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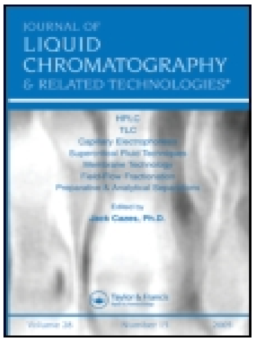

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Development of an Ion Chromatographic Method for Monitoring Fertilizer Industry Wastewater Quality

**Tomislav Bolanča,[1],* Štefica Cerjan-Stefanović,[1]
Goran Srečnik,[2] Željko Debeljak,[3] and Milko Novič[4]**

[1]Laboratory of Analytical Chemistry, Faculty of Chemical Engineering
and Technology, University of Zagreb, Zagreb, Croatia
[2]PLIVA, Pharmaceutical Industry, Zagreb, Croatia
[3]Department of Medicinal Biochemistry, Clinical Hospital Osijek,
Osijek, Croatia
[4]National Institute of Chemistry, Ljubljana, Slovenia

ABSTRACT

The aim of this work is to develop an ion chromatographic method for monitoring of fluoride, chloride, nitrite, sulfate, nitrate, and phosphate in fertilizer industry wastewater. A developed method was optimized and better separation within a reasonable analysis time was obtained. Optimization was performed by using retention models obtained with artificial neural networks in combination with several criteria functions

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*Correspondence: Tomislav Bolanča, Laboratory of Analytical Chemistry, Faculty of Chemical Engineering and Technology, University of Zagreb, Marulićev Trg 20, 10000 Zagreb, Croatia; E-mail: tbolanca@fkit.hr.

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for evaluation of separation, resulting with a fast and accurate optimization procedure. By performing a validation procedure and number of statistical tests, it is shown that the developed ion chromatographic method has superior performance characteristics: linearity $R^2 \geq 0.998$, recovery $= 99.49-100.12\%$, repeatability RSD $\leq 1.14\%$. This result proves that the proposed method can be used for monitoring of fertilizer industry wastewater.

Key Words: Ion chromatography; Fertilizer; Wastewater; Quality.

INTRODUCTION

Fluoride, chloride, nitrite, sulfate, nitrate, and phosphate are commonly monitored for environmental protection purposes in wastewater. Nitrite, nitrate, and phosphate, owing to their high solubility and mobility within the soil, are gradually increasing eutrophication of natural waters.[1–3] A contentious health concern related to these agents is the possible formation of cancerogenic nitroamines as a result of the reaction of nitrite with secondary or tertiary amines present in the human body.[4,5] The presence of nitrate in foods is mainly due to plants taking nitrogen from the soil in this ionic form. The use of nitrogen containing fertilizers increases the nitrate concentration in the soil and, therefore, the nitrate content in plants grown therein is above the normal level. For this reason, it is essential to develop analytical methods that allow the simultaneous determination of these compounds in fertilizer industry wastewater. The content of fertilizer industry wastewater is highly dependent on the selection of raw material for fertilizer production and on fertilizer production process control.

Several methods have been proposed for simultaneous determination of phosphate, nitrite, nitrate, sulfate, chloride, and fluoride, based on flow-injection analysis[6–8] and ion chromatography.[9,10] Representative surveys of the scientific literature covering the detection of these important analytes have been compiled over recent years.[11–13] Performance characteristics of ion chromatographic methods used for analysis of anions in wastewater are dependent on ion chromatographic set ups used for the analysis. Reported performance characteristics of such methods are in the range of: linearity $R^2 \geq 0.0967$ to $R^2 \geq 0.9982$; recovery $= 88-105\%$ to $93-119\%$.[14]

Despite the methodology used for determination of anions in fertilizer wastewater, it is essential to optimize the method. By using the computer optimization procedures, it is possible both to speed up method development, by reducing unnecessary experimentation, and to improve performance characteristics of ion chromatographic determination (better separation within shorter analysis time). Most computer assisted optimization procedures are based on retention modeling.[15–18] The retention model that describes the relationship between retention time (t_R or capacity) and investigated parameter allows retention times to be predicted for any set of parameters in a search area.[19–22] The readability of these predicted retention times is dependent on the suitability of the retention model used.[17,19,22]

The aim of this work is development of an ion chromatographic method for monitoring of fluoride, chloride, nitrite, sulfate, nitrate, and phosphate in fertilizer industry wastewater. The developed method was optimized by using an artificial neural network in combination with different chromatographic separation criteria functions, enabling fast and accurate optimization of separation and analysis time. The performance characteristic of the optimized ion chromatographic method was determined by performing a complete validation procedure. The following validation parameters were determined: selectivity, linearity, accuracy, and precision.

EXPERIMENTAL

Instrumentation

The Dionex DX500 chromatography system (Sunnyvale, CA) equipped with quartenary gradient pump (GP50), eluent generator module (EG40), chromatography module (LC25), and detector module (ED40) was used in all experiments. Separation and suppressor columns used were Dionex IonPac AG15 ($4 \times 50\,\text{mm}^2$) guard column, IonPac AS15 ($4 \times 250\,\text{mm}^2$) separation column, and ASRS-ULTRA-4mm suppressor column, working in recycle mode, were used, respectively. The sample-loop volume was 50 μL. The eluent flow rate was 1.00–1.95 mL/min and concentration of KOH (OH^-) in eluent was 25.00–60.00 mmol/L. The whole system was computer controlled through PeakNet 5.1 software.

The data for further evaluation were obtained by exporting the appropriate chromatograms into ASCII files. ASCII data files were further evaluated using a Microcal Origin (Microcal Software, USA) software package. The program for neural network retention model and optimization procedure was made by the authors in MATLAB environment (MATLAB 6.0, MathWorks, Sherborn, MA). The calculations were performed on the IBM compatible personal computer equipped with 800 MHz Pentium III processor, and 512 MB RAM.

Reagents and Solutions

Stock solutions of fluoride (1.0000 g/L), chloride (1.0000 g/L), nitrite (1.0000 g/L), sulfate (1.0000 g/L), nitrate (1.0000 g/L), and phosphate (1.0000 g/L) were prepared from the air-dried (at 105°C) salts of individual anions of p.a. grade (Merck, Darmstadt, Germany). Appropriate amounts of individual salts was weighed into a volumetric flask (100 mL) and dissolved with Milli-Q water. Working eluent solutions were prepared on-line by appropriate dilution of KOH with Milli-Q water. An 18 MΩ cm water (Millipore, Bedford, MA) was used for dilution in all cases.

Real samples were fertilizer industry wastewater TMG 1 and TMG 2 from Petrokemija d.d., Croatia, fertilizer factory:

TMG 1: fertilizer industry wastewater from following processes: production of NPK fertilizer 1, KAN fertilizer 1, nitric acid 1, and process water preparation 1.

TMG 2: fertilizer industry wastewater from following processes: production of NPK fertilizer 2, KAN fertilizer 2, nitric acid 2, sulfuric acid, phosphoric acid, ammonia, urea, and process water preparation 2.

The real samples of fertilizer industry wastewater were diluted with Milli-Q water prior to injection (TMG 1, 30 : 100; TGM 2, 25 : 100).

RESULTS AND DISCUSSION

Optimization of Separation and Selectivity

Optimal conditions for ion chromatographic determination of fluoride, chloride, nitrite, sulfate, nitrate, and phosphate (eluent flow rate 1.0 mL/min, concentration of KOH in eluent 39.52 mmol/L) were determined by using a retention model obtained with artificial neural networks in combination with different criteria functions.[21,22]

Parallel prediction of retention times of fluoride, chloride, nitrite, sulfate, nitrate, and phosphate by using one artificial neural network was applied. MATLAB Neural Networks ToolBox was not adequate for application for retention modeling in this particular case. Therefore, the authors adopted it for retention modeling by programming in MATLAB metalanguage. The following routines were written; the division of experimental data set on training and test set; selection of data for training and test set; Dixon's outlyer test; retraining procedure routine; calculations of relative error. Three layers feed forward neural networks trained with a Levenberg–Marquardt batch error back propagation algorithm has been used to model ion chromatographic retention mechanisms. The advantage of applied batch training methodology is the significant increase in speed of calculation algorithm in comparison with delta rule training methodology. The technique of experimental data selection for a training set was used, allowing improvement of artificial neural network prediction power. Experimental design space was divided into 8–32 subspaces, depending on number of experimental data points used for training set. The number of hidden layer nodes, the number of iteration steps, and the number of experimental data points used for training sets were optimized. Optimized artificial neural networks present the very fast (300 iteration steps) and very accurate (relative error of 0.88% tested with 116 experimental data points in external validation set) retention models, obtained by using small amounts of experimental data (16 experimental data points in training set).

Seven criteria separation functions were used as a basic tool for calculation under optimal conditions: different retention time criteria, sum of retention time differences, product of retention time differences criteria, adjoining distance criteria, chromatography response function criteria, separation factor criteria, and chromatography exponential function criteria. Computer algorithm, developed by the authors, enables external control of analysis time, regardless of criteria function used for optimization. That feature is included into the algorithm to enable optimization of different types of samples without the need for development of new retention models. In other words, it is possible to select short analysis time, in the case of analyzing samples without matrix and with more or less the same concentration of present components, and longer analysis time for complex samples. Fertilizer industry wastewater samples have high ionic strength and significant difference in concentrations of analyzed components. In order to avoid overloading of column capacity and peak overlapping, 25 min was chosen as optimal value for analysis time.

Figures 1 and 2 presents the chromatograms of real samples of fertilizer industry wastewater by using optimal ion chromatographic parameters. It is shown that calculated optimal ion chromatographic parameters enable very good separation within reasonable analysis time (25 min). All components of interest are detected and baseline separated. The significant improvement has been made by spacing the peaks more evenly on the chromatogram (Figs. 1 and 2), enabling good separation of all components. The selectivity of the proposed method is satisfactory and further evaluation of performance characteristic can proceed.

Linearity

Tables 1 and 2 present the linearity test for ion chromatographic determination of fluoride, chloride, nitrite, sulfate, and nitrate in fertilizer industry

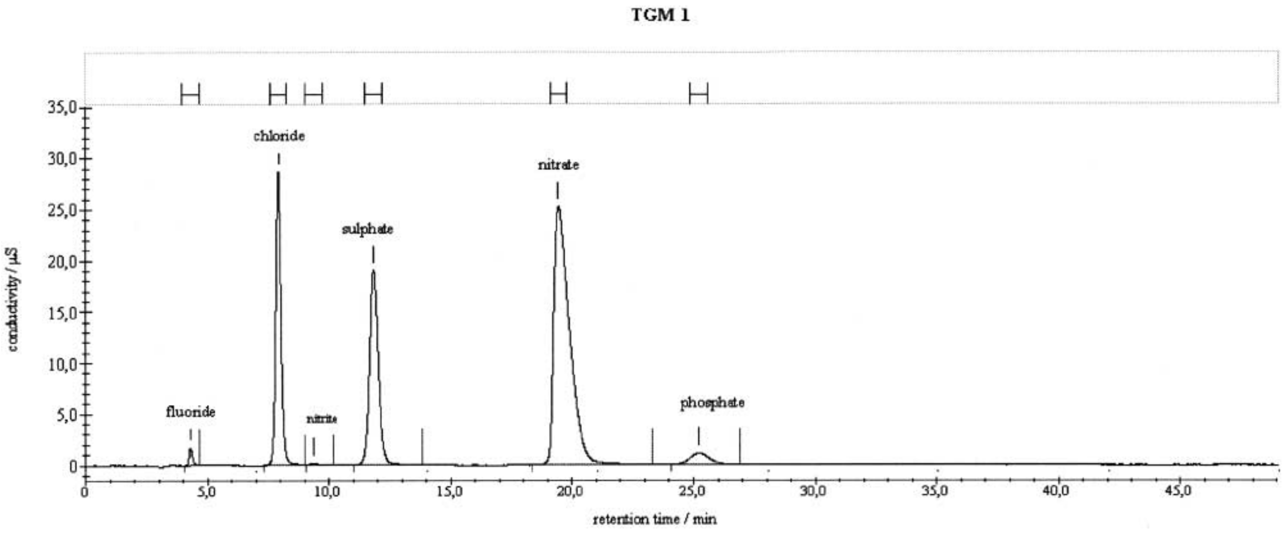

Figure 1. Ion chromatographic determination of fluoride, chloride, nitrite, sulfate, and nitrate in fertilizer industry wastewater TGM 1 obtained by using optimal conditions.

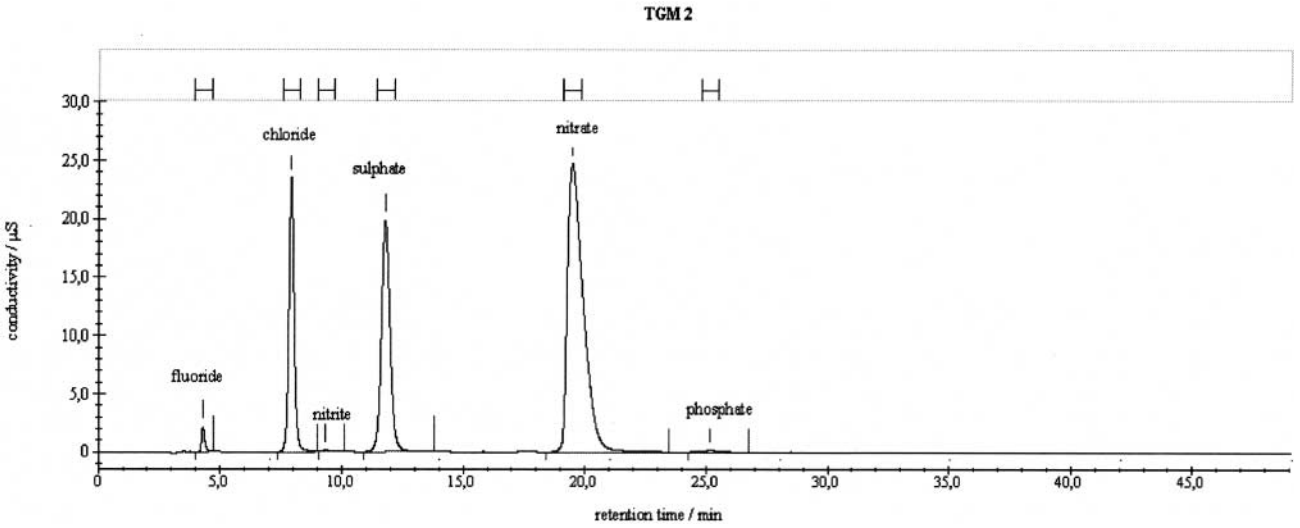

Figure 2. Ion chromatographic determination of fluoride, chloride, nitrite, sulfate, and nitrate in fertilizer industry wastewater TGM 2 obtained by using optimal conditions.

Table 1. Linearity related calculations for ion chromatographic determination of fluoride, chloride, nitrite, sulfate, nitrate, and phosphate in fertilizer industry wastewater TGM 1 under the optimal conditions.

Anion	Fluoride	Chloride	Nitrite	Sulfate	Nitrate	Phosphate
Range (mg/L)	0.11–0.32	5.48–16.43	0.35–1.04	9.51–28.53	12.6–37.80	0.52–1.55
R^2	0.9999	0.9993	0.9991	0.9983	0.9986	0.9997
Slope (μS/mg/min/L)						
Value	538,131	483,721	120,720	236,010	183,624	81,780.9
Lower 95%	536,561	480,007	404.1	3,871.4	181,551.1	81,208.7
Upper 95%	539,700	487,436	1,144.9	54,781.6	185,697.0	82,353.1
Intercept (μS/min)						
Value	234.3	32,035.7	370.4	−4,544.9	589.6	75.63
Lower 95%	−121.6	−11,116.0	−11,776.8	−2,330,695	−54,818.5	−552.59
Upper 95%	590.2	75,187.5	121,776	238,950	55,997.6	703.86
Lack of fit test						
MS_{PE}	147,753	2.05×10^9	20,078,619	4.11×10^9	3.77×10^9	488,319.6
MS_{LOF}	227,255	5.50×10^9	31,026,486	7.22×10^9	3.77×10^9	348,568.1
F-Value	1.5380	2.6860	1.5452	1.7561	0.9978	0.7138
p-Value	0.2194	0.0593	0.2175	0.1710	0.4037	0.5495
F_{crit} (45 observations)	2.8387					

Table 2. Linearity related calculations for ion chromatographic determination of fluoride, chloride, nitrite, sulfate, nitrate, and phosphate in fertilizer industry wastewater TGM 2 under the optimal conditions.

Anion	Fluoride	Chloride	Nitrite	Sulfate	Nitrate	Phosphate
Range (mg/L)	0.16–0.49	4.50–13.50	0.23–0.68	8.40–25.20	14.38–43.13	0.16–0.48
R^2	0.9980	0.9989	0.9992	0.9993	0.9997	0.9985
Slope (μS/mg/min/L)						
Value	456,217	349,080	114,748	230,297	176,789	67,149
Lower 95%	449,970	345,609	113,796	228,474	175,983	66,366
Upper 95%	462,464	352,551	115,700	232,120	177,595	67,932
Intercept (μS/min)						
Value	1,701.1	11,482.9	54.2	152.2	2379.4	139.0
Lower 95%	−463.5	−21,653.0	−402.0	−32,328.5	−22,193.0	−126.7
Upper 95%	3,865.6	44,618.7	510.3	32,632.9	26,951.7	404.7
Lack of fit test						
MS_{PE}	5,809,586	1.38×10^9	266,762.7	1.82×10^8	4.52×10^8	92,724.71
MS_{LOF}	7,847,650	1.01×10^9	52,842.4	2.52×10^8	4.53×10^8	8,150.71
F-Value	1.3508	0.7347	0.1980	1.3900	1.0022	0.0879
p-Value	0.2716	0.5374	0.8970	0.2915	0.2025	0.9662
F_{crit} (45 observations)	2.8387					

wastewater TGM 1 and TMG 2. Since correlation coefficients are the measure of the join variation between two variables, it presents the strength of the proposed linear relationship between a concentration and peak area. It can be seen that correlation coefficients (R^2) have satisfactory values ranging between 0.998 and 0.999, and strong linear relationship between concentration, and peak area for all anions and bought wastewater exist.

The slopes of calibration curves present the sensitivity of the proposed method. If the slope is larger the sensitivity is higher. Values for the slope in Tables 1 and 2 prove the good sensitivity of the method. Lower and upper confidence intervals show the boundaries for expected values with respect to 95% confidence limit.

Lower and upper 95% confidence interval limit boundaries for intercept of calibration curves include value zero. This proves that the intercept of the calibration curve is not significantly different from zero with respect to confidence 95%.

The analysis of variance (ANOVA) was used to detect the lack of fit in the regression, in order to verify whether the model chosen is the correct one (Tables 1 and 2). The total variation of the y-values about the mean value of y was described as the total sum of squares SS_T. Those variations were separated in the two main components, namely sum of squares due to regression (SS_{REG}) and residual sum of squares (SS_R). The results from replicate measurements were available and SS_R was separated into: component which measures the variation do the pure experimental uncertainty, that is, the pure error sum of squares (SS_{PE}); component which measures the variation of the group means of y, about the regression line. This is called sum of squares lack of fit (SS_{LOF}).

All that was arranged in an ANOVA in which the mean squares (MS) were always obtained by dividing the sum of squares by their corresponding degrees of freedom. If MS_{LOF} and MS_{PE} were comparable, the model is justified and bought MS are independent estimates of standard deviation. Consequently, the pooled estimate of variance was used in all subsequent calculations. The values F and p obtained for the lack of fit test proves that lack of fit term is not significant within 95% confidence limit and, consequently, the straight line model is adequate to describe the relationship between concentration and peak area for all investigated anions and bought wastewater samples.

ACCURACY

Tables 3 and 4 present the accuracy related calculation for ion chromatographic determination of fluoride, chloride, nitrite, sulfate, nitrate, and

Table 3. Accuracy related calculations for ion chromatographic determination of fluoride, chloride, nitrite, sulfate, nitrate, and phosphate in fertilizer industry wastewater TGM 1 under the optimal conditions.

Anion	Fluoride	Chloride	Nitrite	Sulfate	Nitrate	Phosphate
R^2	0.9995	0.9992	0.99913	0.9988	0.9991	0.9992
Slope						
Value	0.9962	1.0017	0.9990	0.9997	0.9952	1.0007
Lower 95%	0.9916	0.9960	0.9927	0.9923	0.9889	0.9948
Upper 95%	1.0008	1.0073	1.0052	1.0070	1.0015	1.0065
Intercept						
Value	0.0007	−0.0231	0.0003	0.0283	0.1132	−0.0005
Lower 95%	−0.0003	−0.0889	−0.0042	−0.1197	−0.0559	−0.0070
Upper 95%	0.0017	0.0425	0.0049	0.1764	0.2825	0.0058
Recovery (%)						
Value	99.98	99.91	99.65	99.82	99.72	100.12
Standard deviation	0.64	1.00	0.89	1.13	1.03	0.98

Table 4. Accuracy related calculations for ion chromatographic determination of fluoride, chloride, nitrite, sulfate, nitrate, and phosphate in fertilizer industry wastewater TGM 2 under the optimal conditions.

Anion	Fluoride	Chloride	Nitrite	Sulfate	Nitrate	Phosphate
R^2	0.9993	0.9993	0.9992	0.9993	0.9992	0.9992
Slope						
Value	1.0002	0.9992	0.9975	0.9948	0.9872	0.9967
Lower 95%	0.9945	0.9938	0.9914	0.9893	0.9815	0.9905
Upper 95%	1.0060	1.0047	1.0036	1.0003	0.9930	1.0028
Intercept						
Value	0.0001	0.0032	0.0007	−0.0022	0.2248	0.0010
Lower 95%	−0.0019	−0.0487	−0.0022	−0.1000	−0.0489	−0.0011
Upper 95%	0.0021	0.0551	0.0036	0.0957	0.4008	0.0031
Recovery (%)						
Value	100.04	99.93	99.92	99.49	99.61	100.03
Standard deviation	0.93	0.87	1.12	0.96	1.03	0.98

phosphate in fertilizer industry wastewater. The replicate measurements were made at five different concentration levels and relationships between amounts found (y) against amount added (x) were investigated. If no measurement random errors were made and if there were no bias, this would yield the relationship $y = x$. Since random errors were made, the coefficients of linear relationships were different (intercept was different from zero and/or slope was different from one). There are four possibilities, namely:

If intercept is equal to zero and slope is equal to one, there is no systematic error.

If intercept is equal to zero and slope is different from one, there is proportional systematic error.

If intercept is different from zero and slope is equal to one, there is absolute systematic error.

If there is no linearity, it is necessary to carry out the validation over a shorter concentration range (if this is still compatible with original aim).

Results (Tables 3 and 4) show that values for intercept lower and upper confidence limit (95% confidence) include value zero in all investigated cases. The values for slope lower and upper confidence limit (95% confidence) include value 1 in all investigated cases. The coefficients of correlation have values greater than 0.988 in all investigated cases. This proves that the relationship between amount found against amount added is linear and that there is no systematic error present in the analytical system. Values for recovery (Tables 3 and 4) falls into interval 100% ± 2%, which shows the satisfactory recovery of the method.

Precision

The precision related calculations are shown in Table 5. It can be seen that relative standard deviation is less than 2% in all investigated cases. This proves that precision of determination of anions in fertilizer industry wastewater is satisfactory.

Sample Preparation

The sample preparation procedure consisted of sample dilution. The influence of dilution procedure on final analytical result quality (accuracy and

Table 5. Precision related calculations for ion chromatographic determination of fluoride, chloride, nitrite, sulfate, nitrate, and phosphate in fertilizer industry wastewater under the optimal conditions.

	Relative standard deviation of samples (%)	
Anion	TGM 1	TGM 2
Fluoride	0.65	0.93
Chloride	1.00	0.87
Nitrite	0.90	1.12
Sulfate	1.14	0.97
Nitrate	1.03	1.03
Phosphate	0.98	0.98

precision) was tested by using one-way ANOVA (Tables 6 and 7). The MS errors due to sample preparation are compared with those due to injection. It can be seen from *p*-values, which are greater than 0.05, that MS errors due to dilution are not significantly different from MS errors due to injections, by taking into account 95% confidence. This yields the conclusion that the analytical result quality (accuracy and precision) is not significantly affected by using a sample preparation procedure (dilution).

CONCLUSIONS

This work shows development of an ion chromatographic method for monitoring of fluoride, chloride, nitrite, sulfate, nitrate, and phosphate in fertilizer industry wastewater. The selectivity of the ion chromatographic method plays one of the most important roles in the ion chromatographic analysis. By using artificial neural network retention models in combination with different criteria functions, it was possible to increase separation between all investigated anions within reasonable analysis times. Consequently, the performance characteristic of the proposed method was improved. That was proven by performing validation procedures. Results show that the proposed method is characterized by superior performance characteristics: linearity $R^2 \geq 0.998$, recovery $= 99.49-100.12\%$, repeatability RSD $\leq 1.14\%$, and sample preparation procedure does not influence the analysis result quality. It can be concluded that the developed ion chromatographic method can be recommended and successfully applied for

Table 6. Calculations related sample preparation influence on accuracy of ion chromatographic determination of fluoride, chloride, nitrite, sulfate, nitrate, and phosphate in fertilizer industry wastewater.

Sample	Anion	Fluoride	Chloride	Nitrite	Sulfate	Nitrate	Phosphate
TGM 1	MS between sample preparation	0.2912	0.7465	0.2608	1.1597	0.2384	2.2912
	MS between injections	0.4184	1.2812	1.2876	1.4698	1.2890	0.6590
	p-Value	0.5140	0.5706	0.8188	0.4723	0.8330	0.0575
TGM 2	MS between sample preparation	1.28×10^{-6}	0.0090	1.24×10^{-5}	0.0613	0.0368	2.48×10^{-5}
	MS between injections	1.84×10^{-6}	0.0154	6.13×10^{-5}	0.1264	0.1429	7.13×10^{-5}
	p-Value	0.5140	0.5706	0.8188	0.6252	0.7763	0.0575

Table 7. Calculations related sample preparation influence on precision of ion chromatographic determination of fluoride, chloride, nitrite, sulfate, nitrate, and phosphate in fertilizer industry wastewater.

Sample	Anion	Fluoride	Chloride	Nitrite	Sulfate	Nitrate	Phosphate
TGM 1	MS between sample preparation	0.0871	0.8775	0.0035	0.1372	0.0943	0.5610
	MS between injections	1.0872	0.4192	1.2348	0.5512	0.8554	1.0629
	p-Value	0.9234	0.1578	0.9971	0.7828	0.8964	0.6005
TGM 2	MS between sample preparation	9.484×10^{-7}	0.0071	4.562×10^{-7}	0.0039	0.0078	5.7443×10^{-6}
	MS between injections	1.184×10^{-5}	0.0034	3.835×10^{-5}	0.0156	0.0707	1.0884×10^{-5}
	p-Value	0.9234	0.1578	0.9882	0.7828	0.8964	0.6005

routine monitoring of fluoride, chloride, nitrite, sulfate, nitrate, and phosphate in fertilizer industry wastewater.

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