

DETERMINATION OF SELECTED ATMOSPHERIC AMINES IN THE PRESENCE OF INORGANIC CATIONS BY ISOCRATIC ION CHROMATOGRAPHY

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Abstract

The aim of this study was to optimize and validate the methodology for the determination of selected aliphatic amines in the presence of inorganic cations in environmental samples (rainwater, snow, particulate matter) by isocratic ion chromatography with suppressed conductometric detection. The obtained detection limits for selected aliphatic amines were 4.65 µg/L, 4.46 µg/L, and 12.4 µg/L for methylamine, dimethylamine, and trimethylamine, respectively. The relative standard deviation of repeatability for real samples was less than 6%. The recovery was within the range of 90.3%–100%. The developed methodology was applied to analyse wet deposition and particulate matter samples.

Keywords: atmospheric amines, aliphatic amines, conductometric ion chromatography, method validation and optimization

Introduction

Amines are ammonia derivatives that are formed by replacing one or more hydrogen atoms with an alkyl or aryl groups. Amines are ubiquitous in the atmosphere, in which about 150 amines have been identified. Atmospheric amines are estimated to account for 30% of the total reduced nitrogen in the atmosphere. The most common atmospheric amines are methylamine, ethylamine, dimethylamine, diethylamine, trimethylamine and triethylamine. The low molecular weight amines present in the atmosphere come from anthropogenic and natural emission sources. Biomass burning, vegetation, geological sources (such as soils and volcanic eruptions)

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and oceanic emissions are examples of main natural emission sources. Their main anthropogenic emission sources include industrial combustion, chemical manufacturing, food industry, animal husbandry and agricultural emissions, sewage treatment and leather industries (Ge et al., 2011; Cheng et al., 2018; Shen, 2017; Sullivan et al., 2020).

Atmospheric amines play a role similar to that of ammonia. As atmospheric bases, they can neutralize acids such as nitric acid and sulfuric acid. Low molecular weight amines can contribute to the formation of secondary organic aerosols (SOA) and affect the properties of atmospheric aerosols. Amines present in the atmosphere can be found in the gas and particle phases (fog water, cloud water and aerosol). Given the fact that most amines are well soluble in water and their presence has been detected in rainwater and fog, wet deposition is considered as the main route for removing amines from the atmosphere (Ge et al., 2011; Hertel et al., 2011; Chen et al., 2017; Qiu, Zhang, 2013). Despite the fact that amines are important for human health and atmospheric chemistry, current knowledge about them remains limited (Du et al., 2021).

The predominant species of aliphatic amines in particulate matter and wet deposition, their concentrations and sources in different locations may vary. Examples of studies on the content of aliphatic amines in air have been described in the literature. For example, Huang et al. reported that in autumn 2018 in PM_{2.5} samples collected in an urban area of the Pearl River Delta in China, methylamine was found to be dominating among all measured amines, with an average mass concentration of 243 ± 179 ng/m³, followed by dimethylamine 49 ± 30 ng/m³. These amines occurred mainly as nitrate and sulphate salts (Huang et al., 2022). Cheng et al. (2020) conducted research in Yangzhou urban area, belonging to Yangtze River Delta in China. In this study several aliphatic amines were identified in urban aerosols (PM_{2.5}) collected from April to November 2016. The average concentrations of methylamine, dimethylamine and ethylamine were 1.418 ± 1.341 , 3.623 ± 3.941 and 12.576 ± 10.446 ng/m³, respectively. Their highest variability was observed in spring and the lowest one in autumn. An in-depth analysis has shown that the source areas of the amines were mainly from the oceans and surrounding provinces. In research conducted in Seoul, South Korea, seasonal fluctuation in total amine concentration was observed in PM_{2.5} samples. The highest concentration (5.85 ± 2.90 ng/m³) was recorded in the spring and the lowest in autumn (5.07 ± 1.93 ng/m³) (Choi et al., 2020).

Determination of amines still remains an important challenge for analytical chemists, despite significant progress in the past years. The most popular and useful are methods based on separation techniques, such as high-performance liquid chromatography (HPLC), capillary electrophoresis (CE) and gas chromatography (GC). They are particularly useful given their high separation efficiency and selectivity, as well as their sensitivity and repeatability. Nevertheless, they also have certain some limitations. For the determination of atmospheric amines, methodologies based on ion chromatography with conductometric detection are

often used, usually in gradient mode. Ion chromatography allows simultaneous analyses of organic and inorganic cations. Low ion concentrations, similar retention times of the analytes to be measured, and the method of sample preparation for analyses are the most important problems associated with the determination of low molecular weight amines with the use of ion chromatography. Successful ion separation requires optimising of the determination method and selection of appropriate analytical conditions such as the type of analytical column, the type of eluent and its concentration and flow rate and the method of sample preparation for analysis. Ion chromatography methods provide sufficient sensitivity, selectivity and reproducibility of analysis, as well as offer the possibility of simultaneous determination of multiple cations (Huang et al., 2014; Michalski, 2020; Michalski et al., 2021).

This study aimed to optimize and validate the methodology for the determination of selected aliphatic amines in the presence of inorganic cations by isocratic ion chromatography. The research methodology was based on a simple isocratic ion chromatography kit with conductometric detection, available in most chemistry laboratories. The developed methodology was applied to the analysis of real samples.

2. Materials and methods

2.1. Chemicals and reagents

Standard solutions of inorganic cations were prepared by dilution of their stock solutions (1000 mg/L each, standards for IC Sigma-Aldrich or AccuStandard, USA) in ultrapure deionized water (Hydrolab, Poland). Methylamine hydrochloride ($\geq 98\%$, Sigma-Aldrich, USA), dimethylamine hydrochloride ($\geq 98\%$, Sigma-Aldrich, USA) and trimethylamine hydrochloride (98%, Sigma-Aldrich, USA) were used as a standard for the determination of amines. Methanesulfonic acid (MSA, $\geq 99\%$, Sigma-Aldrich, USA) was used as a mobile phase.

2.2. Ion chromatographic determination of cations

The determination of inorganic cations and selected amines has been carried out on Dionex ICS-1100 (Thermo Fisher Scientific, USA) ion chromatograph equipped with conductivity detector, isocratic pump, cation dynamically regenerated suppressor (Dionex CDRS 600, 4mm diameter) and injection valve with a 25 μL (method optimization) or 100 μL (method validation) sample loop. For method development use was made of Dionex IonPac CS16 column (Thermo Fisher Scientific, USA). The length and diameter of the separation column were 250 mm and 5 mm, respectively. The chromatograms are analysed using the Chromeleon software.

2.3. Method optimization

Standard samples consisting of: lithium (0.5 mg/L), sodium (5 mg/L), ammonium (1 mg/L), potassium (5 mg/L), magnesium (5 mg/L), calcium (5 mg/L), methylamine (1 mg/L), dimethylamine (1 mg/L), trimethylamine (5 mg/L) were used for simultaneously separation and determination of cations by using various separation conditions (different concentration of eluent component, different eluent flow rate, and column temperature). Details have been given in table 1.

Table 1. Optimisation parameters of the separation procedure

Parameter	Condition set number													
	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV
Eluent concentration, mM	50	50	35	35	35	35	30	30	30	30	25	25	25	25
Column temperature, °C	30	40	30	30	40	40	30	30	40	40	30	30	40	40
Flow rate, mL/min	1.0	1.0	1.0	1.5	1.0	1.5	1.0	1.5	1.0	1.5	1.0	1.5	1.0	1.5

2.4. Method validation

The developed method was validated based on the separation capacity of the CS16 column and blank samples, real samples, standard samples of amines and inorganic cations. The performed measurement series were subjected to statistical analysis. Calculations were carried out of method parameters such as limit of detection, limit of quantification, recovery, repeatability precision, accuracy/trueness, intermediate precision, linearity. An analysis of the obtained data and calculations were carried out using the Chromeleon7 program (the program that controls the Dionex ICS-1100 ion chromatograph), LIMS program and Microsoft Excel spreadsheet.

The calibration range was established between 25 µg/L to 250 µg/L for MA and DMA, and from 75 µg/L to 750 µg/L for TMA. Five 10-point calibration curves were prepared over the established concentration range. Plotting was executed of the dependence of the area on subsequent points of the calibration curve (subsequent concentrations). The selected working range was checked by the test for homogeneity of two variances (the F-Snedecor test). A full regression analysis was performed and statistical parameters were established for the linear and non-linear calibration function (number of valid results, mean of concentrations, mean of measured values, correlation coefficient, coefficient a, coefficient b, formula of the linear/non-linear function, residual standard deviation, standard deviation of the method, coefficient of variation of the method). The linearity of the calibration curve was also checked using the F-Snedecor test.

The detection and quantification limits of the method were determined by 10-fold analysis of a mixed solution of 25 µg/L – MA, 25 µg/L – DMA, and 75 µg/L

– TMA. The Dixon test was used for outliers detection. The mean value, standard deviation and coefficient of variation were calculated for a series of measurements. The limit of detection (LOD) and the limit of quantification (LOQ) were calculated from calibration curves of selected amines and were based on equations 1 and 2:

$$LOD = \frac{3.3 \times S_d}{a} \quad (1)$$

$$LOQ = \frac{10 \times S_d}{a} \quad (2)$$

where: S_d – the standard deviation of the area under the peak or peak height corresponding to the concentration of a given standard, and a – the directional coefficient of the mean calibration curve.

In order to determine the precision of repeatability, the determination of methylamine, dimethylamine and trimethylamine concentrations was executed in various environmental samples (air – filters, rainwater, snow) with or without the addition of a standard. Several measurement series were performed, with each series consisting of 7 replicates. The Dixon test was used for the detection of outliers. The mean value, standard deviation of repeatability and coefficient of variation of repeatability were calculated for each series. To determine intermediate precision, standards were prepared at two concentration levels for each selected amine (MA: 25 µg/L and 250 µg/L; DMA: 25 µg/L and 250 µg/L; TMA: 75 µg/L and 750 µg/L). Three measurement series were performed for each concentration, with each series consisting of 7 repetitions. The mean value, standard deviation and coefficient of variation were calculated for each series. The Dixon test was used for outliers detection in each series. The mean value, standard deviation of intermediate precision and coefficient of variation of intermediate precision were calculated. To determine the trueness of the method, certified standards were prepared at two concentration levels for each selected amine (MA: 25 µg/L and 250 µg/L; DMA: 25 µg/L and 250 µg/L; TMA: 75 µg/L and 750 µg/L). Three measurement series were carried out for each concentration, with each series consisting of 7 repetitions. The mean value, standard deviation and coefficient of variation were calculated for each series. The Dixon test was used for outliers detection in each series. In addition, for each series a calculation was made of the mean value, standard deviation, and the recovery of the selected component from the matrix. The recovery of standards was checked for each matrix tested (air - filters, rainwater, snow). Real samples and spiked samples were analysed according to the developed methodology. The Dixon test was used for outliers detection in the series of results. The mean recovery value and standard deviations were calculated.

Additionally tests were carried out of the influence of the syringe filter material on the concentration of the determined amines. For this purpose, the concentration of aliphatic amines in the reference sample was measured: unfiltered sample (7 repetitions), sample after filtration through a syringe filter made of

PES (7 repetitions), sample after filtration through a syringe filter made of PVDF (7 repetitions). To compare the results obtained for the unfiltered and filtered sample, use was made of the Student's t-test for dependent samples (one-tailed test, significance level = 0.01).

2.5. Real sample preparation

Selected aliphatic amines (MA, DMA, TMA) were determined according to the developed methodology in air and wet deposition samples – (particulate matter, rainwater, snow). Real samples were collected in the cities of Upper Silesia (Bytom, Zabrze, Piekary Śląskie, Racibórz). Air samples (filters) were extracted with deionized water (10 mL deionized water/sample) for 1 hour using an ultrasonic bath (with cooling), and then for about 16 hours using a mechanical shaker (speed 60 rpm). The extracts were filtered through a syringe filter made of PES with a pore diameter of 0.22 μm . Samples of snow and rainwater were filtered through a syringe filter made of PES with a pore diameter of 0.22 μm before cation analysis.

3. Results and discussion

3.1. Method optimisation

The method was optimized according to the parameters summarized in Table 1. The eluent concentrations ranged from 25 mM to 50 mM MSA. Flow rate of the mobile phase was 1 mL/min or 1.5 mL/min, and the column temperature was 30°C or 40°C. The figure 1 shows example chromatograms of the separation of cations and selected aliphatic amines under different analytical conditions.

The most optimal separation parameters were selected and summarized in Table 2. The developed methodology was validated and applied to the analysis of cations in rainwater, snow and particulate matter samples (air sample filters).

Table 2. Analytical conditions for the determination of inorganic cations and selected aliphatic amines

Analytical Column	Dionex IonPac CS16 (5x250 mm)
Guard column	Dionex IonPac CG16 (5x50 mm)
Eluent	25 mM MSA
Eluent flow rate	1.0 mL/min
Elution	Isocratic
Detection	Suppressed conductivity
Temperature	40°C
Injection volume	100 μL

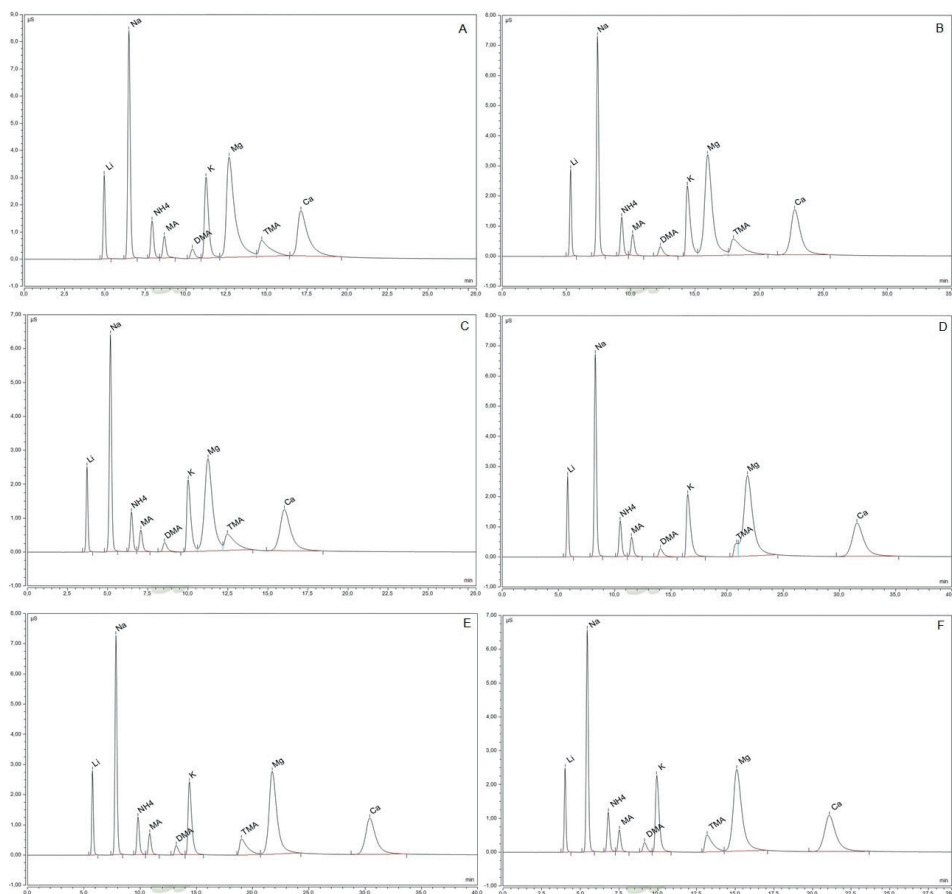


Figure 1. Optimization of the method using Dionex IonPac CS16 column – selected chromatograms (A – eluent: 35 mM MSA, flow rate: 1.0 mL/min, temperature: 40°C; B – eluent: 30 mM MSA, flow rate: 1.0 mL/min, temperature: 30°C; C – eluent: 30 mM MSA, flow rate: 1.5 mL/min, temperature: 30°C; D – eluent: 25 mM MSA, flow rate: 1.0 mL/min, temperature: 30°C; E – eluent: 25 mM MSA, flow rate: 1.0 mL/min, temperature: 40°C; F – eluent: 25 mM MSA, flow rate: 1.5 mL/min, temperature: 40°C).

3.2. Influence of syringe filter material on the veracity of the results

The selection of syringe filter is important because they may influence the results of the analysis. Syringe filters with a 0.22 μm hydrophilic polyvinylidene fluoride (PVDF) and a polyethersulfone (PES) filter membrane by Filtrakon (Poland) were used for the filtration of the real sample. Tests were executed of the influence of the syringe filter material on the concentration of the determined amines. Table 3 shows the results of the Student's t-test of the significance of the differences between the concentrations of selected aliphatic amines in the standard sample without and after being filtered through a syringe filter (PES, PVDF).

Table 3. The results of the Student's t-test

Parameter	PES syringe filter vs. no filtration			PVDF syringe filter vs. no filtration		
	MA	DMA	TMA	MA	DMA	TMA
<i>t</i>	-0.344	-0.280	-0.319	-0.490	-0.319	-0.811
<i>p</i> -value	0.367	0.391	0.376	0.314	0.376	0.212

No significant differences have been ascertained in the results for concentrations of selected aliphatic amines in samples without and after being filtered through a syringe filter. Syringe filters made of PES were used for filtration of real samples due to higher *p*-values.

3.3. Method validation and real sample analysis

The developed method (table 2) was validated based on the separation capacity of the Dionex IonPac CS16 column and blank samples, real samples, standard samples of amines and inorganic cations. The performed measurement series were subjected to statistical analysis. Method parameters such as limit of detection, limit of quantification, recovery, repeatability precision, accuracy/trueness, intermediate precision, linearity were summarized in table 4.

Table 4. The values of selected validation parameters

Parameter		Value			
		MA	DMA	TMA	
Limit of detection, µg/L		4.65	4.46	12.4	
Limit of quantification, µg/L		14.1	13.5	37.6	
Calibration	Coefficient of determination (r^2)	1.000	1.000	0.999	
	Coefficient of variation of method, %	0.267	0.537	0.755	
Precision of repeatability	Particulate matter, %	4.41	5.38	3.79	
	Rainwater, %	1.83	1.01	1.95	
	Snow, %	1.43	2.03	1.66	
Intermediate precision	Check standard (25 µg/L for MA and DMA, 75 µg/L for TMA), %	1.34	1.69	2.78	
	Check standard (250 µg/L for MA and DMA, 750 µg/L for TMA), %	3.40	0.306	3.66	
Trueness	Check standard (25 µg/L for MA and DMA, 75 µg/L for TMA)	Mean value, µg/L	26.7	26.9	78.8
		Coefficient of variation, %	1.34	3.08	0.772
		Recovery, %	93.2	92.5	94.9
	Check standard (250 µg/L for MA and DMA, 750 µg/L for TMA)	Mean value, µg/L	247	254	750
		Coefficient of variation, %	3.40	0.306	3.66
		Recovery, %	98.9	98.3	99.9

Parameter		Value			
		MA	DMA	TMA	
Recovery, %	Particulate matter	Mean value, %	97.3	90.3	106
		Standard deviation, %	1.32	2.85	1.15
	Rainwater	Mean value, %	108	89.5	97.6
		Standard deviation, %	9.43	4.77	3.78
	Snow	Mean value, %	98.0	105	111
		Standard deviation, %	10.1	6.96	1.90

The ion chromatography method described above proved suitable for the determination of selected aliphatic amines in wet deposition and particulate matter extract present at concentrations above 14.1 $\mu\text{g/L}$, 13.5 $\mu\text{g/L}$, and 37.6 $\mu\text{g/L}$ (LOQs) for methylamine, dimethylamine, and trimethylamine, respectively. The working ranges were checked between 25 $\mu\text{g/L}$ to 250 $\mu\text{g/L}$ for MA and DMA, and from 75 $\mu\text{g/L}$ to 750 $\mu\text{g/L}$ for TMA and showed linear calibration curves (figure 2.) characterized by coefficients of determination (r^2) above 0.999 and coefficients of variation of method below 1 %.

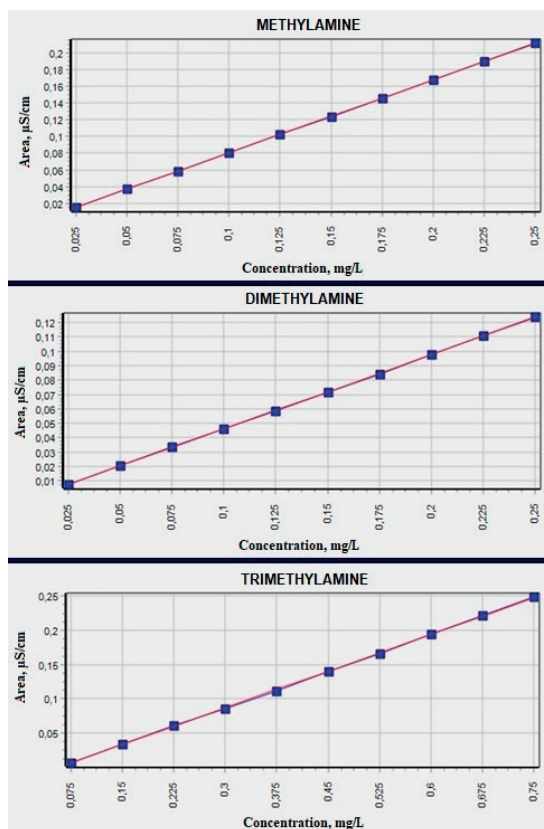


Figure 2. Linear calibration curves

The precision of repeatability was determined for each selected environmental sample (air – filters, rainwater, snow) after seven replicate injections of every sample within one analytical run. The obtained values ranged from 1.43 to 4.41%, from 1.01% to 5.38%, from 1.66% to 3.79%, for MA, DMA, and TMA respectively. This indicates that the developed method is highly reproducible. The intermediate precision was assessed by the interday variability. Two different concentration levels of control standard solutions (MA, DMA, TMA) were prepared. The distributions of the coefficients of variation of intermediate precision were 1.34–2.78%, and 0.306–3.66%, at levels 1 and 2, respectively. Control standards (at two concentration levels) were prepared for validity assessment, in which MA, DMA and TMA concentrations were determined. The recovery of the standards ranged from 98.3 % to 99.9 %, and the coefficients of variation were all below 4%. For the assessment of the recovery, a real sample (air – filters, rainwater, snow) were spiked with known concentrations of MA, DMA, and TMA. Recovery rates for selected matrix tested ranging from 90.3 to 106%, from 89.5% to 108%, from 98.0% to 111%, for MA, DMA, and TMA respectively.

The developed and validated method was verified by analysis of the content of selected aliphatic amines in environmental real samples. The results for several of them are presented in the following table (Table 5).

Table 5. Concentrations of selected aliphatic amines in real samples

Matrices	Sample number	Concentration		
		MA	DMA	TMA
Particulate matter	1	88.0 ng per sample	44.8 ng per sample	160 ng per sample
	2	100 ng per sample	56 ng per sample	187 ng per sample
	3	95.0 ng per sample	< 44.6 ng per sample	< 124 ng per sample
	4	104 ng per sample	< 44.6 ng per sample	< 124 ng per sample
	5	96.0 ng per sample	61.0 ng per sample	454 ng per sample
Rainwater	1	< 4.65 µg/L	9.80 µg/L	< 12.4 µg/L
	2	< 4.65 µg/L	< 4.46 µg/L	< 12.4 µg/L
	3	5.33 µg/L	8.76 µg/L	< 12.4 µg/L
	4	< 4.65 µg/L	< 4.46 µg/L	< 12.4 µg/L
	5	< 4.65 µg/L	9.74 µg/L	< 12.4 µg/L
Snow	1	7.40 µg/L	< 4.46 µg/L	< 12.4 µg/L
	2	34.4 µg/L	10.0 µg/L	< 12.4 µg/L
	3	< 4.65 µg/L	< 4.46 µg/L	< 12.4 µg/L
	4	5.63 µg/L	7.72 µg/L	< 12.4 µg/L
	5	< 4.65 µg/L	< 4.46 µg/L	< 12.4 µg/L

Among the matrices analysed, particulate matter presented higher contents of selected aliphatic amines (most of the results above the LOQs of the method). Lower concentrations of selected amines (mostly below the LOQs of the method) were recorded in snow and rainwater. This is likely due to sample dilution and can be compensated by injecting more concentrated samples or using a larger injection loop. A typical chromatograms of a rainwater sample and particulate matter extract are presented in figure 3.

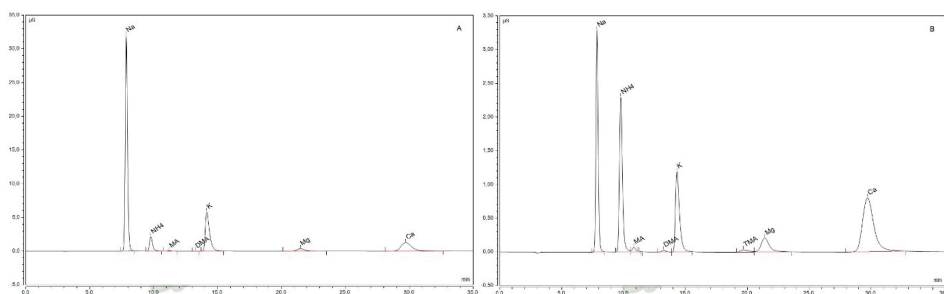


Figure 3. Examples of chromatograms obtained during the analysis of real samples: rainwater (A), particulate matter (B)

4. Conclusion

Ion chromatography with conductometric detection can be used to determine atmospheric amines. Methods based on ion chromatography provide adequate reproducibility of analysis, sensitivity, and selectivity, and offer the possibility of determining multiple cations simultaneously. The Dionex IonPac CS16 column is characterized by separation capabilities that allow quantitative and qualitative analysis of methylamine, dimethylamine and trimethylamine. With overall recoveries ranging from 89.5 to 111% and repeatability precision < 6%, the optimized method was a well suitable tool for the analysis of selected aliphatic amines in environmental samples collected in areas where they could be emitted (for example in the proximity of landfills, sewage treatment plants, wastewater treatment plants, fertilizer plants, and areas of the seas and oceans).

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OZNACZANIE WYBRANYCH AMIN ATMOSFERYCZNYCH W OBECNOŚCI KATIONÓW NIEORGANICZNYCH METODĄ IZOKRATYCZNEJ CHROMATOGRAFII JONOWEJ

Abstrakt

Celem pracy była optymalizacja i walidacja metodyki oznaczania wybranych amin alifatycznych w obecności nieorganicznych kationów w próbkach środowiskowych (woda deszczowa, śnieg, pył zawieszony) metodą izokratycznej chromatografii jonowej z detekcją konduktometryczną. Granice wykrywalności dla wybranych amin alifatycznych wyniosły 4,65 µg/L, 4,46 µg/L i 12,4 µg/L, odpowiednio dla metyloaminy, dimetyloaminy i trimetyloaminy. Precyzja powtarzalności dla próbek rzeczywistych była < 6%. Odzysk mieścił się w zakresie 90,3%–100%. Opracowana metodyka została zastosowana do analizy próbek depozycji mokrej (śnieg, deszcz) oraz próbek pyłu zawieszonego.

Słowa kluczowe: aminy atmosferyczne, aminy alifatyczne, chromatografia jonowa, walidacja i optymalizacja metod

