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CARBONATE ELUENTS IN ION CHROMATOGRAPHY. 1. ELUENT COMPOSITION — RETENTION TIME RELATIONSHIPS

In our previous report [1] we (i) measured the retention times of chloride, nitrate, phosphate and sulfate ions using 25 carbonate eluents, i. e. aqueous solutions containing sodium carbonate and sodium bicarbonate at different concentrations, and (ii) applied the principal component analysis to the retention times measured. It was found that only one factor was necessary to describe the retention times of every ion studied. This enables reproduction of the retention times measured within the experimental errors ($\pm 3\%$). Now we would like to demonstrate how the results from [1] may be used for predicting the retention times of Cl^-, NO_3^-, HPO_4^{2-} and SO_4^{2-} ions when a carbonate eluent of arbitrary composition is applied.

The principal component analysis yielded [1] the following equation for the retention time of the ion studied

$$T(\mathrm{ION}) = r_i \cdot c_j \cdot s_j + \bar{t}_j, \tag{1}$$

where r_i is the value of the first row vector (R_1) at the ratio $Z = C_{NaHCO_3}/C_{Na_2CO_3}$ value, c_j is the first column vector (C_1) value at the chosen sum of concentrations $C = C_{NaHCO_3} + C_{Na_2CO_3}$, $\bar{t}_j$ is the mean retention time at a fixed C value, and s_j is the root mean deviation of the T(ION) values at a fixed C. It has been found [1] that for all the ions studied c_j is a constant (equal to 0.447 ± 0.007 at the confidence level $P = 0.95$).

Using the data from [1] we found that the parameters r_i, s_j and $\bar{t}_j$ in Eq. (1) may be presented as respective empirical functions $\varphi = f(C \text{ or } Z)$. For example, in the case of nitrate ions we found that

$$r_i = -1.85 + 1.91 \cdot Z, \tag{2}$$

$$s_j = 10^{(1.385 + 1.092/C)}, \tag{3}$$

$$\bar{t}_j = 10^{(2.792 - 0.460 \cdot \log C)}. \tag{4}$$

Substituting these empirical equations into Eq. (1) we obtained the following equation for the retention time of nitrate ions:

$$T(NO_3^-) = (20.72 \cdot Z - 20.10) \cdot 10^{1.092/C} + 619.0 \cdot 10^{-0.460 \cdot \log C}. \tag{5}$$

In a similar way the corresponding equations for the other ions studied were constructed:

$$T(Cl^-) = (9.42 + 9.05 \exp(-7.1 \cdot Z) - 11.15) \cdot 10^{1.17/C} + 272.2 \cdot 10^{-0.266 \cdot \log C}, \tag{6}$$

$$T(HPO_4^{2-}) = 7.46 + 364.0/C + 407.0 \cdot Z/C + 8.35 \cdot Z + 1000.0/(5.43 \cdot \log C - 0.67), \tag{7}$$

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$$T(SO_4^{2-}) = (-99.79 + 99.79 \cdot Z) \cdot 10^{2.17/C} +$$
$$+ 9772.0 \cdot 10^{(-2.352 \cdot \log C + 0.9481 \cdot (\log C)^2)}. \quad (8)$$

Eqs. (5—8) were used to calculate 25 retention times for each ion studied. The closeness of the calculated and measured [1] retention times was estimated by the relative error

$$e = (T(\mathrm{ION})_{\mathrm{calc.}} - T(\mathrm{ION})_{\mathrm{meas.}})/T(\mathrm{ION})_{\mathrm{meas.}} \quad (9)$$

The root mean deviation values of e (Eq. (9)) were found to be: Eq. (5) 4.1%, Eq. (6) 1.3%, Eq. (7) 17.7%, and Eq. (8) 9.7%. It is obvious that for HPO_4^{2-} and SO_4^{2-} ions we were not able to find any good empirical relationships for r_i, s_j and $\bar{t}_j$ (See Eqs. (2, 3, 4)). Therefore we slightly modified Eqs. (7 and 8) and estimated the numerical values of coefficients involved by a nonlinear regression method [2]:

$$T(HPO_4^{2-}) = 372.98 \cdot Z/C - 0.1681 \cdot (C - 2.833)^2 +$$
$$+ 1000.0/(5.30 \cdot \log C - 0.9153/C), \quad (10)$$
$$T(SO_4^{2-}) = (100.88Z + 56.94) \cdot 10^{2.142/C} +$$
$$+ 10.0^{(3.025 - 1.111 \cdot \log C + 0.2444(\log C)^2)}. \quad (11)$$

Eqs. (10) and (11) enable us to calculate the retention times rather close to the measured ones [1]: the corresponding root mean deviation values of e (Eq. (9)) are for Eq. (10) 4.4% and for Eq. (11) 5.8%.

Eqs. (5, 6, 10, and 11) are of a quite complicated mathematical form. This has stimulated us to construct simpler, purely empirical equations which would be almost as good for the reproduction of measured data as Eqs. (5, 6, 10, and 11) are. After some experimentation on a computer (EC1036) we found the following empirical relationships for the ions studied:

$$T(Cl^-) = 146.97 + 28.51 \cdot Z - 2.558 \cdot C + 38.746/\ln C - 1.957 \cdot C \cdot Z, \quad (12)$$
$$T(NO_3^-) = 219.74 + 63.04 \cdot Z - 8.599 \cdot C + 133.90/\ln C - 3.835 \cdot C \cdot Z, \quad (13)$$
$$T(HPO^{2-}) = 127.53 + 485.0 \cdot Z/C + 690.44/\ln C - 12.000 \cdot Z +$$
$$+ 8.438 \cdot C \cdot Z - 19.625 \cdot C \cdot Z/\ln C, \quad (14)$$
$$T(SO_4^{2-}) = -189.72 + 1150.0 \cdot Z/C + 949.72/\ln C -$$
$$- 2241.0 \cdot Z - 285.13 \cdot C \cdot Z + 1187.6 \cdot C \cdot Z/\ln C. \quad (15)$$

The root mean deviation values of e (Eq. (9)) for these equations are: Eq. (12) 4.6%, Eq. (13) 3.7%, Eq. (14) 5.2% and Eq. (15) 5.4%.

If the experimental conditions differ from those used in [1], the respective corrections should be made as suggested in [1].

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KARBONAATSED ELUENDID IOONKROMATOGRAAFIAS. 1. RETENTSIOONIAEGADE SÕLTUVUS ELUENDI KOOSTISEST

Võttes aluseks varem karbonaatsete eluentidega mõõdetud Cl^--, NO_3^--, HPO_4^{2-}- ja SO_4^{2-}-ioonide retentsiooniajad, on tuletatud empiirilised võrrandid uuritud ioonide retentsiooniaegade arvutamiseks.

Юло ХАЛДНА

КАРБОНАТНЫЕ ЭЛЮЕНТЫ В ИОННОЙ ХРОМАТОГРАФИИ. 1. ЗАВИСИМОСТИ ВРЕМЕН УДЕРЖИВАНИЯ ОТ СОСТАВА ЭЛЮЕНТА

Исходя из ранее измеренных времен удерживания хлорид-, нитрат-, фосфат- и сульфат-ионов выведены эмпирические уравнения для предсказания времен удерживания изученных ионов.