

OPTIMIZATION OF ISOCRATIC ION CHROMATOGRAPHY METHODS FOR SIMULTANEOUS INORGANIC ANIONS AND CARBOXYLIC ACIDS DETERMINATION

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Abstract. As a part of preliminary studies, the possibility of quantitative oxidation of aldehydes to carboxylic acids and their determination by isocratic ion chromatography with conductometric detection has been tested. A methodology for the simultaneous separation of inorganic anions (F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) and carboxylic acids (formate, acetate and oxalate) by using isocratic ion chromatography with conductivity detection have been developed and validated. Six anion-exchange columns were tested. The best results were achieved for Dionex IonPac AS10 column with 50mM NaOH eluent and flow rate of $1.0 \text{ mL}\cdot\text{min}^{-1}$.

Keywords: anions, ion chromatography, validation, optimization.

1. Introduction

Carboxylic acids and their derivatives are examples of compounds that are more frequently analyzed using ion chromatography and related techniques. Their occurrence in the environment can be of natural or anthropogenic origin. They are broadly used in various industries and daily life.¹ Due to the broad range of applications, carboxylic acids and their derivatives are present in different food, biomedical and environment samples. Organic acids are ubiquitous in the atmosphere and occur in the gas, water and aerosol phases.² Sources of carbonyl compounds (including carboxylic acids) in the atmosphere include emissions from the combustion of biomass, biofuels, and fossil fuels, as well as natural sources, including plant vegetation and microbiological activity.³

Analytical methods and techniques used for their determination are, for example, spectrophotometric and enzymatic methods. However, the most useful are chromatographic techniques, such as: gas chromatography (GC), liquid chromatography (LC), and capillary

electrophoresis (CE).⁴ Particularly helpful is ion chromatography (IC) and related techniques.⁵

Ion chromatography is a variant of high-performance liquid chromatography. Its most popular applications include determinations of the inorganic anions and cations and some organic ions in different types of liquid samples. Development of new types of stationary phases with various separation mechanisms, sample preparation methods and detection modes helps to extend the range of ion chromatography applications to practically all ionic and inorganic substances, also in gaseous and solid samples.⁶ The main advantages of ion chromatography include short time needed for analyses, possibility of analysis of small volume samples, high sensitivity and selectivity, and possibility of simultaneous separation and determination of a few ions or ions of the same element at different degrees of oxidation. Moreover, ion chromatography eliminates the need to use hazardous reagents that are often involved in wet chemical methods. Taking into account the above advantages, ion chromatography is routinely used for the analysis of ionic compounds in water and wastewater.^{7,8} Except of these routine applications of ion chromatography it is applied in food industry^{9,10} and medicinal and pharmacy research.^{11,12}

On standard anion-exchange stationary phases carboxylic acids, such as formate and acetate elute between fluoride and chloride. It is difficult to separate them under isocratic conditions and determine by conductivity detection. This is a problem for most laboratories with only standard IC equipment. Each developed method should be validated before application for real samples. The main aim of the study was to develop and validate a method for the simultaneous determination of selected carboxylic acids (formate, acetate and oxalate) and inorganic anions (F^- , Cl^- , NO_2^- , Br^- , NO_3^- , PO_4^{3-} , SO_4^{2-}) by using isocratic ion chromatography with conductivity detection. The research methodology developed has been verified during the analysis of real samples. A preliminary study on possible oxidation of aldehydes to carboxylic acids has been carried out. The possibilities and limitations of the use of isocratic IC for the determination of

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carbonyl compounds are known and described in textbooks. The novelty of our work concerns optimization with the use of several analytical columns with different characteristics. This gives laboratories with only basic equipped IC the opportunity to perform such analyzes in a specific range.

2. Experimental

2.1. Reagents and Materials

Standard solutions of organic and inorganic anions were prepared by dilution of their stock solutions (1000 mg·L⁻¹ each, standards for IC Sigma Aldrich, USA) in Milli-Q-Gradient ultrapure deionized water (Millipore, Merck). Na₂CO₃ and NaHCO₃ for eluent preparation were purchased from SPC Science AccuSPEC (ACS Grade, France). NaOH solution (50 % in water) was purchased from Sigma Aldrich (USA). Acetaldehyde (ACS reagent, ≥99.5 %, Sigma Aldrich, USA) was used as a standard for

aldehydes determination. Syringe filters with a 0.22 μm hydrophilic polyvinylidene fluoride (PVDF) and a polyethersulfone (PES) filter membrane from Filtrakon (Poland) were used for the real samples filtration. The influence of the syringe filter material on results reliability was checked.

2.2. Instrumentation

Determination of inorganic and organic anions has been carried out on Dionex ICS-1100 (Thermo Scientific, USA) ion chromatograph equipped with conductivity detector, isocratic pump, anion dynamically regenerated suppressor, and injection valve with a 25 μL sample loop. For the method development six anion-exchange columns were tested: Metrohm Metrosep A Supp 5 (Switzerland) and five from Dionex: IonPac AS9-HC, IonPac AS22, IonPac AS14, IonPacAS4A-SC, and IonPac AS10 (Thermo Scientific, USA). The chromatograms are analysed using the Chromeleon software. The analytical conditions recommended by Metrohm and Dionex for the separation of inorganic and organic anions are reported in Table 1.

Table 1. The analytical conditions recommended by Metrohm and Dionex for the separation of inorganic and organic anions

| Column | Eluent | Eluent flow rate, mL·min ⁻¹ |
|---------------------------|------------------------------------------------------------------|----------------------------------------|
| Metrohm Metrosep A Supp 5 | 3.2mM Na ₂ CO ₃ + 1.0mM NaHCO ₃ | 0.7 |
| Dionex IonPac AS9-HC | 9.0mM Na ₂ CO ₃ | 1.0 |
| Dionex IonPac AS22 | 4.5mM Na ₂ CO ₃ + 1.4mM NaHCO ₃ | 1.2 |
| Dionex IonPac AS14 | 3.5mM Na ₂ CO ₃ + 1.0mM NaHCO ₃ | 1.2 |
| Dionex IonPac AS4A | 1.7mM NaHCO ₃ +1.8mM Na ₂ CO ₃ | 2.0 |
| Dionex IonPac AS10 | 80mM NaOH | 1.0 |

Table 2. Optimization parameters of the separation procedure

| Column | Eluent | Eluent flow rate, mL·min ⁻¹ |
|---------------------------|------------------------------------------------------------------|----------------------------------------|
| Metrohm Metrosep A Supp 5 | 3.2mM Na ₂ CO ₃ + 1.0mM NaHCO ₃ | 0.4–0.7 |
| | 2.1mM Na ₂ CO ₃ + 2.1mM NaHCO ₃ | 0.7 |
| | 1.0mM Na ₂ CO ₃ + 3.2mM NaHCO ₃ | 0.7 |
| Dionex IonPac AS9-HC | 9mM Na ₂ CO ₃ | 0.4–1.0 |
| | 3.6mM Na ₂ CO ₃ | 0.7 |
| | 4.5mM Na ₂ CO ₃ + 4.5mM NaHCO ₃ | 1.0 |
| | 1mM Na ₂ CO ₃ + 8mM NaHCO ₃ | 1.0 |
| Dionex IonPac AS22 | 4.5mM Na ₂ CO ₃ + 1.4mM NaHCO ₃ | 0.5–1.2 |
| | 1.5mM Na ₂ CO ₃ + 4.5mM NaHCO ₃ | 1.2 |
| | 1.4mM Na ₂ CO ₃ + 4.5mM NaHCO ₃ | 1.2 |
| | 3.0mM Na ₂ CO ₃ + 2.9mM NaHCO ₃ | 1.2 |
| Dionex IonPac AS14 | 3.2mM Na ₂ CO ₃ + 1.0mM NaHCO ₃ | 0.5–1.0 |
| | 1.0mM Na ₂ CO ₃ + 3.2mM NaHCO ₃ | 1.0 |
| | 1.5mM Na ₂ CO ₃ + 1.0mM NaHCO ₃ | 1.2 |
| Dionex IonPac AS4A | 1.8mM Na ₂ CO ₃ + 1.7mM NaHCO ₃ | 1.0 |
| | 1.0mM Na ₂ CO ₃ + 2.5mM NaHCO ₃ | 1.0 |
| | 3.5mM NaHCO ₃ | 1.5 |
| | 0.5mM NaHCO ₃ | 2.0 |
| Dionex IonPac AS10 | 25–50 mM NaOH | 1.0 |

2.3. Real Samples

Bulk deposition samples were collected in October 2018 in Bytom (Upper Silesia, Poland), using polyethylene bottles. Samples were filtered through a 0.22 μm PVDF syringe filter and were stored at 4 $^{\circ}\text{C}$ before analyses. Bulk deposition samples were used for method validation process.

2.4. Method Optimization

Standard sample consisting of: fluoride (5 $\text{mg}\cdot\text{L}^{-1}$), formate (5 $\text{mg}\cdot\text{L}^{-1}$), acetate (15 $\text{mg}\cdot\text{L}^{-1}$), chloride (5 $\text{mg}\cdot\text{L}^{-1}$), nitrite (5 $\text{mg}\cdot\text{L}^{-1}$), nitrate (10 $\text{mg}\cdot\text{L}^{-1}$), bromide (5 $\text{mg}\cdot\text{L}^{-1}$), sulfate (10 $\text{mg}\cdot\text{L}^{-1}$), phosphate (5 $\text{mg}\cdot\text{L}^{-1}$), and oxalate (10 $\text{mg}\cdot\text{L}^{-1}$) were used for simultaneous separation and determination of anions by using separation conditions recommended by manufacturer of tested analytical columns (Table 1) and under various conditions (different concentration of eluent components and eluent flow rates). Details are given in Table 2.

2.5. Method Validation

Validation parameters such as repeatability, limit of detection, limit of quantification, linearity and correlation coefficient, and recovery were calculated. Repeatability was calculated for concentrations of all anions in real bulk deposition samples after ten injections of bulk deposition sample within one analytical run. Coefficient of variation was used to express the method repeatability. Limits of detection and limits of quantification were calculated from calibration curves of anions and were based on Eqs. (1) and (2):

$$L_{OD} = \frac{3.3 \cdot S_d}{b} \quad (1)$$

$$L_{OQ} = \frac{10S_d}{b} \quad (2)$$

where LOD is a limit of detection; LOQ is a limit of quantification; S_d is a standard deviation value; b is the slope of the calibration curve.

The standard deviation values were determined for 10 times analysis of the standard solutions at concentrations 0.06 $\text{mg}\cdot\text{L}^{-1}$, 0.2 $\text{mg}\cdot\text{L}^{-1}$, 0.4 $\text{mg}\cdot\text{L}^{-1}$, 0.6 $\text{mg}\cdot\text{L}^{-1}$, 0.4 $\text{mg}\cdot\text{L}^{-1}$, 0.1 $\text{mg}\cdot\text{L}^{-1}$, 0.1 $\text{mg}\cdot\text{L}^{-1}$, 0.5 $\text{mg}\cdot\text{L}^{-1}$, 0.1 $\text{mg}\cdot\text{L}^{-1}$, and 0.75 $\text{mg}\cdot\text{L}^{-1}$ for formate, acetate, oxalate, fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate, respectively. The linearity of the method was checked at ten concentration levels: from 0.06 to 0.6 $\text{mg}\cdot\text{L}^{-1}$, from 0.2 to 2.0 $\text{mg}\cdot\text{L}^{-1}$, from 0.4 to 4 $\text{mg}\cdot\text{L}^{-1}$, from 0.06 to 0.6 $\text{mg}\cdot\text{L}^{-1}$, from 0.4 to 4 $\text{mg}\cdot\text{L}^{-1}$, from 0.1 to 1 $\text{mg}\cdot\text{L}^{-1}$, from 0.1 to 1 $\text{mg}\cdot\text{L}^{-1}$, from 0.5 to 5 $\text{mg}\cdot\text{L}^{-1}$, from 0.1 to 1 $\text{mg}\cdot\text{L}^{-1}$, and from 0.75 to 7.5 $\text{mg}\cdot\text{L}^{-1}$ for formate, acetate, oxalate,

fluoride, chloride, nitrite, bromide, nitrate, phosphate, and sulfate, respectively. The calibration curve was constructed by plotting the concentrations of the anions standard ($\text{mg}\cdot\text{L}^{-1}$) versus the peak area ($\mu\text{S}\cdot\text{min}$). The correlation coefficient (r) of each calibration curve was calculated. The recovery was determined with measurements of the real samples spiked with known amounts of anions standard solutions.

2.6. Determination of Aldehyde by Ion Chromatography

Aldehydes could not be directly determined by isocratic ion chromatography with conductivity detection, because they do not exist in ionic form. It is necessary to oxidize them to suitable carboxylic acids. Determination of acetaldehyde by ion chromatography, indirectly after their prior oxidation to acetate using hydrogen peroxide as the oxidant was performed according to method described by Tanaka *et al.*¹³ The diagram of the applied method is shown in Fig. 1.

The oxidation of acetaldehyde (1 $\text{mg}\cdot\text{L}^{-1}$) to acetate was carried out with 1% H_2O_2 and 0.25M Na_2CO_3 . Sodium carbonate was added to the solution to produce an alkaline pH. The effect of oxidation on the content of formate, acetate, and oxalate in sample was investigated. The samples were spiked with known amounts of acetaldehyde (1 $\text{mg}\cdot\text{L}^{-1}$), formate (0.5 $\text{mg}\cdot\text{L}^{-1}$), acetate (0.5 $\text{mg}\cdot\text{L}^{-1}$), and oxalate (1 $\text{mg}\cdot\text{L}^{-1}$) standard solutions and next were oxidized. The recovery for each ion was calculated.

3. Results and Discussion

3.1. The Influence of the Syringe Filter Material on Results Reliability

The selection of syringe filter is important because they may influence results of analysis. Differences between formate and acetate concentrations after sample filtering through 0.22 μm PES syringe filter and 0.22 μm PVDF syringe filter were observed (Fig. 2).

Syringe filters made of PES are commonly used in sample preparation process, but they are not suitable for sample preparation in case of low molecular carboxylic acids. It was noticed that formate and acetate concentrations were higher when the sample was filtered through 0.22 μm PES syringe filter than through 0.22 μm PVDF syringe filter. Thus, syringe filters made of PVDF were used for sample preparation in further study.

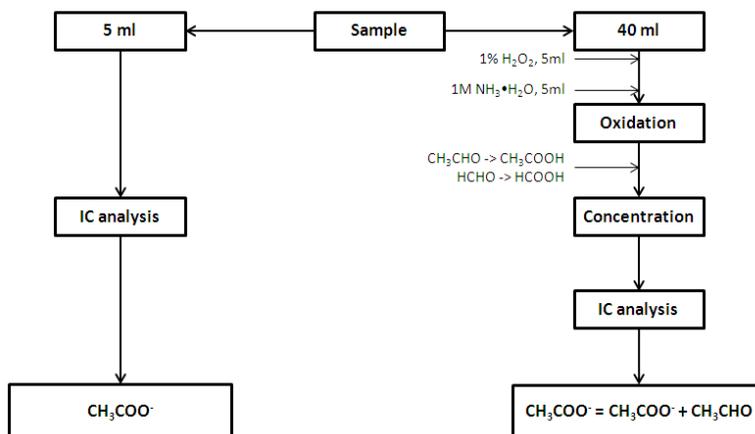


Fig. 1. Scheme of the method of acetaldehyde to acetate oxidation¹³

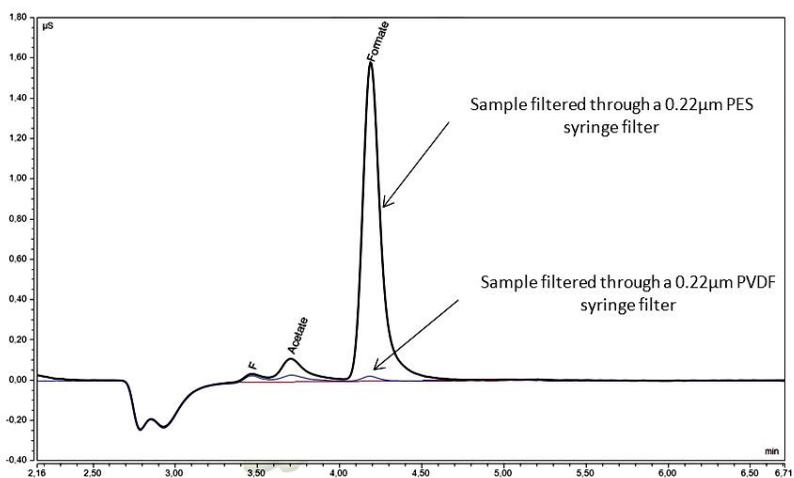


Fig. 2. The influence of syringe filter types used in the sample preparation on acetate and formate concentrations

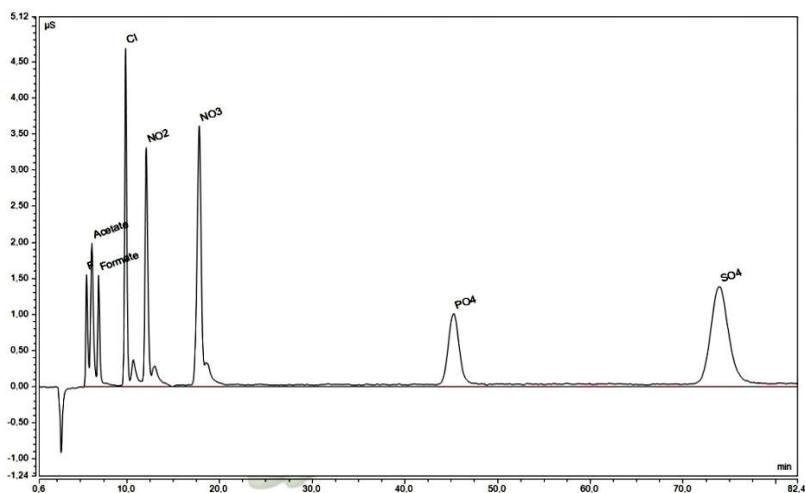


Fig. 3. Separation of selected organic and inorganic anions for Dionex IonPac AS9-HC column (eluent: 1mM Na₂CO₃ + 8mM NaHCO₃; eluent flow rate: 1 mL·min⁻¹)

3.2. Simultaneous Separation of Inorganic Anions and Carboxylic Acids – Method Optimization

Methods optimization by using Dionex IonPac AS4-SC, Metrohm Metrosep A Supp 5 and Dionex IonPac AS14 columns in various conditions given in Table 2 did not yield satisfactory results. Better results were obtained for the columns Dionex IonPac AS9-HC, Dionex IonPac AS22, and Dionex IonPac AS10. Examples of chromatograms for these columns are shown in the Figs. 3-5. According to manufacturer, Dionex IonPac AS9-HC column is recommended for the analysis of inorganic anions and oxyhalides including bromate, chlorite, and chlorate. For this column the best separation has been achieved with 1mM Na_2CO_3 + 8mM NaHCO_3 eluent and its flow rate of $1 \text{ mL}\cdot\text{min}^{-1}$. Anyway, due to very long retention times for sulfate and oxalate ($> 70 \text{ min}$) these conditions are not suitable for routine analysis.

The chromatograms of standard samples for Dionex IonPac AS22 column is shown in Fig. 4. The best

separation for this column has been obtained with 0.6mM Na_2CO_3 + 5.5mM NaHCO_3 eluent, and flow rate of $1.2 \text{ mL}\cdot\text{min}^{-1}$. Unfortunately, retention times for sulfate and oxalate are also very long ($> 60 \text{ min}$).

The best results for carboxylic acids have been obtained for Dionex Ion Pac AS10 column. Example chromatograms are given in Fig. 5.

In the case of that column the best separation was achieved with 25mM NaOH eluent and its flow rate $1.0 \text{ mL}\cdot\text{min}^{-1}$, but the time of analysis of sample was too long. A better option is using 50mM NaOH as a mobile phase. The Dionex IonPac AS10 column was selected as the best column for chromatographic separations of real samples.

3.3. Method Validation

The method was validated on a Dionex IonPac AS10 column using 50mM NaOH as mobile phase at the flow rate of $1.0 \text{ mL}\cdot\text{min}^{-1}$. The method was validated in terms of precision, linearity, limit of detection, limit of quantification, and recovery.

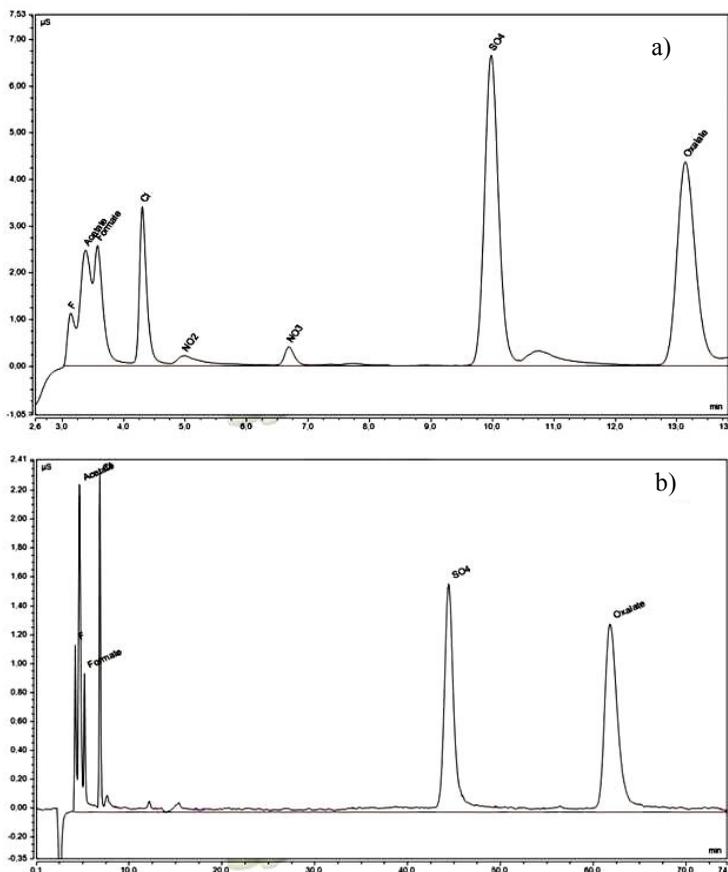


Fig. 4. Chromatograms of standard sample for Dionex IonPac AS22 column: a – eluent: 4.5mM Na_2CO_3 + 1.4mM NaHCO_3 , eluent flow rate: $1.2 \text{ mL}\cdot\text{min}^{-1}$; b – eluent 0.6mM Na_2CO_3 + 5.5mM NaHCO_3 ; eluent flow rate: $1.2 \text{ mL}\cdot\text{min}^{-1}$

The satisfactory recovery values were reached in analysis of the spiked bulk deposition samples and water samples. Recoveries at the level of 91–102 % with relative standard deviation of below 13 % were achieved. Precision of repeatability expressed as relative standard deviations was <10 % for all analyzed anions. Deter-

mination of organic and inorganic anions showed a linear calibration curve within the concentration range described in Method validation section. Correlation coefficients for all analyzed anions were higher than 0.998. Calculated LOD values and other method validation parameters are summarized in Table 3.

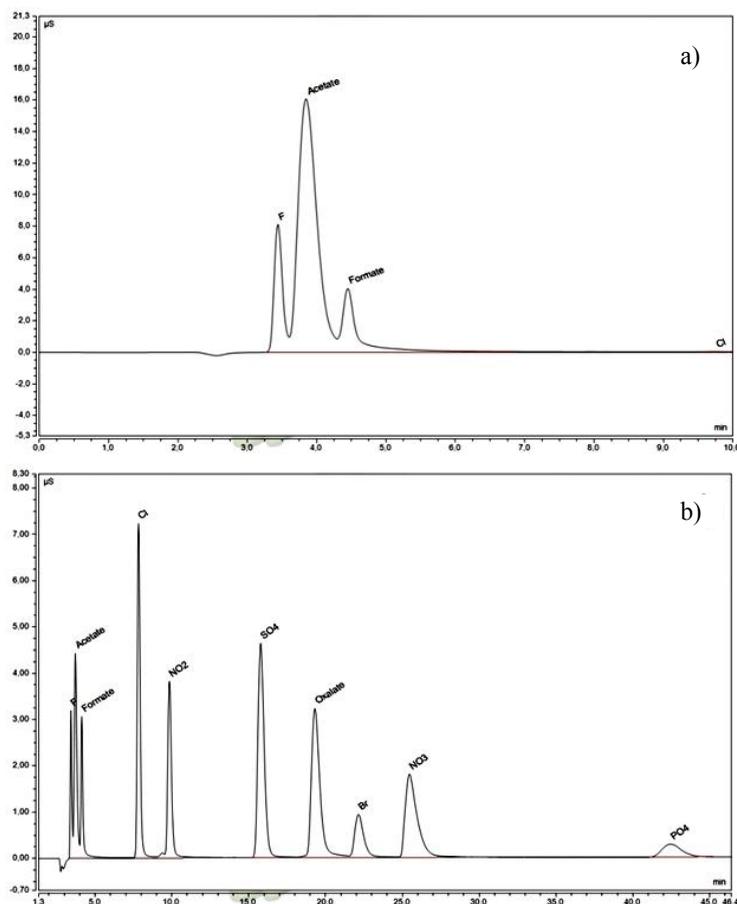


Fig. 5. Chromatograms of standard sample for Dionex IonPac AS10 column (a – eluent: 25 mM NaOH, eluent flow rate: 1.0 mL min⁻¹; b – eluent 50 mM NaOH, eluent flow rate: 1.0 mL min⁻¹)

Table 3. Selected method validation parameters

| Anion | Parameter | | | | |
|-----------|-------------------------------------------------|-------------------------|-------------------------|-------------------------|--------------------|
| | Relative standard deviation of repeatability, % | LOD, mg·L ⁻¹ | LOQ, mg·L ⁻¹ | Correlation coefficient | Recovery, % (± SD) |
| Formate | 7.86 | 0.020 | 0.061 | 0.999 | 94.0 ± 12.4 |
| Acetate | 9.12 | 0.028 | 0.084 | 0.999 | 102.4 ± 13.4 |
| Oxalate | 8.60 | 0.044 | 0.130 | 0.998 | 91.9 ± 12.3 |
| Fluoride | 7.34 | 0.021 | 0.063 | 0.999 | 91.2 ± 9.3 |
| Chloride | 4.07 | 0.063 | 0.191 | 0.999 | 97.2 ± 6.5 |
| Nitrite | 8.41 | 0.027 | 0.082 | 0.998 | 92.1 ± 9.3 |
| Bromide | 9.87 | 0.028 | 0.086 | 0.999 | 92.3 ± 8.7 |
| Nitrate | 5.07 | 0.115 | 0.348 | 0.999 | 96.4 ± 7.4 |
| Phosphate | 7.77 | 0.032 | 0.097 | 0.998 | 93.4 ± 9.6 |
| Sulfate | 4.82 | 0.160 | 0.486 | 0.999 | 97 ± 6.1 |

3.4. Research onto Aldehydes Determination by Isocratic Ion Chromatography

The mean oxidation efficiency of acetaldehyde to acetate is 74.9 % with RSD below 5 %. Chromatogram of oxidation products of acetaldehyde, acetate, formate, and oxalate is shown in Fig. 6.

The effect of oxidation on the content of formate, acetate and oxalate in sample was investigated. Recovery

for each organic ion is given in Table 4. The acetate recovery was calculated assuming that the oxidation efficiency of acetaldehyde was 75 %. The mean acetate recovery was 72.9 % with RSD of 2.19 %. It was observed that the acetate recovery was significantly lower than formate and oxalate recovery. The formate and oxalate recoveries were very similar, and were 112 % and 111 % for formate and oxalate, respectively (RSD were 15.5 % and 4.07 %, respectively).

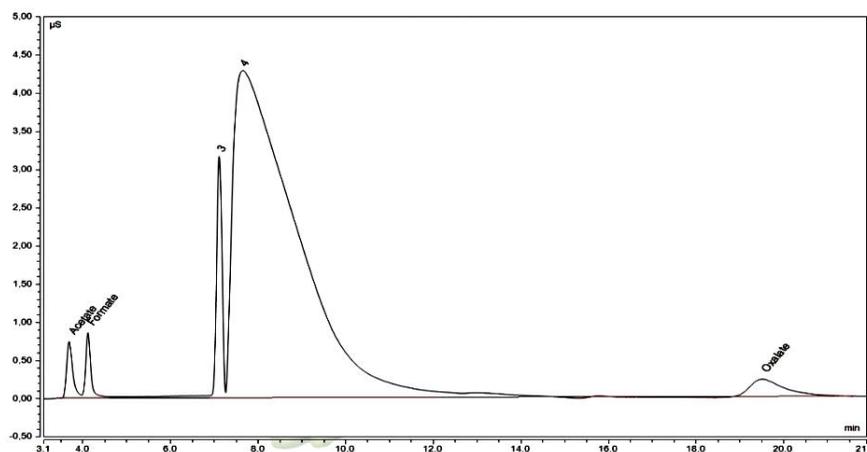


Fig. 6. Chromatogram of oxidation products of acetaldehyde, acetate, formate, and oxalate

Table 4. Recovery of acetate, formate, and oxalate after oxidation by H_2O_2

| Sample | Recovery, % | | |
|---------|-------------|---------|---------|
| | Acetate | Formate | Oxalate |
| 1 | 72.8 | 126 | 119 |
| 2 | 75.4 | 126 | 115 |
| 3 | 70.3 | 120 | 110 |
| 4 | 73.9 | 122 | 109 |
| 5 | 72.1 | 119 | 106 |
| 6 | 73.5 | 85.0 | 106 |
| 7 | 72.3 | 89.9 | 110 |
| Mean, % | 72.9 | 112 | 111 |
| RSD, % | 2.19 | 15.5 | 4.07 |

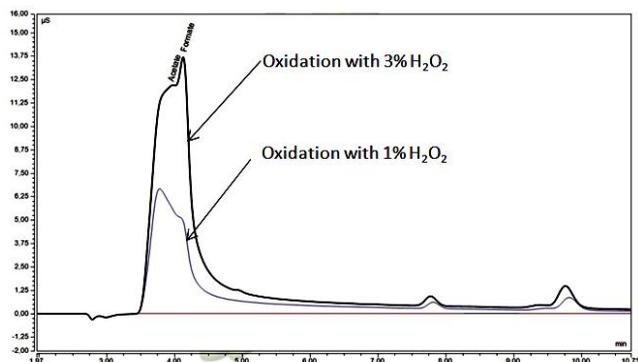


Fig. 7. The influence of H_2O_2 on the size and shape of peaks

Due to the lack of knowledge about the concentration of aldehydes in real samples, H_2O_2 has been added to the sample in excess. It was observed that hydrogen peroxide has a negative effect on stationary phase in analytical column. Fig. 7 presents the influence of H_2O_2 on the analytical column performance.

Due to the negative influence of H_2O_2 peroxide on stationary phase in analytical column, the studies have been interrupted.

4. Conclusions

Isocratic ion chromatography with suppressed conductometric detection for simultaneous separation and

determination of formic and acetic acids, as well as the main inorganic anions was developed and validated. The conclusions of the research are as following:

- Three out of six tested columns from Dionex (IonPac AS9-HC, IonPac AS22, IonPac AS10) allows to satisfactory simultaneously separate formate, acetate, oxalate, and common inorganic anions. The best results were obtained for Dionex IonPac AS10 column. Optimized separation conditions were used for method validation.

- The accuracy of the developed method was evaluated by recovery measurement on spiked bulk deposition samples (recovery results 91–102 % with relative standard deviation of below 13 % were achieved). Precision of the method expressed as RSD was <9 %. LODs values were: 61, 84 and 119 $\mu\text{g}\cdot\text{L}^{-1}$ for formate, acetate, and oxalate, respectively.

- Indirect analysis of aldehydes in bulk deposition samples by oxidation of aldehydes to carboxylic acids with H_2O_2 and determination of reaction products could irreversibly change the performance of the analytical column and the membrane suppressor.

- Filtration of samples through filters made of PES significantly increases the concentration of formate and affects the concentration of acetate in the sample. A good alternative is syringe filters made of PVDF.

- There is a necessity in further optimization of the developed method so that it can be used during the analysis of bulk deposition samples (e.g. using a larger injection loop).

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ОПТИМІЗАЦІЯ МЕТОДІВ ІЗОКРАТНОЇ ЙОННОЇ ХРОМАТОГРАФІЇ ДЛЯ ОДНОЧАСНОГО ВИЗНАЧЕННЯ НЕОРГАНІЧНИХ АНІОНІВ І КАРБОНОВОЇ КИСЛОТИ

Анотація. Перевірено можливість кількісного окиснення альдегідів до карбонових кислот та їх визначення методом ізократної йонної хроматографії з кондуктометричним детектором. З використанням хроматографії розроблена і перевірена методологія одночасного розділення неорганічних аніонів (F-, Cl-, NO₂-, Br-, NO₃-, PO₄³⁻, SO₄²⁻) та карбонових кислот (форміат, ацетат та оксалат). Проведені випробування шести аніонообмінних колонок. Встановлено, що найкращі результати отримані для колонки Dionex IonPac AS10 з 50мМ елюентом NaOH і швидкістю потоку 1,0 мл·хв⁻¹.

Ключові слова: аніони, йонна хроматографія, валідація, оптимізація.