

ION CHROMATOGRAPHIC ASSESSMENT OF DISSOLVED INORGANIC NITROGEN FROM ENVIRONMENTAL SAMPLES

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Abstract

Speciation analysis of nitrogen in water samples is an important task for environmental studies, many classical methods being available nowadays for the determination of inorganic nitrogen species NO_2^- , NO_3^- and NH_4^+ ; most of these methods are time-consuming and labor-intensive, needing also large sample volumes and big amounts of reagents. Because of its high accuracy and reliability, ion chromatography is nowadays one of the most powerful tools for analysis of environmental samples. This paper presents an advantageous analytical alternative to the classical methods, based on the ion – exchange separation of inorganic nitrogen species, followed by conductivity detection of these, enabling the simultaneous determination of ammonium, nitrite and nitrate in less than 25 minutes in a single run, using a minimal sample workup. Analyses were performed on a dual-channel Shimadzu system, using two columns: an Allsep Anion 7u column for separation of nitrite and nitrate and an Universal Cation 7u column for the separation of ammonia, both columns being maintained at 40°C; the mobile phase for the nitrite and nitrate separation was a 4 mM 4-hydroxybenzoic acid solution with pH-ul adjusted to 7.5 with a 0.1 M LiOH solution, at a flow rate of 0.85 mL/min, while the mobile phase for ammonium separation was a 3 mM HNO_3 solution at 0.5 mL/min. This method was successfully applied for assessing the inorganic nitrogen status from Fizes watershed lakes. The method has potential to be used in water quality surveys for drinking waters, surface waters and underground waters, as well as in municipal and industrial waste waters.

Keywords: ion chromatography, surface waters, environment, lakes, inorganic nitrogen, nitrate, nitrite, ammonium

1. INTRODUCTION

Nowadays there is an increasing interest in monitoring chemical pollutants and ionic species in natural aquatic systems, for a better understanding of the relationship between anthropogenic releases and their long-term impact on the environment. For this purpose, chemical analysis is usually employed to assess the distribution of various chemical species and of the outputs generated by the physical, chemical and biological processes developed within the water systems. Among the chemical indicators, the ionic species hold an important place, determining largely the behavior and evolution of the aquatic system.

The nitrogen cycle being of particular significance for biological and nonbiological processes in the environment, speciation analysis of nitrogen in water samples is an important task for environmental studies, many classical methods being available nowadays for the determination of inorganic nitrogen species

NO_2^- , NO_3^- and NH_4^+ . Most of these methods are time-consuming and labor-intensive, needing also large volume of sample and big amounts of reagents: they require many analytical methods, including spectrophotometry, gravimetry, titrations or ion-selective electrode potentiometry [7]. Among the classical methods for nitrates determination, the most utilized are the colorimetric ones, reduction in a cadmium column or the potentiometric method using an ion-selective electrode; the common method for determination of nitrites in water samples is based on generation of an intense red color azo dye, while ammonium ions are often determined by a colorimetric indophenol titration method, by potentiometry with ion-selective electrode or using the old colorimetric method, with Nessler reagent. These methods proved to be insufficiently sensitive or selective, inaccurate, while the repetability of determinations is poor. Other problems arise because of low analytes' concentrations, a direct analysis being not always possible; thus,

preliminary sample preparation may be needed, this being usually time consuming and laborious and while performed incorrectly, it can be a source of significant errors.

The classical analytical methods, besides being time consuming, are quite expensive, a faster and cheaper alternative being more advantageous. Ion chromatography (IC) delivers a more precise and convenient measurement of the various inorganic species; it is a high-performance ion-exchange chromatography technique for the separation and quantification of low-molecular-weight ions, being in use for over 35 years [8]. Because of its high accuracy and reliability, IC is nowadays one of the most important method for the determination of alkaline, alkaline earth and some transition metal ions [1-6, 9, 10].

However, in IC, nitrate and nitrite determination is accompanied by determination of other ions present in the sample, such as fluoride, chloride, phosphate, bromide and sulphate, while the ammonium determination is accompanied by the determination of other cations such as lithium, sodium, potassium, magnesium and calcium. Usually, the concentrations of these ions are much higher than that of the target analytes and peaks' overlapping can occur, masking the peaks of interest; irrespective of the column used, the main problems are related to a proper separation of analytes accompanying ions – especially those with retention times close to the target ones. These problems can be solved by optimizing the conditions of analysis, such as changing the composition of the eluent, flow rate or column type.

Due to its advantages, this technique was selected in order to develop a method for assessing the inorganic nitrogen in the system of lakes and fishing ponds from Fizes watershed. Fizes catchment, part of Somes catchments' tributary of Tisa watershed, is located in Transylvania Plain, in the northern part of Romania. The major pollution sources are represented by sediments (generated by erosion) and diffuse sources (originated from agricultural activities and the improper septic systems of the localities). An IC method with

conductivity detection was developed, enabling the simultaneous determination of ammonium, nitrate and nitrite in a single run, saving thus analytical time, sample pre-treatment and reagents.

2. MATERIALS AND METHODS

Mobile phases were prepared from high purity reagents: 4-hydroxybenzoic acid (Acros Organics), lithium hydroxide (Scharlau) and nitric acid (Merck). Ultrapure water with a specific resistance of 18.2 MΩ/cm was utilized for preparation of mobile phases as well as for sample dilution, being obtained from a Direct Q 3UV Smart (Millipore). All solutions were stored in polyethylene bottles which had been thoroughly rinsed with ultrapure water. Mobile phases were filtered through a 0.45 μm membrane (Millipore), and then degassed using an Elmasonic S30 H ultrasonic bath before use. Standard working calibration solutions were prepared daily by dilution from a “six cation standard-II” and a “seven cation standard-II” (both from Dionex Corporation). A LGC6020, SPS ww2 certified reference material was used for validation.

Water samples were collected during the summer of 2008, in 0.5 L polyethylene bottles, according to International Standard Organization methods [11, 12]; all samples were stored at 5°C, for maximum 24 hours, prior to analysis. Samples were collected in triplicates from the center of the lakes, from a depth of two meters, being passed through a 0.45 μm membrane filter (Millipore) before IC analysis: the samples with ion concentrations exceeding the calibration range were diluted accordingly and re-analyzed.

Analyses were performed on a Shimadzu system, consisting from: a Prominence DGU 20As online degasser, a Prominence LC-20AP solvent delivery module, an automatic sample injector SIL-10AF, a conductivity detector CDD-10Avp, a Prominence CTO-20A column oven, a FCV-10AH2 valve unit, an Allsep Anion 7u column (150 x 4.6 mm), an Universal Cation 7u (100 x 4.6 mm) and a Prominence CBM-20A system controller. Instrument

control, data acquisition and data analysis were accomplished by a computer running „LCsolution” ver.1.2. software. 300 μ L samples were injected in each case; using a temperature of 40⁰C, an Allsep Anion 7u column with a mobile phase of 4-hydroxybenzoic acid 4 mM solution with pH-ul adjusted to 7.5 with LiOH 0.1 M, at 0.85 ml/min, a total separation of 23 min. was effective for a good resolution for all seven anions from the mixed standard solution (fluoride, chloride, nitrite, bromide, nitrate, phosphate and sulphate); similarly, with a Universal Cation 7u

column, using as mobile phase a 3 mM HNO₃ solution, at 0.5 mL/ min for all six cations (lithium, sodium, ammonium, potassium, magnesium and calcium), all peaks being baseline separated. The external standard method was used for quantification, calibrations being achieved using five levels of concentration for accurately determine the concentration of target ions. The calibration curves show a good linearity with R > 0.9985 for nitrite to 0.9998 for nitrate and ammonium.

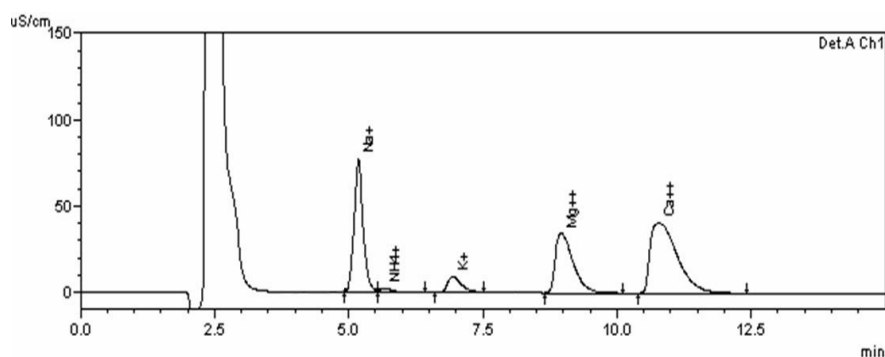


Figure 1. Separation of cations from water samples originating from Geaca lake

3. RESULTS AND DISCUSSION

From the three analytes, the lowest levels were recorded for nitrite – which was detected in only one sample, in Taga Mare lake. For ammonium, concentrations ranging from 0.28 ppm (in Taga Mare lake) and 0.52 ppm (for Geaca lake) were recorded. For nitrate, the lowest concentration was found in Saint Florina lake, while the maximum one in Taga Mare lake.

Table 1 summarizes the ions' concentrations, while figures 1 and 2 reveals the chromatographic profile of two representative water samples. The recorded values were attributed to the diffusion pollution sources originated by manure and animal breeding located in the areas of Catina, Geaca, Taga Mare and Taga Mică lakes.

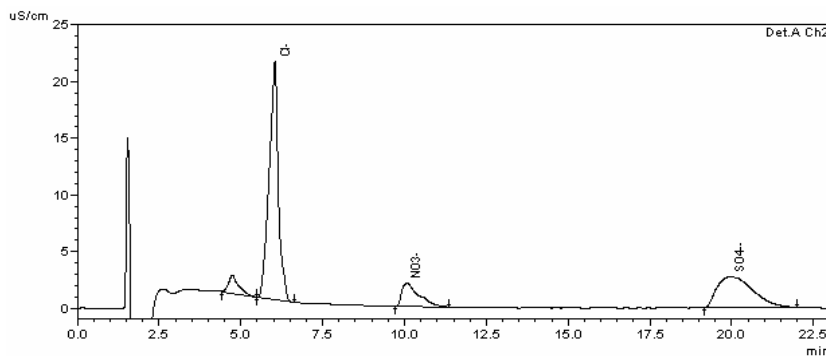


Figure 2. Separation of anions from water samples originating from Cătina lake

Table 1: Concentrations of inorganic nitrogen species in the lakes from Fizeş watershed (mean values \pm SD)

Lakes	NH ₄ ⁺ [ppm]	NO ₃ ⁻ [ppm]	NO ₂ ⁻ [ppm]
Catina	0.45 \pm 0.02	5.24 \pm 0.29	0
Taul Popii	0	0.96 \pm 0.05	0
Saint Florian	0	0.28 \pm 0.01	0
Geaca	0.52 \pm 0.03	6.45 \pm 0.29	0
Sucutard	0	0.83 \pm 0.04	0
Taga Mare	0.44 \pm 0.03	12.79 \pm 0.58	0.21 \pm 0.01
Taga Mica	0.28 \pm 0.01	1.77 \pm 0.09	0
Stiucii	0.49 \pm 0.03	7.66 \pm 0.04	0

4. CONCLUSIONS

Using the proposed IC method can offer an easy, fast, small sample volume demanding and fit-for purpose tool for the determination of inorganic nitrogen in surface water samples, in a large dynamic range. This technique enables the simultaneous determination of inorganic nitrogen ionic species in a short time, with a good reproducibility of results, high sensitivity and selectivity, using small volume samples and a minimal sample processing. The method has potential to be used in water quality surveys for drinking waters, surface waters and underground waters, as well as in municipal and industrial waste waters. It was applied for revealing the inorganic nitrogen status in the Fizeş watershed lakes.

Definite advantages of this method is the low cost of analyses, relatively simple and cheap apparatus and hence the possibility of use in most laboratories. The simultaneous determination of inorganic nitrogen ion species provides more comprehensive information for the studied samples.

5. REFERENCES

- [1] Cickarik D., Dersek-Timotic I., Onjia A., Rajakovic I., Development of ion chromatography methods for the determination of trace anions in ultra pure water from power plants. Journal of the Serbian Chemical Society, 2005; 70 (7), 995-1003.
- [2] Connolly D., Paull, B. Rapid determination of nitrate and nitrite in drinking water samples using ion interaction liquid chromatography. Analytica Chimica Acta, 2001; 441, 53-62.
- [3] Gjerde D.T., Fritz, J.S. Ion Chromatography. Hüthig, Heidelberg, 2000.
- [4] Jackson P.E., Chassaniol K. Advances in the determination of inorganic ions in potable waters by ion chromatography. Journal of Environmental Monitoring, 2002, 4, 10-15.
- [5] Miskaki P., Lytras E., Kousouris L., Tzoumerkas P., Data quality in water analysis: validation of ion chromatographic method for the determination of routine ions in potable water. Desalination, 2007, 213, 182-188.
- [6] Park H.M., Kim Y.M., Lee D.W., Lee S.W., Lee K.B. Ion chromatographic determination of inorganic anions in environmental samples of Korea. Analytical Sciences, 2002; 18, 343-346.
- [7] Skoog D.A., Holler F.J., Nieman T.A. Principles of Instrumental Analysis. Toronto, Ontario, Brooks/Cole, 1998.
- [7] Moorcroft M.J., Davis J., Compton R.G. Detection and determination of nitrate and nitrite: a review. Talanta, 2001, 54, 785 – 803.
- [8] Small H., Stevens T.S., Bauman W.C. Novel ion exchange chromatographic method using conductometric detection. Analytical Chemistry, 1975, 47, 1801–1809.
- [9] Small H. Ion chromatography: an account of its conception and early development. Journal of Chemical Education. 2004, 81, 1277-1284
- [10] Weiss J. Ion Chromatography, VCH, Weinheim, 1995.
- [11] International Standards Organization. Water quality – sampling, part 1: guidance on the design of sampling programs. ISO 5667-1-1980, Geneva, Switzerland, 1980.
- [12] International Standards Organization. Water quality – sampling, part 2: guidance on sampling techniques. ISO 5667-2-1991, Geneva, Switzerland, 1991.