NITRATE DETERMINATION IN SEA WATER BY ON-COLUMN MATRIX ELIMINATION

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Abstract. An ion chromatographic determination of nitrate ions in sea water has been carried out, using the method of on-column matrix elimination. The lowest detection limit obtained by this method while running the UV-detector at the 206 nm was 13 ppb NO_3^-. Applying this technique, the nitrate concentration in a sea water sample taken from the Baltic Sea near Tallinn was found to be 2.1—2.5 ppm (February, 1993).

Key words: ion chromatography, ultraviolet detector, on-column elimination, nitrate determination.

The nitrate concentration in sea water may be considered a measure of sea pollution, especially for semi-isolated bays. Using ion chromatography for nitrate ions determination, we are faced with the problem of the determination of a trace component in the presence of very high levels of potentially interfering sample matrix components. The best solution to the problem seems to be the use of the method of on-column matrix elimination of high levels of chloride and sulphate ions [1]. This means that high levels of matrix anions in sea water (chloride and sulphate ions) are chromatographed using an eluent containing approximately the same concentrations of the above ions. Our previous work has shown that the content of Cl^- and SO_4^{2-} in the water of the Baltic Sea in Tallinn Bay is 2560 and 362 ppm respectively. In this work, therefore, we decided to use an aqueous solution whose content of Cl^- and SO_4^{2-} is 3033 ppm (5.00 g NaCl/l) and 245 ppm (0.362 g Na_2SO_4/l), as an eluent. The detection method to be employed must be selective and sensitive. Therefore, we used the UV-absorption at 206 nm where the NO_3^- absorption maximum in water-sodium chloride mixtures is located.

EXPERIMENTAL

A model 11 ion chromatograph (Design Office, Estonian Academy of Sciences, Tallinn) was used. This ion chromatograph was equipped with an UV-detector, i.e. a variable wavelength monitor from Knauer (Germany). Chromatograms were recorded on a Servogor S recorder (Goerz, Germany). A home-made RC filter was used between the UV-detector and the recorder ($R = 220$ kΩ, $C = 10 + 2$ mF) which reduced the noise level by a factor of 4—5. The separator column (4×250 mm) used was packed with HIKS-1 resin (Khimifil, Tallinn) and had a capacity of 0.052

mequiv./cm³. A 430 μl sample loop was used for all injections. All solutions were prepared from analytical reagent grade chemicals by dissolving them in CO_2-free distilled water. The eluent was an aqueous solution (containing 5.00 g of NaCl/l and 0.362 g of Na_2SO_4/l). These Cl^- and SO_4^{2-} concentrations approximately matched to the respective Cl^- and SO_4^{2-} concentrations in the Baltic Sea water near Tallinn. The latter quantity was determined using the same ion chromatograph with the respective standard conductometric detector (JD-1), a suppressor column (4×250 mm, packed with Dowex 16 WX resin), and a carbonate eluent (0.43 g Na_2CO_3/l).

RESULTS AND DISCUSSION

The UV-detector (Spectromonitor II from Data Control, FL) has been shown to be able to detect nitrate anions at the 0.1 ppm level and higher [2]. This detection limit has been obtained with a 100 μl loop [2].
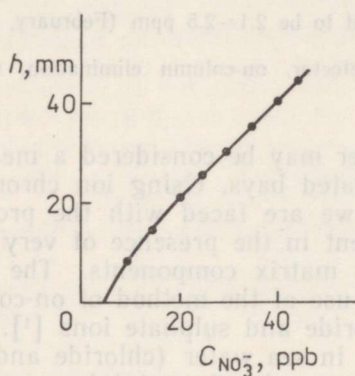

Fig. 1. A calibration graph for low nitrate concentrations: peak height vs. NO_3^- concentration, ppb. The NO_3^- sample solutions were prepared in the eluent used. The latter was an aqueous solution containing 5.00 g of NaCl/l and 0.362 g of Na_2SO_4/l. The flow rate was 2.0 ml/min, back pressure 20 kg/cm². The detector settings used were: 206 nm, range 0.16 AUFS. Recorder 20 mVFS.
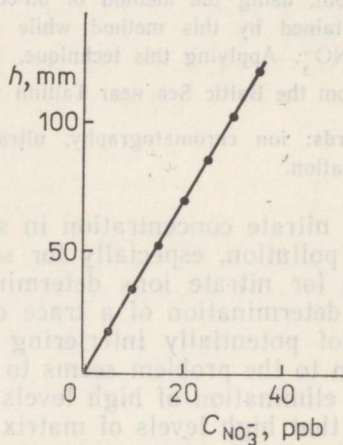
Fig. 2. A calibration graph for high nitrate concentrations: peak height vs. NO_3^- concentration, ppb. The NO_3^- sample solutions were prepared in the eluent used. The latter was an aqueous solution containing 5.00 g of NaCl/l and 0.362 g of Na_2SO_4/l. The flow rate was 2.0 ml/min, back pressure 20 kg/cm². The detector settings used were: 206 nm, range 0.16 AUFS. Recorder 500 mVFS.
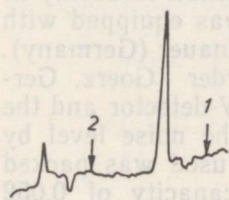

Fig. 3. Chromatograms of samples whose content of NO_3^- were 1 — 25 and 2 — 13 ppb respectively. The eluent and the settings used were the same as in Fig. 1. It should be noticed that at low nitrate concentrations the linearity between peak height and concentration is not exactly followed — see Fig. 1. That is the reason why the peak at 13 ppb is more than 2 times smaller than at 25 ppb.

If the injected volume is as large as 430 µl, the NO_3^- detection limit should be 0.023 ppm = 23 ppb. Fig. 1 shows the calibration graph obtained with a 430 µl loop volume. The linearity between the NO_3^- concentration and measured peak heights is better for higher NO_3^- concentrations (see Fig. 2). The detection limit of NO_3^- with the equipment used is 13 ppb NO_3^- (see Fig. 3). This detection limit should be compared to the NO_3^- content of the sea water: 30—1200 ppb [3]. The conclusion is that single-column ion chromatography with a matched $NaCl + Na_2SO_4$ eluent may be used for NO_3^- determinations in sea water.

The method described above has been applied to NO_3^- determination in the water of the Baltic Sea. The water samples were taken from the neighbourhood of the city of Tallinn and filtered through the paper filter. The NO_3^- content of the three samples analysed were found to be 2.1—2.5 ppm (in winter 1993). This is a very high NO_3^- concentration in comparison with the respective concentrations in open sea (below 0.10 ppm NO_3^-). This result may be due to the pollution coming from the city of Tallinn (more than 400 thousand people in winter 1993).

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NITRAATIOONIDE KONTSENTRATSIOONI MÄÄRAMINE MEREVEES KASUTADES MAATRIKSI ELIMINEERIMIST KOLONNIS

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Ioonkromatograafilise analüüsi abil on määratud nitraatioonide sisaldus Tallinna lahe vees. 1993. aasta veebruaris oli see näitaja 2,1—2,5 ppm. Nitraatioonide määramise alumine tundlikkuspiir oli 13 ppb, kui ultraviolettdetektor töötas lainepikkusel 206 m.

ОПРЕДЕЛЕНИЕ СОДЕРЖАНИЯ НИТРАТ-ИОНОВ В МОРСКОЙ ВОДЕ ЭЛИМИНИРОВАНИЕМ МАТРИЦЫ В КОЛОНКЕ

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Методом ионной хроматографии, в частности элиминированием матрицы в колонке, определено содержание нитрат-ионов в воде Таллиннского залива. На февраль 1993 г. оно составляло 2,1—2,5 части на миллион. С помощью УФ-детектора (длина волны 206 нм) найден нижний предел определения нитрат-ионов — 13 частей на миллиард.