A Simultaneous Determination Method for the Analysis of Chloride and Nitrate Ions in Air Samples by PLS1

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Abstract: This study describes a multi-ion-selective electrode system for the simultaneous determination of nitrate and chloride ions in air samples by using multivariate calibration methods. The measurement system was constituted of two ion-selective electrodes, an Ag/AgCl double-junction reference electrode and a multi-potentiometer. The measurements were performed at pH 5.0 acetic acid/sodium acetate buffer. The obtained data were evaluated by using Partial Least Squares (PLS1). The system was used to analyze the synthetic samples and fume-hood samples in terms of the amount of chloride and nitrate. The percentage recovery values obtained from fume-hood samples were 93.8% ± 3.8 and 102.4% ± 2.5 for chloride and nitrate, respectively. The presented system could be an easy-to-use approach for monitoring the amount of chloride and nitrate species in the scope of occupational health and safety analysis.

INTRODUCTION

Chloride and nitrate ions are frequently encountered in environmental samples such as water, soil and air, and these components affect human health. These ions are also found in the structure of strong acids such as hydrochloric acid and nitric acid.

Nitric acid is used in explosives and ammonium nitrate production for fertilization. In addition, it is used in organic synthesis, metallurgy, ore flotation (separation of free ore grains in liquid by flotation method, etc.), and reprocessing of spent nuclear fuels. Nitric acid is highly corrosive to most metals. Reactions between nitric acid and various organic metals are often highly exothermic and explosive. In addition, toxic gases are released when nitric acid reacts with metals.

The chloride ion is often used to purify drinking water and wastewater treatment. On the other hand, hydrochloric acid is used as an industrial acidifier. It is also used for refining tantalum and tin ores, converting corn starch to syrup, removing stones formed in heat exchangers and boilers in the industry.

The analysis of these and similar ions has always attracted attention. For example, ion chromatography is one of the most used methods (1). In addition, there are other studies conducted by capillary electrophoresis (2) and voltammetric (3) or potentiometric ion-selective electrodes (4, 5) in order to do anion analysis.

Nowadays, special attention is paid to occupational health and safety issues, and some sanctions are applied when necessary. For example, in the industry, the employer has to make some analyses done in the work environment to save the employees' health. According to the Occupational Safety and Health Administration (OSHA), about 32 million workers work with and are potentially

exposed to one or more chemical hazards (6). It is also known that chemical exposure may cause or contribute to many serious health effects such as heart ailments, kidney and lung damage, cancer, burns, and rashes.

Chemicals have exposure limits in the scope of occupational health and safety. For example, the legal airborne permissible exposure limit (PEL) for hydrochloric acid is 5 ppm and can not be exceeded at any time (7). On the other hand, the PEL value is lower for nitric acid, and it is 2 ppm averaged over an 8-hour work shift (8). In such cases, the sampling for air should be done from the environment near the employee's breathing zone, where the ions are most intense.

Analyses can be conducted when a lot of types of components are together in the matrix. The analyses may result in errors due to the species that cause interference. To prevent this, the species that have an interfering effect should be removed from the matrix or masked. After these sample preparations, analysis is carried out by single-variate calibration techniques. However, this situation leads to loss of time and extra cost, and as the number of processes increases, systematic error possibility rises. In order to prevent these adverse effects, multivariate calibration methods can be an alternative (9).

Multivariate calibration methods have been preferred several times by the researchers that carry out spectroscopic studies (10-13). In addition, the use of these techniques with electrochemical studies such as anodic or cathodic differential pulse voltammetry have been reported before (14, 15). Many of these methods, especially spectroscopic ones, have advantages such as repeatability and sensitivity. On the other hand, the main handicaps of spectroscopic techniques are being overpriced, having complex procedures, and being more suitable for benchtop analysis. Potentiometry has become a good alternative for multivariate calibration studies since it has a small and uncomplicated design that allows field measurements. Moreover, compared to the other methods, it is relatively cheap and can be applied easily (16).

The technology, which is created by using multi-ion selective electrode arrays and multivariate calibration methods together, calls "electronic tongue" (17). Electronic tongues benefit the cross sensitivities of different ion-selective electrodes involving a sensor array and evaluate the results by a chemometric database. Although the use of multi-ISE arrays and chemometrics for the qualitative and quantitative analysis of different cations have been reported frequently (18-25), there are limited studies about the anion analyses by using the multi-ISE arrays (26-31). Some of these reported studies are only for anion analysis, while others are based on the analysis of both anions and cations. Also, in some cases, while the

study was designed for the simultaneous determination of more than one anion, researchers could not get that point by virtue of the interfering effect of analytes on each other (32).

Different multivariate calibration methods can be used during the electronic tongue studies, such as Classical Least Squares (CLS), Principal Component Regression (PCR) and Partial Least Squares (PLS1). Among all these methods, PLS1 is one of the most preferred multivariate calibration methods for the simultaneous determination of interfering species. It has also been previously reported that, in many different respects, PLS can be considered as a first-stop convenience method because it is well known and used (33).

In the study described here, a multi-ion-selective electrode array (multi-ISE array) was designed for the simultaneous determination of chloride and nitrate anions in the air samples. The system was used for analyzing the fume-hood samples, and the obtained results were evaluated by PLS1. While there are previously reported studies with the application in various samples such as water, beverages, honey, etc., to the best of our knowledge, this is the first study in which simultaneous determination of chloride and nitrate ions has been conducted in air samples by using a multi-ISE array and multi-variable calibration methods.

EXPERIMENTAL SECTION

Reagents and Solutions
Acetic acid, ammonium acetate, disodium hydrogen phosphate (Na_2HPO_4), potassium dihydrogen phosphate (KH_2PO_4), hydrochloride acid, nitric acid, sodium acetate, sodium chloride, sodium hydroxide, and sodium nitrate were purchased from Merck. Deionized water (Mes Mp Minupure Basic pure) was used to prepare stock solutions, buffer solutions, and synthetic samples.

Equipment
The potential measurements were conducted by a Lawson EMF-16 multiplexer, and the obtained data was recorded in a computer via EMF program. During the measurements, a double junction Ag/AgCl electrode (Thermo Orion) was used as a reference electrode. A Sentek P11 pH electrode was used for pH measurements. The chloride-selective electrode (Sentek) and the nitrate-selective electrode (Sentek) used in the study were commercially available. The fume-hood samples were prepared by using an air sampling pump (GirlAir-PLUS).

Preparation of the training set solutions
Chloride and nitrate stock solutions were prepared from sodium salts. A two-factor/five-level experimental design was used to prepare the training set solutions, and the five-level experimental design was simplified to 25 calibration solutions as described in the literature

(34). The level and concentration values of training set solutions are given in Table 1. 5 mL of chloride and nitrate stock solutions (ten times concentrated according to the concentrations stated in Table 1) and 5 mL of pH=5.0 acetic acid/sodium acetate buffer were placed into a volumetric flask, and the final volume was completed to 50 mL with deionized water.

Table 1: Level and concentration values for the calibration solutions.

Level Values	Cl⁻ (mol/L)	NO₃⁻ (mol/L)
-2	0.0001	0.0001
-1	0.0003	0.0003
0	0.0010	0.0010
1	0.0030	0.0030
2	0.0100	0.0100

Preparation of synthetic samples
Both synthetic chloride and nitrate samples were prepared with a concentration of 0.002 mol/L. 5 mL synthetic sample stock solution (ten times concentrated stock solutions) and 5 mL pH=5.0 acetic acid/sodium acetate buffer were mixed in a volumetric flask, and the final volume was completed to 50 mL with deionized water.

Preparation of fume-hood samples
The air sample collection mechanism used during the study is shown in Figure 1. 0.001 mol/L 200 mL NaOH solution was put into the washing flask of the mechanism. The mechanism was placed in a fume-hood and kept at the specified time. Hydrochloric acid and nitric acid solutions were placed in a glass beaker and heated by a heater to evaporate more quickly. The air sampling pump, which was adjusted to 3000 mL per minute, was attached to the washing flask. The air sample was collected in the washing flask for three hours and thirty minutes.

5 mL of air sample collected in NaOH solution and 5 mL of buffer solution were mixed in a volumetric flask, and the final volume was adjusted to 50 mL with deionized water.

Figure 1: The air sample collection mechanism.

Potentiometric measurements
The multi-ISE array consists of a chloride-selective commercial electrode, a nitrate-selective commercial electrode and a double junction Ag/AgCl reference electrode. Potentiometric measurements were conducted in the presence of acetic acid/ sodium acetate buffer solution (pH=5.0). The EMF measurement of the multi-ISE

array was compared against the reference electrode. The changes in the EMF were measured twice consecutively with the Lawson L-EMF DAQ 3.0 software of the multiplexer, and these changes were recorded on a computer.

Data Processing

The acquired data were evaluated by using PLS1. A training set and a potential matrix with basic codes written in the laboratory in Octave 5.1.0 free licensed software compatible MATLAB were used in order to perform the multivariate calibration techniques (9, 34). The EMF values of the training set, synthetic samples, and the fume-hood samples were recorded in the computer. The predicted values were calculated, and the differences between the known and the predicted concentrations were used to evaluate the EMF values.

First, a cross-validation process was performed with the results of training set solutions. After that, the number of principal components was found by plotting the predicted residual error of sum of squares (PRESS) values against the factor numbers. Chloride and nitrate concentrations were estimated in the training, synthetic and fume-hood sample sets with PLS1 by applying a cross-validation process again with the number of principal components obtained by the graphical results.

Analysis of the synthetic and fume-hood samples

The synthetic samples and the fume-hood samples were analyzed with the prepared multi-electrode array. In order to calculate the recovery values, the standard addition method was used. Chloride and nitrate standard solutions (1 mol/L) were spiked to both synthetic and fume-hood samples after the calibration with the training set. Standard additions were conducted by using 50 µL, 100 µL, 100 µL, 100 µL volumes respectively. Percentage recoveries of both chloride and nitrate anions were obtained using the difference between the anion concentrations calculated at the end of the standard addition and the initially calculated anion concentrations.

RESULTS AND DISCUSSION

Performance characteristics of the ion-selective electrodes

In nitrate and chloride calibration solutions, the slopes, correlation coefficients (R^2), and linear working ranges of each ion-selective electrode composing a multi-ISE array were determined separately. Calibration solutions were prepared in the range of $1,0 \times 10^{-1}$ mol/L - $1,0 \times 10^{-6}$ mol/L. Also, the selectivity coefficients of electrodes against other analyte ions were determined by using the IUPAC recommended separate solution method (35). The selectivity coefficients and the performance characteristics calculated from calibrations are given in Table 2.

Table 2: Performance characteristics of the ion-selective electrodes.

Ion-selective electrode	Slope (mV per decade)	R^2	Working Range (mol/L)	log K $_{A,B}$*
Chloride	51.48	0.9999	1×10^{-1} - 1×10^{-3}	0.205
Nitrate	51.15	0.9964	1×10^{-1} - 1×10^{-4}	1.054

$$^*E_2 - E_1 / \pm s = \log K_{A,B}$$

The effect of pH on the performance of ion-selective electrodes

To determine the effect of pH on the performance of the ion-selective electrodes, the measurements were carried out in the solutions that contained no buffer, pH=7.0 buffer (ammonium acetate), pH=6.8 (KH_2PO_4/Na_2HPO_4) buffer and pH=5.0 (acetic acid/sodium acetate) buffer. When the obtained data were evaluated, it was observed that the best slope, intercept and R^2 values were gained at pH=5.0. The results are detailed in Table 3.

Table 3: The effect of pH on the performance of the multi-ISE array.

Buffer Solution	Ion	Slope	R^2	Intercept
No Buffer	NO_3^-	0.9929	0.9862	0.0003
	Cl$^-$	**0.9847**	**0.9725**	**0.0005**
pH=7.0 Buffer	NO_3^-	0.9829	0.9973	0.0002
	Cl$^-$	0.7864	0.8647	0.0004
pH=6.8 Buffer	NO_3^-	0.9903	0.9942	0.0003
	Cl$^-$	0.9739	0.9741	0.0008
pH=5.0 Buffer	NO_3^-	0.9962	0.9987	0.00008
	Cl$^-$	0.9972	0.9938	0.00007

Data Processing

Cross-Validation: To perform the cross-validation of the method "leave-one-out" technique was used. In accordance with this purpose, one of the 25 training set solutions was accepted as a sample, and the remaining 24 training set solutions were used in calibration. In the calibration made with 24 training solutions, the content of the 25th solution was determined. The same procedure was repeated for each solution.

PRESS values and the factor numbers were plotted by using distinctions between known and predicted concentrations in each solution. The principal

component numbers were appointed from the minimum points of these graphs. The obtained graphs are given in Figure 2. The principal component numbers were six for both chloride and nitrate by PLS1.

The concentrations of the analytes in synthetic samples were estimated via PLS1 by applying a cross-validation process with the principal component numbers. The percentage recovery values calculated according to described in Experimental Section were found 103.8% ± 3.5 and 103.1% ± 1.6 for chloride and nitrate, respectively.
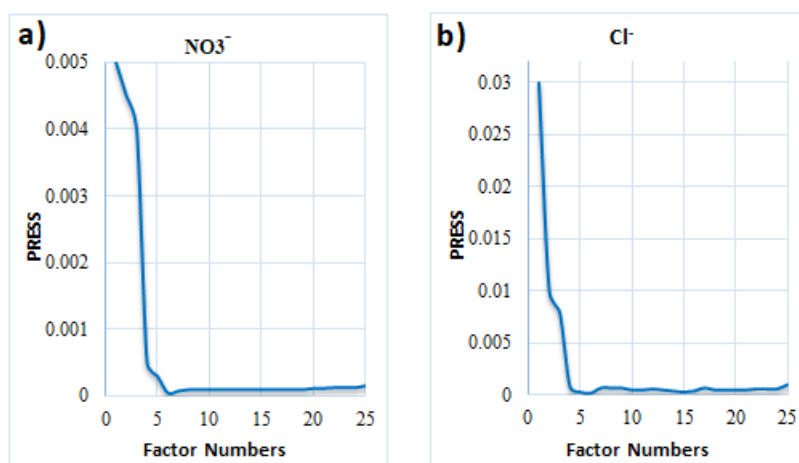

Figure 2: The number of factors according to PRESS values for PLS1 method.

Analytical application of the multi-ISE array to the fume-hood samples

The C_{known} – $C_{predicted}$ graphs obtained by PLS1 are given in Figure 3. Measurements were taken with multi-ISE in six different fume cupboard samples prepared according to described in Experimental

Section. The chloride and nitrate concentrations were calculated by PLS1, and according to these calculations, 0.63 m³ of air was drawn from the fume-hood and 41.87 mg chloride ions and 77.46 mg nitrate ions were found in 1 m³ air.
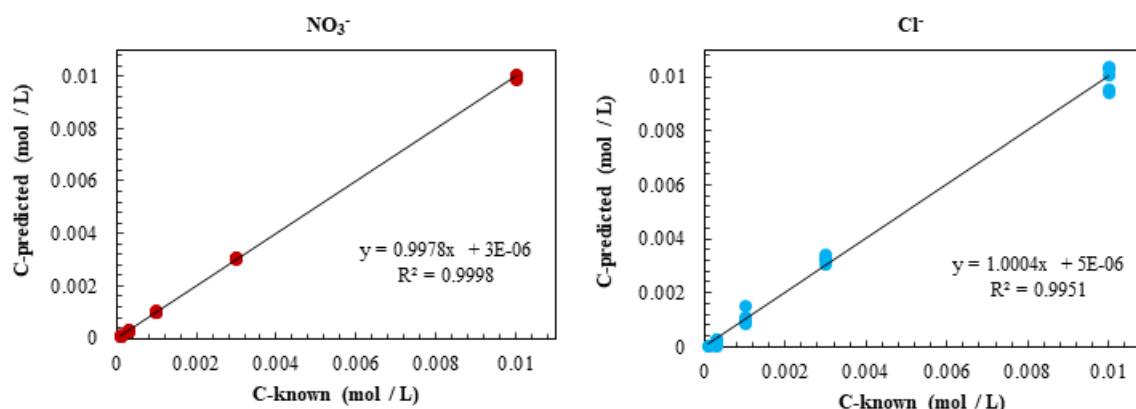

Figure 3: The concentration values calculated by PLS1 against the known concentrations.

When the percentage recovery values calculated from the standard addition were evaluated, it was observed that these values were 93.8% ± 3.8 and 102.4% ± 2.5 for chloride and nitrate, respectively. In addition, the percentage recovery results were

checked for systematic errors using the *t-test* and it was determined that there was no systematic error at 99% confidence level (degree of freedom (DF):3) in the results obtained from the multi-ISE array (Table 4). According to these results, it can

be concluded that the use of multi-variable calibration methods with the multi-ISE array is could be a good alternative for the anion analysis because it is not only easy and cheap but also gives good recovery values.

Table 4: Statistical comparison of the nitrate and chloride concentrations in fume-hood samples.

$$t_e = \frac{\mu - \overline{x}}{\frac{s}{\sqrt{n}}}$$

Analyte	Recovery%	t_e	t_c	$t_c > t_e$
NO$_3^-$	102.4 ± 2.5	1.92	5.84	5.84 > 1.92
Cl$^-$	**93.8 ± 3.8**	**3.26**	**5.84**	**5.84 > 3.26**

There are many commercially available anion and cation-selective electrodes on the market. The costs of these electrodes are quite affordable compared to more complex analytical devices, which are suitable for benchtop analysis. In fact, the proposed system can be used in different sample matrices for different anions/cations with the help of a chemometric approach and different ion-selective electrodes. On the other hand, in the light of this study, laboratories can also develop similar systems with ion-selective electrodes, which they designed.

Results obtained from single ion-selective electrodes
Both nitrate and chloride concentrations in the fume-hood samples were determined using single ion-selective electrodes. To that end, potential readings were acquired in the calibration solutions of the analytes to each ion-selective electrode sensitive, and concentration values were obtained by using the created calibration curves and the Nernst equation. As indicated in Table 5, there is a significant difference between the results obtained from single ion-selective electrodes and multi-ISE array, especially for nitrate concentrations.

Table 5: The percentage recoveries of Cl$^-$ and NO$_3^-$ in fume hood samples by using single ISEs.

	ISE	Analyte	Recovery%	t_e	t_c	$t_c > t_e$
$t_e = \dfrac{\mu - \overline{x}}{s/\sqrt{n}}$	Nitrate ISE	NO$_3^-$	60.3 ± 3.1	25.61	5.84	5.84 < 25.61
DF : 3	Chloride ISE	Cl$^-$	104.1 ± 5.3	1.55	5.84	5.84 > 1.55

According to these results, it can be concluded that the use of a multi-ISE array in the analysis could be more advantageous. Also, more accurate results can be gained compared to a single electrode.

CONCLUSION

In this study, we proposed a multi-ISE array for the simultaneous determination of chloride and nitrate anions in air samples. The system was used to analyze the synthetic samples and fume-hood samples in terms of the amount of chloride and nitrate anions. The measurement system was consisted of two ion-selective electrodes, an Ag/AgCl double-junction reference electrode, and a multi-potentiometer. The obtained data were evaluated by using PLS1. The application of the multi-ISE array was demonstrated by the simultaneous determination of nitrate and chloride ions in air samples obtained from a fume-hood with good recoveries. The presented sensor could be an easy to use approach for monitoring the amount of chloride and nitrate in the scope of occupational health and safety analysis.

While it is possible to analyze samples taken from air samples by chromatography systems combined with thermal desorption, it is possible to conduct the analysis more straightforward and cheaper with the system proposed in the study. To the best of our knowledge, this is the first study in which simultaneous determination of chloride and nitrate ions has been carried out in air samples by a multi-ISE array and multi-variable calibration methods. Considering the benefits of the proposed system, such as reducing costs and minimizing the need for extensive facilities and number of personnel, we believe that this study will elucidate future studies and will be of interest to most laboratories that carry out similar analyses.

CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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