Carbonate interferences by ion chromatographic determination of anions in mineral waters

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Abstract

The high content of hydrogen carbonate anions and dissolved CO_2 in some mineral waters interfere with the determination of anions in such samples by ion chromatography. It was found that the irreproducibility of retention times of all anions present in the samples was caused by on-column neutralisation of CO_3^{2-} to HCO_3^- by CO_2. Microbubbles of CO_2 released downstream by the suppressor inhibited exchange of Na^+ with H_3O^+ resulting in lower conductivity and consequently in the decrease of chloride peak. To avoid peak deformation and overlapping caused by carbonate species, they should be removed by acidification followed by CO_2 elimination in a gas separation unit. To prevent sample contamination by the anion of the added acid, the electrodialytic clean-up procedure was applied. The liberated CO_2 was removed in a microporous Gore-Tex semipermeable tubing connected in series with the dialytic cell. The developed dialytic clean-up procedure was applied to the analysis of some typical mineral waters.

Keywords: Mineral water; Water analysis; Carbonate

1. Introduction

Mineral waters are used frequently in peoples' daily diet, and that is why their chemical composition should be known in detail. For anion determinations, direct ion chromatography (IC) analysis can be a method of choice, but only for those samples which do not contain complex matrices. High concentrations of hydrogen carbonate and/or carbonate anions and dissolved CO_2 in some samples interfere with some anions of interest [1] and for that reason these species should be removed prior to IC analysis. Dissolved CO_2 can be simply removed by sonication in an ultrasonic bath, while the most effective way for hydrogen carbonate and carbonate removal seems to be their conversion to H_2CO_3 by appropriate ion-exchange procedures with subsequent CO_2 elimination. Dual ion-exchange procedures rather than classical Donnan dialysis is recommended in the literature [2,3]. In this procedure a resin slurry is used instead of an electrolyte as the ion reservoir. This modification had to be done due to non-complete perm-selectivity of the separating membrane that can cause the contamination of the sample with the co-ion present in the electrolyte. Dual ion-exchange procedures as well as Donnan dialysis were expanded to other sample pre-treatment procedures in IC analysis, e.g., the neutralisation of strongly alkaline samples [4], other matrix modification and sample pre-concentration [3,5].

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In order to improve the exchange of cations with H_3O^+ or anions with OH^- in the neutralisation procedure, an electric field was applied across the dialysis cell [6]. Non-ideal perm-selectivity of the separating membranes caused sample contamination with anions or cations from the reagent compartment. The problem of the non-ideal perm-selectivity of the charged membrane was solved recently with the development of an electrolytic micromembrane suppressor device for continuous suppression in IC [7,8]. Using an electrodialytic cell, exchangeable active species H_3O^+ and OH^- are generated in the cell by water electrolysis, and subsequently, sample contamination with anion or cation co-ion is avoided [9].

In the present work the use of a self-regenerating anion micromembrane suppressor for the electrodialytic pre-treatment of hydrogen carbonate/dissolved CO_2 buffered samples is described. The influence of sample dialysis time and the appropriate on-line removal of electrodialytically liberated CO_2 was investigated. The developed procedure was applied to the analysis of some carbonate-containing mineral waters.

2. Experimental

2.1. Reagents

All reagents were of analytical reagent grade. Sodium hydrogen carbonate–carbonate based eluent was prepared according to the Dionex instructions [10]. Stock solutions of inorganic anions (F^-, Cl^-, Br^-, NO_3^-, and SO_4^{2-}) were prepared by dissolving appropriate amounts of their sodium salts, dried at 103°C, in Milli-Q water. Working solutions were obtained by corresponding dilution of the stock solutions with 18 MΩ cm^{-1} deionised water.

2.2. Chromatographic conditions

Anions were separated on HPIC-AG4A SC (4×50 mm) and HPIC-AS4A SC (4×250 mm) guard and separation columns (Dionex). Eluent conductivity was chemically suppressed on a ASRS-1 (4 mm, Dionex) self-regenerating suppressor, current setting 1 or 2, and operating in the auto-suppression external
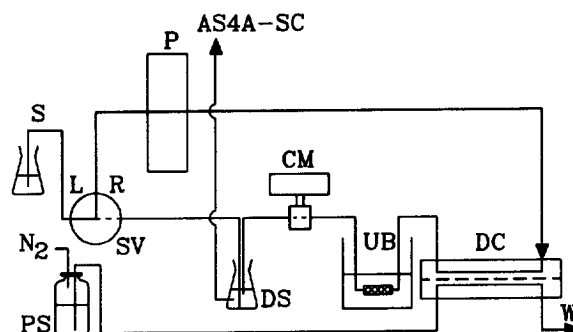

Fig. 1. The scheme of the off-line electrodialytic system used for the acidification of carbonate based mineral waters. S, sample; P, peristaltic pump; PS, pneumatic Milli-Q water delivery system; N_2, purging gas; SV, selecting valve; DC, electrodialytic cell; UB, ultrasonic bath with CO_2 separator; CM, conductivity meter; DS, dialysed sample; AS4A-ASC, analytical system.

water mode. The sample loop volume was 50 µl. Eluent and H_3O^+ donor flow-rates were 2 ml/min and 3 ml/min, respectively. Chromatograms were obtained using a conductivity detector (Dionex) and UV/VIS spectrophotometer (Spectrasystem UV 2000, Spectra-Physics). The electrodialytic apparatus is schematically shown in Fig. 1. It consists of a peristaltic pump P (IPN12, Ismatec), pneumatic Milli-Q water delivery system PS (Dionex), electrodialytic unit DC (ASRS-1, 4 mm, Dionex), a selecting valve SV (Rheodyne injection valve re-plumbed into the selecting valve), CO_2 separator installed in an ultrasonic bath UB (Iskra) and conductometer CM (Iskra), connected in series by PTFE tubing (0.5 mm I.D.). Liberated CO_2 was removed in the CO_2 separator by the Gore-Tex microporous PTFE membrane tube, which was 10 cm long with an inner diameter of 1 mm and pore size of 3 µm. The separator was installed immediately after the dialytic unit and placed into an ultrasonic bath filled with the deionised water.

3. Results and discussion

3.1. The effects of dissolved carbonate/hydrogen carbonate and CO_2 on the retention behaviour of anions

The majority of mineral waters in Slovenia contain

very high concentrations of dissolved hydrogen carbonate (2–3 g/l) and CO_2 (3–4 g/l). As published by Weiss [1], increased concentrations of hydrogen carbonate can cause some problems in the IC determination of fluoride. This was confirmed also by our experiments. Additionally, we have found that dissolved carbonate species diminished and broadened the chloride peak and caused strongly irreproducible retention times of chloride and other anions (Br^-, NO_3^- and SO_4^{2-}) which made automatic detection impossible. Typical chromatograms of a mineral water and a synthetic sample of a similar chemical composition as a mineral water (0.5 mg/l F^-, 50.0 mg/l Cl^-, 0.1 mg/l Br^-, 0.2 mg/l NO_3^- and 90.0 mg/l SO_4^{2-}) but without any carbonate species added, are shown in Fig. 2. Curves A and B represent the chromatograms of a mineral water, containing approx. 3.5 g/l CO_2, obtained without and after degassing (15 min in a ultrasonic bath), respectively. Curve C represents the chromatogram of a synthetic sample. From Fig. 2 it is evident that dissolved CO_2 causes the prolongation of retention times of anions which are more strongly retained than fluoride and increases the peak width of chloride. The partial removal of CO_2 (curve B) did not shorten the retention time of chloride and at the same time it did not recover chloride peak shape. The retention times of all anions with the exception of F^- remained too long in comparison with the retention

times when the synthetic sample without carbonate were analysed.

To explain this phenomenon, a series of a synthetic samples containing 0.5 mg/l F^-, 50.0 mg/l Cl^-, 0.1 mg/l Br^-, 0.2 mg/l NO_3^- and 90.0 mg/l SO_4^{2-} and individual carbonate species was analysed. Fig. 3 contains the chromatograms of the synthetic sample in Milli-Q water (A), the same sample with 5.0 g/l HCO_3^- (B) and with 2.0 g/l CO_3^{2-} (C). As expected the fluoride peak was overlapped by the system peak, composed mostly of cations and carbonate and hydrogen carbonate, displaced from the stationary phase and which were not completely removed in the suppressor. Evidently hydrogen carbonate prolonged chloride retention time without affecting its peak width. At the same time hydrogen carbonate had only minimal influence on the retention time and peak shape of sulphate. Carbonate anions caused shorter retention time of chloride and sulphate and increased their peak width (especially sulphate peak width). Bromide and nitrate were not monitored during this experiment. Chloride and sulphate retention behaviour could be explained by taking into account the self-elution process combined with the on-column change of the eluent. When samples containing higher concentrations of hydrogen carbonate or carbonate (5.0 g/l and 2.0 g/l, respectively) are injected, the self-elution effect of both anions prevents other anions from being retained by the stationary phase. This process continues until the sample plug becomes diluted enough
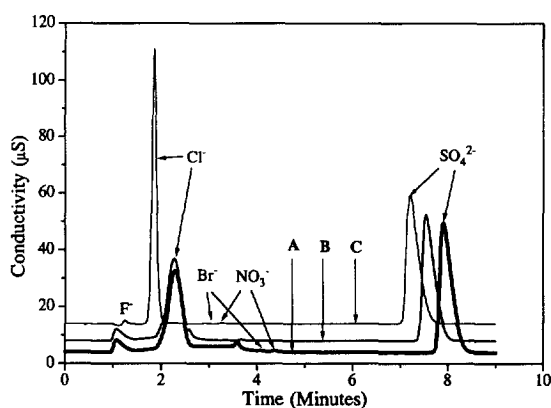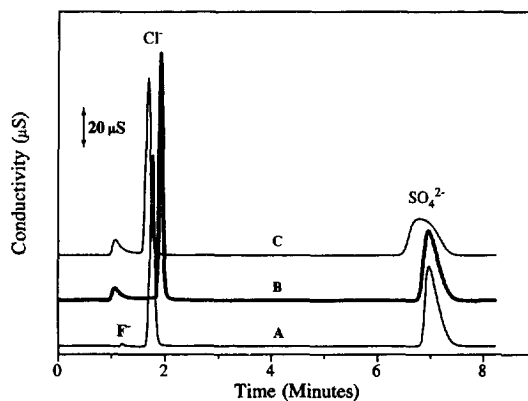

Fig. 2. Chromatograms of a mineral water (A), degassed mineral water (B) and synthetic sample having approximately the same chemical composition as mineral water (0.5 mg/l F^-, 50.0 mg/l Cl^-, 0.1 mg/l Br^-, 0.2 mg/l NO_3^- and 90.0 mg/l SO_4^{2-}) but with no carbonate species added (C).

Fig. 3. Chromatograms of a synthetic sample (the same as described in Fig. 2) without carbonate species added (A), with 5 g/l of HCO_3^- added (B) and 2.0 g/l of CO_3^{2-} added (C).

by the eluent, so that the anions are retained. As a result of this process shorter retention times are expected. At the same time, the stationary phase is converted to mostly hydrogen carbonate or the carbonate form. The eluent which follows the sample plug, reconverts the stationary phase back to hydrogen carbonate/carbonate form. Depending on the carbonate species, retained anions are eluted for a certain period of time with the eluent enriched with hydrogen carbonate (low elution capacity) or carbonate (high elution capacity) anions. This phenomenon was called on-column change of the eluent [11]. The combination of both effects i.e. self-elution effect and on-column change of the eluent, prolong retention times of anions when hydrogen carbonate is present in higher amounts (the low elution capacity of hydrogen carbonate prevails over the self-elution effect). Conversely, the retention times of anions are shortened in the case when carbonate is present as the interfering anion (high self-elution capacity, high elution capacity of the eluent containing mostly carbonate anions).

For the investigation of the effect of CO_2, the same synthetic sample, saturated with CO_2, was used. CO_2 saturation was achieved by bubbling the sample with CO_2 for 30 min at 20°C. After the bubbling was finished, the sample was placed in an ultrasonic bath for 15 min. Chromatograms of the synthetic sample, with (curve B) and without CO_2 saturation (curve A), are shown in Fig. 4. As evident, CO_2 caused a significant prolongation of the re-
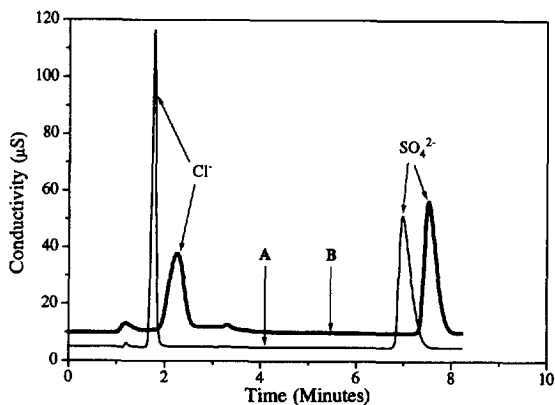
tention time of chloride and sulphate and at the same time it broadened markedly the chloride peak. Curve B on Fig. 4 has practically the same shape as curve B on Fig. 2, signifying that dissolved CO_2 represents the largest influence on the retention behaviour of chloride and other anions. This is a quite unexpected phenomenon because it was supposed that dissolved CO_2 should be co-eluted with the system void volume thus having minimal influence on the retention behaviour of other anions. This means that there should be a mechanism according to which the dissolved CO_2 prolongs the retention times of all investigated anions and broadens the chloride peak. The suggestion for the appropriate explanation can be made when chromatograms of pure demineralised water (A) and water saturated with CO_2 (B) were compared (Fig. 5). On chromatogram A only a water peak (a) can be observed while on chromatogram B, a broad peak (b) (extending from 1.8 to nearly 5 min) with a sharp maximum (c) at 3 min was observed. Because pure CO_2 saturated water was injected, this peak could only belong to the dissolved CO_2. Taking this fact into account and knowing the composition and the structure of the AS4A-SC stationary phase [12–14], the prolongation of the retention times of anions in the mineral waters, containing high concentration of HCO_3^- and dis-

Fig. 4. Chromatograms of a synthetic sample (the same as in Fig. 2) without carbonate species added (A) and saturated with CO_2 (B).
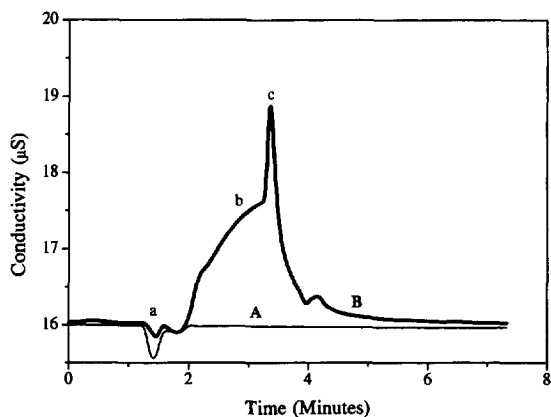

Fig. 5. Chromatograms of the sample of Milli-Q water (A) and of the same sample saturated with CO_2 (B). Negative peak (a) (curves A and B) corresponds to the water peak, peak (b) (curve B) to the eluted CO_2 and peak (c) (on chromatogram B) to the fraction of the dissolved CO_2 which diffused (due to the greatest difference in partial pressure of CO_2) the most intensively into the pores of the stationary phase.

solved CO_2, can be explained as follows. When a sample plug reaches the stationary phase, anions (other than hydrogen carbonate), are not retained for a certain period of time because of the self-elution effect of HCO_3^-. At the same time, dissolved CO_2 converts CO_3^{2-} in the eluent and CO_3^{2-} groups attached to the stationary phase into HCO_3^- groups. Because there is an excess of CO_2 over CO_3^{2-} ions (the concentration of CO_3^{2-} ions in the eluent is 1.7 mM and the total capacity of the AS4A-SC column is about 20 μeq, while the concentration of CO_2 in the analysed mineral waters was above 20 mM) the rest of the dissolved CO_2 diffuses into the pores of the hydrated surface-sulfonated polystyrene–divinylbenzene substrate carrying latex particles. In this way CO_2 is retained in the stationary phase and therefore it does not move through the column within the sample plug. When the sample plug moves down the column, CO_2 retained by stationary phase starts to diffuse from the interior of the stationary phase back to the bulk of the fresh incoming eluent and converts CO_3^{2-} into HCO_3^-. In this way the sample plug is followed by the eluent enriched with HCO_3^- which possesses a lower elution power than the original HCO_3^-/CO_3^{2-} eluent. The higher the concentration of dissolved CO_2 in the sample, the greater the CO_2 retained by the stationary phase and more CO_3^{2-} is converted to HCO_3^- and more intensive on-column eluent conversion results in greater prolongation of retention times of the individual anions. The transformation of carbonate/hydrogen carbonate eluent to hydrogen carbonate eluent is therefore the main reason for the prolongation of the retention times of all anions present in the sample.

To obtain support for the proposed mechanism the conductivity and the pH value of the eluent immediately after the separator column was measured. The presence of the dissolved CO_2 should diminish the overall conductivity (due to the conversion of CO_3^{2-} to HCO_3^-) and the pH value of the eluent should decrease indicating the change of the eluent composition from CO_3^{2-}/HCO_3^- to HCO_3^-/CO_2). The results of the conductivity measurements are shown in Fig. 6. Two samples were injected, distilled water (curve A) and a degassed mineral water (curve B). When distilled water was injected, only a small drop in conductivity was obtained [negative peak (a) on curve A], while in the case of the degassed mineral
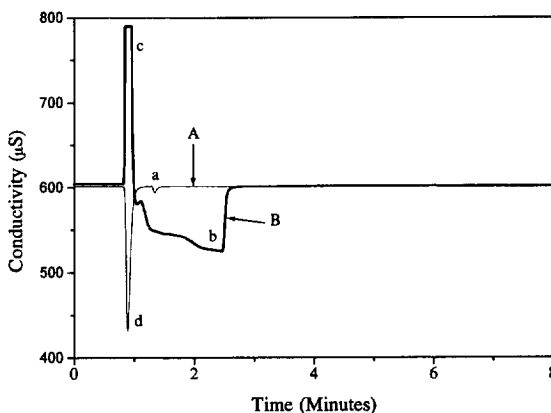

Fig. 6. Recordings of the conductivity detector outputs when distilled water (curve A) and degassed mineral water (curve B) were injected. (a and b), decrease of conductivity caused by the conversion of CO_3^{2-} to HCO_3^- by CO_2; (c), system peak; (d), water peak.

water the decrease of the eluent conductivity was rather broad and intensive in the time interval between 1 and 2.6 min [peak (b)]. Peak (c) is a system peak, caused mostly by eluted HCO_3^-, while peak (d) is a water peak.

To verify that the diminution of the conductivity corresponds to the acidification of the eluent by the retained CO_2, pH of the eluent was monitored by post-column addition of the indicator Thymol blue (0.1 g of Thymol blue in 50 ml of ethanol and 50 ml of water). The indicator used has the colour transition range between pH values 8.0 (yellow colour) and 9.6 (blue colour). The pH value of the original CO_3^{2-}/HCO_3^- eluent was found to be 9.9. Indicator solution was added to the eluent immediately after the separator column using a reagent delivery module (Dionex) at the flow-rate 0.5 ml/min. As a detector, a Spectrasystem UV 2000 (Spectra-Physics) spectrophotometer was used. By recording the spectra it has been found that Thymol blue in deprotonated form absorbs strongly at 595 nm, while in protonated form it absorbs strongly at 430 nm and it practically does not absorb at 595 nm. The differences in absorbance of protonated and deprotonated indicator were used for on-line detection of pH change. Chromatograms of the degassed mineral water (Fig. 7) at 595 nm (curve A) and at 430 nm (curve B) confirm clearly the acidification of the eluent. Due to the drop of the pH value of the eluent,
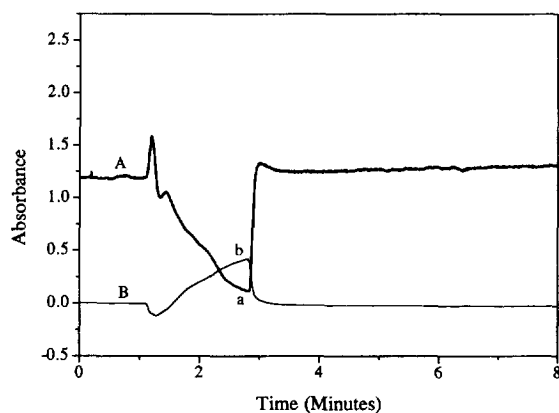
Fig. 7. Absorbance of the eluant with post-column added indicator Thymol blue. The injected sample was degassed mineral water. Absorbance was measured at 595 nm (curve A) and at 430 nm (curve B).

the indicator converts from the deprotonated to the protonated form. Decreases in absorbance at 595 nm (curve A) and an increase at 430 nm (curve B) between 1.5 and 3 min indicated pH changes due to the elution of an excess of CO_2.

By comparing Figs. 5–7 it can be concluded that most of the dissolved CO_2 is never eluted within the system void volume. It elutes in a broad time interval between 1.5 to 3 min. Under the described experimental conditions, the CO_2 peak reaches its maximum at about 3 min [peak (a) in Fig. 5; minimal conductivity (b) in Fig. 6 and minimal (a)/maximal (b) absorbance in Fig. 7]. On this basis the only possible explanation for the retention of dissolved CO_2 was its diffusion into the pores of the stationary phase.

By comparison of Figs. 2 (curve A an B), 5, 6 and 7 it can also be concluded that chloride is always co-eluted with CO_2 when present in increased concentrations, and the explanation for the change, i.e., decrease of the chloride peak height and increase in peak width could be proposed. When the plug of the eluent rich in CO_2 enters the micromembrane suppressor, an additional quantity of CO_2 is formed by the neutralisation of the eluent constituents (CO_3^{2-} and HCO_3^-). This plug therefore becomes supersaturated with respect to CO_2. Because of the pressure drop downstream of the suppressor column, microbubbles of CO_2 are evolved which partially block the surface of the membrane thus preventing the

exchange of Na^+ with H_3O^+. Therefore the conductometric cell reaches a segment of eluent containing mixture of Na^+, H_3O^+ and Cl^- ions instead of H_3O^+ and Cl^- only. Since the equivalent conductivity of sodium ions is much lower than that of H_3O^+ ions, this results in the corresponding decrease of the detector signal. When the plug rich with dissolved CO_2 is flushed out, ion-exchange processes are restored and the suppressor starts to operate in a normal way. The experimental evidence for this prediction was found after collecting fractions of the eluent (after the suppressor column) and determining the Na^+ content in them. Sodium was determined by flame atomic emission spectrophotometry. Three kinds of eluent fractions were collected i.e. pure eluent (prior to the sample injection), the fraction in which chloride was eluted and the fraction in which sulphate was eluted. In the fraction of pure eluent and in the fraction in which sulphate was eluted, sodium was not detected (below 0.01 mg/l) while in the fraction of the eluent in which chloride was eluted, the concentration of sodium was found to be 0.13 mg/l (the average of four measurements). On the basis of these results it can be concluded that the exchange of Na^+ by H_3O^+ in the suppressor column within the zone where CO_2 is eluted, is partially inhibited. Co-elution of CO_2 (broad peak) and Cl^- (sharp peak) is also the most probable reason for the broadening of the Cl^- peak.

3.2. Electrodialytic removal of dissolved carbonate species

For the elimination of the described matrix effects caused by dissolved carbonate species, electrodialytic sample acidification was tested. The acidification was carried out by the apparatus schematically shown in Fig. 1.

3.2.1. Analytical procedure

Samples were transferred into a 100 ml volumetric flask and sonicated for 15 min in an ultrasonic bath. The whole dialytic system was rinsed with the degassed sample. In valve position "LOAD" (L, Fig. 1) about 5 ml of sample was collected into a volumetric flask (DS, Fig. 1). In valve position "RECYCLE" (R, Fig. 1) the sample from the volumetric flask was re-dialysed (usually 15–20 min)
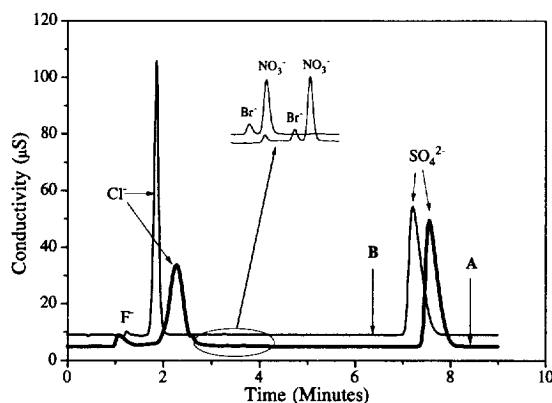
Fig. 8. Chromatograms of a degassed mineral water (A) and electrodialytically pre-treated mineral water (B). On the inset, part of a chromatogram obtained by UV/VIS spectrophotometric detection is presented.

Table 2
Relative standard deviations of retention time, peak area and peak height of anions after electrodialytic sample acidification ($n=6$)

Anion	Retention time (min)	Peak area	Peak height
F^-	1.55 ± 0.01	40 ± 4	5.1 ± 0.4
	$s_{rel}=0.6\%$	$s_{rel}=8.9\%$	$s_{rel}=7.8\%$
Cl^-	2.07 ± 0.01	660 ± 7	83 ± 1
	$s_{rel}=0.5\%$	$s_{rel}=1.1\%$	$s_{rel}=1.4\%$
Br^-	2.84 ± 0.01	284 ± 1	42.1 ± 0.4
	$s_{rel}=0.4\%$	$s_{rel}=0.4\%$	$s_{rel}=1.0\%$
NO_3^-	3.15 ± 0.01	1639 ± 10	215 ± 4
	$s_{rel}=0.3\%$	$s_{rel}=0.6\%$	$s_{rel}=1.6\%$
SO_4^{2-}	6.16 ± 0.02	866 ± 12	52.8 ± 0.7
	$s_{rel}=0.3\%$	$s_{rel}=1.4\%$	$s_{rel}=1.3\%$

until constant conductivity was reached. Liberated CO_2 was removed in a microporous gas separator installed in the ultrasonic bath. The concentration of individual anions in the dialysate (Cl^-, Br^-, NO_3^- and SO_4^{2-}) was determined by the injection of 50 µl of the dialysed sample into an IC, using calibration curves and by standard addition.

The effects of electrodialytic acidification of carbonate based sample can be observed in Fig. 8. Retention times of all anions present in the sample became stable and reproducible (Fig. 8, curve B) and what is even more important, chloride and fluoride peak areas were recovered. The inset in Fig. 8 shows the influence of sample acidification on the retention times of bromide and nitrate. Both anions were detected by UV/VIS spectrophotometer.

Using the proposed sample pre-treatment different mineral waters were analysed and the results obtained compared to the declared values. Quantitative evaluation was carried-out by calibration curve and

standard addition. Samples of mineral waters were electrodialysed, analysed and concentrations of anions were read out from the calibration curves prepared from the standard solutions of anions in Milli-Q water. In the second set of experiments, standard solutions of anions with three concentration ranges were added to the degassed samples which were then electrodialysed and analysed. The concentration of anions were calculated from the peak area increase due to the standard addition. The results presented in Table 1 confirmed that there was no significant difference in the determination of individual anion either by using calibration curve or standard addition. This means that electrodialytic acidification eliminated carbonate interference and showed that there was no loss of anions in the dialytic cell. In order to check this finding, the repeatability of retention times, peak areas and peak heights for five anions (F^-, Cl^-, Br^-, NO_3^- and SO_4^{2-}) in one mineral water was determined. Six samples were taken from one mineral water, electrodialysed and chromatographed. The results are summarised in Table 2. Standard deviations with the

Table 1
The comparison of determined and declared concentration of anions in one mineral water

Anion	Calibration curve (mg/l)	Standard addition (mg/l)	Declared value (mg/l)
F^-	–	0.29	0.24
Cl^-	46.0	45.9	44.2
Br^-	0.42	0.42	0.36
NO_3^-	0.15	0.15	0.08
SO_4^{2-}	88.7	88.1	87.1

exception of fluoride, are very close to the relative standard deviations which are usually obtained when anions are determined by using IC without any sample pre-treatment. This means that electrodialytic neutralisation does not influence the overall uncertainty much. In the case of fluoride it should be pointed out that the reproducibility of fluoride determination (using AS4A-SC column) is relatively low even without any sample pre-treatment because of its co-elution with the system void volume.

4. Conclusions

Dissolved CO_2 in mineral waters causes in IC analysis prolonged retention times and irreproducible peak shapes and peak areas of anions. Chloride and fluoride can not be determined without sample pre-treatment. The automatic detection of other anions is rendered more uncertain due to irreproducible retention times.

After the electrodialytic acidification and the removal of the released CO_2, the results of IC determination of F^-, Cl^-, Br^-, NO_3^- and SO_4^{2-} anions in mineral water were within the limits declared by the producer.

It was found that dissolved CO_2 caused the prolongation of the retention times of anions due to the on-column change of the eluent from carbonate/hydrogen carbonate to mostly the hydrogen carbonate form. CO_2 from the sample neutralised CO_3^{2-} anions to HCO_3^- anions and the surplus of CO_2 is retained by the stationary phase due to diffusion into the pores of the stationary phase. In the segment of eluent which follows the sample plug, CO_2 diffused back into the eluent, converting CO_3^{2-} again into HCO_3^-, and subsequently diminished the elution strength of the eluent.

The decrease of the peak area of the anions which are co-eluted with CO_2, e.g., chloride, is explained by the formation of CO_2 microbubbles in the suppressor column which block the suppressor membrane surface and physically prevent exchange of Na^+ with H_3O^+. The higher fraction of Na^+ in the eluted sample plug results in a lower conductivity than in the case when all Na^+ ions are replaced by H_3O^+.

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