LINEAR CALIBRATION IN ION CHROMATOGRAPHY BY CALCULATING TOTAL AMOUNTS OF SAMPLE FROM MEASURED CONDUCTIVITY DATA

M. J. VAN OS* and J. SLANINA

Netherlands Energy Research Foundation (ECN), Petten, N.H. (The Netherlands)

C. L. DE LIGNY and J. AGTERDENBOS

Laboratory for Analytical Chemistry, State University, Croesestraat 77A, Utrecht (The Netherlands)

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SUMMARY

Calibration graphs in ion chromatography are generally not linear, if a suppressor column and a conductivity detector are employed. The main reason for this is that the dissociation equilibrium of the eluent (which is a weak acid after eluent suppression) is shifted by H^+ ions from the sample, which are formed in the suppressor column. Therefore a formula is derived in which the suppression of the eluent dissociation by the sample is considered. Application of this formula for chloride, nitrate and sulphate samples in succinate and carbonate eluents results in linear calibration graphs in the range 0—40 mg l⁻¹ when peak areas are used.

Ion chromatography, introduced by Small et al. in 1975 [1], is a useful and sensitive method for the determination of inorganic anions, and has found widespread application, especially in environmental analyses [2]. When a conductometric cell is used as a universal detector, the use of a suppressor column improves sensitivity and detection limit. Unfortunately, in the eluate from the suppressor column, the eluent is a weak acid and the sample is a strong acid, the H^+ ions of which suppress the ionization of the weak acid. Consequently, the contribution of the eluent to conductivity is not constant, but decreases with increasing sample concentration. As a result, calibration graphs, whether based on peak heights or peak areas, cannot be expected to be linear. This was observed in earlier work [3].

In this report a formula is derived, by which the sample concentration can be calculated from the measured conductivity. The displacement of eluent ions from the separator column by sample ions and the eluent dissociation after suppression are considered in the calculation of linear calibration graphs.

THEORETICAL CONSIDERATIONS

In ion chromatography with eluent suppression and conductivity detection, the following processes take place. A mixture of anions X^-, Y^- and Z^- is injected into an eluent stream which flows through an anion-exchange column, where the separation occurs. If the sample anions are eluted with a salt of a dibasic acid, H_2B, then in the eluate from the separator column X^-, Y^- and Z^- are present as the sodium salts NaX, NaY and NaZ, together with an excess of Na_2B, NaHB (and a small amount of H_2B). To reduce the eluent contribution to the conductivity, a second column (suppressor column) is inserted between separator column and detector. This is a cation-exchange column in the H^+-form, where all cations are exchanged for H^+. In the eluate from the suppressor column, the sample ions are present as strong acids (HX, HY and HZ) and the eluent as a weak acid H_2B. Since the equivalent conductance of H^+ is $7 \times$ higher than that of Na^+, the contribution of the sample ions (X^- together with H^+) to the conductivity signal is increased, but the contribution of the eluent (determined by the degree of ionization of the weak acid H_2B) is reduced. Thus, eluent suppression improves the sensitivity and reduces the background conductivity. Consequently, the detection limit also is improved.

It has been shown [4] that the elution of the sample ions is governed by the concentration of divalent B^{2-} ions in the eluate. Thus the ion-exchange column can be considered as in dynamic equilibrium with the divalent eluent ions B^{2-}. After sample injection on the top of the column (Fig. 1a), a dynamic equilibrium is set up in which the sample ions partition between the mobile phase and the stationary phase, an equivalent number of eluent ions B^{2-} being displaced from the stationary phase. Thus the eluent concentration in the stationary phase is locally reduced and the eluent concentration in the mobile phase is locally increased (Fig. 1b). When $\Delta C_{B^{2-}, s}$ is the decrease of eluent concentration and $C_{X^-, s}$ is the sample concentration in the stationary phase, then

$$\Delta C_{B^{2-}, s} = 1/2 C_{X^-, s} \tag{1}$$

The local deficit of eluent ions in the stationary phase equals the local excess of eluent $\Delta C_{B, m}$ (where $\Delta C_{B, m} = \Delta C_{B^{2-}, m} + \Delta C_{HB^-, m} + \Delta C_{H_2B, m}$) in the mobile phase, hence

$$\Delta C_{B^{2-}, s} \, V_s = \Delta C_{B, m} \, V_m \tag{2}$$

where $\Delta C_{B, m}$ is the increase of the eluent concentration in the mobile phase and V_s and V_m are the volumes of the stationary and mobile phases in the column, respectively. The eluent ions in the mobile phase are not retarded by the resin in the B^{2-} form and the eluent peak is eluted after V_m ml of eluent has been added (Fig. 1c). Transport of the sample ions through the column is accompanied by the transport of the local deficiency of eluent ions in the stationary phase (Fig. 1c). When the sample ions X^- are eluted
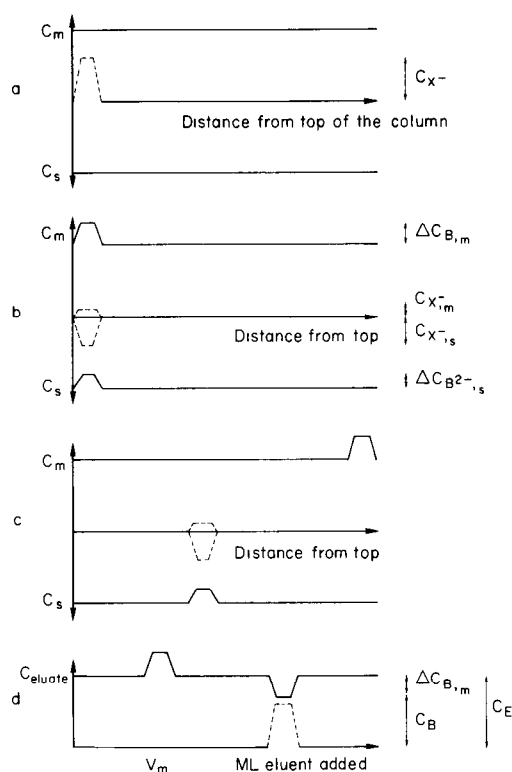
Fig. 1. Displacement of eluent ions from the separator column by sample ions: (——) eluent; (- - -) sample. (a) Situation in the column after injection of the sample and before equilibration; (b) after equilibration; (c) after the addition of V_m ml of eluent; (d) situation in the eluent after elution of the sample.

from the separator column, the concentration of X^- in the eluate (C_{X^-}) can be calculated as follows. For the last section of the column, containing a volume dV_m of mobile phase and a volume dV_s of stationary phase, and $dn_{X^-,m}$ moles of sample ions in the mobile phase and $dn_{X^-,s}$ moles of sample ions in the stationary phase, it holds that

$$dn_{X^-,m} + dn_{X^-,s} = c_{X^-,m}dV_m + c_{X^-,s}dV_s \qquad (3)$$

Division by dV_m gives

$$dn_{X^-,tot}/dV_m = c_{X^-,m} + c_{X^-,s}V_s/V_m \qquad (4)$$

If the increase in peak width that occurs during elution of the sample peak is neglected, then when a volume dV_m of eluent flows into (and out of) the column, $dn_{X^-,tot}$ moles of ions leave the last section and enter the eluate (while $dn'_{X^-,tot}$ moles of ions enter the last section from the preceding section). The concentration of the sample ions in the eluate c_{X^-} is equal to $dn_{X^-,tot}/dV_m$, so that $c_{X^-} = c_{X^-,m} + c_{X^-,s}V_s/V_m$. The capacity factor k' is defined as

$k' = c_{X^-,s} V_s / c_{X^-,m} V_m$. Combination of the expressions for c_{X^-} and k' yields

$$c_{X^-,s} = [k'/(k' + 1)] c_{X^-} V_m / V_s \qquad (5)$$

Then $\Delta c_{B^{2-},m}$ can be calculated as a function of c_{X^-}, by using Eqns. 1, 2 and 5: $\Delta c_{B,m} = 0.5 [k'/(k' + 1)] c_{X^-} = \gamma c_{X^-}$, with $\gamma = 0.5 [k'/(k' + 1)]$. When c_B is the actual eluent concentration in the eluate, (where $c_B = c_{B^{2-}} + c_{HB^-} + c_{H_2B}$), the sum of c_B and $\Delta c_{B,m}$ is equal to the original eluent concentration c_E (Fig. 1d):

$$c_E = c_B + \Delta c_{B,m} = c_B + \gamma c_{X^-} \qquad (6)$$

It should be realized that Eqn. 6 is valid not only in the absence but also in the presence of sample ions X^-.

In the situation considered, a sample anion X^- is eluted with B^{2-} and, in the eluate of the suppressor column, the sample anion is present as a strong acid HX and the eluent is present as a weak acid H_2B. The equilibrium for the weak acid is $H_2B \rightleftharpoons H^+ + HB^-$, with the equilibrium constant $K_{a1} = c_{H^+} c_{HB^-} / c_{H_2B}$. The second ionization step is neglected (see below). After eluent suppression, the total eluent concentration c_E can be written (see Eqn. 6) as $c_E = c_{HB^-} + c_{H_2B} + \gamma c_{X^-}$. Further, because of electroneutrality, $c_{H^+} = c_{X^-} + c_{HB^-}$. In the eluate of the suppressor column, c_{OH^-} is negligibly small (see below). Thus, from these expressions for K_{a1}, c_E and c_{H^+},

$$c_{H^+} = 0.5 \{ c_{X^-} - K_{a1} + [(c_{X^-} + K_{a1})^2 + 4K_{a1}(c_E - \gamma c_{X^-})]^{1/2} \} \qquad (7)$$

$$c_{HB^-} = 0.5 \{ -c_{X^-} - K_{a1} + [(c_{X^-} + K_{a1})^2 + 4K_{a1}(c_E - \gamma c_{X^-})]^{1/2} \} \qquad (8)$$

The conductivity detector measures the sum of the conductivities of all the ions in the eluate. When c_i is the concentration of ion i in the eluate, Λ_i is its equivalent conductance and S_T is the measured total conductivity, including the contribution of the eluent, S_T is given by

$$\sum_i c_i \Lambda_i = c_{X^-} \Lambda_{X^-} + c_{H^+} \Lambda_{H^+} + c_{HB^-} \Lambda_{HB^-} = P S_T \qquad (9)$$

where P is the cell constant of the conductivity cell. If S_E is the eluent conductivity (with zero sample concentration), then $P S_E = c_{H^+} \Lambda_{H^+} + c_{HB^-} \Lambda_{HB^-}$, which can be rewritten, using the expressions for K_{a1} and c_E, as

$$P S_E = 0.5 (\Lambda_{H^+} + \Lambda_{HB^-}) [-K_{a1} + (K_{a1}^2 + 4c_E K_{a1})^{1/2}] \qquad (10)$$

If S_N is the conductivity, compensated for the background eluent conductivity, then $S_N = S_T - S_E$ and S_N is equal to

$$S_N P = c_{X^-} \Lambda_{X^-} + c_{H^+} \Lambda_{H^+} + c_{HB^-} \Lambda_{HB^-} - 0.5 (\Lambda_{H^+} + \Lambda_{HB^-}) [-K_{a1}$$
$$+ (K_{a1}^2 + 4c_E K_{a1})^{1/2}] \qquad (11)$$

When c_{H^+} and c_{HB^-} are both expressed in terms of c_{X^-} (with Eqns. 7 and 8), then

$$S_N P = c_{X^-} \Lambda_{X^-} + 0.5 \Lambda_{H^+} \{ c_{X^-} - K_{a1} + [(c_{X^-} + K_{a1})^2 + 4K_{a1}(c_E - \gamma c_{X^-})]^{1/2} \}$$

$$+ 0.5\Lambda_{HB^-}\{-c_{X^-} - K_{a1} + [(c_{X^-} + K_{a1})^2 + 4K_{a1}(c_E - \gamma c_{X^-})]^{1/2}\}$$

$$-0.5(\Lambda_{H^+} + \Lambda_{HB^-})[-K_{a1} + (K_{a1}^2 + 4c_E K_{a1})^{1/2}] \qquad (12)$$

Equation 12 can be rearranged to a quadratic equation in the unknown concentration c_{X^-}

$$Ac_{X^-}^2 + Bc_{X^-} + C = 0 \qquad (13)$$

where $A = (\Lambda_{H^+} + \Lambda_{X^-})(\Lambda_{X^-} - \Lambda_{HB^-})$ \qquad (14)

$$B = -0.5(2\Lambda_{X^-} + \Lambda_{H^+} - \Lambda_{HB^-})(\Lambda_{H^+} + \Lambda_{HB^-})(K_{a1}^2 + 4c_E K_{a1})^{1/2}$$

$$-S_N P(2\Lambda_{X^-} + \Lambda_{H^+} - \Lambda_{HB^-}) - 0.5K_{a1}(\Lambda_{H^+} + \Lambda_{HB^-})^2 (1 - 2\gamma) \qquad (15)$$

$$C = (S_N P)^2 + S_N P (\Lambda_{H^+} + \Lambda_{HB^-})(K_{a1}^2 + 4c_E K_{a1})^{1/2} \qquad (16)$$

c_{X^-} is calculated with the square root formula:

$$c_{X^-} = -B + (B^2 - 4AC)^{1/2}/2A \qquad (17)$$

This means that c_{X^-} can be calculated from the measured conductivity S_N with Eqns. 14—17. The physical constants Λ_{H^+}, Λ_{HB^-}, Λ_{X^-} and K_{a1}, the eluent concentration c_E, the cell constant P and the value of γ (or the capacity factor k') must be known. The capacity factor is calculated from chromatographic retention data and P is determined by calibrating the conductivity cell with KCl solutions of known concentrations.

The effect of the suppression of the ionization of the weak acid is illustrated for two weak acids, succinic acid and carbonic acid. These acids originate after suppression of succinate and carbonate eluent, respectively. Figure 2 shows the effects of increasing chloride concentration (c_{Cl^-}) in the suppressor eluate on the H^+ concentration (c_{H^+}) and on the concentrations of the monobasic eluent ions hydrogensuccinate (c_{HSu^-}) and hydrogen carbonate ($c_{HCO_3^-}$), respectively. The value of c_{H^+} is calculated with Eqn. 7; c_{HSu^-} and $c_{HCO_3^-}$ are calculated from Eqn. 8 with $c_E = 1.4 \times 10^{-3}$ mol l^{-1} and $c_E = 3 \times 10^{-3}$ mol l^{-1}, respectively (eluent concentrations commonly used in ion chromatography). The pK_{a1} values applied were 4.16 for succinic acid and 6.37 for carbonic acid. Capacity factors for chloride were 1.26 in 1.4 $\times$ 10^{-3} mol l^{-1} sodium succinate and 1.52 in 3 $\times$ 10^{-3} mol l^{-1} sodium carbonate.

Some results are as follows. First, as carbonic acid is a much weaker acid than succinic acid, both c_{HB^-} and c_{H^+} are smaller in carbonic acid. Second, the pH in the succinic acid eluate is 3.56 or lower and in the carbonic acid eluate 4.45 or lower. It is clear that c_{OH^-} is extremely small and can be neglected in the equation $c_{H^+} = c_{X^-} + c_{HB^-}$. Third, the p$K_{a2}$ values for succinic and carbonic acids are 5.61 and 10.25, respectively, and the pH of the two eluates is $\leqslant 3.56$ and $\leqslant 4.45$, respectively, which means that the ratio $c_{B^{2-}}/c_{HB^-}$ for both eluates is less than 1%. For this reason, the second ionization step, $HB^- \rightleftharpoons H^+ + B^{2-}$, of the weak acid H_2B is not considered in the equation $c_E = c_{HB^-} + c_{H_2B} + \gamma c_{X^-}$.

In Fig. 3, the total ionic conductivities $\Sigma_i c_i \Lambda_i$ in succinic and carbonic

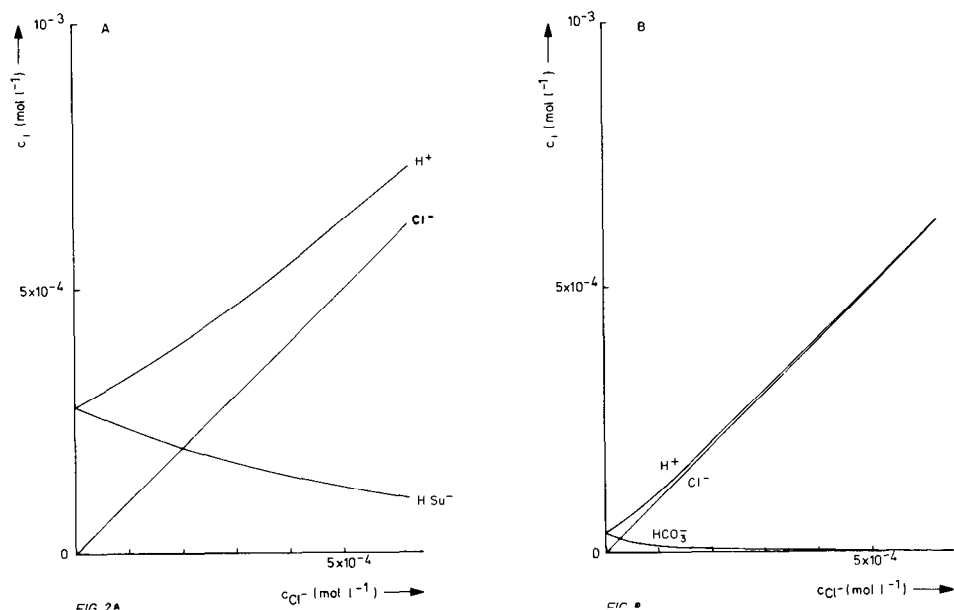Fig. 2. Dissociation of (A) 1.4×10^{-3} mol l^{-1} succinic acid and (B) 3×10^{-3} mol l^{-1} carbonic acid as a function of chloride concentration.
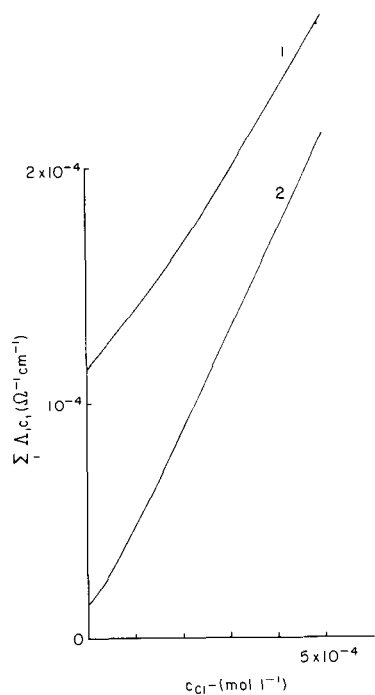

Fig. 3. Total ionic conductivity in 1.4×10^{-3} mol l^{-1} succinic acid (curve 1) and 3×10^{-3} mol l^{-1} carbonic acid (curve 2) as a function of chloride concentration.

acids are calculated as a function of c_{Cl^-}, using Eqn. 9. The Λ_i values applied were 76.3 Ω^{-1} cm^2 eq^{-1} for chloride, 350 for H$^+$, 60 for hydrogensuccinate and 44.5 for hydrogencarbonate ions [5]. As can be seen, both plots are curved.

EXPERIMENTAL

Chemicals

Zipax SAX, a pellicular anion exchanger with a particle diameter of 25—37 μm and a capacity of about 12 μeq g^{-1} dry material (DuPont de Nemours) was used in the separation column. The cation exchanger AG 50W-X16 (BioRad), with a capacity of about 5 meq g^{-1} dry resin was used in the suppressor columns. Sodium succinate ("Baker grade") and sodium carbonate (99.6%) were obtained from Baker Chemicals.

Column packing and measuring procedure

The ion chromatograph and column packing apparatus are described in detail elsewhere [4]. A 200 × 4.5 mm column was packed with Zipax SAX beads and two 150 × 2.0 mm suppressor columns were packed with AG 50W-X16 using the slurry technique [4]. A 100 × 4.0 mm glass column was packed by pumping over Dionex anion-exchange material from a 250 × 4.5 mm prepacked Dionex column. The separation column, suppressor column and detector cell were thermostated at 25.0°C.

Eluents were prepared by dissolving 1.0599 g of sodium carbonate and 2.7015 g of sodium succinate hexahydrate, respectively, in 1 l of deionized water. These solutions were then diluted to 3 × 10^{-3} mol l^{-1} sodium carbonate and 1.4 × 10^{-3} mol l^{-1} sodium succinate, respectively.

A FORTRAN computer program (available on request) was written to calculate the total amount of sample in the eluate from conductivity data. The program consists of the following parts. First, conductivity is measured at regular time intervals. This time interval is increased after each peak, because the peak width increases with the retention time. Second, a peak search routine indicates the start, maximum and end of each peak. The baseline is determined before and after the peak and the mean value of the baseline is subtracted from each point on the chromatogram. Third, the sample concentration in each point is calculated with Eqn. 17. Finally, the total amount of sample is obtained by integrating the calculated sample concentrations over the total eluted peak volume.

RESULTS AND DISCUSSION

The cell constant P was determined by measuring the conductivity S of 10^{-4} mol l^{-1} KCl at 25.0°C. The response of the conductivity cell was linear up to 5 × 10^{-4} mol l^{-1} KCl according to the relation $S \times P = 10^3 \, c(\Lambda_{K^+} + \Lambda_{Cl^-})$ wherein Λ_{K^+} and Λ_{Cl^-} are 73.5 and 76.3 Ω^{-1} eq^{-1} cm^2, respectively, c is

the KCl concentration (mol l^{-1}) and S is the conductivity (μmho). P was found to be 1.69 cm^{-1}.

Capacity factor data for chloride, nitrate and sulphate were calculated with the equation $k' = (V_R - V_M)/V_m$, wherein V_R and V_M are the retention volumes of the retarded component and water, respectively, in the separator-suppressor column combination. The k' values, listed in Table 1, were determined by injecting 2 μg of each sample ion.

Calibration graphs for chloride, nitrate and sulphate were prepared for both a 200 × 4.5 mm Zipax SAX column and a 100 × 4.0 mm Dionex column. The eluents were 1.4 × 10^{-3} mol l^{-1} sodium succinate and 3 × 10^{-3} mol l^{-1} sodium carbonate, respectively. A 150 × 2.0 mm AG 50W-X16 suppressor column was used in both cases. Samples with concentrations ranging from 1 to 40 mg l^{-1} were injected with a 200-μl or 500-μl loop.

In Table 2, experimental plate heights are listed for chloride, as well as the ratios S_p/c_0 and c_p/c_0, where c_0 is the known chloride concentration in the sample, S_p is the conductivity at the peak maximum, and c_p is the calculated chloride concentration at the peak maximum. It appears that on the Zipax column, S_p/c_0 increases with c_0 for c_0 = 1 to 10 mg l^{-1} and decreases for $c_0 > 10$ mg l^{-1}. Obviously the Zipax column is overloaded if more than 10 mg l^{-1} is injected and as a result the eluted peak is broadened. This is

TABLE 1

Capacity factors (k') for chloride, nitrate and sulphate on a Zipax SAX column and a Dionex column
Eluents: 1.4 × 10^{-3} mol l^{-1} sodium succinate and 3 × 10^{-3} mol l^{-1} Na$_2$CO$_3$, respectively)

Ion	Cl$^-$	NO$_3^-$	SO$_4^{2-}$
k' (Zipax)	1.26	5.46	8.38
k' (Dionex)	1.52	6.23	13.21

TABLE 2

Calibration for chloride on a Zipax SAX column and a Dionex column, based on conductivity data at the peak maximum[a]

c_0	Zipax SAX			Dionex		
	H	S_p/c_0	$10^5 c_p/c_0$	H	S_p/c_0	$10^5 c_p/c_0$
1	0.12	6.88	2.37	0.18	8.70	2.66
2	0.13	7.03	2.38	0.18	9.55	2.63
5	0.13	7.18	2.33	0.18	11.01	2.58
10	0.13	7.21	2.20	0.19	11.82	2.53
20	0.17	6.77	1.91	0.21	12.19	2.47
40	0.25	5.73	1.49	0.25	11.63	2.29

[a]c_0: concentration of chloride injected (mg l^{-1}). H: plate height (mm). S_p: peak height (μmho). c_p: peak height (mol l^{-1}). Injected sample volume: 200 μl.

affirmed by the measured plate heights: H is constant (0.13 mm) for c_0 = 1 to 10 mg l^{-1} but increases for $c_0 > 10$ mg l^{-1}. Consequently, c_p/c_0 is constant only for c_0 = 1 to 5 mg l^{-1} and decreases when $c_0 > 5$ mg l^{-1}. The same reasoning applies for the Dionex column. It is concluded that, because of peak broadening, a calibration based on calculated sample concentrations at the peak maximum is not linear over the range 1—40 mg l^{-1}.

The effect of peak broadening on the calibration is eliminated if the total amount of constituent under the peak is determined. Total amounts of chloride, nitrate and sulphate were so determined from conductivity measurements and the results are listed in Table 3 (n_1 data). For convenience, the amounts of sample injected (n_0) and the n_1/n_0 ratios are also given, as well as the conductivities at the peak maximum S_p and the S_p/c_0 ratios. The results in Table 3 indicate again that calibration graphs based on peak heights are curved. It can be seen that the n_1/n_0 ratios are all about 1.0. Thus the amount of sample that is injected can be accurately determined by conductivity. In principle, no standards are required once the cell constant has been measured, but this kind of absolute calibration can be applied successfully only if the eluent flow rate, the loop volume and the capacity factors are all accurately known and if the temperature remains constant. In practice, the capacity factors vary somewhat whenever a fresh eluent or a fresh suppressor column is used. Therefore a relative calibration with two standards is advisable.

The linear regression technique was used to test the calibration graphs. Inspection of the n_1/n_0 values in Table 3 shows that 6 out of the 12 data at the lowest concentration are rather low. Therefore, the results obtained at c_0 = 1 mg l^{-1} were not considered for the regression. The n_1 values obtained at the other values of c_0 are probably beset with a constant relative error. (The main contribution to the error of n_1 stems from the error of the conductivity measurements; generally, the relative error of conductivity measurements is constant.) The error in n_0 is negligible, and the values of n_1/n_0 are about constant. Therefore, if the relative error of n_1 is constant, the absolute error of n_1/n_0 is constant. Accordingly, the regression equation used was $n_1/n_0 = a + bc_0$. The results are shown in Table 4. It appears that the intercepts a are just significant statistically, so that a single-point calibration is not warranted. Two-point calibration gives values of s_{n_1/n_0} of about 0.02, i.e., an accuracy of 2%. Thus a linear calibration graph with a standard deviation of 2% can be obtained when the proposed formula is applied.

Conclusions

In ion chromatography with eluent suppression, non-linear relations between sample concentrations and conductivity values are found if the usual procedures are applied. Linear relations are found if three modifications are applied: consideration of the suppression of the eluent dissociation by the sample ions, consideration of the displacement of eluent ions in the separator column by the sample ions, and integration of the calculated

TABLE 3

Calibration of chloride, nitrate and sulphate on Zipax SAX and Dionex columns, based on integration of conductivity data over the peak volume[a]

Ion injected	c_0 (mg l^{-1})	n_0 (μg)	S_p (μmho)	S_p/c_0 (μmho mg^{-1} l)	n_1 (μg)	n_1/n_0
(a) Zipax SAX (1.4 × 10^{-3} mol l^{-1} sodium succinate eluent at 1.86 ml min^{-1}; 200 μl injected)						
Chloride	1	0.2	6.88	6.88	0.194	0.97
	2	0.4	14.07	7.03	0.398	0.99
	5	1.0	35.90	7.18	0.990	0.99
	10	2.0	72.05	7.21	1.983	0.99
	20	4.0	135.4	6.77	4.00	1.00
	40	8.0	229.0	5.73	8.02	1.00
Nitrate	1	0.2	1.03	1.03	0.188	0.94
	2	0.4	2.08	1.04	0.390	0.98
	5	1.0	5.20	1.04	0.981	0.98
	10	2.0	10.27	1.03	1.989	0.99
	20	4.0	19.83	0.99	4.05	1.01
	40	8.0	37.40	0.94	8.10	1.01
Sulphate	1	0.2	0.96	0.96	0.209	1.05
	2	0.4	1.93	0.97	0.425	1.06
	5	1.0	4.85	0.97	1.045	1.05
	10	2.0	9.84	0.98	2.07	1.04
	20	4.0	20.06	1.00	4.16	1.04
	40	8.0	40.54	1.01	8.29	1.04
(b) Zipax SAX (1.4 × 10^{-3} mol l^{-1} sodium succinate as eluent at 1.85 ml min^{-1}; 500 μl injected)						
Chloride	1	0.5	16.50	16.50	0.490	0.98
	2	1.0	33.39	16.70	0.983	0.98
	5	2.5	81.26	16.25	2.464	0.99
	10	5.0	148.6	14.86	4.92	0.98
	20	10.0	250.7	12.54	9.90	0.99
	40	20.0	379.3	9.48	19.81	0.99
Nitrate	1	0.5	2.55	2.55	0.477	0.96
	2	1.0	5.11	2.56	0.985	0.99
	5	2.5	12.45	2.49	2.459	0.98
	10	5.0	23.77	2.38	4.96	0.99
	20	10.0	44.73	2.24	9.98	1.00
	40	20.0	84.17	2.10	19.93	1.00
Sulphate	1	0.5	2.42	2.42	0.512	1.02
	2	1.0	4.87	2.44	1.031	1.03
	5	2.5	12.42	2.48	2.578	1.03
	10	5.0	25.29	2.53	5.15	1.03
	20	10.0	51.82	2.59	10.24	1.02
	40	20.0	104.6	2.62	20.26	1.01

TABLE 3 (continued)

Ion injected	c_0 (mg l^{-1})	n_0 (μg)	S_p (μmho)	S_p/c_0 (μmho mg^{-1} l)	n_1 (μg)	n_1/n_0
(c) Dionex (3 × 10^{-3} mol l^{-1} sodium carbonate as eluent at 1.91 ml min^{-1}, 200 μl injected)						
Chloride	1	0.2	8.70	8.70	0.206	1.03
	2	0.4	19.09	9.55	0.414	1.03
	5	1.0	55.05	11.01	1.022	1.02
	10	2.0	118.2	11.82	2.05	1.02
	20	4.0	243.7	12.19	4.09	1.02
	40	8.0	465.3	11.63	8.09	1.01
Nitrate	1	0.2	1.14	1.14	0.194	0.97
	2	0.4	2.30	1.15	0.400	1.00
	5	1.0	5.76	1.15	1.013	1.01
	10	2.0	11.66	1.17	2.04	1.02
	20	4.0	23.98	1.20	4.10	1.02
	40	8.0	50.37	1.26	8.16	1.02
Sulphate	1	0.2	0.84	0.84	0.200	1.00
	2	0.4	1.71	0.86	0.414	1.04
	5	1.0	4.45	0.89	1.025	1.02
	10	2.0	9.35	0.94	2.05	1.03
	20	4.0	19.99	1.00	4.12	1.03
	40	8.0	40.56	1.01	8.17	1.02
(d) Dionex (3 × 10^{-3} mol l^{-1} sodium carbonate as eluent at 1.92 ml min^{-1}, 500 μl injected)						
Chloride	1	0.5	23.41	23.41	0.507	1.01
	2	1.0	52.13	26.06	1.015	1.02
	5	2.5	139.3	27.90	2.531	1.01
	10	5.0	273.1	27.31	5.03	1.01
	20	10.0	494.4	24.72	9.98	1.00
Nitrate	1	0.5	2.74	2.74	0.492	0.98
	2	1.0	5.48	2.74	1.005	1.01
	5	2.5	13.81	2.76	2.513	1.01
	10	5.0	28.51	2.85	5.03	1.01
	20	10.0	60.69	3.03	9.96	1.00
	40	20.0	126.9	3.17	19.96	1.00
Sulphate	1	0.5	2.11	2.11	0.503	1.01
	2	1.0	4.35	2.18	1.012	1.01
	5	2.5	11.72	2.34	2.542	1.02
	10	5.0	24.44	2.44	5.06	1.01
	20	10.0	48.87	2.44	9.97	1.00
	40	20.0	92.83	2.32	19.87	0.99

[a]n_0: amount of sample injected. n_1: amount of sample found. Further legend as in Table 2.

concentrations over the total eluted peak area. Linear calibration based on peak heights cannot be obtained as the peak width increases with the sample concentration when constant volumes are injected. With these modifications, linear calibration graphs were obtained for chloride, nitrate and sulphate ions in both succinate and carbonate eluents.

TABLE 4

Results obtained in calibration for chloride, nitrate and sulphate on Zipax and Dionex columns

Separation column/ injection loop	Chloride			Nitrate			Sulphate		
	a	b	s_{n_1}/n_2	a	b	s_{n_1}/n_2	a	b	s_{n_1}/n
Zipax/200 µl	0.99	0.0003	0.005	0.98	0.0010	0.018	1.05	—0.0005	0.011
Zipax/500 µl	0.98	0.0002	0.004	0.99	0.0004	0.007	1.03	—0.0005	0.008
Dionex/200 µl	1.03	—0.0005	0.009	1.01	0.0004	0.010	1.03	—0.0002	0.005
Dionex/500 µl	1.02	—0.0010	0.008	1.01	—0.0002	0.005	1.02	—0.0006	0.010

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