

Short communication

Simultaneous determination of fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulfate in aqueous solutions at 10^{-9} to $10^{-8}\%$ level by ion chromatography

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Abstract

The method of simultaneous determination of F^- , Cl^- , NO_2^- , Br^- , NO_3^- , HPO_4^{2-} , SO_4^{2-} ions on trace level by IC using preliminary concentration and water removal from concentrating column was proposed. Detection limits were 10^{-9} to $10^{-8}\%$ for sample volume 10 ml depending on the anion.

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1. Introduction

Determination of anions on the trace level in ultrapure water is of prime interest. Now ion chromatography (IC) is high selective, high sensitive and fast method of anion content determination in water. This method allows direct determination of anions in water on the level of 10^{-6} to $10^{-4}\%$, depending on anion, sample volume and instrument [1–5]. However, direct determination of anions in water by IC cannot provide sensitivity necessary for ultrapure water analysis. Therefore, preliminary concentration on a concentrating column is necessary.

Nowadays discrepancy of detection limits (10^{-8} to $10^{-7}\%$) in various works is observed [6–8]. In these publications, the data on blank experiment using large sample volume injection were absent, and simultaneous determination of F^- , Cl^- , NO_2^- , Br^- , NO_3^- , HPO_4^{2-} , SO_4^{2-} anions in water was not considered. Due to interferences with negative water peak, the obtained chromatograms were unable to provide the accurate registering of fluoride and chloride peaks. The attempt to decrease water dip interference thanks to partial removal of water from concentrating column was performed [6] but separation of water peak and F^- anion peak was not achieved.

Detection limits for chloride, nitrate and sulfate in article [9], according to the authors, were on the $10^{-10}\%$ level. However, examination of chromatograms of the mixture of the anions in water on the level $(8-70) \times 10^{-10}\%$, given in the article shows that the presented data are not agreed with those claimed at this level.

The purpose of this work was to investigate the possibility of simultaneous determination of F^- , Cl^- , NO_2^- , Br^- , NO_3^- , HPO_4^{2-} , SO_4^{2-} in water on the ultratrace level by IC using preconcentration.

2. Experimental part

2.1. Instrumentation

The investigation was carried out on an ion chromatograph “761 Compact IC” (Metrohm, Herisau, Switzerland) with anion self-regenerating suppressor Metrohm Suppressor Module MSM (Fig. 1) and conductivity detector. Separation of anions was carried out on a column “Star-Ion-A300” (100 mm \times 4.60 mm) (Phenomenex, Torrance, USA). A “Metrosep A PCC 1 HC” column (12.5 mm \times 4.0 mm) (Metrohm, Herisau, Switzerland) was used for preconcentration.

The sample loop of 20 μ l volume was used in our work. Sample injection of anion mixtures into the ion chromatograph was carried out using 5 ml “Becton Dickinson” syringe (Fraga, Spain).

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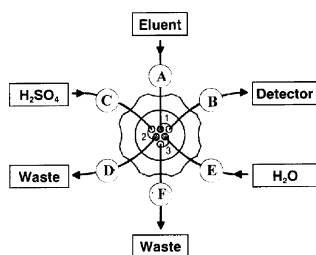


Fig. 1. Connections at suppressor module “Metrohm Suppressor Module MSM” (Metrohm). (1, 2, 3) Suppressor columns; (A) suppressor inlet capillary for eluent; (B) suppressor outlet capillary for eluent; (C) suppressor inlet capillary for H_2SO_4 ; (D) suppressor outlet capillary for H_2SO_4 ; (E) suppressor inlet capillary for H_2O ; (F) suppressor outlet capillary for H_2O .

2.2. Chemicals

Respective salts (Merck, Darmstadt, Germany) were used for preparation of anion standard solutions (concentration range 5×10^{-3} to $5 \times 10^{-8}\%$). Na_2CO_3 and NaHCO_3 (Merck, Darmstadt, Germany) were used for the preparation of eluent. Regenerating solution (20 mM H_2SO_4 , Boris Avogadro, Moscow, Russia) was prepared using high concentrated sulfuric acid. Deionized water with a specific resistance of $18.2 \text{ M}\Omega \text{ cm}$ from Milli-Q water purification system (Millipore, Bedford, USA) was used for preparation of all aqueous solutions. All standard solutions were stored in quartz glassware.

3. Results

Various combinations of Na_2CO_3 and NaHCO_3 were tested as eluent (flow rate 0.5–1.5 ml/min). Detection limits for the ions in case of injection of aqueous solution (20 μl sample loop) into the ion chromatograph were determined. Optimum detection limits and separation of anions were obtained using 3.6 mM NaHCO_3 /3.75 mM Na_2CO_3 eluent and 0.5 ml/min flow rate. The dependence of peak height on anion concentration was linear through all concentration range (5×10^{-3} to $5 \times 10^{-6}\%$). Detection limits were 3.5×10^{-7} , 0.6×10^{-6} , 1.7×10^{-6} , 2.4×10^{-6} , 2.0×10^{-6} , 0.8×10^{-5} and $1.1 \times 10^{-6}\%$, for F^- , Cl^- , NO_2^- , Br^- , NO_3^- , HPO_4^{2-} , SO_4^{2-} , respectively (sample volume 20 μl). Standard relative deviation was within 20% ($n = 3, P = 0.95$). Example of the chromatogram, obtained on injection of anion model solution is given in Fig. 2A.

The possibility of preconcentration of anions using an ion-exchange concentrating column (12.5 mm \times 4.0 mm) was investigated. It was connected to ion chromatograph instead of the sample loop.

Content of chloride in deionized water was about $0.5 \times 10^{-7}\%$. No peaks of the other anions in question were detected in deionized water on the detection limit level (sample volume 10 ml). Example of the chromatogram, obtained on injection of 10 ml of water sample containing all the tar-

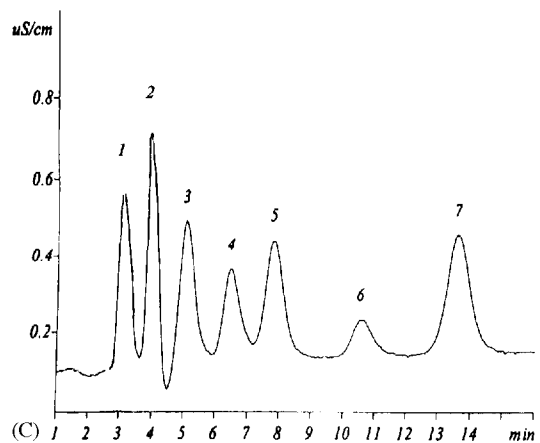
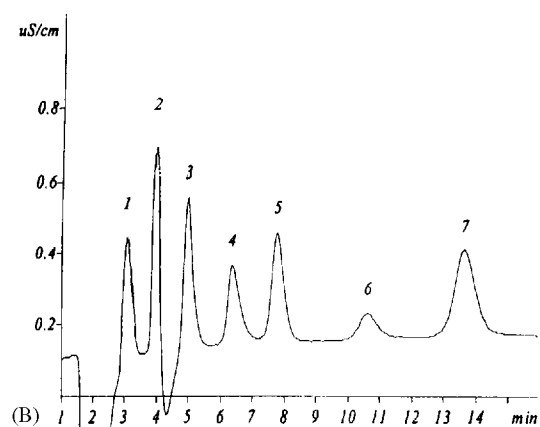
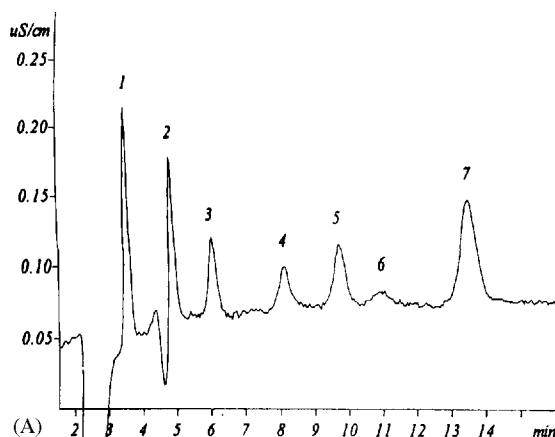


Fig. 2. Chromatogram obtained on injection of sample anions (eluent 3.6 mM NaHCO_3 /3.75 mM Na_2CO_3 , 0.5 ml/min flow rate). (A) sample loop volume 20 μl : (1) fluoride ($0.50 \times 10^{-5}\%$), (2) chloride ($0.60 \times 10^{-5}\%$), (3) nitrite ($0.70 \times 10^{-5}\%$), (4) bromide ($0.68 \times 10^{-5}\%$), (5) nitrate ($0.74 \times 10^{-5}\%$), (6) phosphate ($0.69 \times 10^{-5}\%$), (7) sulfate ($1.1 \times 10^{-5}\%$). (B) 10 ml of sample anions using preconcentration without water eliminating from preconcentrating column: (1) fluoride ($2.7 \times 10^{-8}\%$), (2) chloride ($0.6 \times 10^{-7}\%$), (3) nitrite ($1.0 \times 10^{-7}\%$), (4) bromide ($0.8 \times 10^{-7}\%$), (5) nitrate ($0.9 \times 10^{-7}\%$), (6) phosphate ($1.2 \times 10^{-7}\%$), (7) sulfate ($0.9 \times 10^{-7}\%$). (C) 10 ml of sample anions using preconcentration and water eliminating from preconcentrating column. The concentrations of all the anions were same as in (B).

get anions is given in Fig. 2B. It clearly shows that the water dip interferes with peaks of fluoride and chloride. The intermediate washing of concentrating column with eluent before sample injection into the analytical column for decreasing the water dip interference was investigated. Optimum eluent volume was found to be 500 μ l. Example of the chromatogram, obtained on successive injection of 10 ml of water sample containing all the target anions and 500 μ l of eluent is given in Fig. 2C. Under these conditions the reliable determination of F^- and Cl^- was provided. Concentration detection limits were 0.8×10^{-9} , 5.0×10^{-8} , 0.4×10^{-8} , 0.5×10^{-8} , 0.6×10^{-8} , 1.4×10^{-8} and 0.3×10^{-8} %, for F^- , Cl^- , NO_2^- , Br^- , NO_3^- , HPO_4^{2-} , SO_4^{2-} . Detection limit of chloride was confined by its content in deionized water.

4. Conclusion

The method of simultaneous determination of F^- , Cl^- , NO_2^- , Br^- , NO_3^- , HPO_4^{2-} , SO_4^{2-} anions on the trace

level by ion chromatography using preconcentration and water eliminating from preconcentrating column was investigated. Concentration detection limits for these anions were 10^{-9} to 10^{-8} %, depending on anion (sample volume 10 ml).

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