Fig. 5. Dependence of chloride retention on mobile phase flow-rate. Packing: VARS-2, 12.7 $\mu$equiv./ml. Column: 250 × 4 mm. Sample: 20 $\mu$l, 3.55 mg/l Cl$^-$. Flow-rates: ——, 0.5; ×—×, 1.0; ...., 2.0; -.-, 3.0; ---, 5.0 ml/min.
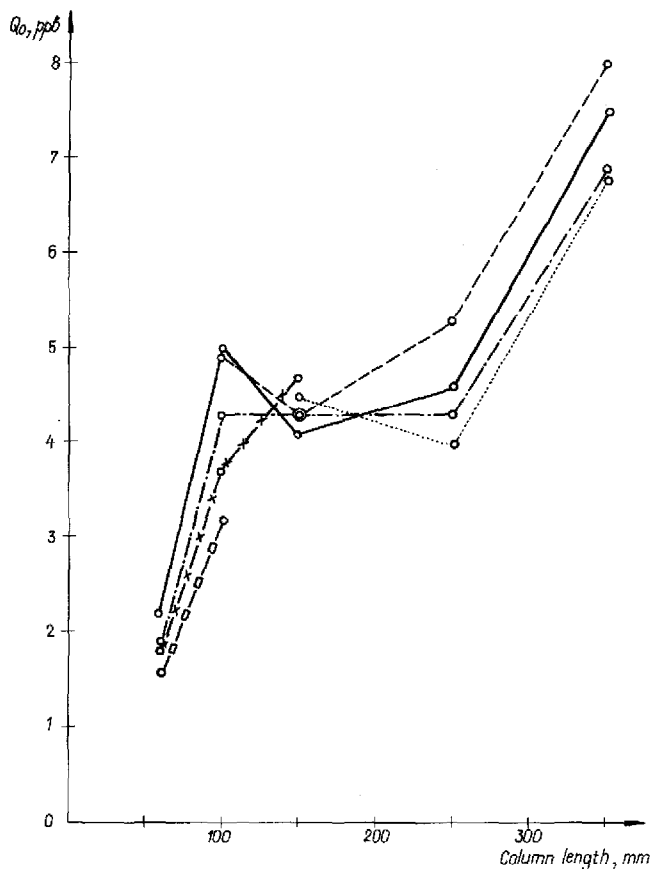


Fig. 6. Plot of LOD of Cl$^-$ vs. column length at different mobile phase flow-rates. Packings: VARS-2, 38.0 $\mu$equiv./ml. Flow-rates: □—□, 0.5; ×—×, 1.0; ...., 1.5; -.-, 2.0; ——, 3.0 and ---, 4.0 ml/min.

TABLE II

LIMIT OF DETECTION OF Cl⁻ UNDER DIFFERENT EXPERIMENTAL CONDITIONS

Column: 250 × 4 mm, capacity 12.7 μequiv./ml. Sample: 20 μl of standard solution (14.2 mg/l Cl⁻).

| Mobile phase flow-rate, $F$ (ml/min) | Column inlet pressure (MPa) | $W_h$ (min) | Peak height, $h$ (mm) | Peak area, $S$ (mm²) | $F \cdot S$ (mm² · ml/min) | LOD (ppb) |
|---|---|---|---|---|---|---|
| 0.5 | 4.21 | 12.3 | 98 | 1199 | 600 | 4.4 |
| 2.0 | 4.21 | 4.0 | 76 | 302 | 604 | 5.7 |
| 3.0 | 4.21 | 3.0 | 67 | 200 | 600 | 6.6 |
| 4.0 | 4.21 | 2.4 | 63 | 150 | 600 | 6.8 |
| 5.0 | 4.21 | 2.0 | 60 | 120 | 600 | 7.1 |
| 1.0 | 1.37 | 8.5 | 76 | 646 | 646 | 5.6 |
| 1.0 | 2.45 | 8.5 | 74 | 629 | 629 | 5.8 |
| 1.0 | 5.39 | 8.7 | 72 | 626 | 626 | 5.9 |
| 1.0 | 7.25 | 8.7 | 74 | 644 | 644 | 5.8 |
| 1.0 | 0.96 | 5.7 | 58 | 661 | 661 | 3.7 |
| 2.0 | 1.34 | 3.5 | 48 | 333 | 666 | 4.5 |
| 3.0 | 2.21 | 2.5 | 42 | 210 | 630 | 5.1 |
| 4.0 | 2.88 | 2.0 | 38 | 152 | 608 | 5.6 |

been investigated in more detail. It was found that a decrease in the mobile phase flow-rate results in an increase in the peak height, therefore causing a decrease in the LOD of Cl⁻ (Figs. 5 and 6). The results are summarized in Table II. In these analyses the separation column was 250 × 4 mm (12.7 μequiv./ml) and 20 μl of a standard solution (14.2 mg/l Cl⁻) were injected by the loop injector. According to the results, a 10-fold decrease in the mobile phase flow-rate causes a 63% increase in peak height and a decrease in the LOD of Cl⁻. At the same time the product of the peak area and mobile phase flow-rate remains constant, a characteristic of concentration detectors. At a constant mobile phase flow-rate, a change in the inlet pressure has little influence on the peak height. When the change in mobile phase flow-rate is accompanied by a change in inlet pressure, a 4-fold increase in mobile phase flow-rate causes a 34% decrease in peak height. Under these conditions the product of the peak height and mobile phase flow-rate is not constant, but decreases at higher flow-rates and inlet pressures. This may be connected with the change in mobile phase viscosity and temperature at the higher pressures[5].

The length of the suppression column has little influence on the LOD. Experiments were made using a separation column of 60 × 4 mm (38.0 μequiv./ml) and two suppression columns, 60 × 4 and 150 × 4 mm. A 10-μl volume of standard solution (5.0 mg/l Cl⁻) was introduced by the loop injector. In the case of the 60 × 4 mm suppression column at mobile phase flow-rates of 1.0, 1.5 and 2.0 ml/min, the LOD of Cl⁻ was 3.6, 3.9 and 4.2 ppb, respectively. In the case of the 150 × 4 mm suppression column the corresponding LOD values were 3.6, 3.8 and 4.1 ppb.

To enable very dilute samples to be analyzed reliably without prior preconcentration, the use of large injection volumes is necessary. The results in Fig. 7 show
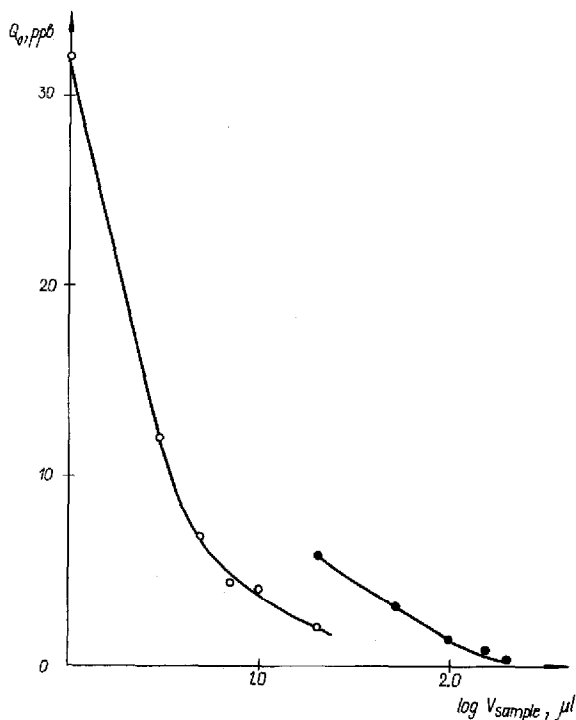
Fig. 7. Dependence of the limit of detection of $Cl^-$ on sample size. Mobile phase flow-rate: 1.5 ml/min. O—O, Column 60 × 3 mm (38.0 μequiv./ml), sample 53.25 mg/l $Cl^-$; ●—●, column 250 × 4 mm (12.7 μequiv./ml), sample 14.2 mg/l $Cl^-$.

that the lowest LOD obtained for $Cl^-$ was 0.6 ppb when the 200-μl loop injector was used.

In the calculations of the separation factor, $\alpha$, the adjusted retention times were used. The separation factor characterizes the position of the chloride peak relative to those of $F^-$ and $NO_3^-$. The values of $\alpha_{Cl^-/F^-}$ and $\alpha_{NO_3^-/Cl^-}$ did not depend on the length of the separation column. A decrease in mobile phase flow-rate caused an increase in the values of $\alpha$: 4.0 ml/min, $\alpha_{NO_3^-/Cl^-}$ was 2.5 and $\alpha_{Cl^-/F^-}$ 2.0; at 2.0 ml/min the corresponding values were 3.0 and 5.7.

The peak resolution, $R_S$, was calculated as the ratio of the distance between the peak maxima of $Cl^-$ and $NO_3^-$ to the mean value of the peak width at the base[6]. At a mobile phase flow-rate of 3.0 ml/min for the 60-mm column the value of $R_S$ was 1.6, for 250-mm column it was 3.7. By lowering the mobile phase flow-rate it is possible to increase the value of $R_S$.

For the practical use of dual-column IC in the analysis of $Cl^-$ in aqueous solutions it can be said that the plot of the amount of chloride vs. peak height is linear up to 4 μg injected. The analysis time varies from 1.5 to 20 min, depending on the column length, mobile phase linear velocity, suppression column size, mobile phase concentration, column inlet pressure and sample concentration. As the LODs of $Cl^-$, $F^-$ and $NO_3^-$ are almost of the same order, to get a good separation their

concentrations should not differ by more than a factor of $10^2$. In the case of very concentrated solutions, dilution is recommended.

REFERENCES

1 G. O. Franklin, *Int. Lab.*, 7/8 (1985) 56–67.
2 P. R. Haddad and A. L. Heckenberg, *J. Chromatogr.*, 318 (1985) 279–288.
3 R. E. Majors, H. G. Barth and C. H. Lochmüller, *Anal. Chem.*, 56 (1984) 300R–349R.
4 E. Katz and R. P. W. Scott, *J. Chromatogr.*, 253 (1982) 159–178.
5 E. Katz, K. Ogan and R. P. W. Scott, *J. Chromatogr.*, 260 (1983) 277–295.
6 R. W. Yost, L. S. Ettre and R. D. Conlon, *Practical Liquid Chromatography. An Introduction*, Perkin-Elmer, 1980, p. 45.