ISSN 0027-1314, Moscow University Chemistry Bulletin, 2008, Vol. 63, No. 1, pp. 30–35. © Allerton Press, Inc., 2008.
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Interference of Anions in On-Line Sorption Ion Chromatographic Determination

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Received September 6, 2007

Abstract—A technique for investigation of the interference of ions in on-line sorption ion chromatographic determination has been proposed. The technique involves choice of a mathematical model for describing the sorption dynamics, calculation of the thermodynamic and kinetic properties of ion sorption in a given system, and plotting of sorption isotherms of a microcomponent in a wide range of concentrations of interfering macrocomponents. The technique has been used for studying the sorption of nitrate in the presence of bicarbonate and sulfate ions. It has been shown that the nitrate sorption dynamics is adequately described by the external diffusion model. The data obtained have been used for predicting the recovery levels of nitrate as a function of the sample volume containing sulfate. The accuracy of the prediction has been proved experimentally.

DOI: 10.3103/S0027131408010070

Analysis of waters and solutions requires the determination of inorganic and organic ions. The most universal method of solving these problems is ion chromatography (IC) [1]. Among the advantages of this method are a high sensitivity (detection limits for some ions are 0.5–1.0 μg/L without preliminary concentration), the possibility of relatively rapid simultaneous determination of a large number of ions in a small analyte volume, a wide range of determined ion concentrations, and complete automation of determination. Among the disadvantages of the method are complicated synthesis of ion exchangers for ion separation and lower efficiency of ion separations compared to HPLC [2].

The IC method affords determination of inorganic anions and cations, as well as the ions of organic acids and bases. Typical objects of IC analysis are natural and waste waters, atmospheric precipitation, and different processing solutions in which anions, for example, inorganic ones (fluoride, chloride, nitrate, bromide, and sulfate), should be quantified. The concentration ranges of inorganic anions in waters can be rather wide, from trace concentrations in special purity water, for example, from a few micrograms per liter of chloride and sulfate in the water circulating in heat-transfer loops of power plants [3], to macroconcentrations, for example, to tens of grams per liter of chloride in seawater [4]. To enhance the sensitivity of ion determination, solutions are concentrated (sorption is most often used for concentration).

Analyte ions are also concentrated in analysis of solutions containing large amounts of accompanying components that exist in solution in ionic form. The task is complicated by the low selectivity of ion-exchange processes and the low capacity of sorption columns used for concentration.

This work deals with the development of methods for considering and predicting the interference of ions in the course of concentration.

EXPERIMENTAL

Solutions and Reagents. Eluents and model solutions of ions were prepared using deionized water with a resistivity of no less than 18.0 MΩ.

1 M sodium carbonate and bicarbonate solutions were prepared by dissolving weighed portions of the corresponding salts in deionized water. The purity of the salts (Merck, Germany) was GR for analysis. Nitrate and sulfate solutions were prepared by dilution of certified solutions with the concentration 1 mg/mL (Ekoanalitika, Russia).

Eluents were prepared immediately before the experiments from 1 M sodium carbonate and bicarbonate solutions by dissolving them with deionized water. To suppress the background conductivity of the eluent, a 0.05 M sulfuric acid (chemically pure, Khimmed, Russia) solution in distilled water was used.

All solutions were prepared in Vitlab plasticware (polyethylene).

Equipment. Sorption IC analysis was carried out on a setup composed of commercial modules (Aquilon, Russia). The setup included three precision high-pressure pumps (Staier of series I and series II), a CD-510 conductivity detector with analog (integrator) output, an E-18 AQU ADC external two-channel 18-bit analog-to-digital converter, an AMP-01 anion capillary suppressor of eluent conductivity, two Rheodyne Model 9740-001 six-port injection valves, and a

Phenomenex Star-Ion A300 chromatographic column (100 × 4.6 mm). A protection column for Star-Ion A300 (10 × 4.6 mm) was used as the column for concentration. Both columns were packed with the same sorbent (based on a styrene–divinylbenzene copolymer with quaternary amino groups). The sorbent grain size was 7.5 μm.

Dissolved gases were removed from solutions by using an ultrasonic bath with a volume of 1.3 L (Sapfir PKF, Russia). An analogous procedure was used for faster dissolution of compounds.

For recording chromatograms and dynamic elution curves, the Multichrom 2.4 software (Ampersand Ltd., Russia) was used. Direct and inverse problems of sorption dynamics were solved using the Matlab 7.0 (Mathworks, Inc.) and Femlab/Comsol 3.2 (Comsol AB) softwares.

RESULTS AND DISCUSSION

In accord with the objective of this work, we studied the interference of inorganic anions in on-line sorption ion chromatographic determination and developed an approach that provides the prediction of ion interference with the use of mathematical models of sorption dynamics.

In sorption IC analysis of solutions, microcomponent ions should often be determined in the presence of considerable amounts of other ions. In this case, due to the low selectivity of ion-exchange processes, the recovery level of the analyte component, as a rule, decreases. For estimating the systematic error of determination of ions under such conditions, it is expedient to develop a mathematical description of the sorption process, which will allow one to predict the recovery level of a microcomponent in the presence of various concentrations of macrocomponents. To do this, we used so-called determinate models of sorption dynamics based on partial differential equations. These equations and methods of their solution have been discussed in monographs [5–7].However, analytical solutions can be obtained only in a few special cases; in more complicated cases, numerical methods are used. In this work, sets of equations were solved numerically with the use of the Femlab software.

Mathematical models of sorption dynamics. The models used involve three basic equations: the material balance equation and the equations of mass transfer kinetics and thermodynamics. The material balance equation for a one-component system takes the form [8]

$$\frac{f}{V'_g}\frac{\partial c}{\partial x} + \varepsilon\frac{\partial c}{\partial t} + \frac{\partial a}{\partial t} = \frac{D_l \partial^2 c}{V_g^2 \partial x^2}, \tag{1}$$

where ν is the geometrical volume of an empty column from its beginning ($\nu = 0$) to a given point, f is the solution flow rate, ε is the fraction of the free volume in a sorbent-packed column, D_l is the longitudinal diffusion coefficient, V_g is the total geometric volume of the column without a sorbent, and $c(x)$ and $a(x)$ are the averaged concentrations of a microcomponent in a phase (of the solution and sorbent, respectively) in the unit cross section with the x coordinate. Concentrations in solution were calculated per unit volume of the solution and those in the sorbent, per unit volume of the entire medium (column).

The mass transfer of a component from the solution phase to the sorbent was described in terms of external diffusion kinetics. In so doing, we assumed that the concentration change rate of the microcomponent in the sorbent is proportional to the difference between the current and equilibrium concentrations of the microcomponent in the solution [8]:

$$\frac{\partial a}{\partial t} = \beta(c(x, t) - c_{\mathrm{e}}(x, t)), \tag{2}$$

where β is the external diffusion mass transfer coefficient, s^{-1}.

If the sorption isotherm of the microcomponent is linear, the distribution coefficient is

$$K_{\mathrm{d}} = \frac{a_{\mathrm{e}}}{c_{\mathrm{e}}} = \mathrm{const.} \tag{3}$$

Taking into account Eq. (3), Eq. (2) can be rewritten as

$$\frac{\partial a}{\partial t} = \beta\left(c(x, t) - \frac{a(x, t)}{K_{\mathrm{d}}}\right). \tag{4}$$

Equations describing diffusion mass transfer coefficients as a function of the sorbent packing factor were derived in [9]. In the case of the external diffusion model, this dependence is expressed is follows:

$$\beta = \frac{\beta_1}{a + \beta_2}. \tag{5}$$

For further calculations, we used both Eq. (4) (the external diffusion model with constant parameters; hereinafter, model 1) and Eqs. (4) and (5) (the external diffusion model with variable parameters, model 2).

Calculation of model parameters. To find the values of the model parameters, we solved so-called inverse problems of sorption dynamics. In the framework of mathematical physics, these problems are attributed to the inverse problems of identification of constant coefficients [7]. No universal and correct methods for solving such problems are currently available. However, the most frequently used (and recom-

Table 1. Values of $\delta/N \times 10^4$ calculated for different DECs and models 1 and 2

$c_{HCO_3^-}$, mmol/L	Model	
	1	2
0.5	2.3	4.2
1.0	6.6	0.9
1.4	6.4	2.2
1.7	7.0	1.0
2.0	8.3	2.5

mended) method for solving similar problems is iterative optimization [7]. This method was used in the present work.

Let us write the structure of the sorption dynamics model in the general form:

$$c(x, t) = M[c_{\text{init}}(x), c_{\text{inlet}}(t), p], \qquad (6)$$

where $c(x, t)$ is the solution of the set of equations M at the specified initial distribution of the microcomponent concentration over the system $c_{\text{init}}(x)$, concentration of the microcomponent at the column inlet $c_{\text{inlet}}(t)$, and vector of the equation parameters p. From the dynamic experiment, we obtain the function $c_{\text{exp}}(x, t)$ (as a rule, its section at some point $c_{\text{exp}}(x_0, t)$). In the further consideration, variable coordinates will be omitted. By the identification of parameters is usually meant the search for such a vector p_{opt} at which

$$c_{\text{exp}} = M[c_{\text{init}}, c_{\text{inlet}}, p_{\text{opt}}]. \qquad (7)$$

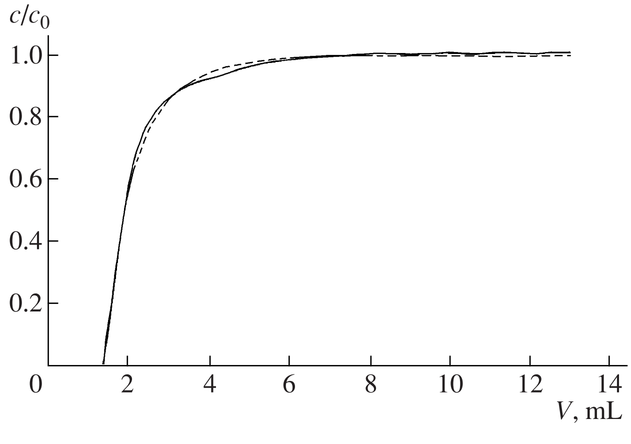

Fig. 1. Comparison of the experimental DEC and the DEC calculated using model 2. The solid line corresponds to the experimental data, and the dashed line corresponds to the calculated values (c/c_0 is the ratio nitrate concentration at the outlet of the column to the initial concentration). The experimental DEC of nitrate sorption (2.0 mg/L) was obtained on a Star-Ion A300 column ($c_{HCO_3^-}$ = 2.0 mmol/L, the sample flow rate was 1 mL/min).

Inasmuch as experimental data always contain random errors, it is evident that, even in the case of complete identity of the model and the experimental system, Eq. (7) cannot be solved in the general form. Therefore, let us formulate the problem in a different way: the search for such a vector p_{opt} for which the distance (δ) between the c and c_{exp} functions determined by some method is minimal. In most cases, the experimental results are expressed as the set of the k pairs of $\{t_i, c_i\}_{1<i<k}$ points; i.e., they are not a function but a vector of the function values at the points $\{t_i\}$; therefore, it makes sense to determine the distance between the c and c_{exp} functions in the following way:

$$\delta = \|c, c_{\text{exp}}\| = \frac{1}{k}\sum_{i}^{k}(c(t_i) - c_{i,\text{exp}})^2. \qquad (8)$$

The search for p_{opt} when the analytical form of the $c(p)$ dependence is unknown (this is the case for most problems of sorption dynamics) is performed by means of different iteration procedures [10].

Preliminary experiments. The volume of a solution in the column for concentration (the hold-up volume of the column V_m) was determined. To do this, 20 μL of water was introduced into the flow of a bicarbonate solution, and the hold-up volume of the column was calculated from the water peak retention time with taking into account the hold-up volume of the system without the column for concentration.

To determine the amount of nitrate sorbed on the column for concentration, we obtained the dependence of the nitrate peak area in the chromatogram on its amount in an injected sample. Calibration dependences were plotted upon direct IC determination of nitrate. To do this, 20 μL of a nitrate solution was applied to a Star-Ion A300 column and chromatograms were recorded.

Study of nitrate sorption kinetics and thermodynamics. To calculate the kinetic and thermodynamic parameters of nitrate sorption on the Star-Ion A300 sorbent, a series of dynamic elution curves (DECs) at different concentrations of the supporting electrolyte: $c_{HCO_3^-}$ = 0.5–2.0 mol/L and the constant nitrate concentration 2.0 mg/L. To do this, a sample was passed though a column at a constant rate of 1 mL/min and the conductivity of the solution at the outlet of the column was measured as a function of the volume of the introduced sample. Rather good reproducibility of DECs was observed. Inverse problems of sorption dynamics were solved for calculation of parameters of models 1 and 2.

At the first stage, we compared the qualities of description of the experimental data obtained in models 1 and 2: we compared the δ/N values (N is the number of experimental points in a DEC) obtained upon optimization (Table 1). The quality of description can be visually assessed from Fig. 1.

As follows from Table 1, model 2 provides the best fit between the theoretical and experimental DECs. Therefore, this model was used for further calculations. Table 2 presents the values of the parameters of model 2 calculated for all DECs measured.

The sorption of nitrate from solutions in which its concentration is at the level of micrograms per liter is of practical interest. However, at such concentrations, the above direct method of measuring DECs is inapplicable because of the insufficient sensitivity of the detector. To check the predictive power of model 2, we studied the sorption of nitrate at its low concentrations (2 μg/L) and compared the data obtained with those calculated by model 2 using the found parameter values.

To study the dynamics of sorption of low concentrations of ions, a specified sample volume was passed through the concentration column, then the extracted ions were desorbed with a chromatographic eluent and transferred to the analytical column, and a chromatogram was recorded. From the resulting chromatograms, the amount of the recovered nitrate was calculated. The theoretical dependence of the sorbed nitrate on the volume of the sample passed through the column was calculated. To do this, model 2 was used, and its parameters were taken to be $\beta_1 = 0.4$ s^{-1}, $\beta_2 = 0.7$, and $K_d = 3.1$ mL/mL. The experimental and theoretical curves are shown in Fig. 2, which demonstrates that the calculated curve fits well the observed one. Thus, this model can also be considered valid for description of the sorption of low concentrations (on the order of μg/mL) of nitrate ions.

Plotting of sorption isotherms. The major physicochemical parameter determining the behavior of the microcomponent in a sorption system is the distribution coefficient or, in the general case, the sorption isotherm. The concentrations of the analyte ion and accompanying ions in actual samples can vary in wide ranges; therefore, to predict the recovery levels of the microcomponent, we should obtain isotherms of its sorption in the presence of different amounts of interfering anions.

The sorption isotherms of nitrate in the presence of different concentrations of sulfate and bicarbonate were plotted. To do this, a solution with different contents of HCO_3^- and SO_4^{2-} ions was passed through the concentration column until equilibrium was achieved. Then, 20 μL of a solution containing 4–20 mg/L of nitrate was injected into the flow using a loop dispenser. The distribution coefficient of nitrate was determined from the retention time. The distribution coefficients were calculated by Eq. (9):

$$K_d = \frac{V'_r}{V_s} = \frac{V_r - V_m}{V_s}, \quad (9)$$

where V'_r is the corrected retention volume of the nitrate peak. Over the entire concentration range studied, the nitrate sorption isotherms are linear ($R^2 > 0.999$).

Table 2. Parameters of model 2 calculated for different concentrations of the supporting electrolyte

$c_{HCO_3^-}$, mmol/L	β_1, s^{-1}	β_2	K_d, mL/mL
0.5	0.9 ± 0.1	2.7 ± 0.5	10 ± 2
1.0	0.6 ± 0.1	1.6 ± 0.5	5.5 ± 0.5
1.4	0.48 ± 0.04	1.7 ± 0.1	3.4 ± 0.3
1.7	0.38 ± 0.06	1.6 ± 0.4	4.6 ± 0.2
2.0	0.4 ± 0.1	0.7 ± 0.4	3.1 ± 0.4

To consider the effect of interfering ions on the nitrate sorption, we obtained a set of distribution coefficients of nitrate in the presence of various concentrations of sulfate ions (0–6 mg/L) and the supporting electrolyte ($c_{HCO_3^-}$ = 0.5–1.7 mmol/L). Thus, we obtained the dependence of the nitrate distribution coefficient on bicarbonate and sulfate concentrations (Fig. 3).

Prediction of the recovery level of nitrate as a function of the sample volume in the presence of sulfate. The above information on the kinetics (dependence of coefficients β on the bicarbonate concentration) and thermodynamics (dependence of K_d on the

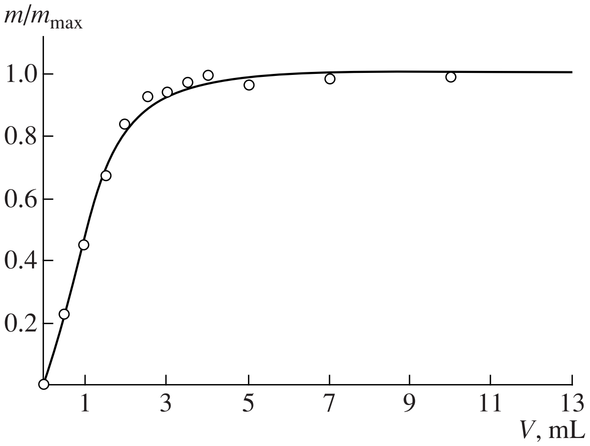

Fig. 2. Amount of nitrate ions recovered on the Star-Ion A300 column vs. the sample volume passed through the column at the stage of sorption. Open circles denote experimental values; the solid line corresponds to the calculated values. $c_{HCO_3^-}$ = 1.7 mmol/L, $c_{NO_3^-}$ = 2.0 μg/L (the sample flow rate is 1 mL/min; m/m_{max} is the ratio of the amount of nitrate sorbed on the column to the maximal amount of nitrate sorbed in the course of a given experiment).

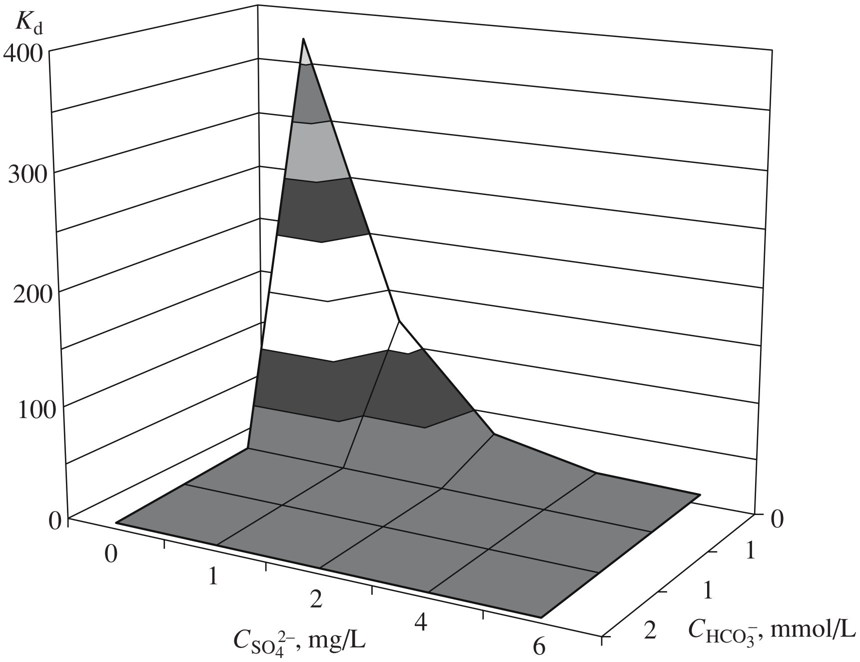

Fig. 3. Nitrate distribution coefficient vs. the bicarbonate and sulfate concentration.

bicarbonate and sulfate concentration) of nitrate sorption was used for predicting the nitrate recovery (*R*) as a function of the sample volume passed though the column. A typical dependence is shown in Fig. 4. To verify the validity of the prediction procedure, we compared the calculated and experimental *R* values. As follows from Fig. 4, the calculated recovery values fit rather well the experimental values.

Thus, we suggested a technique for investigation of interference of ions in their on-line sorption ion chromatographic determination. The technique involves the following major steps: choice of a mathematical model, calculation of the mass transfer and distribution coefficients of the microcomponent, and plotting of the sorption isotherms of the microcomponent in a wide range of concentrations of interfering components in a sample. The technique has been used for predicting the recovery levels of nitrate as a function of the change in concentrations of interfering ions in a wide range. The adequacy of the prediction has been proved experimentally.

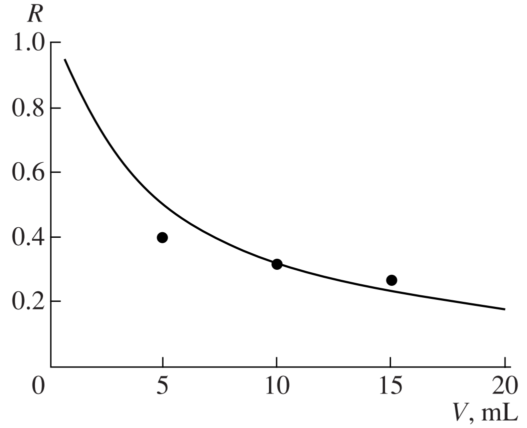

Fig. 4. Comparison of experimental and calculated recovery levels of nitrate on the Star-Ion A300 sorbent. The solid line corresponds to the calculated values, and solid circles correspond to the experimental values.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research (project no. 06-03-32178a) and the Council for Grants of the President of the Russian Federation for support of leading scientific schools (grant no. NSh-8627.2006.3).

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