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TRACE LEVEL DETERMINATION OF INORGANIC ANIONS AND CATIONS IN WATER

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OZNACZANIE ŚLADÓW NIEORGANICZNYCH ANIONÓW I KATIONÓW W WODACH

Analiza ultraśladowa wymaga stosowania ekstremalnie czystych odczynników, w tym wody. Jakość wody stosowanej w laboratoriach decyduje o wiarygodności uzyskiwanych wyników. W laboratoriach chemicznych i biologicznych, jak również przemysłowych, stosowana jest woda destylowana, redestylowana i dejonizowana. Ważnym parametrem określającym jakość wody jest zawartość nieorganicznych jonów. Jedną z najbardziej odpowiednich metod analitycznych w zakresie oznaczania nieorganicznych anionów i kationów jest chromatografia jonowa. W pracy opisano zastosowanie chromatografii jonowej do oznaczania śladowych ilości nieorganicznych anionów (fluorków, chlorków, azotanów(V), fosforanów i siarczanów(VI) oraz kationów (litu, sodu, amonu, potasu, magnezu i wapnia) w wodach destylowanych, redestylowanych i dejonizowanych.

Summary

Ultratrace analysis requires the use of extremely clean reagents, including water. Quality of water used in laboratories is crucial element of obtained reliable results. In chemical and biological laboratories, as well as industry, distilled, re-distilled and deionized waters are used. Important factor of water quality is the content of inorganic ions. One of the most competitive analytical techniques for trace analysis of inorganic anions and cations is ion chromatography. In the work ion chromatographic method for the determination of common inorganic anions (fluoride, chloride, nitrate, phosphate and sulfate) and cations (lithium, sodium, ammonium, potassium, magnesium and calcium) in distilled, re-distilled and deionized water has been developed and validated.

INTRODUCTION

Due to the increased sensitivity of instrumentation analytical detection limits can now reach ng/dm^3 (ppt) levels in routine basis, and even pg/dm^3 (ppq) levels under certain conditions [1].

The boundaries of trace analysis are described by the definition of "trace element" in the IUPAC Compendium of Chemical Terminology – "*Any element having an average concentration of less than about 100 parts per million atoms or less than 100 μg/g*". There is no agreement about the range of ultratrace analysis and no rigorous definition. Within the literature, the term "ultratrace analysis" is used for the definition of elements at mass fractions less than 10^{-6} and 10^{-8} g/g (1 ppm and 10 ppb).

Water is omnipresent variable in many chemical analyses, whether it is used as a reagent, eluent mobile phase, cleaning agent, sample solvent or reference material. Its composition must be well-characterized and controlled in order to obtain sensitive, precise, accurate and error-free results. To maintain the purity from the high-quality production, storage containers must be chosen that do not leach contaminants and are impermeable to atmospheric gases.

Water quality is testified by the national and international norms that have been developed for the specification of purified water for different applications. ISO 3696:1987 [3], for example, specifies three different types of water. Type 1 is the highest analytical grade for high-purity analysis such as High Performance Liquid Chromatography (HPLC) and Ion Chromatography (IC) trace analysis and is largely free of dissolved impurities (inorganic and organic), colloidal impurities, specified for conductivity, UV adsorption at 254 nm and SiO_2 content.

Type 2 water contains very low inorganic, organic or colloidal contaminants and is suitable for sensitive analytical purposes including atomic absorption spectrometry (AAS) and the determination of constituents in trace quantities. This water type can be produced by multiple distillation, ion exchange or reverse osmosis followed by distillation. Type 3 water is suitable for most laboratory wet chemistry work and preparation of reagent solutions. It can be produced by single distillation, by ion exchange, or by reverse osmosis.

From the practical point of view, the most important parameters affecting water quality and possibilities of its using is the content of inorganic anions and cations, which determine water electrical conductivity.

Classical "wet" chemical methods are not suitable for trace level analysis, thus ion chromatography has become the most important instrumental method. The sensitivity of ion chromatography makes it ideal for low-ppm level quantification, and also for trace analysis, it therefore creates the requirements for high purity eluents and well-defined standards [2, 8]. Ion chromatography, combined with conductivity measurement, has become a reliable and popular method for analyzing a large variety of anions and cations in environmental samples [5–7].

Although cations are usually determined by spectroscopic techniques such as Atomic Spectrometric Absorption (AAS) or Inductively Coupled Plasma (ICP), simultaneous determination of ammonium and inorganic anions can be analyzed on trace level concentration only by ion chromatography.

The aim of the presented work is application of ion chromatography for the determination of trace levels of inorganic anions (F^-, Cl^-, NO_3^-, PO_4^{3-} and SO_4^{2-}), and cations (Li^+, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+}) in several distilled, re-distilled and deionized waters.

EXPERIMENTAL

Ion chromatographic separations were performed on Metrohm ion chromatography system (Herisau Metrohm AG, Switzerland) consisting of: 818 IC Pump, 837 IC Eluent Degasser, 830 IC Interface, 820 IC Separation Center, Rheodyne injection valve, Metrodata 2.3 software, autosampler (838 Advanced Sample Processor), MSM suppressor, and conductivity detector (819 IC).

For inorganic anions determination analytical grades of: Na_2CO_3, $NaHCO_3$ used for eluent preparation and 95% H_2SO_4 as a regenerant solution were obtained from Fluka (Fluka, Steinheim, Switzerland). Standard solutions of inorganic anions were prepared by dissolving suitable salts in water. Analytical grades of: KF, NaCl, $NaNO_3$, K_3PO_4 and Na_2SO_4 were purchased from Fluka (Fluka, Steinheim, Switzerland).

For inorganic cations determination analytical grades of: tartaric acid and 1,2-dipicolinic acid used for eluent preparation were obtained from Fluka (Fluka, Steinheim, Switzerland). Standard solutions of inorganic cations were prepared by dissolving suitable salts in water. Analytical grades of: LiCl, NaCl, NH_4Cl, KCl, $Mg(NO_3)_2$ and $Ca(NO_3)_2$ were purchased from Fluka (Fluka, Steinheim, Switzerland).

Water used in the experiments was purified using Millipore equipment (Millipore, Bedford, MA, USA) and had an electrical conductivity < 0.05 µS/cm.

All standard solutions were stored in a refrigerator at 2°C to 8°C. Calibration solutions of analyzed inorganic ions were prepared by diluting the stock standard solution to the required concentration just before use.

Method optimization

Within the confines of method optimization several ion-exchange columns were examined. The separation columns used in the optimization test were: Metrosepp Supp 5 (150 x 4 mm I.D.), Metrosepp Supp 5 (250 x 4 mm I.D.), Metrosepp Supp 3 (250 x 4 mm I.D.) and Metrosepp C-2 (250 x 4 mm I.D.) from Metrohm (Metrohm, Herisau, Switzerland) as well as Ion Pac AS9-SC (250 x 4 mm I.D.), IonPac AS 14 (250 x 4 mm I.D.) and IonPac CS12 (250 x 4 mm I.D.) from Dionex (Dionex, Sunnyvale, USA).

Within the confines of method optimization, two eluent concentrations (1.7 mM Na_2CO_3 + 1.5 mM $NaHCO_3$ and 3.5 mM Na_2CO_3 + 1.0 mM $NaHCO_3$), and two eluent flow rates (0.8 cm^3/min; 1.0 cm^3/min) were tested. The column oven was maintained at 32°C. Samples were injected using $100 \cdot 10^{-6}$ dm^3 loop injector. The best chromatographic performances were obtained for the following analytical conditions:

Anions separation:
Analytical column – Metrohm Metrosepp Supp 3
Eluent – 3.5 mM Na_2CO_3 + 1.0 mM $NaHCO_3$
Flow rate – 1.0 cm^3/min
Detection – Suppressed conductivity
Suppressor – MSM
Cations:
Analytical column – Metrosepp C2-250
Eluent – 8.0 mM tartaric acid + 1.5 mM 1,2-dipicolinic acid
Flow rate – 0.9 cm^3/min
Detection – Non-suppressed conductivity

Analyzed water samples

The objects of research were 5 distilled waters, 3 re-distilled waters and 5 deionized waters obtained from different users (commercial and government laboratories from Upper Silesia, Poland). Distilled water was obtained usually from 1–4 year old distillation and re-distillation apparatus.

Table 1. Method validation parameters

Parameter	F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Li^+	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Concentration range [mg/dm³]	0.02–0.2	0.3–3.0	0.02–0.2	0.01–0.1	0.1–1.0	0.01–0.1	0.3–3.0	0.05–0.5	0.1–1.0	0.1–1.0	0.3–3.0
Standard deviation [mg/dm³]	0.002	0.003	0.003	0.002	0.017	0.003	0.044	0.007	0.027	0.016	0.049
Coefficient of variation [%]	2.17	2.94	2.37	2.92	3.09	3.02	2.66	3.24	4.98	2.98	2.99
Limit of detection [mg/dm³]	0.005	0.007	0.006	0.004	0.038	0.007	0.099	0.008	0.062	0.037	0.111
Limit of quantification [mg/dm³]	0.019	0.022	0.021	0.013	0.134	0.023	0.356	0.035	0.210	0.130	0.390
Linearity (r)	0.9993	0.9987	0.9971	0.9967	0.9966	0.9964	0.9969	0.9974	0.9963	0.9967	0.9956

Table 2. Concentrations of common inorganic anions and cations in analyzed water (n = 3)

Sample number	pH	Electrical conductivity [µS cm⁻¹]	Ion concentrations [mg/dm³]										
			F^-	Cl^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Li^+	Na^+	NH_4^+	K^+	Mg^{2+}	Ca^{2+}
Distilled water													
1	5.65	1.462	< 0.005	0.212	0.047	< 0.004	1.231	< 0.007	0.149	< 0.008	< 0.062	< 0.037	0.564
2	6.52	3.643	0.012	0.211	0.056	< 0.004	1.586	< 0.007	0.351	< 0.008	< 0.062	0.165	0.817
3	6.16	2.601	< 0.005	0.334	0.043	< 0.004	1.617	< 0.007	0.223	0.053	< 0.062	0.219	0.482
4	6.14	2.310	< 0.005	0.375	0.028	< 0.004	1.094	< 0.007	0.257	< 0.008	< 0.062	0.188	0.712
5	6.07	9.460	0.017	0.766	0.094	< 0.004	2.316	< 0.007	0.186	0.184	< 0.062	0.272	0.936
Re-distilled water													
6	5.08	2.180	< 0.005	0.153	< 0.021	< 0.004	1.723	< 0.007	< 0.099	< 0.008	< 0.062	< 0.037	< 0.111
7	6.18	2.225	< 0.005	0.126	0.034	< 0.004	1.321	< 0.007	< 0.099	< 0.008	< 0.062	< 0.037	< 0.111
8	5.76	1.109	< 0.005	0.181	< 0.021	< 0.004	1.559	< 0.007	< 0.099	< 0.008	< 0.062	< 0.037	< 0.111
Deionized water													
9	6.65	5.109	< 0.005	0.525	0.046	< 0.004	1.185	< 0.007	0.146	< 0.008	< 0.062	0.133	0.148
10	6.24	2.789	< 0.005	0.226	< 0.021	< 0.004	0.675	< 0.007	0.323	< 0.008	< 0.062	< 0.037	< 0.111
11	5.84	0.623	< 0.005	0.084	< 0.021	< 0.004	0.272	< 0.007	< 0.099	< 0.008	< 0.062	< 0.037	< 0.111
12	6.29	0.916	< 0.005	0.105	< 0.021	< 0.004	0.558	< 0.007	< 0.099	< 0.008	< 0.062	< 0.037	< 0.111
13	6.11	1.068	< 0.005	0.137	< 0.021	< 0.004	1.042	< 0.007	0.026	< 0.008	< 0.062	< 0.037	< 0.111
Water used for calibration solution and eluent preparation													
0	6.34	0.065	< 0.005	0.010	< 0.021	< 0.004	0.141	< 0.007	< 0.099	< 0.008	< 0.062	< 0.037	< 0.111

Deionized water was obtained from: Millipore, Labconco, Smart 2000 and Istran GmBH manufacturers. According to producers and users data all of them had electrical conductivity better than 0.1 μS/cm.

Calibration and method validation

Validation was carried out with responses for peaks areas collected and evaluated. 10 calibration solutions of analyzed inorganic anions and cations prepared in deionized water were injected into the eluent stream.

Concentration ranges of analyzed anions and cations in calibration solutions, standard deviations, coefficients of variation, limits of determination, limits of quantification and regression coefficients are given in Table 1.

The limit of detection (LOD) and the limit of quantification (LOQ) were calculated as six and ten times, respectively, the ratios between the standard deviation of the regression and the slope of the calibration line.

The concentrations ranges have been chosen according to the expected concentration of analyzed distilled and deionized water samples. All samples and calibration solutions were analyzed in triplicate under optimalized chromatographic conditions.

The average concentrations of analyzed water samples including uncertainty of measurement are given in Table 2. An example chromatogram of separated anions of sample no. 3 compared with standard no. 5 is given in Figure 1. An example chromatogram of cations (repeatability, n = 3) of sample no. 9 is shown in Figure 2.

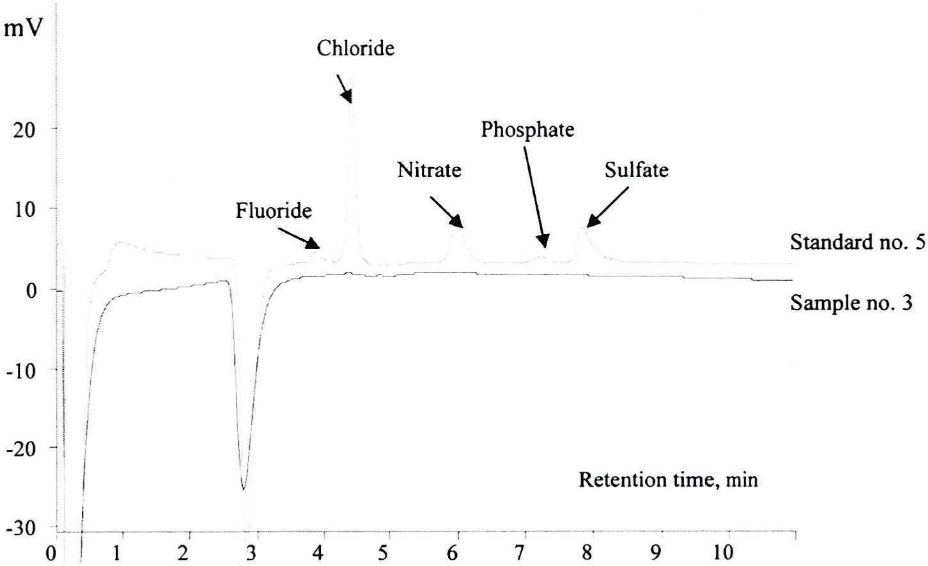

Fig. 1. Chromatograms of anions in standard no. 5 and sample no. 3

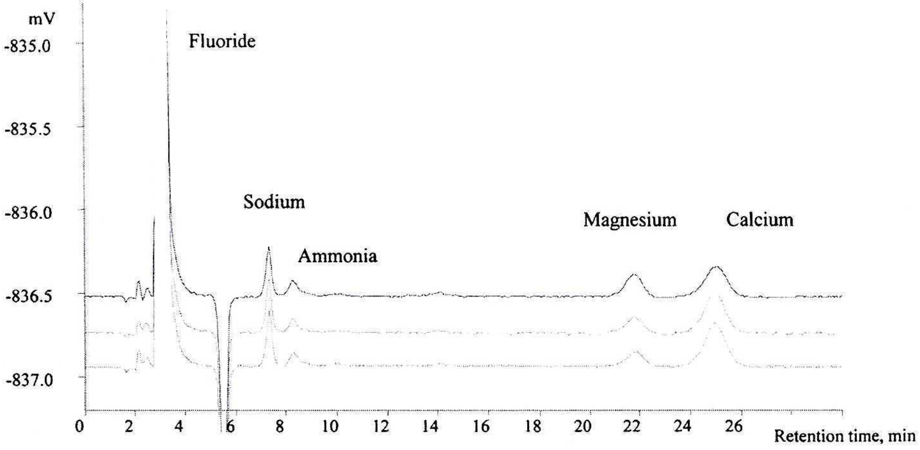

Fig. 2. Chromatograms of repeatability of cations determination in sample no. 9

RESULTS AND DISCUSSION

Water is one of the most important reagents because it is used in so many applications. Because of this broad range of application and volumes required, extreme care must be taken with water quality. In particular, in trace analysis, constant and reproducible high purity water, free of residual ions, is necessary.

High quality ultrapure water is necessary to meet all the requirements of ultratrace analysis, as required for critical cleaning and preparation of blanks and standard solutions. Water use for such purposes is usually distilled, re-distilled and deionized water. On the basis of the obtained results, the following can be concluded:

1. Isocratic ion chromatography with suitable separation columns, eluents and conductivity detection mode is fast, accurate and sensitive method for simultaneous inorganic anions and cations analysis. Determination of ions on trace level without preconcentration or other pretreatment procedure is possible using appropriate high capacity and selectivity columns (e.g. Metrohm Metrosepp Supp 3, and Metrosepp C2).
2. Analytical conditions applied for the determination of common inorganic anions and cations in analyzed water samples allows for their determination on trace μg/dm^3 levels. RSD method for all analyzed ions is below 5% (Tab. 1), and repeatability is high (Fig. 2).
3. Electrical conductivity was the highest in sample no. 5 (distilled water) and sample no. 9 (deionized water). Both samples were stored several days before measurement and probably its relatively high conductivity is concerned with CO_2 absorption from ambient air. Chloride and sodium are ubiquitous elements and they were determined in all samples. Next, phosphate and lithium were not found in any sample.
4. In general, according to the results shown in Table 2, re-distilled water is better than distilled water and even than deionized water. The best performance shows fresh prepared deionized water from new deionizer apparatus (blank sample no."0" and sample no. 11) which was used for eluent and standard preparations.

5. Depending on water use (analysis of organic compounds, metals or inorganic ions) different parameters are crucial for its quality. The quality of water depends on type and general conditions of used apparatus, however, the most important parameters are time and manner of water storage. In any case water used for trace level analysis should be freshly prepared.

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