Determination of UV-Absorbing Anions in Environmental Samples by Microcolumn High-Performance Liquid Chromatography

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Abstract—The chromatographic retention and separation of NO$_2^-$, Br$^-$, NO$_3^-$, and I$^-$ anions on a column packed with Nucleosil 100-5 C18 dynamically modified with trimethyloctadecylammonium bromide (TMODAB) was studied using direct UV detection. A procedure was developed for the determination of the above anions in the concentration range 0.06–2500 µg/L without preconcentration. Sample preparation involved only the elimination of organic impurities (if present) from the test sample. The procedure was used for the determination of NO$_2^-$ and NO$_3^-$ anions in Baikal Lake water and in an aerosol extract.

The problem of determining low concentrations of nitrates and nitrites (less than 50 µg/L) in slightly mineralized waters is of current interest. This stems from the fact that their concentrations in natural reservoirs are prone to seasonal fluctuations and attain a minimum during the vegetation period. The application of conventional methods, which determine down to 3 µg/L of nitratior, involves various interfering effects [1]. Nitrates and nitrites can be determined without preconcentration at concentrations down to 5 µg/L by ion chromatography. Conductometric and UV detectors are used for detection, and direct UV detection provides very low detection limits [2, 3]. Sometimes, a conductometric detector and an UV detector are connected in series to increase the reliability of the results [4]. There are also published data on the determination of UV-absorbing anions by reversed-phase ion-pair chromatography with direct UV detection [5].

In this work, we continue the investigation of properties of dynamically modified reversed phases [6] and examine the possibility of using these phases for the determination of UV-absorbing anions (NO$_2^-$, NO$_3^-$, Br$^-$, and I$^-$) on standard chromatographs with direct multiwavelength UV detectors.

EXPERIMENTAL

Chromatographic experiments were performed on a Milikhrom A-02 microcolumn liquid chromatograph (ZAO EkoNova, Novosibirsk, Russia) with a 75 × 2-mm column packed with a Nucleosil 100-5 C18 sorbent modified with trimethyloctadecylammonium bromide (TMODAB) (Aldrich Chemical Co., Inc., USA). The eluent flow rate was 100 µL/min. Detection was carried out at wavelengths of 202, 204, and 226 nm, corresponding to the absorption maximums of bromide, nitrate, and iodide. All reagents were of analytical or chemically pure grade.

The sorbent was modified according to [6]. At the last stage, the column was washed with a 0.5 M solution of NaF (pH 7.5) with 10% of methanol or 0.2 M of NaCl to a constant value of absorbance at a wavelength of 210 nm.

RESULTS AND DISCUSSION

Solutions of potassium or sodium sulfate, phosphate, acetate, carbonate, fluoride, chloride, and perchlorate were studied as eluents. Quality chromatograms were obtained only when chloride and fluoride were used. The column performance (by iodide, the last eluted anion of the analytes) was 2500–3000 theoretical plates, and the peak asymmetry factor was 1.03. Eluting with acetate and carbonate produced strong baseline noise, eluting with perchlorate resulted in poor separation, and diffuse and asymmetric peaks were observed upon eluting with phosphate and sulfate. With consideration for high corroding properties of chloride solutions, it is preferable to use fluoride solutions in 10% methanol (pH 7.5). When it is necessary to change the composition of the eluents, a long time is necessary for column conditioning to achieve stable values of the retention time. Such behavior of a dynamically modified reversed phase was already noticed [6, 7], and it was recommended to pass a flow of an eluent through the column for one night before the analytical use of the dynamically modified column. This is possibly because the applied modifier slowly changes its conformation upon a change in the ionic strength of the eluent. The use of eluents (except for the chloride one) without an