-1}, sample metal concentration = 110 μg l^{-1} and HCl volume = 2.60 ml.

aluminium recovery rate between 90 and 95% was acceptable, but the desirability was equal to 0 if Y_3 was lower than 90%. This function was physically mapped over the domain for X_1, X_2, X_3, X_4, X_5 and X_6 (Fig. 6), giving a reliable general picture of the acceptable region. From these desirability functions and by combining each response, it has been possible to establish an application domain of each factor for at least 95% aluminium recovery rate.

In order to determine analytical features and study application of the optimized extraction procedure, factors were then fixed with following values: a flow-through sample volume of 1.5 ml, a sample percolation (or extraction) flow-rate of 2 ml min^{-1}, a HCl volume of 2 ml, an elution flow-rate of 3 ml min^{-1} and a HCl concentration of 0.10 mol l^{-1}.

3.5. Analytical features

The calibration graph under the conditions previously quoted is given as $A = 3.38 \times 10^{-1} + 4.6 \times 10^{-3} C$ in the range of 2.2–200 μg l^{-1} (A is aborbance of complex, C is aluminium con-

centration in solution, μg l^{-1}). The precision of the procedure, determined as the relative standard deviation in sample solutions containing between 10 and 150 μg l^{-1} of aluminium is in the range of 9.3–2.8%, respectively, calculated by 10 measurements. The limit of detection (LOD), defined as the aluminium concentration that gives a response equivalent to three times the standard deviation (s) of the blank ($n = 11$) was found to be 1.1 μg l^{-1} in 1.5 ml of sample solution.

3.6. Effect of foreign ions

The effect of potential interfering species in the determination of 100 μg l^{-1} Al(III) was studied. Amounts of each species were considered tolerable, when the signal in the presence of the species resulted in a deviation of the absorbance less than 5%, compared with the signal for aluminium alone. Cations Fe^{3+} (3 mg l^{-1}) and Fe^{2+} (5 mg l^{-1}) are potential interfering ions, but these concentrations are not allowed in finished waters, according European legislation for waters intended for human consumption [1]. It is the same for all the other cations (Mn^{2+},
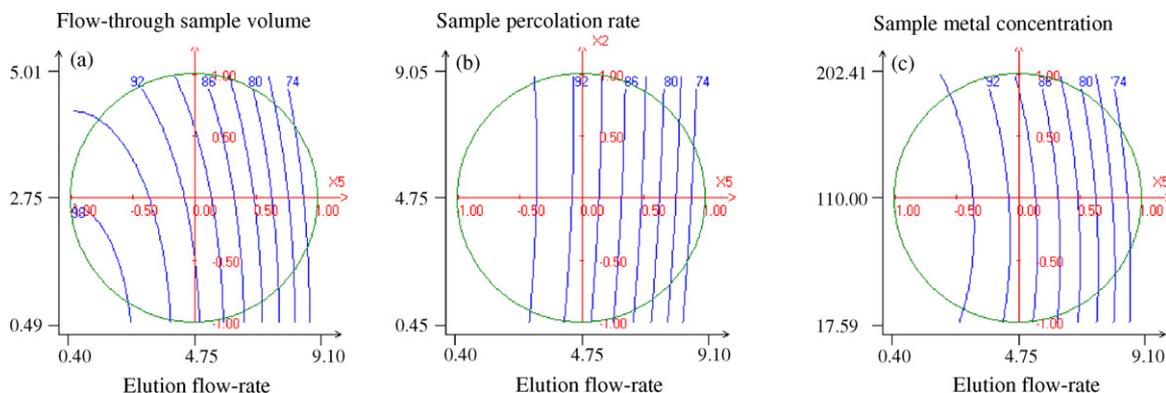
Fig. 5. Study of extraction parameters (a) variation of the response-Y_3 in the plane: X_1 (flow-through sample volume), X_5 (elution flow-rate) and fixed factors, sample percolation rate = 4.75 ml min^{-1}, sample metal concentration = 110 μg l^{-1}, HCl volume = 2.60 ml and HCl concentration = 0.30 mol l^{-1}. (b) Variation of the response-Y_3 in the plane: X_2 (sample percolation rate), X_5 (elution flow-rate) and fixed factors, flow-through sample volume = 2.75 ml, sample metal concentration = 110 μg l^{-1}, HCl volume = 2.60 ml and HCl concentration = 0.30 mol l^{-1}. (c) Variation of the response-Y_3 in the plane: X_3 (sample metal concentration), X_5 (elution flow-rate) and fixed factors, flow-through sample volume = 2.75 ml, sample percolation rate = 4.75 ml min^{-1}, HCl volume = 2.60 ml and HCl concentration = 0.30 mol l^{-1}.
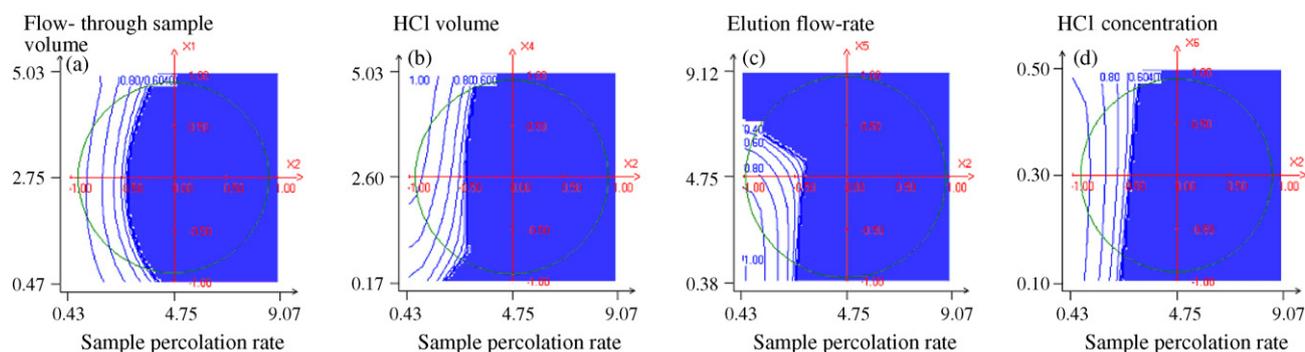
Fig. 6. Study of the desirability (a) variation of the desirability in the plane X_1, X_2 (sample volume, sample percolation rate) with fixed factors: X_3 (sample metal concentration) = 121.05 μg l^{-1}; X_4 (HCl volume) = 3.05 ml; X_5 (elution flow-rate) = 3.32 ml min^{-1}; X_6 (HCl concentration) = 0.30 mol l^{-1}. (b) Variation of the desirability in the plane X_4, X_2 (HCl volume, sample percolation rate) with fixed factors: X_1 = 2.94 ml; X_3 = 121.05 μg l^{-1}; X_5 = 3.32 ml min^{-1}; X_6 = 0.30 mol l^{-1}. (c) Variation of the desirability in the plane X_5, X_2 (elution flow-rate, sample percolation rate) with fixed factors: X_1 = 2.94 ml; X_3 = 121.05 μg l^{-1}; X_4 = 3.05 ml; X_6 = 0.30 mol l^{-1}. (d) Variation of the desirability in the plane X_6, X_2 (HCl concentration, sample percolation rate) with fixed factors: X_1 = 2.94 ml; X_3 = 121.05 μg l^{-1}; X_4 = 3.05 ml; X_5 = 3.32 ml min^{-1}.

Cu^{2+}, Ni^{2+}, Zn^{2+}, K^+, Na^+) tested during these experiments. Method is nevertheless sensitive to waters containing Mg^{2+} above 100 mg l^{-1} and Ca^{2+} above 250 mg l^{-1}. Method is not sensitive to the presence of PO_4^{3-} but presence of fluoride ions may have an impact by the formation of Al–F complexes [28]. The whole results of system selectivity are given Table 3.

3.7. Application

In order to evaluate the accuracy of the developed procedure, aluminium was determined at the outlet of a potable water treatment unit operating with aluminium polychloride as a floculating reagent (Vallon Dol Water Treatement Unit, Société des Eaux de Marseille, Marseille, France – 170 000 m^3 raw water treated each day).

During these procedures, aluminium amounts were determined successively determined by our developed procedure – flowing through microcolumn, acid desorption and spectrophotometric determination – and by GF–AAS. Aluminium amounts found by both procedures varied between 41 and 68 μg l^{-1} (Table 4).

The results from GF–AAS and the proposed method are in good agreement, and the statistical comparison applied showed no significant difference between the two methods ($r^2 = 0.9979$). These results proved that the procedure could be applied satisfactorily for aluminium determination in finished waters.

Table 3
Maximum tolerable amounts of foreign ions in on-line system using SA-XAD microcolumn (aluminium concentration = 100 μg l^{-1})

Substance	Maximum tolerable amount (mg l^{-1})
Fe^{3+}	0.5
Mn^{2+}, F^-, Fe^{2+}	1
Cu^{2+}, PO_4^{3-}	5
Ni^{2+}, Zn^{2+}	10
Mg^{2+}	100
Ca^{2+}, SO_4^{2-}, Cl^-	250
K^+, Na^+	1000

Table 4
Results obtained for aluminium determination at the outlet of a potable water treatment unit

Sample	Reference method (μg l^{-1})	Proposed method (μg l^{-1})	Recovery (%)
1	44.1 ± 0.3	44.8 ± 0.2	−1.59
2	43.3 ± 0.1	44.6 ± 0.1	−3.00
3	48.1 ± 0.2	48.7 ± 0.4	−1.25
4	41.2 ± 0.1	41.9 ± 0.3	−1.70
5	47.5 ± 0.1	48.6 ± 0.1	−2.32
6	64.6 ± 0.1	64.8 ± 0.1	−3,19
7	67.5 ± 0.2	67.7 ± 0.1	−0.31
8	65.7 ± 0.3	65.1 ± 0.2	0.91
9	68.2 ± 0.3	68.4 ± 0.3	−0.30
10	67.4 ± 0.1	67.9 ± 0.1	−0.74

Confidence interval: 95%.

4. Conclusion

The use of an experimental design to determine global optimum to retain at least 95% of initial amount of aluminium has allowed us to obtain this result in only 43 experiments, while being sure not to privilege one parameter against another one. On-site validations have allowed us to assess the relevance of factors tested during the exprimental design approach: flow-through sample volume, sample percolation rate, sample metal concentration, eluent volume, elution flow-rate and concentration of eluent. However, results obtained from this study show that the elution step is largely predominant upon the extraction step. Moreover, it has been proved that it is HCl concentration and/or HCl volume which is the most influential parameter when operating with this modified chelating resin.

The fact that extraction yield value as a function of metal amount in the range 20–200 μg l^{-1} is quasi-independent is an important result, and shows that the modified resin is well suited for the extraction of aluminium at the outlet of potable water treatment units.

This work has also demonstrated the potentialities of functionalized SA-XAD resin combined with spectrophotometry and

a flow injection system for aluminium determination in aqueous samples such as effluents from potable water treatment unit. Further experiments are needed to enlarge potentialities of such a device.

Acknowledgements

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