An experimental design to optimize the flow extraction parameters for the selective removal of Fe(III) and Al(III) in aqueous samples using salicylic acid grafted on Amberlite XAD-4 and final determination by GF-AAS

P. Vanloot [a], J.-L. Boudenne [a,*], C. Brach-Papa [b], M. Sergent [c], B. Coulomb [a]

[a] *Laboratoire de Chimie et Environnement, FRE2704, Université de Provence, CNRS, Aix-Marseille I, 3 Place Victor Hugo, Case 29, 13331 Marseille Cedex 3, France*
[b] *European Commission, Joint Research Centre, Institute for Reference Materials and Measurements Isotope Measurements Unit, Retieseweg 111, 2440 Geel, Belgium*
[c] *Laboratoire de Méthodologie de la Recherche Expérimentale, UMR 6171, Université Paul Cézanne, Avenue Escadrille Normandie Niemen, 13397 Marseille Cedex 20, France*

Abstract

In this paper, a multivariable approach has been applied for the selective removing of Fe(III) and Al(III), in the range 0–200 $\mu g\,l^{-1}$, in water samples onto a modified organic support (salicylic acid grafted on XAD-4). An empirical mathematical model was designed which establishes the relationship between the variation of the responses (extraction yields), and the variation of three factors (sample volume, sample percolation flow rate and amount of metallic ions present in the sample). To estimate the coefficients of the developed model, an uniform shell Doehlert design has been applied; these experiments consisted in GF-AAS determination of aluminium and iron amounts in eluates after percolation of samples through modified support. Results show a similar behaviour of the resin towards aluminium and iron with a preponderant effect of the percolation flow rate value; however this one is crucial for aluminium extraction and should be maintained below to 0.55 ml min^{-1} to reach a 95% Al^{3+} extraction yield (versus 2.25 ml min^{-1} for Fe^{3+}).

The optima determined by this experimental design approach have been further applied to the selective extraction of aluminium and iron from multielement synthetic samples and from real samples at the outlet of potable water treatment units.
© 2007 Elsevier B.V. All rights reserved.

Keywords: Aluminium; Chelating resin; Iron; Response surface methodology

1. Introduction

Presence of trace metals – such as aluminium and iron – in waters can originate in two main sources: an occurrence resulting from natural mineralization and activities of microorganisms, that leads to low levels in groundwaters and surface waters (below 2 mg l^{-1} for iron and below 0.1 mg l^{-1} for aluminium) [1], and an exacerbated occurrence resulting from human intervention. Increased levels in groundwater may actually result from diffuse source emissions from industry but primarily from

acid deposition caused by sulfur dioxides, nitrogen oxides, and ammonia (mobilisation of aluminium is observed if the pH gets below a value of 4.2) [2]. Recent studies in Europe [3] and Australia emphasize the recent and important disturbance and oxidation of soils with high levels of iron sulfide minerals resulting in acidification and causing the mobilization of metals into groundwater [4], with very high levels of Al (37 mg l^{-1}) and iron (1200 mg l^{-1}).

In addition to the environmental interest of removing these two metals from waters, a sanitary and statutory benefit arises when considering waters intended for human consumption: World Health Organization has fixed a sanitary security limit for iron to 2 mg l^{-1} [5] and European Legislation has established a maximum contaminant level (MCL) at 200 $\mu g\,l^{-1}$ for these two cations [6]. These values originate from aesthetic reasons for

* Corresponding author. Tel.: +33 4 91106140; fax: +33 4 91106378.
E-mail addresses: boudenne@univ-provence.fr,
boudenne@up.univ-mrs.fr (J.-L. Boudenne).

iron (coloration of water) or from safety reasons for aluminium. This last one is associated with various health problems in numerous studies, from gastrointestinal damage and phosphate deficiency to dialysis encephalopathy, renal oestrodistrophy and Alzheimer's disease [7,8], and its removing from dialysis fluids has received increasing attention in the last years. It has been established that aluminium accumulates in the tissues of some patients with chronic renal failure, and this accumulation is associated with a subsequent development of toxic phenomena [9].

Removal or recovery of iron or aluminium from wastewaters or treated waters may be reached by different processes: by sorption onto natural or modified supports [10,11], by physico-chemical and/or biological methods [12,13], by precipitation or co-precipitation [14,15], by ion exchange [16], by membrane treatment techniques [17,18] or liquid–liquid extraction [19]. All these methods rarely allow one to remove selectively these compounds. However, when considering potable, mineral or dialysis waters, it is important that aluminium and iron, when present, are removed without other metallic compounds, known as essential mineral nutrients for human body.

One way to selectively uptake metals of interest is obviously the use of chelating sorbents, and especially sorbents onto which specific ligands have been grafted or immobilized [20–23]. Using of such chelating sorbents may be interesting in analytical field too, as a separation support in solid-phase extraction (SPE) or in solid-phase microextraction (SPME). Coupling SPE or SPME technics with spectroscopic, liquid-chromatography or electrochemical methods thus permit to decrease detection limits of targeted compounds [24–27] thanks to extraction and/or preconcentration.

Whatever aim these sorbents are used, most of papers consider optimization strategies based in a single variable approach (SVA) [28–31]. This step by step approach can lead to erroneous conclusions about the importance of certain factors on the removal process, and, above all, can lead to carry out numerous experiments to find optimized extraction parameters.

Primary aims of this paper were to validate the use of a recently modified sorbent [32] for selective flowing retention of iron and aluminium present in aqueous samples in the range 20–200 μg l^{-1}, to simultaneously optimize extraction parameters of targeted analytes by reducing number of experiments needed (Green Chemistry Principles [33]), to check with synthetic and real samples during laboratory and on-site validations that no influencing parameters have been forgotten.

To reach these objectives, a multivariate approach (MVA) – that, to our knowledge, has never been applied to extraction processes – has been used to the simultaneous study of three parameters affecting targeted analytes extraction (sample volume, sample percolation flow rate and amount of metallic ions present in the sample) with an objective to reach at least a 95% extraction yield both for aluminium and iron. An empirical mathematical model was designed which establishes the relationship between the variation of the responses (extraction yields), and the variation of the factors (three parameters presented above). To estimate the coefficients of the developed model, an uniform shell Doehlert design, consisted in a set of 13 distinct experiments, has been applied; these experiments consisted in GF-AAS determination of aluminium and iron amounts in eluates after percolation of samples through modified support.

Once parameters optimized, procedure validation has been carried out in presence of interfering ions and by varying extraction temperatures: in laboratory with synthetic multielement samples, and on-site (two different potable water treatment units), during cold and warm seasons.

2. Experimental

2.1. Resin

Sorbent used in this study is a modified commercial resin (Amberlite® XAD-4) onto which we have chemically bond a chelating function (salicylic acid) [32]. Salicylic acid has often been chosen for Al(III) and Fe(III) spectrophotometric determination in water samples [34,35], its complexation constants towards these two metallic ions are very well known [36,37]. This new resin has been packaged into a methyl polymetacrylate micro-column of 6 mm inner diameter and 10 mm length, affording thus flow-through percolation of samples. Physico-chemical characteristics of the modified resin are shown in Table 1.

Resin was washed with HCl 1N and then rinsed with ultrapure water between each experiment.

2.2. Instrumentation

The manifold used for extraction of aluminium and iron is composed of two modules: an automatic burette CRISON Microbur BU1S (Crison Instruments, Alella, Spain) equipped with a 5 ml syringe (for aspiration and dispense through the column) and an eight-port selection valve CRISON 2045 (for selection between sample, eluent and water). Tubings, 0.8 mm i.d., are made of Teflon. The modules are connected to a computer via a RS-232C interface and controlled by the Autoanalysis Station 3.0 software (SCIware, Palma, Spain).

Graphite furnace-atomic absorption spectrometry (GF-AAS) was used to determine the extraction yields of sorbent towards aluminium and iron.

GF-AAS measurements were carried out on a Perkin-Elmer 1100B spectrometer equipped with an HGA700 graphite furnace. A Perkin-Elmer aluminium or iron 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.

Table 1
Physico-chemical characteristics of the modified resin [23]

Mean specific area	800 m^2 g^{-1}	BET method
Mean porous volume	0.9 ml g^{-1}	Mercury intrusion porosimetry
Mean porous diameter	4 nm	
Mean bead diameter	350 nm by sieving	
Adsorption capacity (batch method)	Al^{3+} (pH 2.5)	Fe^{3+} (pH 2.0)
	4.4 ± 0.3 mg g^{-1}	14.1 ± 0.1 mg g^{-1}

2.3. Reagents

All solutions were prepared with ultra-high quality deionised water (Millipore, resistivity > 18 MΩ cm). All chemicals used in this work were of analytical grade. Suprapur acids were used throughout the work. Fe^{3+} stock solution was prepared by dissolution of ferric chloride salt and a commercial stock solution of $1\,g\,l^{-1}$ 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) is constituted of 17 elements (As, Be, Ca, Cd, Co, Cr, Cu, Mg, Mo, Ni, Pb, Sb, Se, Ti, Tl, V, Zn) at $10\,mg\,l^{-1}$ ($\pm 0.08\,mg\,l^{-1}$).

2.4. Experimental design

2.4.1. Experimental factors

Preliminary studies have shown that three parameters could be considered as influential on the extraction yield: the sample volume, the percolation flow rate and the trace metal amount.

The domain of variation for each factor was determined based on knowledge of the system acquired from initial experimental trials and is described as follows:

- X_1: sample volume: 0.5–5 ml;
- X_2: percolation flow rate: 0.5–$9\,ml\,min^{-1}$;
- X_3: sample metal amount: 20–$200\,\mu g\,l^{-1}$;

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

2.4.2. Experimental design methodology

The aim of this study was to determine the best conditions of extraction, 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:

$$\eta = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2$$
$$+ \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3$$

where β_i, β_{ii} and β_{ij} are coefficients of the linear, quadratic and cross-product terms, respectively and $N = i$, $j = 3$ is the number of factors.

To estimate the coefficients of this model, we need a set of experiments well spread in the domain, that is a design of experiments 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 [38]. This design consists of a set of 13

distinct experiments and has different interesting properties, that make them particularly suitable for solving certain problems. For instance, it includes the possibility of adding additional factors without any adverse effects on the quality of the design. The central point of the experimental domain was repeated nine times to evaluate the repeatability of the measurements. For each studied response (Y), the estimates (β_i, β_{ii}, β_{ij}) were calculated using a multilinear regression. The calculations have been performed with the Nemrod-W software (LPRAI, Marseille, France), which was developed for building and processing designs of experiments [39].

3. Results and discussion

3.1. Fixed parameters

3.1.1. Mass of sorbent

Extraction columns have been conditioned with 40 mg of functionalized resin. This amount has been fixed according to the future applications of these columns: they are aimed to be used for the detection of aluminium and iron – used as floculating agents – at the outlet of potable water treatment units, and be interfaced with a SIA (sequential injection analysis) system. Sample volumes that will be used in this kind of system will not exceed 5 ml and tolerable amount of aluminium and iron authorized by European Legislation intended for human consumption is $200\,\mu g\,l^{-1}$ [6]. From data extracted from Table 1, it can be concluded that the resin packed is able to retain up to $560\,\mu g$ Fe and up to $180\,\mu g$ Al. Considering volumes traditionaly used in SIA system, concentrations up to $112\,mg\,l^{-1}$ Fe or up to $36\,mg\,l^{-1}$ Al can be retained by this resin. Forty milligrams of resin is thus supposed to be sufficient to retain these two metals and the potential interfering ions present in aqueous samples.

3.1.2. Influence of pH

When operating with a chelating resin, the main phenomenon of retention of metallic ions is directly linked to their complexation constants versus pH. This pH value should then be chosen as a function of the formation constants of the metals with the investigated chelating agent and can be chosen to prevent interfering ion complexation [40] and was thus considered as a parameter not to be included in the experimental design, and was fixed to 2.5 for aluminium retention and to 2.0 for iron for further experiments.

3.2. Experimental design

3.2.1. Experimental results

The experimental conditions and the experimental results are regrouped in Table 2. From these results, coefficients estimation were calculated, for the two extraction yields:

$$Y_1(\text{Fe extraction}) = 90.96 + 0.66 X_1 - 5.00 X_2 + 0.98 X_3$$
$$- 0.16 X_1^2 + 2.24 X_2^2 + 0.89 X_3^2$$
$$- 0.58 X_1 X_2 + 3.08 X_1 X_3 - 4.56 X_2 X_3$$

Table 2
Doehlert design and experimental results

Exp. no.	Sample volume (ml)	Percolation flow rate (ml min^{-1})	Sample metal amount (μg l^{-1})	Fe extraction (%)	Al extraction (%)
1	5.00	4.75	110.0	92.8	88.2
2	0.50	4.75	110.0	88.8	89.3
3	3.88	8.45	110.0	88.4	79.8
4	1.63	1.05	110.0	96.3	96.5
5	3.88	1.05	110.0	97.9	96.0
6	1.63	8.45	110.0	87.8	83.7
7	3.88	6.00	185.0	90.1	83.7
8	1.63	3.50	35.0	93.5	86.9
9	3.88	3.50	35.0	88.7	91.5
10	2.75	7.20	35.0	91.1	82.3
11	1.63	6.00	185.0	90.2	85.5
12	2.75	2.30	185.0	97.8	93.4
13	2.75	4.75	110.0	91.2	86.3
14	2.75	4.75	110.0	92.3	86.3
15	2.75	4.75	110.0	90.1	85.2
16	2.75	4.75	110.0	91.2	86.3
17	2.75	4.75	110.0	91.2	86.3
18	2.75	4.75	110.0	90.1	85.2
19	2.75	4.75	110.0	90.1	86.3
20	2.75	4.75	110.0	92.3	86.3
21	2.75	4.75	110.0	90.1	85.2

$$Y_2(\text{Al extraction}) = 85.93 - 0.48X_1 - 8.55X_2 + 0.39X_3$$
$$+ 2.82X_1^2 + 3.15X_2^2 + 0.43X_3^2$$
$$- 1.96X_1X_2 - 3.23X_1X_3 - 1.23X_2X_3$$

The experimental results and the predicted values could be compared – from two last columns in Table 2 – and they match properly (S.D. = 1.281 for Y_1, 1.194 for Y_2).

These models have also been validated using analysis of variance (ANOVA). In these ANOVA tests, the regression mean squares (227.5391 for iron and 478.0070 for aluminium) and the residual mean square (1.6404 for iron and 1.4251 for aluminium) allowed the calculation of the Fisher ratios for assessing the sta-

tistical significance. The regression was good: 99.3% for iron extraction rates and 98.6% for aluminium extraction rates. That means that the variation of the response was due to the variation of the parameters and not only due to the experimental error.

3.2.2. Response surface regression analysis

From these models, contour plots (2D) and response surface plots (3D) have been drawn.

3.2.2.1. Factors influencing iron extraction yield.

Fig. 1 shows the variation of the Y_1 response as a function of sample volume (X_1) and percolation flow rate (X_2), while the sample iron amount is fixed at 110 μg l^{-1}. Percolation flow rate appears to be a critical parameter, as small increases in the flow rate result in a
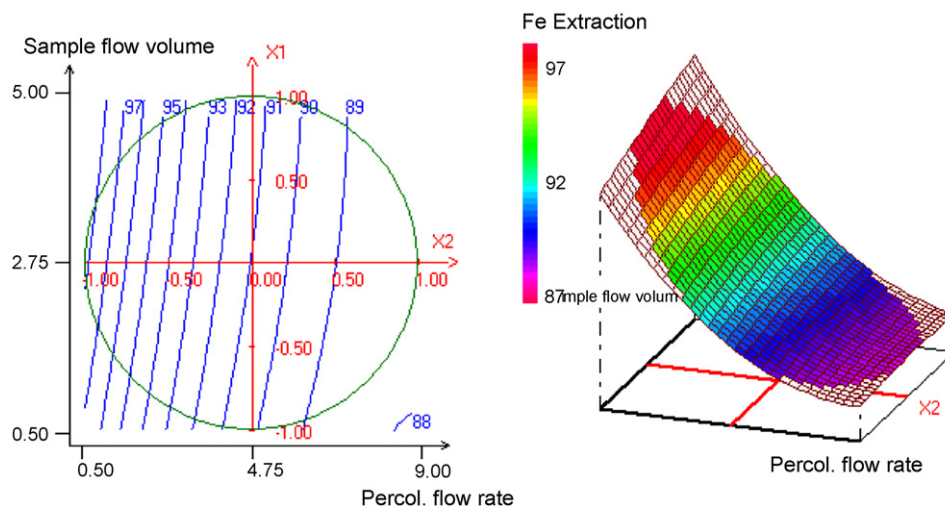

Fig. 1. Contour plot (left) and response surface plot (right) showing the variation of response Y_1 (Fe extraction) as a function of sample volume (X_1) and percolation flow rate (X_2). The sample metal amount is fixed at 110 μg l^{-1}.
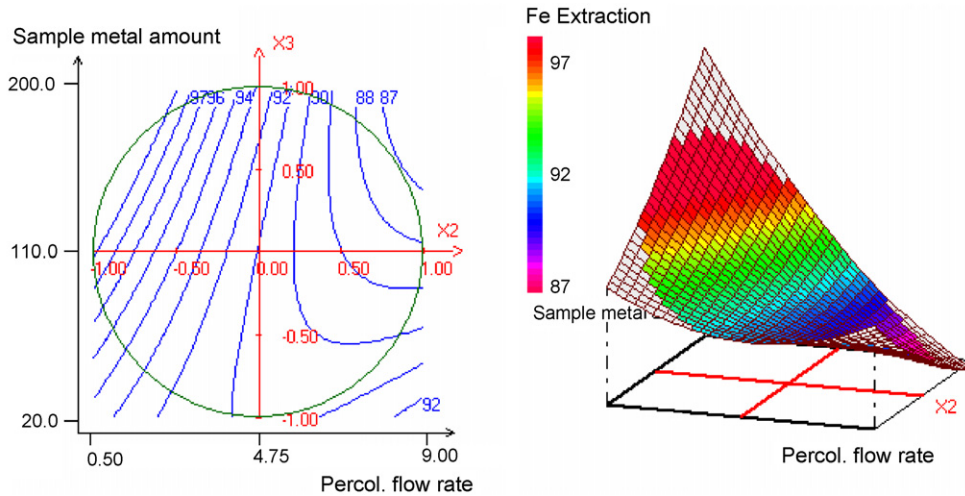
Fig. 2. Contour plot (left) and response surface plot (right) showing the variation of response Y_1 (Fe extraction) as a function of percolation flow rate (X_2) and sample metal amount (X_3). The sample volume (X_1) is fixed at 2.75 ml.

rapid decrease in the Fe extraction, as illustrated by *iso*-response curves nearly perpendicular to the X_2 axis in the contour plot. The influence of the sample volume, in this variation domain, seems to be negligible on the Fe extraction yield.

Fig. 2 shows the variation of the Y_1 response as a function of percolation flow rate (X_2) and sample metal amount (X_3), while the sample flow volume is fixed at 2.75 ml. It indicates that percolation flow rate remains the limiting factor: an increase of iron concentration from 20 to 200 $\mu g\, l^{-1}$ leads to a slight increase in extraction yield of 3%, whereas an increase of percolation rate from 0.5 to 9 ml min^{-1} leads to a 10% extraction yield decrease.

To conclude upon influences of the two recessive factors, Fig. 3 presents the variation of the Y_1 response as a function of sample volume (X_1) and sample metal amount (X_3), while the percolation flow rate is fixed at 4.75 ml min^{-1}. These ones have a slight and similar effect: an increase of one of them in the domain previously defined leads to a small extraction yield increase of about 3%, and when increased together, to a small extraction yield increase of 5%.

From this study it can be concluded that it is the iron mole number present in the sample which directly influences extraction yield and not the iron concentration or sample volume.

To reach the desired Fe extraction, i.e. an extraction at least equal to 95%, the percolation flow rate should be maintained smaller than 2.25 ml min^{-1}, whatever the values of the two others factors.

3.2.2.2. Factors influencing aluminium extraction yield. Figs. 4 and 5 show the variation of the Y_2 response as a function of sample volume (X_1) and percolation flow rate (X_2) or sample aluminium amount (X_3). These response surface show the preponderant factor influencing aluminium extraction yield is the percolation flow rate. An increase of aluminium amount from 20 to 200 $\mu g\, l^{-1}$ leads to a slight increase in extraction yield of 2%, whereas an increase of percolation rate from 0.5 to 9 ml min^{-1} leads to a 16% extraction yield decrease.

Study of variation of the Y_1 response as a function of sample volume (X_1) and sample metal concentration (X_3) leads to the
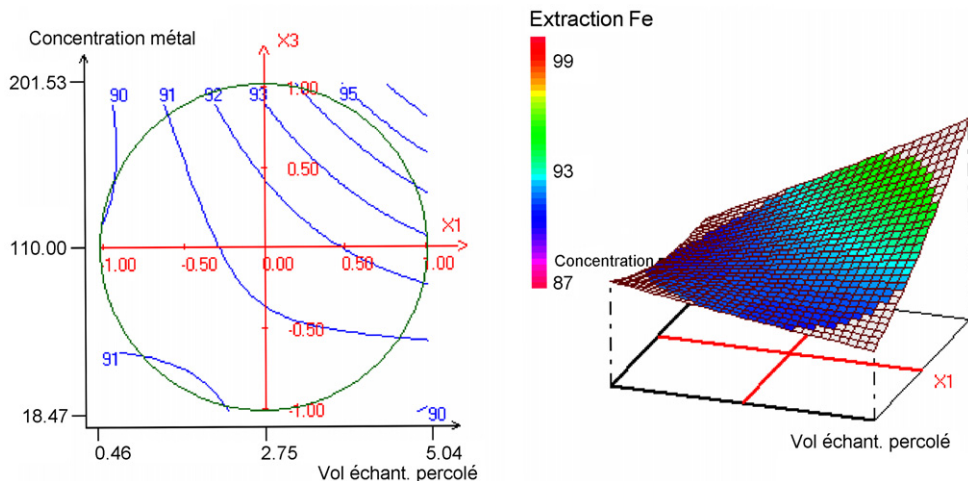

Fig. 3. Contour plot (left) and response surface plot (right) showing the variation of response Y_1 (Fe extraction) as a function of sample volume (X_1) and sample metal amount (X_3). The percolation flow rate (X_2) is fixed at 4.75 ml min^{-1}.
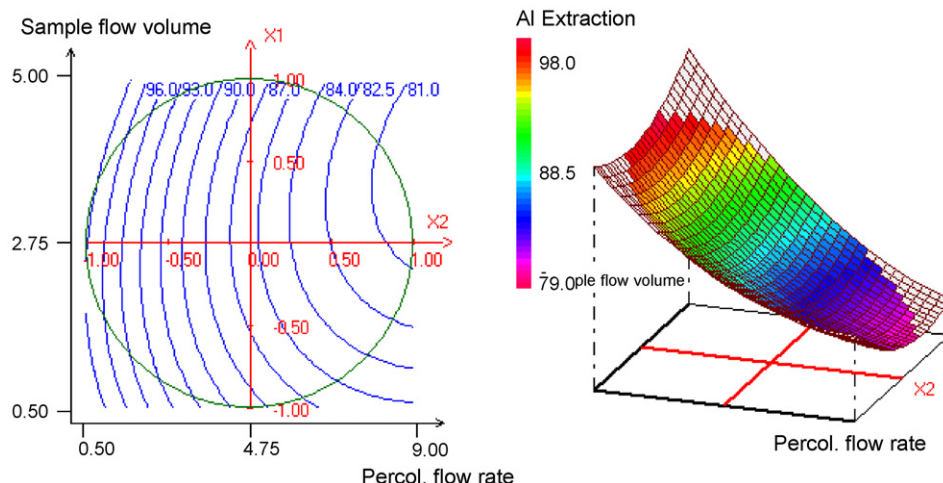
Fig. 4. Contour plot (left) and response surface plot (right) showing the variation of response Y_2 (Al extraction) as a function of sample volume (X_1) and percolation flow rate (X_2). The sample metal amount is fixed at $110 \, \mu g \, l^{-1}$.

same conclusion as for iron: an increase of aluminium extraction yield of about 4%, when these parameters are simultaneously increased.

To obtain an extraction yield at least equal to 95%, a percolation flow rate smaller than $0.55 \, ml \, min^{-1}$ should be maintained.

The preponderance of the percolation flow rate is more pronounced in case of aluminium ($0.55 \, ml \, min^{-1}$ for Al^{3+} versus $2.25 \, ml \, min^{-1}$ for Fe^{3+}) and is certainly linked to the difference of complexation constant values between salicylic acid and aluminium or iron. Complexation kinetics of salicylic acid with iron seems to be faster and could explain the differences observed between the two cations. This influence of percolation flow rate could efficiently used to favour selectivity of this resin, either towards aluminium or towards iron.

The optimized factors – determined thanks to this experimental design – have been applied during lab and on-site experiments.

3.3. Application

3.3.1. Laboratory application

These experiments have been carried out with samples constituted of Al^{3+} and Fe^{3+} at four different concentrations (50, 100, 200 and $300 \, \mu g \, l^{-1}$). Samples were acidified at pH 2.5 during aluminium recovery tests and at pH 2.0 during iron ones, before being flowed through functionalized resin with five replicates. During these experiments, sample volumes were fixed at 5 ml.

Extraction yields of aluminium and iron – determined by GF-AAS – are presented (Table 3). Results obtained were consistent with those estimated thanks to the experimental design, with extraction yields between 96.05% and 97.85%, whatever initial metal concentration.

A second set of experiments were conducted to study influences of potential interfering ions and of temperature on the extraction yields of Al^{3+} and Fe^{3+}. Multielement synthetic
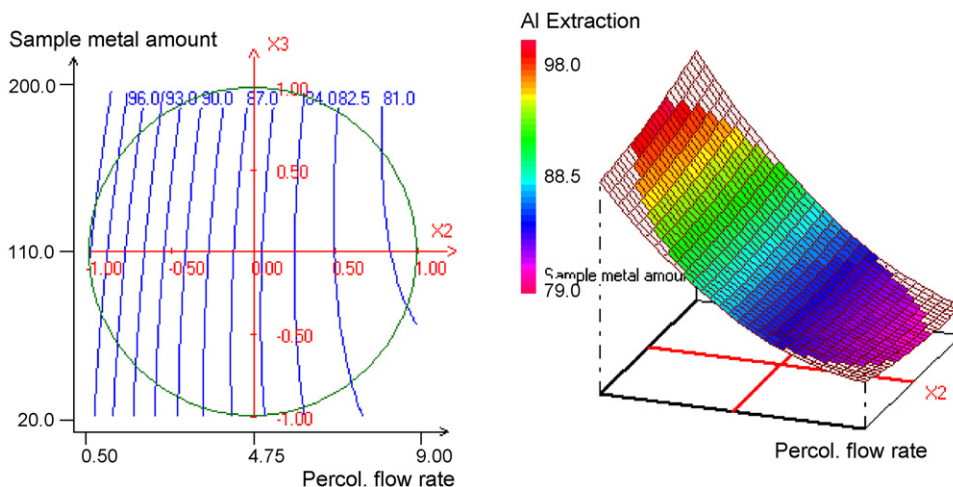

Fig. 5. Contour plot (left) and response surface plot (right) showing the variation of response Y_2 (Al extraction) as a function of percolation flow rate (X_2) and sample metal amount (X_3). The sample volume (X_1) is fixed at 2.75 ml.

Table 3
Influence of initial concentration of metal on the extraction yield (laboratory validation)

	Average extraction yield (%)
$[Fe^{3+}]_0$ ($\mu g\, l^{-1}$)	
50	97.50
100	97.85
200	96.53
300	97.50
$[Al^{3+}]_0$ ($\mu g\, l^{-1}$)	
50	96.05
100	96.70
200	96.40
300	97.85

solutions at a $100\,\mu g\, l^{-1}$ concentration were flowed through modified resin, in presence of $100\,\mu g\, l^{-1}$ Al^{3+} or Fe^{3+} and adjusted to pH 2.0 (when used with Fe^{3+}) and to pH 2.5 (when used with Al^{3+}). Two solution temperatures have been tested (7 and 25 °C) and were chosen to mimic temperatures of raw waters coming into drinking water treatment units, observed during winter and summer seasons (in Marseille, France).

Results (Table 4) agreed with those obtained from the experimental design, with an average extraction yield of Fe^{3+} between 96.68 and 96.78%, and between 95.94 and 96.60% for Al^{3+}. The residual standard deviation obtained when working at the two different temperatures lead us to conclude that the extraction process is not influenced by temperature (in the range 7–25 °C).

3.3.2. On-site application

On-site applications have been carried out at the outlet of two potable water treatment units: one operating with ferric chloride as a floculating reagent (Sainte-Marthe Water Treatement Unit, Société des Eaux de Marseille, Marseille, France—420 000 m^3 raw water treated each day); the other one operating with aluminium polychloride (Vallon Dol Water Treatment Unit, Société des Eaux de Marseille, Marseille, France—170 000 m^3 raw water treated each day).

During these procedures, aluminium and iron amounts were determined at the outlet of the units by GF-AAS, before and after flowing through column. The amounts varied from 22 to 39 $\mu g\, l^{-1}$ for iron, and from 41 to 68 $\mu g\, l^{-1}$ for aluminium. These tests were carried in winter and in summer. Extraction yields—presented Table 5 reached between 95.78 and 96.80%, whatever water temperature.

Table 4
Influences of temperature and of potential interfering ions (multielement synthetic solution) on Al^{3+} and Fe^{3+} extraction yield (laboratory validation)

	$[Fe^{3+}]_0$ ($100\,\mu g\, l^{-1}$)		$[Al^{3+}]_0$ ($100\,\mu g\, l^{-1}$)	
	$T = 7\,°C$	$T = 25\,°C$	$T = 7\,°C$	$T = 25\,°C$
Average extraction yield (%)	96.68	96.78	95.94	96.60
Residual standard deviation (%)	0.99	0.79	0.83	0.78

Table 5
On-site validation: influence of temperature on Al^{3+} and Fe^{3+} extraction yields

	$[Fe^{3+}]_0$ (22–$39\,\mu g\, l^{-1}$)		$[Al^{3+}]_0$ (41–$68\,\mu g\, l^{-1}$)	
	$T = 7\,°C$	$T = 25\,°C$	$T = 7\,°C$	$T = 25\,°C$
Average extraction yield (%)	95.78	96.80	95.88	96.56
Residual standard deviation (%)	1.19	0.98	1.16	1.58

4. Conclusion

The use of an experimental design to determine global optimum to retain at least 95% of initial amount of aluminium or iron has allowed us to obtain this result in only 21 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 experimental design approach: percolation flow rate, sample volume and amount of metallic ions. However, results obtained from this study show that only two parameters have to be studied when operating with a chelating resin: percolation flow rate and sample volume.

The fact that extraction yield value as a function of metal amount in the range 20–200 $\mu g\, l^{-1}$ is quasi-independent is an important result, and shows that the modified resin is well suited for the extraction of these metals at the outlet of potable water treatment units. Application of this resin to treatment of dialysis fluids can although be envisaged: the experimental design has proven that extraction yields do not depend on the initial amount of metal present in solution but only on the percolation flow rate. The Maximum Tolerable Amount of aluminium authorized in dialysis fluids ($30\,\mu g\, l^{-1}$) should be attained with this modified resin.

About potential analytical applications, it seems that this resin can be efficiently used as a sample pre-treatment column, allowing removal or preconcentration of aluminium and iron from samples. Indeed, the experimental design has although proven that the sample volume is not a preponderant factor in the range 0.5–5 ml facing extraction yields. That certainly means a high preconcentration factor can be reached, if this sorbent is coupled with aluminium and iron detection methods.

References

[1] A. Misund, B. Frengstad, U. Siewers, C. Reimann, Variation of 66 elements in European bottled mineral waters, Sci. Tot. Environ. 243 (1999) 21–41.
[2] W.L. Lindsay, Chemical Equilibria in Soils, Wiley, New York, 1979.
[3] L. Rosen, D. Wladis, D. Ramaekers, Risk decision analysis of groundwater protection alternatives on the European scale with emphasis on nitrate and aluminium contamination from diffuse sources, J. Hazard. Mater. 61 (1998) 329–336.

[4] A.L. Hinwood, P. Horwitz, S. Appleyard, C. Barton, M. Wajrak, Acid sulphate soil disturbance and metals in groundwater: implications for human exposure through home grown produce, Environ. Pollut. 143 (2006) 100–105.

[5] Rolling revision of the WHO guidelines for drinking water quality, Nutrient minerals in drinking-water and the potential health consequences of long-term consumption of demineralized and remineralized and altered mineral content drinking-waters, 2003.

[6] Directive 98/83/EC on the quality of water intended for human consumption.

[7] K. Berend, G. Van der Voet, W.H. Boer, Acute aluminium encephalopathy in a dialysis center caused by a cement mortar water distribution pipe, Kidney Int. 59 (2001) 746–751.

[8] T.P. Flaten, Aluminium as a risk factor in Alzheimer's disease, with emphasis on drinking waters, Brain Res. Bull. 55 (2001) 187–196.

[9] D. Bohrer, A. Giods, R. Binotto, P.C. Do Nasciemento, On-line separation and spectrophotometric determination of low levels of aluminum in high-salt content samples: application to analysis of hemodialysis fluids, Anal. Chim. Acta 362 (1998) 163–169.

[10] B. Das, P. Hazarika, G. Saikia, H. Kalita, D.C. Goswami, H.B. Das, S.N. Dube, R.K. Dutta, Removal of iron from groundwater by ash: a systematic study of a traditional method, J. Hazard. Mater. 141 (2007) 834–841.

[11] M. Loan, O.M.G. Newman, R.M.G. Cooper, J.W. Farrow, G.M. Parkinson, Defining the paragoethite process for iron removal in zinc hydrometallurgy, Hydrometallurgy 81 (2006) 104–129.

[12] A.H. Abdul, M.S. Yusoff, M.N. Adlan, N.H. Adnan, S. Alias, Physico-chemical removal of iron from semi-aerobic landfill leachate by limestone filter, Waste Manage. 24 (2004) 353–358.

[13] A.G. Tekerlekopoulou, I.A. Vasiliadou, D.V. Vayenas, Physico-chemical and biological iron removal from potable water, Biochem. Eng. J. 31 (2006) 74–83.

[14] S. Santos, R. Machado, M. Joana Neiva Correia, J.R. Carvalho, Treatment of acid mining waters, Miner. Eng. 17 (2004) 225–232.

[15] J.O. Claassen, E.H.O. Meyer, J. Rennie, R.F. Sandenbergh, Iron precipitation from zinc-rich solutions: defining the Zincor process, Hydrometallurgy 67 (2002) 87–108.

[16] J.S. Kim, M.A. Keane, Ion exchange of divalent cobalt and iron with NA-Y zeolite: binary and ternary exchange equilibria, J. Colloid Interf. Sci. 232 (2000) 126–132.

[17] K.H. Choo, H. Lee, S.J. Choi, Iron and manganese removal and membrane fouling during UF in conjunction with prechlorination for drinking water treatment, J. Membr. Sci. 267 (2005) 18–26.

[18] A.G. Pervov, E.V. Dudkin, O.A. Sidorenko, V.V. Antipov, S.A. Khakhanov, R.I. Makarov, RO and NF membrane systems for drinking water production and their maintenance techniques, Desalination 132 (2000) 315–321.

[19] E. Rodil, R. Dumortier, J.H. Vera, Removal of aluminium from aqueous solutions using sodium di-(*n*-octyl) phosphinate, Chem. Eng. J. 97 (2004) 225–232.

[20] B. Saad, C.C. Chong, A.S.M. Ali, Md.F. Bari, I. Ab Rahman, N. Mohamad, M.I. Saleh, Selective removal of heavy metal ions using sol–gel immobilized and SPE-coated thiacrown ethers, Anal. Chim. Acta 555 (2006) 146–156.

[21] S. Sengupta, A.K. Sengupta, Chelating ion-exchangers embedded in PTFE for decontamination of heavy-metal-laden sludges and soils, Colloid Surf. A 191 (2001) 79–95.

[22] H.A. Abd El-Rehim, E.A. Hegazy, A. El-Hag Ali, Selective removal of some heavy metal ions from aqueous solution using treated polyethylene-g-styrene/maleic anhydride membranes, React. Funct. Polym. 43 (2000) 105–116.

[23] S. Boussetta, C. Branger, A. Margaillan, J.L. Boudenne, B. Coulomb, Comparative study on metal extraction properties of Emporte SDB-XXC and Amberlite XAD-4 grafted by salicylic acid and its derivatives via different bridges, Sep. Sci. Technol. 41 (2006) 1619–1633.

[24] N.C. Dias, M.D. Porter, J.S. Fritz, Principles and applications of colorimetric solid-phase extraction with negligible depletion, Anal. Chim. Acta 558 (2006) 230–236.

[25] Z. Legnerova, D. Satinsky, P. Solich, Using on-line solid phase extraction for simultaneous determination of ascorbic acid and rutin trihydrate by sequential injection analysis, Anal. Chim. Acta 497 (2003) 165–174.

[26] M. Luo, S. Bi, Solid phase extraction–spectrophotometric determination of dissolved aluminum in soil extracts and ground waters, J. Inorg. Biochem. 97 (2003) 173–178.

[27] G. Yang, Z. Huang, Q. Hu, J. Yin, Study on the solid phase extraction of Co(II)-QADEAB chelate with C_{18} disk and its application to the determination of trace cobalt, Talanta 58 (2002) 511–515.

[28] A. Economou, Sequential-injection analysis (SIA): a useful tool for on-line sample-handling and pre-treatment, Trend Anal. Chem. 24 (2005) 416–425.

[29] C. Brach-Papa, B. Coulomb, C. Branger, A. Margaillan, F. Théraulaz, P. Vanloot, J.-L. Boudenne, Fluorimetric determination of aluminium in water by sequential injection through column extraction, Anal. Bioanal. Chem. 378 (2004) 1652–1658.

[30] C. Barzen, A. Brecht, G. Gauglitz, Optical multiple-analyte immunosensor for water pollution control, Biosens. Bioelectron. 17 (2002) 289–295.

[31] D.T. Rossi, N. Zhang, Automating solid-phase extraction: current aspects and future prospects, J. Chromatogr. A 885 (2000) 97–113.

[32] J.-L. Boudenne, S. Boussetta, C. Brach-Papa, C. Branger, A. Margaillan, F. Théraulaz, Modification of a poly(styrene-co-divinylbenzene) resin by grafting of an aluminium selective ligand, Polym. Int. 51 (2002) 1050–1057.

[33] N.D. Anastas, J.C. Warner, The incorporation of hazard reduction as a chemical design criterion in green chemistry, Chem. Health Saf. 12 (2005) 9–13.

[34] G. Cathalifaud, J. Ayele, M. Mazet, Etude de la complexation des ions aluminium par des molécules organiques: Constantes et stoechiométrie des complexes. Application au traitement de potabilisation des eaux (Aluminium ions/organic molecules complexation: formation constants and stoichiometry Application to drinking water production), Water Res. 31 (1997) 689–698.

[35] K.-W. Cha, K.-W. Park, Determination of iron(III) with salicylic acid by the fluorescence quenching method, Talanta 46 (1998) 1567–1571.

[36] R. Belcher, H. Friser, Metallochromic Indicators, Pergamon Press, 1972, pp. 209–435.

[37] S. Giroux, S. Aury, P. Rubini, S. Parant, J.-R. Desmurs, M. Dury, A spectroscopic investigation of the complexing ability of catecholate or salicylate derivatives towards aluminium(III), Polyhedron 23 (2004) 2393–2404.

[38] D.H. Doehlert, Uniform shell designs, Appl. Stat. 19 (1970) 231–245.

[39] G.A. Lewis, D. Mathieu, R. Phan-Tan-Luu, Pharmaceutical Experimental Design, Drugs and the Pharmaceutical Sciences, Marcel Dekker Inc., New York, 1999.

[40] V. Camel, Solid-phase extraction of trace elements, Spectrochim. Acta B 58 (2003) 1177–1223.