Review

Suppressed ion chromatographic analysis of anions in environmental waters containing high salt concentrations[1]

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Abstract

The literature on the application of suppressed ion chromatography for the analysis of low concentrations of anions in the presence of a high concentration of matrix ions is critically reviewed. It is reported in the literature that suppressed ion chromatographic determinations of anions such as sulfate, arsenate, oxalate, etc., give erroneous results when low concentrations are quantified in the presence of high salt concentrations. In many cases this is believed to arise from overloading of the column by matrix ions, typically by matrix anions.

However, as discussed in this review, the erroneous results in the suppressed ion chromatographic determination of small concentrations of anions such as sulfate, oxalate and molybdate in matrices having very high salt concentrations are not caused by column overloading but are due to some anion–proton interactions within the suppressor. Determination of anions of strong acids such as Cl^-, Br^-, and I^- is not affected and they can be accurately quantified by suppressed ion chromatography in aqueous matrices containing high salt concentrations.

Suppressed ion chromatography as a tool for the accurate analysis of small concentrations of anions in the presence of high ionic strength matrices, such as subsurface waters, well waters, and aqueous extracts of sandy soils has also been reported.

Keywords: Reviews; Suppressed ion chromatography; Water analysis; Environmental analysis; Anions; Sea water; Subsurface brines; Geothermal brines; High salinity groundwaters; Soil extracts

Contents

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1. Introduction

Ion chromatography (IC) was developed by Small et al. [1] by making use of suppressed ion conductivity detection and pellicular ion-exchange packings. At present there are two main types of ion chromatography: (1) suppressed ion chromatography and (2) non-suppressed or single-column chromatography. The basic principles of each technique have been presented elsewhere [2–5] and are not part of the discussion herein.

Soon after its introduction, IC was used for different applications in various fields. Although the major use of IC has been in the analysis of environmental waters, it has also been applied to the analysis of numerous other matrices. For ultimate detection limits, generally in the $mg\,l^{-1}$ to $\mu g\,l^{-1}$ ranges, suppressed IC is normally superior to single-column or non-suppressed IC. Therefore, the use of suppressed IC has been more widespread than the applications of non-suppressed methods.

Since its invention in 1975, suppressed ion chromatography has become the workhorse laboratory instrument for the determination of anions. This important role is reflected in a large number of publications, reviews [6–14] and books [2,3], [15–18]. Its determination of common anions is so well established that the reliability of suppressed IC is often taken for granted.

The determination of anions such as fluoride, chloride, bromide, iodide, nitrate, sulfate, carbonate, phosphate, oxalate, etc., in environmental waters is the largest single area in which suppressed ion chromatography has found applications. In most environmental water samples, analyzed by ion chromatography, the concentrations of anions are within an order of magnitude of each other and therefore simultaneous determination of various anions can be made with good accuracy. However, this is not the case when determining small or trace concentrations of anions in the presence of large concentrations of matrix ions. In these instances suppressed ion chromatography may produce erroneous results in anion quantification. The error is believed to be due to incomplete resolution of the peaks and/or overloading of the column by the matrix ion.

Although an extensive literature, including reviews and books, has been published on IC, critical reviews concerning the determination of small concentrations of anions in the presence of very large concentrations of salt matrices are lacking. Moreover, most review articles have simply reported the literature without critical analysis of the special cases. This prompted us to review the existing literature on the applications of suppressed IC in the analysis of high ionic strength waters and various aqueous matrices.

The objective of this paper was to critically review the application of suppressed IC in the analysis of high ionic strength waters and aqueous matrices.

This review is divided into two parts. Part A contains the review of the literature concerning the suppressed IC determination of known or synthetic solutions. In Part B, we have reviewed the suppressed ion chromatographic analysis of real waters such as subsurface and pore waters generated by oilfield and geothermal energy industries, seawater, ground waters with high salt concentration and extracts of sandy soils containing high salt concentrations. The analysis of these waters (or aqueous matrices) is critical with respect to pollution problems, subsurface formation identification, water compatibilities, water quality control, water flooding, and environmental corrosion.

2. Part A. Suppressed IC determination of small concentrations of anions in the presence of very large salt concentrations

Bynum et al. [19] were the first to investigate the response of a small concentration of sulfate in the presence of large concentration of chloride under standard suppressed IC conditions. These authors reported that the determination of 0–100 mg l^{-1} of sulfate in the presence of 8000 mg l^{-1} or higher chloride was unreliable.

Suppressed IC determination of a small concentration of chloride in large concentrations of sodium hydroxide and sulfuric acid solutions was studied by Smith [20]. He reported that retention time and the peak height of 31.2 mg l^{-1} chloride in the presence of sulfuric acid, equivalent to 0 to 12 200 mg l^{-1} sulfate, increased with increasing concentration of sulfuric acid. The peak height of 12.5 mg l^{-1} chloride was also increased due the presence of 0.8 mol l^{-1} sodium hydroxide. On the basis of these results and the data reported by Bynum et al. [19], Smith [20] concluded that the effect of high concentrations of one anion on the analysis of a small concentration of a second anion was general.

Tan and Dutrizac [21] studied the effect of the concentrations of common anions such as chloride, nitrate and sulfate on the suppressed IC determination of HAsO$_4^{2-}$ anion. On the basis of their experimental data, these authors concluded that high concentrations of anions such as chloride, nitrate, and sulfate affected the determination of arsenate by

suppressed IC. This effect did not appear to be due to peak overlap. It was suggested that the change in the arsenate peak height in the presence of high concentrations of other anions might have occurred due to the competition between the arsenate and other anions for the active sites on the resin in the analytical (or separator) column during the exchange with eluent anions. This competitive effect was observed prior to column overloading, at which point the arsenate peak completely disappeared at very high concentrations of the other anions.

During the course of suppressed ion chromatographic determinations of sulfate in deep subsurface oilfield brines (containing 300 mg l^{-1} sulfate with 140 000 mg l^{-1} chloride) Singh et al. [22], reported that the sulfate analysis was inaccurate at 50 times dilution (containing 2660 mg l^{-1} chloride and 6 mg l^{-1} sulfate) of the brine samples. Although, the
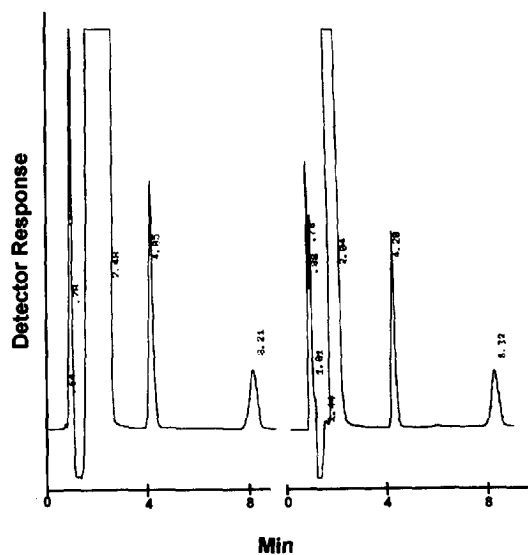
Fig. 1. Ion chromatograms of subsurface oilfield brine at 50 times dilution (first chromatogram showing 19.4 mg l^{-1} Br$^-$ and 4.7 mg l^{-1} SO$_4^{2-}$ peaks in the presence of 2800 mg l^{-1} Cl$^-$) and at 300 times dilution (second chromatogram showing 3.8 mg l^{-1} Br$^-$ and 1.4 mg l^{-1} SO$_4^{2-}$ peaks in the presence of 560 mg l^{-1} Cl$^-$). Dionex 2120 ion chromatograph; injection volume, 50 μl; detector sensitivity, 10 μS full scale (for first chromatogram) and 3 μS full scale (for second chromatogram); analytical column, Dionex AG-4 and AS-4; eluent, a mixture of 3.0 mmol l^{-1} NaHCO$_3$ and 2.4 mmol l^{-1} Na$_2$CO$_3$; flow rate, 2.0 ml min^{-1}; peak integrator, Dionex 4217.

sulfate peak was reasonably sharp and well resolved up to the baseline (Fig. 1), the analytical results were about 30% lower than those obtained by inductively coupled plasma atomic emission spectrometry (ICP-AES). Accurate sulfate quantification was obtained only after 200 times or higher dilution of the analyte sample. Bromide results, however, remained unaltered at various dilutions. To confirm this further, the effect of 2660 mg l^{-1} chloride (0.075 mol l^{-1} sodium chloride) on the determination of 5 mg l^{-1} each of bromide and sulfate was studied. These results, shown in Fig. 2 and Fig. 3, respectively, again indicated that the bromide peak remained unchanged by the presence of 2660 mg l^{-1} chloride. However, a decrease of about 12% was observed in the peak height of sulfate in the presence of 2660 mg l^{-1} chloride (due to the use of a brand new AS-4 column, the sulfate results reported in Fig. 3 were

Fig. 3. Ion chromatograms: (a) 5 mg l^{-1} sulfate, and (b) 5 mg l^{-1} sulfate + 0.075 mol l^{-1} sodium chloride (2660 mg l^{-1} chloride). IC conditions same as in Fig. 1 (this figure was reproduced from Ref. [22]).

Fig. 2. Ion chromatograms: (a) 5 mg l^{-1} bromide, and (b) 5 mg l^{-1} bromide + 0.075 mol l^{-1} sodium chloride (2660 mg l^{-1} chloride). IC conditions same as in Fig. 1 (this figure was reproduced from Ref. [22]).

slightly different than reported for the brine sample in Fig. 1).

On the basis of the data reported in the above paragraph it is clear that the effect of high concentrations of one anion on the analysis of a small concentration of a second anion cannot be generalized as concluded by Smith [20]. This is because small concentrations of bromide were not affected by the large concentration of salt (sodium chloride) as long as all anion peaks were resolved to the baseline. These observations prompted Singh and Abbas [23] and Singh [24] to investigate the response of other

anions such as: (1) the determination of nitrate, iodide, oxalate and molybdate in the presence of a large concentration of sodium chloride, and (2) the determination of a small concentration of chloride and sulfate in the presence of a large concentration of sodium hydroxide. The results of these investigations revealed that oxalate and molybdate peak heights were considerably decreased in the presence of sodium chloride in comparison to their peaks in its absence. The effect of sodium chloride on these ions was similar to the effect of sulfate [19,22] and arsenate [21]. The presence of sodium chloride, however, had no effect on the suppressed IC determination of a small concentration of iodide. In the presence of 0.08 mol l^{-1} sodium hydroxide, the chloride peak remained unchanged, while the sulfate peak was reduced by 20%. The behavior of chloride in sodium hydroxide and iodide in sodium chloride were similar to that observed for bromide in sodium chloride [22].

3. Critical analysis of the data reported in Part A and characterization of the problem

3.1. Critical analysis

Critical analysis of the data reported in Part A revealed: (1) that the effect of a high concentration of one anion on the analysis of a small concentration of a second anion cannot be generalized, as the effect is not the same for each anion; (2) that the peak heights of small concentrations of anions such as chloride, bromide and iodide remain unchanged in the presence and absence of large concentrations of salts as long as a baseline resolution is obtained; (3) that the presence of a large concentration of salt greatly affected the determination of small concentrations of sulfate, oxalate, arsenate and molybdate by causing a resultant decrease in peak height; and (4) it was difficult at times to even identify the error (Fig. 1).

Normally in liquid chromatography the error in the determination of analytes is caused either by incomplete resolution of peaks or by overloading of the analytical column by the matrix analytes. In the absence of peak overlapping, the error in the de-

termination of small concentrations of one anion in the presence of salt matrices by suppressed IC was suggested to be due to column overloading [25] or to competition between small concentrations of analyte anions and a large concentration of matrix anions for active sites on the column [21].

The error in quantification due to column overloading is possible, because high concentrations of chloride or other matrix anions can overload the separator column, by occupying all or most of the exchange sites on the column. The overloading of the column can result in a broadening or asymmetry in the peak of the minor anion. However, on the basis of the results reported in Table 1 (data obtained from Fig. 1), the possibility of column overloading due to a large concentration of chloride was ruled out, as the bromide concentration of 968.7 mg l^{-1} determined at 50 times dilution (first chromatogram, Fig. 1) did not differ from that of 953.1 mg l^{-1} determined at 250 (second chromatogram, Fig. 1) or higher dilutions. However, the sulfate concentration of 237.3 mg l^{-1} determined at 50 times dilution was 30% lower as compared to 340.3 mg l^{-1} determined at 250 times dilution. These results demonstrated that the lower than expected values obtained in the suppressed ion chromatographic determination of sulfate in 50 times diluted brine were not caused by column overloading by chloride. If the column overloading had occurred, the bromide peak height should have been reduced more than the sulfate peak, because bromide elutes before sulfate, and therefore has less affinity for the column than does sulfate. Similar conclusions can be drawn from the analysis of small concentrations of chloride and sulfate in the presence of a large concentration of sodium hydroxide.

Table 1
Determination of bromide and sulfate in presence of different concentration of chloride present as NaCl, CaCl$_2$ and MgCl$_2$

Dilution of brine (times)	Chloride[a] (mg l^{-1})	Concentration[a] (mg l^{-1})	
		Bromide	Sulfate
50	2800 (140 000)	19.4 (968)	4.7 (237.3)
250	560 (140 000)	3.8 (953.1)	1.4 (340.3)

[a] Numbers within brackets represent the concentration in undiluted brine sample.
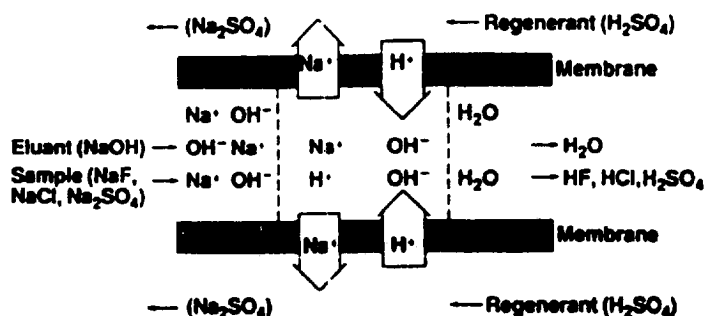
Fig. 4. Anion micromembrane suppressor; eluent cations are exchanged for H^+ to form low-conductivity solution; solute cations are also exchanged for H^+ to form strong acids (this figure was reproduced from Ref. [27a]).

3.2. Characterization of the problem

The results reported clearly suggested that the reduction in peak height of a small concentration of sulfate in the presence of a large concentration of sodium chloride or sodium hydroxide was not caused by overloading of the analytical column by the matrix anions, such as chloride and hydroxide. We suspect that the suppressed ion chromatographic determination of sulfate in the presence of very high concentrations of sodium chloride and sodium hydroxide was not affected by the large concentration of chloride and hydroxide but due to the large concentration of the corresponding cation, i.e. sodium.

It has been mentioned in the literature [26,27a,28] that in suppressed ion chromatography, the suppressor column or anion micro membrane suppressor (AMMS) exchanges all the influent cations for H^+. In doing so, the suppressor column reduces the eluent (typically a mixture of sodium bicarbonate and sodium carbonate for anion analysis) background to that of weakly conducting H_2CO_3 and converts the common anions such as Cl^-, Br^-, I^- and SO_4^{2-} to strongly ionized acids (HCl, HBr, HI and H_2SO_4, respectively). For quantitative analysis, complete and fast exchange of cations for H^+ ions at the surface of the suppressor column is required. However, when the cationic concentration in the influent suddenly increases due to the presence of large amounts of cations such as Na^+ in the analyte sample, a significant accumulation of H^+ ions occurs on the surface of the suppressor during the ion-exchange process as suggested by Mercurio-Cason et al. [29].
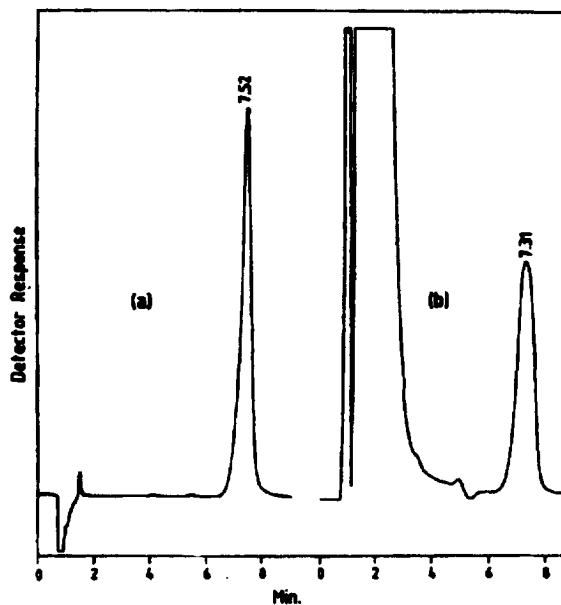
Fig. 5. Ion chromatograms: (a) 10 mg l^{-1} oxalate, and (b) 10 mg l^{-1} oxalate+0.128 mg l^{-1} sodium chloride (4538 mg l^{-1} chloride). IC conditions same as in Fig. 1 (this figure was reproduced from Ref. [22]).

This phenomenon is illustrated in Fig. 4 [27a].

Accumulation of hydrogen ions at the surface of the suppressor will cause the formation of the HSO_4^- ion pair after reaction with analyte sulfate ions. The formation of the HSO_4^- ion pair will cause a decrease in the conductivity of sulfate ions due to the reduction in total ionic charge. In addition, the process of proton–sulfate association may result in broadening of the sulfate peak. (Fig. 4, Fig. 5)

If the explanation given holds true, the determi-

Table 2
Proton–anion association equilibria

H_3O^+–anion association equilibria	Log K
$H_3O^+ + I^- \leftrightarrow HI + H_2O$	-9.5
$H_3O^+ + Cl^- \leftrightarrow HCl + H_2O$	-6.0
$H_3O^+ + Br^- \leftrightarrow HBr + H_2O$	-9.0
$H_3O^+ + HSO_4^{2-} \leftrightarrow HSO_4^- + H_2O$	1.9
$H_3O^+ + HC_2O_4^{2-} \leftrightarrow HC_2O_4^- + H_2O$	4.2
$H_3O^+ + MoO_4^{2-} \leftrightarrow HMoO_4^- + H_2O$	–

nation of anions, which are capable of forming a strong ion pair with protons as shown in Table 2 27b, in the presence of large concentrations of cations should also be affected. This was found, as reported above. Oxalate, arsenate ($HAsO_4^{2-}$) and molybdate anions, each capable of forming a strong ion pair with a proton (Table 2), were affected when their small concentrations were determined in the presence of sodium chloride. For example, a marked decrease of approximately 40% in oxalate peak height, shown in Fig. 6, associated with a small
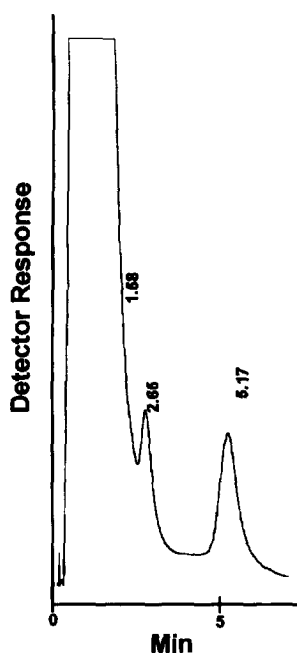
Table 3
Effect of different concentrations of metal salts on the peak height of 2.0 mg l^{-1} oxalate with 250 μl injection volumes (reproduced from Ref. [22])

Metal salt	Concentration		Peak-height counts	Reduction[a] (%)
	Salt (mol l^{-1})	Anion (mg l^{-1})		
None	0	0	785 556	
NaCl	0.028	Cl, 992.7	705 286	10.2
CaCl$_2$	0.014	Cl, 992.7	231 679	70.5
CaCl$_2$	0.0036	Cl, 255.3	735 040	6.4
NaNO$_3$	0.0036	NO$_3$, 223.2	750 604	4.4
Mn(NO$_3$)$_2$	0.0018	NO$_3$, 223.2	595 397	24.2

[a] % Reduction as compared to the peak height counts of the peak of pure oxalate.

amount of peak broadening, can be attributed to the $HC_2O_4^-$ ion pair, similar to the formation of the HSO_4^- ion pair as suggested above. However, the accuracy of the determination of anions which do not form strong ion pairs with protons (Table 2), was unaffected by the presence of a large salt concentration.

To further confirm that the decrease in oxalate peak height in the presence of sodium chloride was not caused by chloride, the effect of different metal salts on the peak height of 2 mg l^{-1} oxalate was studied. These results, reported in Table 3, show that at the same anion (chloride) concentration, calcium caused a larger change in oxalate peak height than sodium. Similarly the effect of manganese was much higher as compared to sodium when present with oxalate as their nitrate salts (containing the same amount of nitrate). These experimental results demonstrate that it is the cation which is causing a reduction in the oxalate peak height during its determination by suppressed IC when relatively large concentrations of metal salts are present in the analyte matrix.

Fig. 6. Ion chromatogram showing the separation of 0.3 mg l^{-1} thiosulfate peak (5.17 min) from chloride, bromide and sulfate (1.58 min) and iodide (2.65 min). Dionex AG-5 analytical column; 3.0 mmol l^{-1} NaHCO$_3$ +2.4 mM Na$_2$CO$_3$ eluent at a flow-rate of 2.0 ml min^{-1}; detector sensitivity, 1.0 μS with a 250-μl sample injection.

4. Conclusion Part A

On the basis of the results presented in Part A, it is concluded that the error in the determination of small concentrations of anions such as sulfate, oxalate, molybdate etc., each being able to form strong anion–proton ion pairs, in the presence of large

concentrations of salt matrices by suppressed ion chromatography can be very difficult to identify. The error is often not caused by column overloading by matrix anions, but instead may be caused by some anion–proton interactions within the suppressor. Such interactions would cause a decrease in analyte conductivity, resulting, in turn, in smaller and broader analyte peaks. Anions of strong acids such as chloride, bromide, and iodide are not affected by proton–anion interactions, and, as long as peaks are resolved up to the baseline, should be accurately determined by suppressed ion chromatography in water matrices containing high salt concentrations.

Changes in the baseline conductivity would also affect the quantification of analyte anions. For example, strongly acidic analyte solutions will cause a decrease in the baseline conductivity by: $H^+ + CO_3^{2-}$ $\leftrightarrow HCO_3^-$ and $H^+ + HCO_3^- \leftrightarrow H_2CO_3$. This, in turn, would result in higher analyte peaks. Positive error in the determination of chloride in sulfuric acid solutions, observed by Smith [20], can be explained on this basis.

5. Part B. Suppressed IC analysis of real waters of high salinity

5.1. Subsurface waters

5.1.1. Oilfield brines

Petroleum is normally produced with some water, and in some cases, a substantial amount of water is generated [30]. Although the oil industry has recognized its use in the secondary recovery of oil, not all of the produced water is always immediately usable and generally must be disposed of by some method. Since most of the produced or subsurface waters are highly mineralized, they have a great potential to pollute potable water. Pollution, disposal, and other water problems in the petroleum industry have, therefore, necessitated the complete analysis of subsurface brines [31,32].

Subsurface waters are quite variable in their chemical composition, especially, in their major components, as can be seen from the composition of brine recovered from Saudi Arabian oilfields (Table 4). A complete analysis of subsurface brine from the Ghawar field (Saudi Arabia) is shown in Table 5.

Table 4
Concentration of ions in high- and low-salinity subsurface oilfield brines

Solutes	Concentration (mg/l)	
	High salinity	Low salinity
Cations		
Ca^{2+}	30 060	13 600
Mg^{2+}	4375	1600
Na^+	47 300	28 000
Sr^{2+}	1050	560
Anions		
Cl^-	139 500	71 800
HCO_3^-	360	360
SO_4^{2-}	96	400

Through a recent literature search, it was noted that very little has been reported on the suppressed ion chromatographic analysis of subsurface oilfield brines. In a recent paper, Singh et al. [22] have reported on the suppressed IC analysis of deep subsurface waters obtained from Saudi Arabian oil wells. Marr [33] has also reported an IC method for the determination of sulfate in oil-well brines.

There is a slight difference between the procedures used in suppressed IC analysis of highly saline subsurface brines and those used for surface waters having a low salinity (for example drinking water, rain water, snow, river water and lake water). Typically, the simultaneous analysis of all determinant anions is not always possible in subsurface waters due to the very large difference in the concentration of major and minor anions. Since the methods are not well established, the accuracy of suppressed IC for the analysis of subsurface brines cannot be taken for granted. The methods used for the analysis of various anions in subsurface brines are described in the following paragraphs.

5.1.1.1. Determination of chloride. Accurate analysis of chloride in oilfield waters can be carried out using suppressed IC after appropriately diluting the water samples. In Table 6 and Table 7, comparisons of chloride results obtained by a suppressed IC method and those obtained via a silver chloride precipitation method (obtained using an automatic titration system, MemoTitrator) are presented. The good agreement between the two methods revealed the accuracy of suppressed IC for this analysis.

Table 5
Complete analysis of a subsurface water (obtained from Saudi Arabian oilwell), seawater (obtained from Arabian Gulf) and ground water (obtained from Saudi Arabian aquifer)

Solutes	Concentration, mg l^{-1} water		
	Subsurface	Seawater	Ground water
Cations			
Ba^{2+}	8	0.2	0
Ca^{2+}	16 184	660	224
K^+	1747	629	38
Li^+	30	0.3	0.1
Mg^{2+}	1852	2137	98
Na^+	46 937	17 770	847
NH_4^+	595	0.1	<1
Sr^{2+}	829	13	5
Anions			
BO_3^{3-}	276	22	3.3
Br^-	829	1030	3.5
Cl^-	110 500	31 940	1535
F^-	5	<1	240
HCO_3^-	210	140	<1
I^-	31	<1	<1
NO_3^-	–	<1	10
$S_2O_3^{2-}$	34	<1	<1
SO_4^{2-}	255	4550	528
Other parameters			
pH	7.1	7.6	7.9
Density (g ml^{-1})	1.125	1.043	1.004
TDS (mg l^{-1})	180 300	58 900	3500
Ionic strength (mol l^{-1})	3.816	1.154	0.073

5.1.1.2. Determination of bromide and sulfate. Similar to chloride, the determination of bromide in oilfield waters can be accurately carried out by suppressed IC after appropriate dilution of the sample water to achieve baseline resolution of the bromide peak as shown in Fig. 1. However, the determination of the sulfate content of oilfield waters by suppressed IC is not as straightforward as it may seem based on the determination of sulfate in low-salinity waters. The determination of sulfate could be erroneous if proper dilution of the water sample is not made. This is clearly shown in Table 8. Depend-

Table 6
Analysis of chloride in various high-salinity water matrices determined by suppressed ion-chromatography (IC) and Memotirator (MT) methods

Sample identity	Analyzed chloride concentration (mg l^{-1})		Statistical parameters		
	MT±S.D.	IC±S.D.	t	s_m	n
Arab-D (LS)	71 650±280	71 565±910	0.22	298	7
Ground water	2600±1	2577±4	1.2	28	5
Seawater	31 650±95	31 800±286	1.22	469	5
Mixture	90 400±452	91 109±1367	1.21	447	7

Arab-D: oilfield brines obtained from Saudi Arabian oil wells. LS: low salinity. HS: high salinity. Mixture: 60% Arab-D (HS)+20% ground water+20% seawater.

Table 7
Regression statistics comparing the results of chloride analysis of various natural water matrices obtained by suppressed ion chromatography and Memotirator methods

Water matrix	n	Regression line	r	$t_{intercept}$	t_{slope}	S.E.
Mixture[a]	20	$Y=1.006X-1295$	0.9986	0.002	0.42	1238
Ground water	25	$Y=1.011X+4$	0.9976	0.14	1.04	9
Soil extracts	20	$Y=0.993X+33$	0.9999	0.005	2.59	294

[a] Mixtures of ground water, seawater and Arab-D brines in different ratios. S.E.: standard error.

ing on the sulfate and salt content of the oilfield brine, different dilutions are required for accurate analysis. As mentioned earlier, the error in the determination of sulfate in a subsurface brine by suppressed IC may not be identifiable on the basis of visual inspection of ion chromatograms alone. Therefore, initially the accuracy of sulfate results obtained by suppressed IC should be validated by another established method.

5.1.1.3. Determination of thiosulfate. Because of its strong retention on IC columns [34], the determination of thiosulfate in subsurface oilfield waters by suppressed IC is most efficiently carried out using columns of short length [35,36]. Singh and Abbas (unpublished work) developed IC conditions for the accurate determination of thiosulfate in subsurface brines. Fig. 6 presents the ion chromatogram of a brine sample diluted 100 times with deionized water. The thiosulfate peak which eluted at 5.17 min was clearly separated from the other matrix anions (from chloride, bromide and sulfate which eluted together at 1.58 min and iodide which eluted at 2.65 min).

The analysis was run on a Dionex 2120i ion chromatograph. It can be seen in Fig. 6 that the iodide peak, although not resolved up to the baseline, may be used for qualitative analysis of this anion.

Simultaneous analysis of sulfate, iodide and thiosulfate

Singh and Abbas (unpublished work) developed a suppressed IC method for the simultaneous determination of sulfate, thiosulfate and iodide in subsurface oilfield waters. The detector sensitivity was changed during the analysis to give well resolved analyte peaks. Accuracy of the data was assessed by ICP-AES and the method of standard additions. Detection limits were found to be between 10 and 20 $\mu g\,l^{-1}$, obtained without sample preconcentration.

5.1.1.4. Determination of fluoride, borate and carbonate. Accurate determinations of these three ions in high-salinity waters cannot be made by suppressed IC using regular anion-exchange columns. Normally, suppressed ion-exclusion chromatography [37–41] is the method of choice. By using octanesulfonic acid

Table 8
Analysis of sulfate in real Arab-D brine (RAD), high salinity synthetic Arab-D brine (HSSAD) and low salinity synthetic Arab-D brine (LSSAD), at different dilutions as carried out by suppressed ion chromatography (IC) and inductively coupled plasma atomic emission spectroscopy (ICP) (reproduced from Ref. [22])

Dilution factor	RAD, SO_4 (mg l^{-1})			HSSAD, SO_4 (mg l^{-1})			LSSAD, SO_4 (mg l^{-1})		
	ICP	IC	% difference	ICP	IC	% difference	ICP	IC	% difference
50	6.0	4.10	31.7	1.90	0.90	52.6	7.60	7.2	5.3
100	3.0	2.84	5.3	0.95	0.80	15.8	3.80	3.82	-0.5
200	1.5	1.48	2.0	0.48	0.42	12.5	1.90	1.90	0.0
250	1.2	1.2	0	0.38	0.36	5.3	1.27	1.27	0.0

RAD: Na=55 220, K=2055, Mg=2180, Ca=19 050, Sr=1000, Cl=133 000, SO_4=300.
HSSAD: Na=41 600, Mg=4200, Ca=26 320, Sr=900, Cl=123 550, SO_4=95.
LSSAD: Na=28 000, Mg=1600, Ca=13 600, Sr=545, Cl=77 800, SO_4=380.
% difference=[(ICP-IC)/ICP]×100.

(1–1.5 mmol l^{-1} at 0.8–1.0 ml min^{-1}) as eluent, tetrabutylammonium hydroxide (5.0 mmol l^{-1} at 4.0 ml min^{-1}) as regenerent, a Dionex HPICE-AS1 analytical column and an AMMS-ICE as suppressor, we were able to quantify fluoride, borate, and carbonate in Arab-D brines (unpublished work). The accuracy of the method was tested by analyzing these anions by other standard methods. An ion chromatogram showing the separation of fluoride, borate and carbonate anions in a subsurface oilfield brine is depicted in Fig. 7.

5.1.1.5. Determination of organic aliphatic acid anions. The ion-exclusion chromatographic conditions, as reported above, were employed by Fisher [42] for the determination of aliphatic acid anions in deep subsurface waters from eight localities. Formation waters from the Eastern Venezuelan basin, Denver basin, Eastern Green River basin (Red Desert
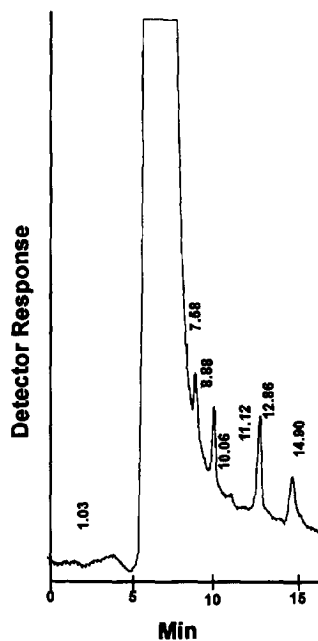

Fig. 7. Ion chromatogram showing the peaks of fluoride (at 8.88 min), borate (10.06 min), formate (11.12 min), acetate (12.86 min) and carbonate (14.90 min) in a 50 times diluted subsurface oilfield water. Dionex HPICE-AS1 analytical column; Dionex AMMS-ICE suppressor; 1 mmol l^{-1} octanesulfonic acid eluent at 0.8 ml min^{-1} flow-rate, 5.0 mmol l^{-1} tetrabutylammonium hydroxide regenerent at 4.0 ml min^{-1} flow-rate; detector sensitivity 1 μS with a 50-μl sample injection.

and Washakie basins, Wamsutter Arch), San Juan basin, Piceance basin, Raton basin, Gulf Coast basin, and the Western Overthrust, were analyzed. The general order of the aliphatic acid anion concentrations in various deep subsurface waters was: acetate≫propionate≳butyrate≳valerate. For coal associated waters, the order of abundance was propionate≳acetate≳butyrate≳valerate.

5.1.1.6. Determination of scale inhibitors. Shuler [43] reported an anion chromatographic method for the determination of phosphate-based scale inhibitors in oil-well waters. In this method, instead of using suppressed conductivity, a post column reactor was used for the determination of scale inhibitors as an iron complex of the inhibitor compound which was detected by UV.

5.1.2. Geothermal brines

Geothermal subsurface fluid is brought to the surface for energy recovery. The cooled effluent from this process may be returned to the ground through reinjection wells. However, the well water samples must be thoroughly characterized in order to estimate corrosion and scaling problems due to this highly mineralized water, as well as to establish any environmental impacts and potential for mineral recovery. Lash and Hill [44] have reported on the suppressed IC analysis of geothermal well waters. Anions such as fluoride, chloride, bromide and sulfate were analyzed in geothermal waters obtained from two sites. The concentrations of these anions in these waters were found to vary greatly. While site A contained about 3600 mg l^{-1} of total dissolved salts, the water from site B was as mineralized as high-salinity subsurface oilfield water containing 132 000 mg l^{-1} Cl, 14 mg l^{-1} F, 95 mg l^{-1} bromide and 59 mg l^{-1} sulfate with major cations being sodium (46 120 mg l^{-1}) and potassium (9700 mg l^{-1}). The results obtained by suppressed IC were compared with other standard methods. Good agreement was found for sulfate quantification in low-salinity water between suppressed IC and other methods. However, IC results for sulfate in high-salinity water were 44% lower in comparison to other methods. The lower results for sulfate in high-salinity brine can be attributed to ion pair formation in the suppressor as mentioned in Part A. The discrepancy in the de-

termination of some anions such as fluoride and
bromide can be attributed to lack of baseline res-
olution. Other workers [45–48] have also reported
on the IC analysis of geothermal brines.

5.1.3. Porewater

Pyen and Fishman [49] examined pore waters
obtained from subsurface cores by suppressed IC.
The high-salinity waters were diluted 50- to 100-fold
prior to analysis. The diluted samples were analyzed
for fluoride, phosphate, nitrate, bromide and sulfate.
Analysis of chloride required a higher dilution. The
analytical results obtained by suppressed IC were
compared with colorimetric methods. Typically, a
good agreement between analytical results obtained
from both methods was found. However, suppressed
IC analysis of the samples containing high salt
concentration and low sulfate concentration showed
lower results as compared with results obtained via
colorimetric methods. This discrepancy may have
also been caused by ion pair formation between
protons and sulfate ions as discussed in Part A.

5.2. Seawater

Analysis of anions such as chloride, bromide and
sulfate present in seawater is critical in the oil
industry, as the seawater is used in the secondary
recovery of oil by flooding the subsurface formation
[32]. The determination of major anions such as
chloride, bromide and sulfate can be quite accurately
carried out by suppressed IC as described in the
literature [12]. The accuracy of chloride determi-
nation in seawater matrices by IC was assessed by a
silver chloride precipitation titration method using an
automatic titrator system. These results are listed in
Table 6 and Table 7.

It is clear from Table 5 that the concentration of
bicarbonate in seawater is small when compared with
sulfate and chloride. The determination of the car-
bonate content of seawater can be carried out by
suppressed ion-exclusion chromatography as re-
ported for oilfield subsurface waters. An ion chro-
matogram of 25 times diluted seawater showing the
separation of carbonate from chloride, bromide and
sulfate ions can be seen in Fig. 8.

Quantification of nitrate in seawater is also im-
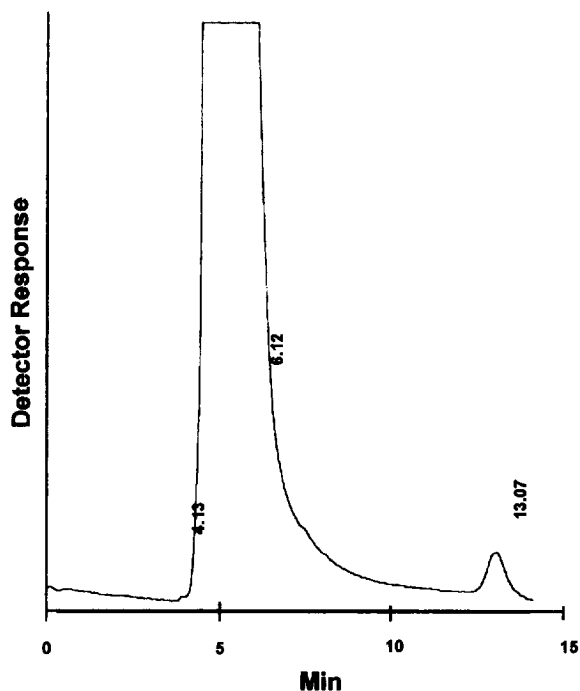portant due to environmental concern. Because of its

Fig. 8. Ion chromatogram showing the peak of carbonate (13.07
min) in a 25 times diluted seawater sample. Dionex HPICE-AS1
analytical column; deionized water eluent at 1 ml min^{-1} flow-rate;
detector sensitivity 3 μS with a 50-μl sample injection. Other IC
conditions same as in Fig. 7.

very low concentration (Table 5), however, its
determination typically is not carried out by sup-
pressed IC. Normally amperometric and UV de-
tection systems are used [50,51]. Singh and Abbas
(unpublished) have developed suppressed IC con-
ditions for the determination of seawater nitrate, as
can be seen in Fig. 9. The method was used for the
accurate determination of nitrate in fish pond water
in which the nitrate concentration is slightly higher
than in seawater.

The simultaneous determination of major anions
(such as chloride and sulfate) and cations (such as
magnesium and calcium) in seawater can be carried
out by suppressed and single-column IC with ethyl-
enediaminetetraacetic acid (EDTA) as eluent [52,53].
By interacting with EDTA, magnesium and calcium
form anionic complexes and can be determined as
anions. This approach can also be applied to the
simultaneous analysis of chloride, bromide, sulfate,
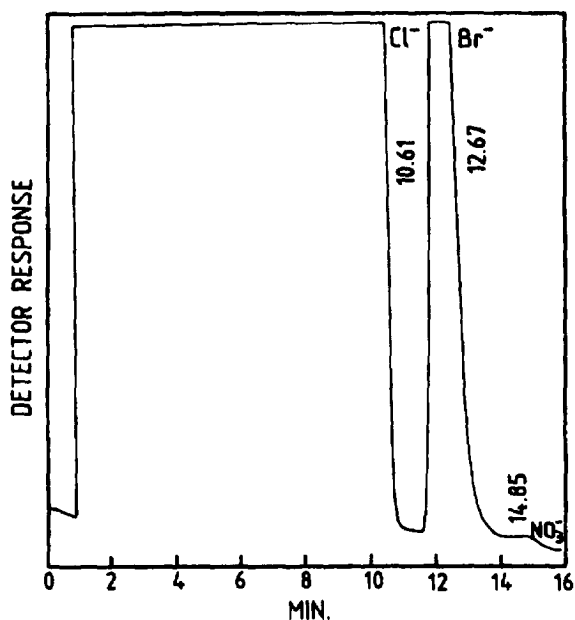magnesium and calcium in subsurface brines.

Fig. 9. Ion chromatogram showing the peaks of chloride (10.61 min), bromide (12.67 min) and nitrate (14.85 min) in a five times diluted seawater sample. Dionex AS-4 analytical column with AG-4 guard column; 0.3 mmol l^{-1} Na$_2$CO$_3$+1.0 mmol l^{-1} NaOH eluent at a flow-rate of 2.0 ml min^{-1}; detector sensitivity 1 μS with a 50-μl sample injection.

5.3. Ground waters of high salinity

Ground water in desert countries like Saudi Arabia contains a very high concentration of salt (Table 5 and Table 9). Use of such waters in petroleum recovery and other applications sometimes results in scaling and corrosion formation due to their high content of chloride, sulfate, and calcium carbonate supersaturation (Table 9). Therefore, characterization of the ionic content of these waters is critical. Like subsurface waters and seawater, ground waters also have large differences in their concentrations of major and minor anions. For example, bromide and nitrate concentrations are typically much lower than sulfate and chloride concentrations. Because of the very high sulfate concentration, low dilutions of the water samples may not be adequate. The sulfate concentration may overload the column resulting in reduced peak height and giving lower results than expected. On the other hand, greater dilution of the water samples may lower the concentrations of

bromide and nitrate to the levels below the detection limits of their determination by suppressed IC. Despite the large difference in anion concentrations, a simultaneous determination is possible as can be seen in Fig. 10 using variable detector sensitivity. Using these suppressed IC conditions accurate results of chloride (Table 6 and Table 7) and sulfate analyses were obtained in various ground waters.

Determination of fluoride cannot be accurately carried out by suppressed anion chromatography and requires suppressed anion-exclusion chromatography, as can be seen in Fig. 11. Suppressed IC, however, can be used for the determination of trace concentrations of iodide in these waters (Fig. 12). Carbonate can be determined simultaneously with fluoride by suppressed anion-exclusion chromatography (Fig. 11).
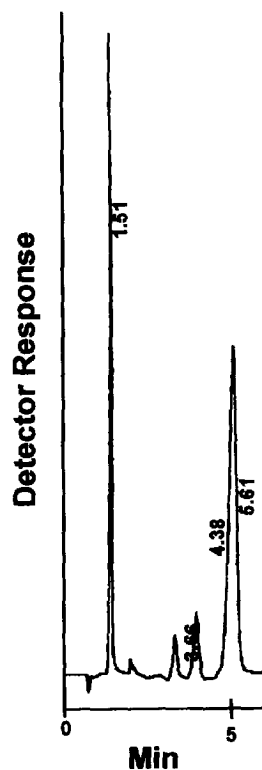

Fig. 10. Ion chromatogram showing the peaks of chloride (1.51 min), bromide (3.66 min), nitrate (4.38 min) and sulfate (5.61 min) in a 50 times diluted ground well water sample. Detector sensitivity 100 μS for chloride, 1 μS for bromide and nitrate and 10 μS for sulfate. Other IC conditions same as in Fig. 1.

Table 9
Ionic strength (IS), cation–anion balance and supersaturation index of calcite in different ground waters, obtained from various ground water wells in Saudi Arabia

Sample	IS (mmol l^{-1})	$f_{Calcite}$	T_{Cation} (mmol l^{-1})	T_{Anion} (mmo l^{-1})	Δ (mmol l^{-1})
1.	36.1	2.214	26.7	26.4	1.1
2.	18.6	0.144	13.4	12.9	3.8
3.	37.3	2.157	27.2	25.9	4.9
4.	20.5	1.493	14.3	14.6	−2.1
5.	23.7	1.556	16.3	16.7	−2.4
6.	19.9	1.328	13.4	13.6	−1.5
7.	23.9	1.582	16.5	16.1	2.5
8.	66.3	1.524	52.5	52.6	−0.2
9.	51.9	1.078	41.5	39.6	4.7
10.	39.4	1.931	29.8	30.3	−1.7
11.	20.2	1.066	14.2	14.3	−0.7
12.	18.8	0.950	13.3	13.4	−0.7
13.	123.7	1.147	94.9	93.4	1.6
14.	43.8	1.558	29.3	29.8	−1.7
15.	21.5	1.397	15.2	15.1	0.7
16.	18.7	1.969	12.8	13.3	−3.8
17.	20.7	1.484	14.6	14.7	−0.7
18.	20.4	0.891	14.2	14.5	−2.1
19.	66.4	0.649	49.9	50.3	−0.8
20.	25.6	0.802	18.4	18.1	1.6
21.	19.5	0.901	13.8	13.6	1.5
22.	23.9	0.554	17.3	20.8	2.9
23.	24.5	1.037	17.4	17.9	−2.8
24.	33.0	1.151	22.4	21.9	2.3
25.	2.7	−51.630	1.8	1.9	−5.4
26.	4.4	0.716	3.1	3.2	−3.2
27.	4.4	0.568	3.0	2.9	3.4
28.	35.5	1.188	23.1	23.6	−2.1

$\Delta = 200(T_{Cation} - T_{Anion})/(T_{Cation} + T_{Anion})$.

5.4. Soil extracts from sandy soil

Analysis of various water-soluble anions in a particular soil is important to check its suitability for growing different crops. These soil solutions are also characterized by high salinity, especially high concentrations of sulfate and calcium ions. Like other high-salinity waters, these waters also have a large difference in the concentration of major and minor anions. For example, nitrite, bromide and nitrate concentrations are much lower (0–20 mg l^{-1}) than sulfate concentrations (300–2500 mg l^{-1}). For the simultaneous determination of these anions, dilution and total loading of various anions on the IC column is critical. Careful sample preparation is needed to retain sufficient amounts (required for their suppressed IC detection) of the trace/small concentration ions in diluted extracts, while protecting the column from overloading due to the high sulfate concentration. Column overloading by sulfate will give lower results for this anion as has been found in the analyses of ground water samples. A suppressed ion chromatogram showing the simultaneous determination of chloride, nitrite, nitrate and sulfate can be seen in Fig. 13. Accuracy of chloride analysis of these extracts was confirmed by a silver chloride precipitation method and the results are presented in Table 7. Analysis of the bicarbonate content of these extracts was carried out by suppressed ion-exclusion chromatography.
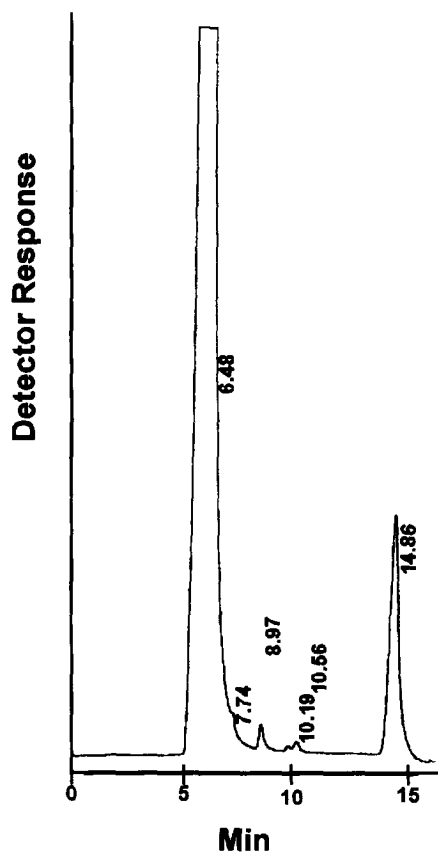
Fig. 11. Ion chromatogram showing the peaks of fluoride (8.97 min) and carbonate (14.86 min) in a twice diluted ground well water. Detector sensitivity 10 μS with a 50-μl sample injection. Other IC conditions same as in Fig. 7.

Fig. 12. Ion chromatogram showing the peak of 0.02 mg l^{-1} iodide (8.49 min) in an undiluted ground well water sample. IC conditions: Dionex AS-5 analytical column and AG-5 guard column; 4.5 mmol l^{-1} NaHCO$_3$+3.0 mmol l^{-1} Na$_2$CO$_3$ eluent at a flow-rate of 2.0 ml min^{-1}; detector sensitivity, 1.0 μS with a 250-μl sample injection.

6. Critical analysis and conclusion of Part B

Based on the results presented in this part, the accurate analysis of low sulfate concentrations in the presence of large concentration of metal chlorides in high-salinity subsurface brines by suppressed ion chromatography needs to be carried out carefully. At lower dilutions (lower than 200 times), suppressed ion chromatography of subsurface Arab-D brines resulted in lower sulfate results despite a baseline resolution of the sulfate peak. The reduction in peak height may be caused by cations, present in large concentrations in Arab-D brine. The interference of metal salts in the suppressed ion chromatographic determination of such anions can be overcome by
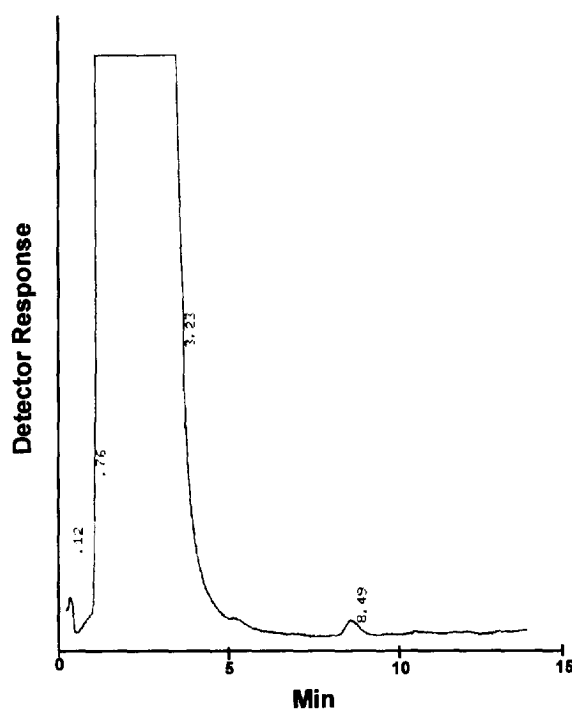
reducing the concentration of metal salts in the medium. Therefore, for the accurate analysis of sulfate in high-salinity brines, such as subsurface Arab-D brines, the IC analysis should be carried out at several dilutions until a constant concentration is obtained. The accuracy of the analysis based on peak sharpness and baseline resolution can be misjudged. For example the sulfate peak shown in the first chromatogram of Fig. 1 (at 50 times dilution of Arab-D water) can be regarded as reasonably sharp, if not compared with the peak obtained at 250 times dilution (second chromatogram in Fig. 1). The accuracy of sulfate results obtained by suppressed IC should be validated by another established method.

Simultaneous determinations of large sulfate concentrations and small concentrations of other anions such as chloride, nitrite, bromide and nitrate in waters, such as ground water and aqueous extracts of
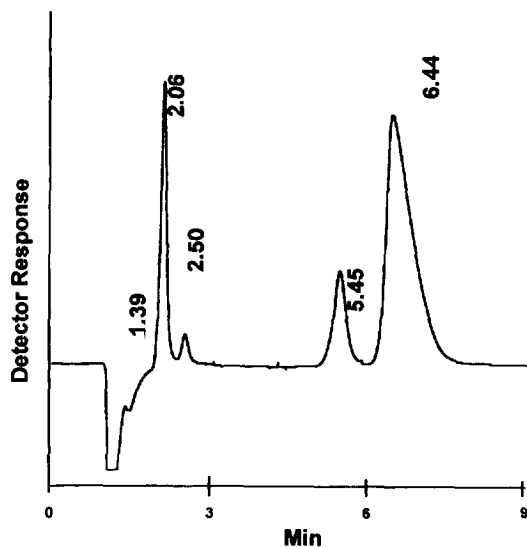
Fig. 13. Ion chromatogram showing the peaks of chloride (2.06 min), nitrite (2.50 min), nitrate (5.45 min) and sulfate (6.44 min) in a 25 times diluted aqueous extracts of sandy soil. Detector sensitivity, 10 μS for chloride and nitrite, 3 μS for nitrate and 300 μS for sulfate with a 150-μl injection volume. Other IC conditions same as in Fig. 1.

soil obtained from desert countries, should also be carried out carefully. Because of its strong adsorption on IC columns, large sulfate concentrations can overload the column. The overloaded sulfate peaks can cause negative errors in sulfate results.

The determination of fluoride in water matrices containing large concentrations of chloride (such as subsurface waters and ground waters obtained from desert countries) required the use of suppressed ion-exclusion chromatography, as baseline resolution of the fluoride peak cannot be obtained by suppressed anion-exchange chromatography. However, there is an advantage of using suppressed ion-exclusion chromatography for the analysis of fluoride in subsurface waters. It allows the simultaneous determination of fluoride with other anions such as borate, aliphatic organic acid anions (such as formate, acetate etc.) and carbonate, all of which are also critical in subsurface waters.

Accurate determination of small concentrations of various anions such as nitrate in seawater, iodide and thiosulfate in subsurface waters may be carried out by suppressed IC using appropriate chromatographic conditions as shown in this section.

7. General conclusion

On the basis of the results presented in this review, it is clear that the determination of small concentrations of anions capable of forming anion–proton ion pairs is affected when analyzed using suppressed IC in the presence of salt matrices. Anions of strong acids such as chloride, bromide and iodide are normally not affected, provided their peaks are well resolved up to the baseline. We have also mentioned that this error is normally caused by the presence of cations in the salt matrices and occurs in the suppressor column. Overloading of the analytical column was normally believed to be the cause of such errors in the past [25].

In the early literature, it is also frequently mentioned that dilution is usually the only pretreatment necessary for the determination of trace sulfate in salt brines and sodium hydroxide [26]. This is true as long as dilution of the sample allows a well separated peak of the determinant anion of sufficient height for accurate integration and determination. For example suppressed IC analysis of 300 times diluted subsurface oilfield waters resulted in a well resolved peak of sufficient height for accurate quantification. However, sometimes accuracy of the analysis based on well resolved peaks can be misleading and therefore accuracy of suppressed IC analyses in aqueous matrices containing high salt, base or acid concentrations cannot be taken for granted.

8. Recommendations

For the quantification of very low levels of sulfate and other anions capable of forming strong ion pairs with protons, of the order of 10 mg l^{-1} or lower in a high-salinity brine, dilution of the water sample may not be adequate. In these situations, removal of salt from the matrix may be required by ion exchange or other methods such as those reported in the literature [25]. The method reported by Cox and Tanaka [25] is ideal for the clean-up of alkaline matrices such as carbonate and hydroxide of alkali metals. For the removal of a chloride salt matrix, an ion-exchange resin in the silver form may be more appropriate.

Recently, Jackson and Jones [54] reported the use of a hollow-fiber membrane-based sample prepara-

tion device for the clean-up of brine samples prior to ion chromatographic analysis. This device uses a cation-exchange hollow fiber made of Nafion per-fluorosulphonate immersed in a counter-ion donating solution of 50 mmol l^{-1} silver p-toluenesulphonate. Total removal of chloride and bromide was achieved with the anions eliminated as silver chloride and silver bromide. This is an ideal system for the clean-up of subsurface waters, since the chloride concentration balances almost the total cation concentration. Removal of the chloride means removal of almost all of the chloride salts (such as NaCl, $CaCl_2$, $MgCl_2$ and KCl). In this method, cations from the brine are exchanged for silver cations which precipitate with chloride (halide) ions. The only anionic salts left in solution are those which do not form a precipitate with silver (such as sulfate in subsurface water). After clean-up, the water samples can be accurately analyzed by suppressed IC. In the same way, matrices containing sodium/calcium sulfate can be separated by barium in place of silver. A cation-exchange column in the barium form can be used to remove sulfate salts from water matrices containing high concentrations of sulfate ions.

Rokushika and Yamamoto [55] used a similar device for the determination of nitrite and carbonate in seawater. These authors used sulfuric acid as an eluent and an Ashipak DDP-50 column (15 cm×4.6 mm, octadecyl-modified polyvinyl alcohol gel column containing 5-μm particles). However, since the sensitivity of the UV detector (210 nm) was very low for carbonate in the acidic eluate, the eluate was passed through a cation-exchange hollow fiber having an alkaline or neutral enhancer solution flowing counter current on the other side. Both ions were well resolved from the matrix ions which eluted near the void volume. The method was also successfully applied to the nitrite and carbonate analysis of seawater.

Determination of trace anions in water matrices containing large concentrations of salts can also be made by multidimensional suppressed IC as described by Hoover and Yager [56]. In this method, trace concentrations of anions can be separated from the matrix anions (such as chloride, nitrate and sulfate in various water matrices) by collecting a selected portion of the ion chromatogram on a concentrator column after suppression and reinject-

ing the concentrated amount of trace anions at the original chromatographic conditions.

Although in this review we have discussed the examples of subsurface waters, high-salinity ground water and aqueous extracts of sandy soils, similar situations of the determinations of small concentrations of a single anion in the presence of high salt concentrations may be encountered in many other aqueous solutions of water pollution concern. Examples include the analysis of biological and pharmaceutical liquids [57–65], chemicals [66–74], ores [75], coal and geological materials [76–79], inorganic materials [69], [80,81], scales and scale inhibitors [82–84], nuclear waste [85–87], waters from thermal power plants [88], explosives [89,90], chemical processes [91,92], aerosols [93–95], sediments [96,97], plants [98], oilshales [35] and aqueous solutions from hydrometallurgical operations [21]. For instance, aqueous leachates (using water, acid or base) of oilshales, metal ores or catalysts may generate an aqueous matrix containing a small concentration of determinant anions in the presence of large concentrations of salt, acid (or salt and acid) or base (or salt and base). Similarly, fusion of inorganic solids (such as sediments, inorganic materials etc.) in the presence of sodium peroxide, sodium hydroxide, sodium carbonate or other fusion mixtures may produce aqueous solutions containing a small concentration of determinant anions in the presence of a large concentration of sodium hydroxide or salt matrices. Some specific examples are the determination of oxalate in urine and plasma, sulfur as sulfate in sediments and geological solids, sulfate in reforming catalysts, chromium as chromate in chromium oxide based catalysts and cements, trace impurities of anions in acids and bases and arsenic in ferric chloride/sulfuric acid leachates of base metal sulfide. Suppressed IC analysis of these samples for desired analytes should be carried out carefully either after appropriate dilution or removal of the matrix by suitable methods.

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