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Simultaneous determination of six inorganic anions in drinking water by non-suppressed ion chromatography[☆]

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Abstract

A non-suppressed ion chromatographic method with conductometric detection is described for the simultaneous determination of six inorganic anions: fluoride, chloride, nitrite, bromide, nitrate and sulphate. The separation was achieved on a low-capacity anion-exchange column Metrohm IC Anion Column Super Sep, with a mobile phase consisting of phthalic acid dissolved in high-purity water, 2-amino-2-hydroxymethyl-1,3-propanediol and acetonitrile. In this work computer optimization procedures, using computer programs to select chromatographic conditions have been used, leading to the achievement of a desired separation. By using the different optimization methods in an integrated manner it is, however, possible to both speed method development, by reducing unnecessary experimentation, and to overcome the many shortcomings of each method, because of the different approaches. The purpose of this work is to improve and characterise the method for simultaneous determination of six inorganic anions in drinking water by non-suppressed ion chromatography, using optimization procedures, in order to be applied to the routine analysis. The proposed method has numerous advantages over the other widely used non-suppressed ion chromatography methods: higher selectivity, shorter analysis time, lower quantitation and detection limits. The performance characteristics of the method were established by determining the following validation parameters: precision and accuracy, linearity, detection limits and quantitation limits. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Small et al. [1] reported the first method for separation and quantitative determination of inor-

ganic ions by high-performance liquid chromatography. This technique, called ion chromatography (IC), used a combination of analytical column and suppressor column to decrease the conductivity of the mobile phase for conductometric detection. Since then significant drawbacks from the chromatographic point of view have been reported regarding this approach, most arising from the suppressor itself. Butytenhuys [2] reported that the number of injections is restricted by the capacity of the suppressor column (if it is used); the suppressor introduces extra band broadening, which results in lower resolution;

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special equipment is needed for ion chromatography; only those buffers can be applied which, after passage through a suppressor, result in low electrical background conductivity. These deficiencies have provided an impetus for the development of chromatographic methods that do not require use of a suppressor column.

Some investigations have been undertaken in an attempt to overcome these disadvantages of suppressed ion chromatography. In particular Gjerde and co-workers [3,4] demonstrated that the suppressor column is not absolutely necessary for high-performance ion chromatography with electric conductivity detection. They used an ion-exchanger having a low exchange capacity and eluent having a very low conductivity. In this way the background conductivity is sufficiently low to allow the separated anions to be detected with a simple conductance detector.

A number of alternative methods have been reported in the literature, all of which use an analytical separator column without suppressor. These methods differ from each other chiefly in the mode of detection employed. Inorganic anions may be separated on a reversed-phase system either by prior formation of organic derivatives or by using ion-pair formation with subsequent direct detection of UV-absorbing ions at low UV wavelengths (210–220 nm). Cortes and Stevens [5] applied this same approach to an amino column, however these methods are not widely applicable since only limited number of inorganic ions show UV absorbance. Papp and Fehervary [6] and Chauret and Hubert [7] proposed the more general methods using reversed-phase ion-pair high-performance ion chromatography with UV-absorbing pairing ions, where samples gave positive or negative peaks, depending on their charge and retention relative to a UV-absorbing pairing ion. Frenzel et al. [8] and Reidmann and Glatz [9] reported that among these techniques, conductometric detection remains the mainstay of high-performance ion chromatography.

Compared to non-chromatography techniques, ion chromatography methodology has the advantages of separation before detection, increased sensitivity, simple sample preparation and faster analysis time [10,11]. It finds general application in power plants, semiconductors, detergents, medicine, food, agricul-

tural, and more importantly in the environmental fields [12–15]. Thus, it has been certified and adopted by the American Society for Testing and Materials (ASTM) and the US Environmental Protection Agency (EPA) [16] in the USA, and Croatian standards HRN EN ISO 10304-3 [17] and HRN EN ISO 1030-4 [18].

In the present paper a non-suppressed chromatographic method with conductometric detection is described for the simultaneous determination of fluoride, chloride, nitrite, bromide, nitrate and sulphate. The purpose of this work is to improve performance characteristic of the method by using optimization of chromatographic parameters (eluent flow-rate, mobile phase) in order to be applied to the routine analysis of drinking water.

The validity of the method was established by determining the following validation parameters: precision and accuracy, linearity, detection limits and quantitation limits.

2. Experimental

2.1. Instrumentation

Samples were analysed using a Metrohm (Herisau, Switzerland) 690 ion chromatograph with conductivity detector, and 100 μ l injection loop, with Metrohm (Herisau, Switzerland) 687 IC pump. The separation column was a Metrohm IC Anion Column Super Sep, 100 \times 4.6 mm, packed with polymethacrylate with quaternary ammonium groups, and was used with a Metrohm IC precolumn cartridge PRP-1. The eluent flow-rate was 1.0–2.0 ml/min. Data acquisition was performed using a Shimadzu (Kyoto, Japan) integrator model C-R5A Chromatopac. The optimization, and mathematical evaluation of experimental data was achieved by an IBM-compatible personal computer using MathCad Professional 7.0 (MathSoft, USA) and Mathematica 3.0 (Wolfram Research, USA) software.

2.2. Reagents

Stock solution of fluoride, chloride, nitrite, bromide, nitrate and sulphate were prepared by dissolving appropriate amounts of analytical reagent grade

sodium or potassium salts in high-purity water. These solutions were diluted to give the multi-anion solutions required (ISO 10304-1, 1992).

The mobile phase was phthalic acid dissolved in high-purity water (1.5–3.5 mmol/l), followed by pH adjustments with 2-amino-2-hydroxymethyl-1,3-propanediol (4.2–4.5), and mixed with acetonitrile (2.5–10%).

Analytical reagent-grade compounds provided by Fluka (Buchs, Switzerland) were used to prepare the eluent system examined in the present study.

3. Results and discussion

3.1. Optimization of the chromatographic system

The chromatographic system for the separation of the six inorganic anions was chosen in order to result in optimum separation regarding the selectivity and detection conditions. The computer assisted double criteria optimization was used for the optimization of chromatographic parameters: eluent flow-rate, pH of eluent, concentration of phthalic acid in eluent and concentration of acetonitrile in eluent.

The mathematical form of the response functions, f , relating the observed response, y (the retention time), to the chromatographic parameters x_n , is unknown:

$$y = f(x_n)$$

In order to describe the response surface in the region where the optimum is to be found by means of a graphic plotting method, the response function was approximated by a generalised polynomial equation of the second order. When the responses are expressed as a function of independent variable, the polynomial equations can be described by a quadratic equation [19]:

$$y = a_0 + a_1x + a_2x^2$$

where x represents a chromatographic parameter (eluent flow-rate, pH of eluent, concentration of phthalic acid in eluent, concentration of acetonitrile in eluent), and y the observed response (retention time). The coefficients a_0 , a_1 , a_2 are constants and they are characteristic of each investigated parameter. The

fitting was performed in six experimental points. Fig. 1 presents experimental data for optimisation of ion chromatographic parameters.

The optimisation procedure deals with the estimation of the coefficients in the polynomial equation in order to describe as well as possible the responses of chromatographic experiments. By using the information contained in the optimized equation an analyst can alter the dependent variables in the desired fashion and calculate wherever one wants, respecting the boundaries of response value.

The coefficients of the polynomial equations must be estimated using statistical methods before the optimal conditions can be calculated in the global optimization process. Since the accuracy of chromatographic response prediction using this model is highly dependent on quality of the estimation of the coefficient, it is thus highly dependent on the algorithms and computing program chosen. The coefficients have been estimated employing the polynomial regression model, using MathCad Professional 7.0 and Mathematica 3.0 software (Table 1).

Two criteria for comparing and evaluating of a chromatograph have been used for double criteria computer-assisted optimization and these are summarised below [19–21].

Minimum t_R difference, expressed as:

$$\Delta t_{R(\min)} = |t_{RFi} - t_{RFj}|$$

where t_R values predicted for chromatographic parameters are used to calculate the values of Δt_R for adjacent pairs of chromatographic peaks. If n is the number of peaks, $(n - 1)$ calculations are performed for each set of chromatographic conditions. The conditions which give maximum value of $\Delta t_{R(\min)}$ present the best separation conditions. If there is more than one maximum, $\Delta t_{R(\min)}$ which has the smallest value has to be selected. The disadvantage of this method is that it considers only the least well separated pair of peaks.

A multipeak separation response (MRF) function is given by the expression:

$$MRF = \frac{[(ht_{RF_{\max}} - ht_{RF_n})(ht_{RF_1} - ht_{RF_{\min}})]}{[(ht_{RF_{\max}} - ht_{RF_{\min}})/(n + 1)]^{n+1}} \times \prod_{i=1}^{n-1} (ht_{RF_{(i+1)}} - ht_{RF_i}) \cdot 100$$

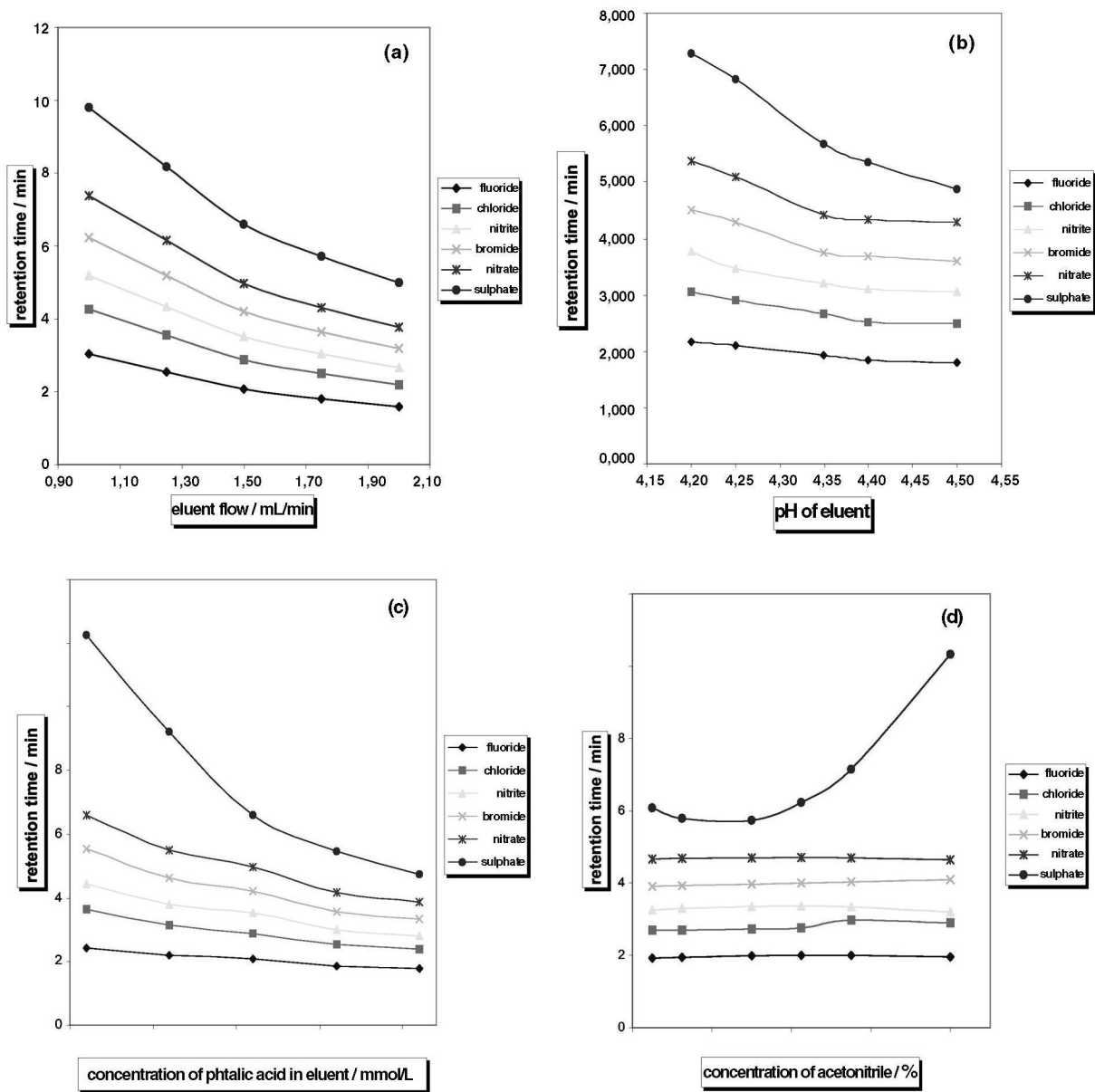


Fig. 1. Experimental data of ion chromatographic parameters. (a) Plot of retention time t_R against eluent flow-rate; (b) plot of retention time t_R against pH of eluent; (c) plot of retention time t_R against concentration of phthalic acid in eluent; (d) plot of retention time t_R against concentration of acetonitrile in eluent.

where ht_R is defined as $100 \times t_R$. Index 1 corresponds to the component of lowest t_R and index n to that of highest t_R . The boundaries of extreme values within which all the other components must lie ($t_{R_{\min}}$ and $t_{R_{\max}}$) can be selected to eliminate the regions near

the origin and the solvent peak, which are subject to greater qualitative and quantitative uncertainty. The criterion is expressed as a percentage. If a peak does not occur within the present interval then the criterion is automatically set to zero. When all components

Table 1

Predicted function with estimated coefficients and correlation factors for correlation between ion-chromatographic parameters and retention times: (A) retention time t_R against eluent flow-rate; (B) retention time t_R against pH of eluent; (C) retention time t_R against concentration of phthalic acid in eluent (D) retention time t_R against concentration of acetonitrile in eluent

Anion	Predicted function	Correlation factors
(A)		
Fluoride	$f(x) = 0.857x^2 - 4.031x + 6.223$	0.999
Chloride	$f(x) = 1.249x^2 - 5.825x + 8.852$	0.999
Nitrite	$f(x) = 1.511x^2 - 7.067x + 10.763$	0.999
Bromide	$f(x) = 1.819x^2 - 8.505x + 12.928$	0.999
Nitrate	$f(x) = 2.167x^2 - 10.123x + 15.357$	0.999
Sulphate	$f(x) = 2.581x^2 - 13.383x + 20.359$	0.999
(B)		
Fluoride	$f(x) = 3.4736x^2 - 31.51x + 73.256$	0.994
Chloride	$f(x) = 6.5333x^2 - 58.793x + 134.76$	0.989
Nitrite	$f(x) = 9.3766x^2 - 83.847x + 190.5$	0.989
Bromide	$f(x) = 11.575x^2 - 103.87x + 236.6$	0.989
Nitrate	$f(x) = 16.375x^2 - 146.27x + 330.89$	0.988
Sulphate	$f(x) = 16.415x^2 - 151.04x + 352.14$	0.995
(C)		
Fluoride	$f(x) = 0.048x^2 - 5.74x + 3.184$	0.991
Chloride	$f(x) = 0.168x^2 - 1.47x + 5.457$	0.995
Nitrite	$f(x) = 0.196x^2 - 1.795x + 6.679$	0.989
Bromide	$f(x) = 0.304x^2 - 2.61x + 8.729$	0.994
Nitrate	$f(x) = 0.378x^2 - 3.254 + 10.615$	0.993
Sulphate	$f(x) = 1.748x^2 - 12.51x + 27.136$	0.998
(D)		
Fluoride	$f(x) = -0.0044x^2 + 0.0595x + 1.8012$	0.989
Chloride	$f(x) = 0.003x^2 - 0.0094x + 2.6993$	0.991
Nitrite	$f(x) = -0.0095x^2 + 0.1108x + 3.0382$	0.995
Bromide	$f(x) = 0.0003x^2 + 0.0219x + 3.8503$	0.994
Nitrate	$f(x) = -0.0032x^2 + 0.037x + 4.5989$	0.985
Sulphate	$f(x) = 0.1406x^2 - 1.1905x + 8.1724$	0.989

are equally spaced from each other and form the chosen boundaries the function has its maximum value of 100%.

The criteria were used for optimization, and behaviour of the two criteria were demonstrated for a separation problem. The response surfaces of criteria is shown in Figs. 2 and 3, and the optimal conditions for ion chromatographic analysis of the fluoride, chloride, nitrite, nitrate, bromide and sulphate are shown in Table 2. The actual chromatogram presenting ion chromatographic analysis of six inorganic

anion under the optimized conditions is shown in Fig. 4.

3.2. Performance characteristics of the proposed method

The system described here was used for the simultaneous determination of fluoride, chloride, nitrite, bromide, nitrate and sulphate. Optimised chromatographic conditions were set and the following characteristics were evaluated: precision and accuracy, linearity, detection and quantification limits.

3.2.1. Precision and accuracy

In order to verify precision and accuracy, four samples with a known concentration of each assayed anion (fluoride, chloride, nitrite, bromide, nitrate and sulphate) were injected into the eluent stream. Statistical evaluation related standard deviation, relative standard deviation, and recovery factor for nine injections of each sample were performed (Tables 3 and 4. Repeatability of the proposed method, in other words precision under the same operating conditions over a short interval of time (one day), is shown in Table 3. Table 4 presents the reproducibility of the proposed method, respectively long term stability of the method over five consecutive days.

3.2.2. Calibration curves

Calibration curves covering the concentration ranges from 0.5 to 50 ppm of each assayed anion were obtained, and the linear relationship between peak area and concentration were experimentally verified. The results of the statistical treatment of calibration data are summarised in Table 5 and shows high values of correlation coefficient for all assayed curves.

3.2.3. Detection and quantitation limit

Several approaches for determining the detection and quantitation limit are possible, depending on whether the procedure is non-instrumental or instrumental. An approach based on standard deviation of response and slope was applied in this study. Detection limit (*DL*) and quantitation limit (*QL*) can be expressed as:

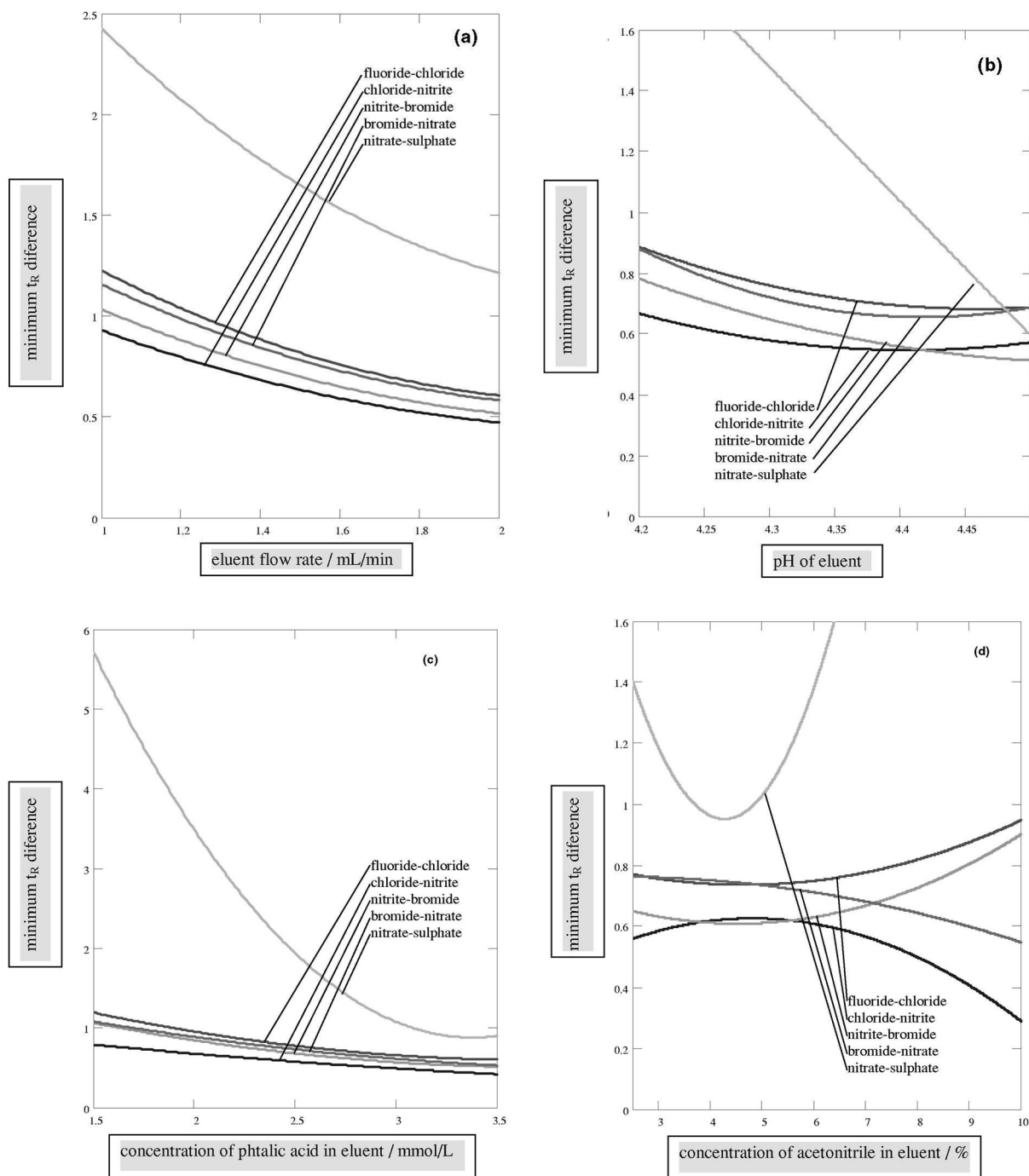


Fig. 2. Ion chromatography response surface as a function of (a) eluent flow-rate; (b) pH of eluent; (c) concentration of phthalic acid in eluent; (d) concentration of acetonitrile in eluent, using minimum t_R difference criteria.

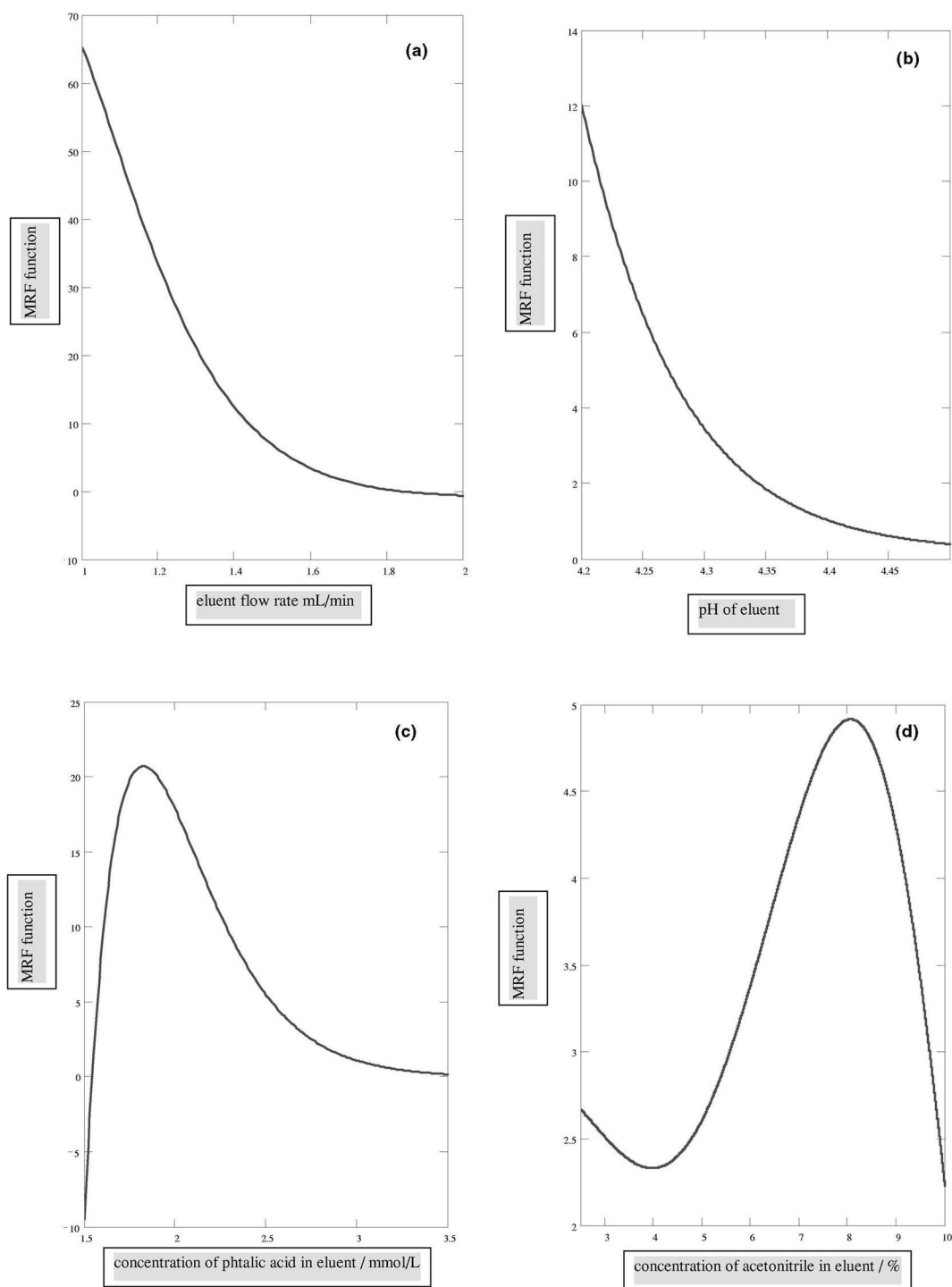


Fig. 3. Ion chromatography response surface as a function of (a) eluent flow-rate; (b) pH of eluent; (c) concentration of phtalic acid in eluent; (d) concentration of acetonitrile in eluent, using MRF criteria.

Table 2

Optimal conditions for ion chromatographic analysis of the fluoride, chloride, nitrite, nitrate and sulphate

Chromatographic parameter	Optimal value
Eluent flow-rate	1.5 ml/min
pH of eluent	4.2
Concentration of phthalic acid in eluent	1.8 mmol/l
Concentration of acetonitrile in eluent	8.1%

$$DL = 3.3 \sigma/S$$

$$QL = 10 \sigma/S$$

where σ presents residual standard deviation of the response, and S present the slope of the calibration curve. The results are shown in Table 6.

4. Conclusions

Six inorganic anions: fluoride, chloride, nitrite, bromide, nitrate and sulphate were separated and analysed by means of non-suppressed single column ion chromatography, with conductometric detection. Four ion chromatographic parameters were opti-

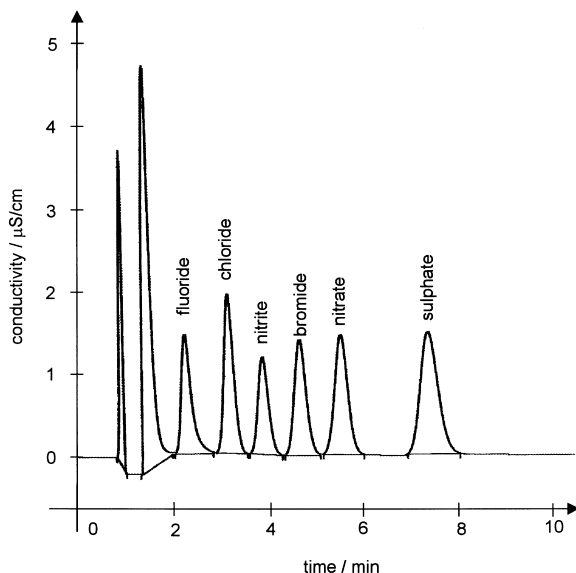


Fig. 4. Ion chromatographic analysis of fluoride (2.50 mg/l), and bromide, nitrate, sulphate (5.00 mg/l), under the optimized conditions: (eluent flow-rate, 1.5 ml/min; pH of eluent, 4.2; concentration of phthalic acid in eluent, 1.8 mmol/l; concentration of acetonitrile in eluent, 8.1%).

Table 3

Repeatability of ion chromatographic determination of fluoride, chloride, nitrite, bromide, nitrate and sulphate

		Concentration of anion (mg/l)			
		1.00	5.00	10.00	50.00
Fluoride	SD	0.05	0.22	0.21	0.63
	RSD (%)	0.05	0.04	0.02	0.01
	Recovery (%)	103	101	102	100
Chloride	SD	0.02	0.15	0.20	0.84
	RSD	0.02	0.03	0.02	0.02
	Recovery (%)	101	101	102	101
Nitrite	SD	0.03	0.14	0.18	0.57
	RSD	0.03	0.03	0.02	0.01
	Recovery (%)	103	101	100	100
Bromide	SD	0.03	0.13	0.21	0.46
	RSD	0.03	0.03	0.02	0.01
	Recovery (%)	101	99	98	99
Nitrate	SD	0.02	0.07	0.12	0.44
	RSD	0.02	0.01	0.01	0.01
	Recovery (%)	100	102	99	100
Sulphate	SD	0.01	0.03	0.11	0.55
	RSD	0.01	0.01	0.01	0.01
	Recovery	101	101	98	100

mised: eluent flow-rate, pH of eluent, concentration of phthalic acid in eluent and concentration of acetonitrile in eluent. Two criteria were used for optimization leading to more accurate estimation of optimal conditions for separation. The criteria minimum, t_R , difference provided information about a peak and its neighbor, so a direct influence can be seen of the particular chromatographic parameter on the separation of two neighboring peaks. This information is very useful for the analysis of samples, with great differences in concentrations of components. On the other hand, the multiplex separation response function has the advantage of taking all the peaks into account at the same time, so it can provide information about the whole analytical system.

The optimization procedure was applied in order to increase the separation, reduce the analysis time, and to decrease the quantitation and detection limits. The optimization procedure allows manipulating with the appearance of the particular peak on the chromatogram. The sulphate peak which elutes last was very distanced from all other peaks (i.e., has a

Table 4
Reproducibility of ion chromatographic determination of fluoride, chloride nitrite, bromide, nitrate and sulphate

		Concentration of anion (mg/l)			
		1.00	5.00	10.00	50.00
Fluoride	SD	1.01	0.24	0.22	0.18
	RSD	0.04	0.05	0.02	0.02
	Recovery (%)	101	101	101	100
Chloride	SD	1.01	0.16	0.19	0.70
	RSD	0.02	0.03	0.02	0.01
	Recovery (%)	101	103	100	101
Nitrite	SD	1.01	0.14	0.19	0.68
	RSD	0.02	0.03	0.02	0.01
	Recovery (%)	101	99	103	101
Bromide	SD	1.01	0.12	0.18	0.56
	RSD	0.02	0.02	0.02	0.01
	Recovery (%)	100	103	102	99
Nitrate	SD	1.00	0.10	0.17	0.48
	RSD	0.02	0.02	0.02	0.01
	Recovery (%)	101	102	100	100
Sulphate	SD	1.01	0.07	0.10	0.49
	RSD	0.02	0.02	0.01	0.01
	Recovery (%)	100	101	99	101

very large retention time), while at the same time all other peaks (fluoride, chloride, nitrite, bromide, nitrate) were poorly separated. The optimization method allows moving the sulphate peak towards the nitrate peak, and at the same time to distribute all other peaks (fluoride, chloride, nitrite, bromide, nitrate) more evenly between the eluent peak and sulphate peak. This results in increasing selectivity of the method, and in a shorter analysis time. Moreover, all peaks have changed elution profiles (increased peak height and decreased peak width), which results in decreasing detection and quantitation limits because the signal/noise ratios increase.

Table 5
Calibration data for ion chromatographic determination of fluoride, chloride, nitrite, bromide, nitrate and sulphate

Parameter	Fluoride	Chloride	Nitrite	Bromide	Nitrate	Sulphate
Concentration range (mg/l)	0.5–50	0.5–50	0.5–50	0.5–50	0.5–50	0.5–50
Slope (1/mg)	5415.9	6477.8	4721.5	3166.5	3696.8	4994.8
Intercept	6236.6	4214.4	1078.4	1169.9	1264.9	4284.8
Correlation coefficient	0.9998	0.9998	0.9999	0.9999	0.9999	0.9998

Table 6
Detection limits and quantitation limits for ion chromatographic determination of fluoride, chloride, nitrite, bromide, nitrate and sulphate

Anion	Detection limit (mg/l)	Quantitation limit (mg/l)
Fluoride	0.004	0.01
Chloride	0.003	0.01
Nitrite	0.003	0.01
Bromide	0.003	0.01
Nitrate	0.003	0.01
Sulphate	0.004	0.01

The appearance of the actual chromatogram under the optimized conditions is shown in Fig. 4.

The developed method has numerous advantages over the other widely used non-suppressed ion chromatography methods: higher selectivity, shorter analysis time, lower quantitation and detection limits. It is characterised by high accuracy, precision and linearity. It is important to emphasize the low cost of operating the proposed method, providing the multi-anion analysis within 8 min. Moreover, no regeneration step has to be included and no special equipment is needed. The separation can be achieved on any liquid chromatograph equipped with a conductometric detector.

5. Nomenclature

- x chromatographic parameters (eluent flow-rate, pH of eluent, concentration of phthalic acid in eluent, concentration of acetonitrile in eluent)
- y response function, relating observed response (retention time) to the chromatographic parameters
- a_0, a_1, a_2 constants, characteristic of each investigated parameter

$\Delta t_{r(\min)}$	minimum t_R difference
t_R	retention time
t_{RFi}	response function of the i^{th} peak
t_{RFj}	response function of j^{th} peak
MRF	multipeak separation response function
h_{tRF1}	response function of first eluting peak $\times 100$
h_{tRFn}	response function of last eluting peak $\times 100$
$h_{tRF_{\min}}$	minimum value of retention time $\times 100$ within which other components must lie
$h_{tRF_{\max}}$	maximum value retention time $\times 100$ within which other components must lie
SD	standard deviation of the method
RSD	relative standard deviation of the method
DL	detection limit
QL	quantitation limit
σ	residual standard deviation of response of the calibration curve
S	slope of the calibration curve

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