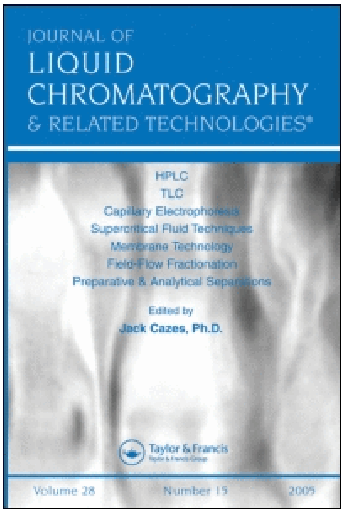

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HIGHLY SELECTIVE SIMULTANEOUS DETERMINATION OF EIGHT INORGANIC ANIONS IN DRINKING WATER BY SINGLE COLUMN HIGH PRESSURE ANION CHROMATOGRAPHY

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ABSTRACT

Ion Chromatography is a well-established analytical technique for the simultaneous determination of ions. This paper focuses on the analytical determination of eight inorganic anions: fluoride, hydrogen carbonate, chloride, nitrite, bromide, nitrate, hydrogen phosphate and sulphate, using conductometric detection.

The separation of the cited anions was achieved on a low capacity anion exchange column Hamilton PRP-X100 100 x 4.1 mm, 10 μm, with a mobile phase consisted of 2.5 mM p-hydroxybezoic acid and 2.0 mM sodium benzoate at a pH 9.0 adjusted with 1N NaOH and 8% CH_3OH as organic modifier, at a flow rate 0.7 ml/min.

For the quantitative determination bromide was used as internal standard at a concentration of 7.8 mg/l. A rectilinear relationship was observed up to 40 mg/l for all ions except for carbonate that was up to 30 mg/l. The detection limits (S/N =3) were 100 μg/l for carbonate and 50 μg/l for the rest of the cited anions, when 50 μl of the samples were injected onto the analytical column.

Recovery of anions in spiked samples ranged from 90.44% to 108.88% with the time of analysis being less than 10 min. The statistical evaluation of the method was examined performing intra-day (n=8) and inter-day calibration (n=10) and found to be satisfactory with high accuracy and precision results.

The applicability of the method was demonstrated on the analysis of drinking water: tap, table and mineral.

INTRODUCTION

The first reported method for separation and quantitative determination of inorganic ions by means of high-pressure liquid chromatography was developed by Small et al (1). This technique called ion chromatography used a combination of an analytical column and a suppressor column to decrease the conductivity of the mobile phase for conductometric detection. Since then significant drawbacks from the chromatographic point of view have been reported regarding this approach, most of which arise from the suppressor column itself(2):

(1) the number of injections is restricted by the capacity of the suppressor column,

(2) the suppressor column introduces extra band broadening, which results in lower resolution,

(3) special equipment is needed for IC,

(4) only those buffers can be applied which, after passage through the suppressor column, result in a low electrical background conductivity.

Solutions containing $NaHCO_3$ and Na_2CO_3 in low concentrations, 1-5 mM are used as eluents in dual column Ion Chromatography (suppressed conductivity).

In addition, packed suppressors require periodic regenaration to restore their ion-exchange capacity and the eluents applicable to suppressed ion chromatography are restricted to those which undergo suitable protonation or other reactions in the suppressor column. These deficiencies have provided an impetus for the development of chromatographic methods for inorganic anion analysis that do not require use of a suppressor column.

Solutions containing $NaHCO_3$ and Na_2CO_3 in low concentrations, 1-5 mM are used as eluents in dual column Ion Chromatography (suppressed conductivity).

Some investigations have been undertaken in an attempt to overcome these disadvantages. In particular Gjerde and co workers demonstrated that a suppressor column is not absolutely necessary for HPIC with electric conductivity detection. They used an anion exchanger having a low exchange capacity and an eluent having a very low conductivity. In this way the background conductivity is sufficiently low to allow the separated anions to be detected with a simple conductance detector(3-5).

A number of alternative methods have been reported in the literature, all of which use an analytical separator column (usually an ion-exchange column) without a suppressor column. These methods differ from each other chiefly in the mode of detection employed . Inorganic anions may be separated on a reversed-phase system either by prior formation of organic derivatives or by using ion-pair formation with subsequent direct detection of UV-absorbing ions at low UV wavelengths (210-220 nm). This same approach has been applied to an amino column (6,7), however these methods are not widely applicable since only a limited number of inorganic ions show UV absorbance. A more general method is the use of reversed-phase ion-pair HPLC with UV-absorbing pairing ions, where samples gave positive or negative peaks, depending on their charge and retention relative to the UV-absorbing pairing ion. Octylamine, cetrimide and alkylammonium salts e.g. tetrabutylammonium-acetate, phthalate or salicylate are most commonly used as eluents with this technique (8-20).

Various detection techniques reported in literature include conductivity, indirect UV photometry, amperometry, potentiometry and refractive index.

Among these techniques conductometric detection remains the mainstay of HPIC (21-23).

The detection of ions by conductance in non-suppressed Ion Chromatography (Single Column Ion Chromatography) is achieved due to the difference in ionic conductances of the sample and eluent ions.

When a large number of determinations are required the application of specific reactions for anions becomes time consuming and the possibility of the simultaneous separation, identification and quantitification of several anions is of interest High Pressure Ion Chromatography (HPIC) with suppressed conductivity detection is one of the most popular methods that satisfy these objectives.

Compared to non-chromatography techniques, Ion Chromatography methodology has the advantages of separation before detection increased detection, increased sensitivty, simple sample preparation and faster analysis time (24,25).

The United States Environmental Protection Agency (EPA) has established regulations and methodology for inorganic contaminants under the Safe Drinking Water Act. Fluoride, nitrite and nitrate are listed as primary pollutants since they can cause adverse health effects. Ion Chromatography has become a well established technique for the determination of nitrite and

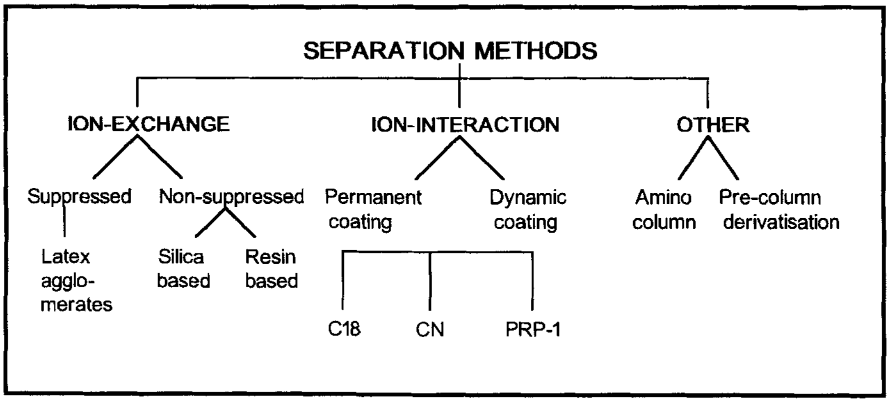


Figure 1. Schematic representation of separation methods used for inorganic anions.

nitrate in drinking water. Chloride and sulphate are listed as secondary contaminants because they are organoleptic (affect the smell, taste or appearance of water). They are not monitored by the EPA, hence, a laboratory can use any method (HPIC, ion selective electrode, flow injection analysis, etc.) to analyze for these analytes. The ability of HPIC to separate the analytes of interest from interferences provides a dinstinct advantage over other analytical techniques in terms of detection, sensitivity and is capable of multi-element analysis (26).

Several separation methods concerning the determination of inorganic anions are described in the literature. Figure 1 shows a schematic representation of these methods (27).

A summary of experimental conditions used in some non-suppressed ion-exchange methods using a variety of column types and detectors is given in table 1.

Detection limits in the range of 0.4-1600 ng are reported in the literature using different eluent and detection systems, while the time of analysis was in the most cases over ten minutes (16, 30).

In the present paper a non-suppressed chromatographic method with conductometric detection is described for the simultaneous determination of eight inorganic anions.

TABLE 1
SUMMARY OF EXPERIMENTAL CONDITIONS USED IN SOME ION-EXCHANGE METHODS USING A VARIETY OF COLUMN TYPES ELUENTS AND DETECTORS

ANIONS	COLUMN	ELUENT*	DETECTION	REF
Br,Cl,NO_3,NO_2,PO_4,SO_4	Nucleosil 5 or 10SB	0.03 M salicylate pH 4.0 0.075 M p-HBA pH 5.6 0.05 M KHP	Indirect Refractive Index	2
Br,Cl,F,PO_4,SO_4	Partisil SAX	0.05M $NaNO_3$ 0.04M KI , 0.05M KIO_3	Indirect UV Absorbance	27
Br,Cl,F,PO_4,SO_4,NO_3	Permutit ZeoKarb 225 Cd Form	0.0025 M $(CH_3COO)_2Cd$	Potentiometry	27
Br,Cl,NO_3,NO_2,PO_4,SO_4,F, CO_3	0.007 mequiv/g resin-based ion exchanger	6.5x 10^{-4} M benzoate 5x 10^{-4} M KHP	Conductivity	4,5
Br,CO_3,NO_3,NO_2,PO_4,SO_4	TSK GEL 620	1.3 mM gluconic acid in borate buffer	Conductivity	25
Cl,F,NO_3,NO_2,SO_4	TSK GEL 620 SA	2mM KOH	Conductivity	27
Br,Cl,NO_3,NO_2,SO_4	TSK GEL IEX 520	1mM citrate pH 5.2 1mM tartrate pH 3.2	Conductivity	28
F,NO_3,NO_2,PO_4,SO_4	TSK GEL IEX 520	0.1 M $NaNO_3$ or 0.05 M $NaNO_3$ in 0.05 M acetate buffer	Post-column reaction using $Fe(ClO_4)_3$	27
Cl,F,NO_3,NO_2,SO_4,PO_4	Surface agglomerated pellicular ion exchanger	1 mM phthalate pH 7.0 or 0.1 mM sulphobenzoate pH 8	Indirect UV absorbance	27
Br,Cl,PO_4,NO_3,NO_2, SO_4	Vydac 302 IC	5 mM KHP pH 4.0	Conductivity, Indirect UV	27
F,Br,Cl,PO_4,NO_3,NO_2,SO_4	Vydac 302 IC	0.5 mM KHP pH 4.6	Conductivity	27
F,Br,Cl,PO_4,NO_3,NO_2,SO_4, CO_3	Wescan 269-001	4 mM KHP pH 3.9	Conductivity	27
Br,Cl,PO_4,NO_3, SO_4	Vydac 302 IC	5 mM KHP pH 4.6	Conductivity, Indirect UV	9
Br,Cl,NO_3,NO_2	Wescan 269-001	10mM methanesulphonate pH5	UV 214 nm	29

*KHP=Potassium hydrogen phthalate
p-HBA= p-hydroxybenzoic acid

The purpose of this work was to characterize the method in terms of sensitivity, detection limits and working range in order to be applied to the routine analysis of drinking water.

The analysis of table water was also investigated and the validity of the method was established by inter-day and intra-day calibration studies.

EXPERIMENTAL

Instrumentation

The ion chromatograph used consisted of an SSI model 222D Pump (SSI, State College PA,USA) and a model Wescan 315 conductometric detector (Alltech, Deerfield, IL, USA) maintained at 35± 0.1 °C.

A Rheodyne model 9125 six-port high pressure switching injection valve (Rheodyne, Cotati, CA, USA) was assempled with a 50 μl injection loop.

The separation column Hamilton PRP-X100 100x 4.1 mm was packed with spherical 10 μm polystyrene-divinylbenzene trimethylammonium anion exchanger (Hamilton, Reno, NV, USA). The capacity of the column was 0.19±0.02 meq/g.

Data aquisition was performed using a Hewllett-Packard integrator, model HP 3396 II (Hewlett-Packard, Avondale, PA, USA).

Statistical evaluation of the experimental data was achieved by a VIP 312 IBM compatible PC.

Reagents

Stock standard solutions (1,000 mg/l) of fluoride, hydrogen carbonate, chloride, nitrite, bromide, nitrate, hydrogen phosphate and sulphate were prepared by dissolving appropriate amounts of analytical reagent grade sodium or potassium salts in de-ionised water. These solutions were subsequently diluted to give the multi-anion solutions required.

Analytical reagent grade compounds provided by Merck (Darmstadt, Germany) were used to prepare the eluent systems examined in the present study.

Stock solutions of 20 mM sodium benzoate and 20 mM p-hydroxybenzoic acid were diluted daily to provide the working concentration of mobile phase 2.0 mM and 2.5 mM respectively.

The pH of the mobile phase was adjusted at 9.0 by adding 4 ml 1N sodium hydroxide solution per 1 liter of eluent. The sodium hydroxide solution was prepared by diluting properly the content of Fixanal ampoule (Riedel-deHaen, Hannover, Germany).

HPLC-grade methanol (Merck, Darmstadt, Germany) was added to the mobile phase at a concentration of 8%.

The mobile phase was filtered through 0.2 μm membrane filters (Schleicher-Schuell, Dassel, Germany).

All standard solutions and samples of drinking water were kept at 4 °C before and after analysis.

RESULTS AND DISCUSSION

Optimization of the chromatographic system

The chromatographic system for the separation of the eight, inorganic anions, was chosen among others, as shown in tables 2 and 3, in order to result in optimum separation regarding to selectivity and detection conditions and it was optimized in terms of its suitability for conductivity detection, considering its effectiveness on displacement of desired species with minimal conductivity.

pH of the mobile phase was sufficiently high in order to eliminate the system peak which is often encountered in SCIC (31). The system peak seems to be due to the elution of neutral molecules of the eluent on injection of a water sample. These molecules are believed to be retained on the chromatographic column by a reversed-phase mechanism, as about 85% of a low-capacity ion-exchange column is unfunctionalized (i.e. has no ionized group). The retention time of this peak depends on several parameters like: nature nad concentration of the eluent, pH of the mobile phase, presence of organic modifier in the eluent etc. Its existence can be a real problem if it overlaps with an analyte peak or it appears late in the chromatogram and it increases the time of analysis. To avoid this peak, the eluent must be completely ionized at the pH chosen.

The eluent anion must be retained by the anion-exchange resin sufficiently strongly that a very low concentration of the eluent salt will move anions to be separated down to the chromatographic column. At the same time the conductance of the eluent should be low so that the separated anions will give a detector signal well above that of the eluent background. The observed background conductivity of the eluent chosen was 12.25 $\mu S \cdot cm^{-1}$.

Keeping all the above practical considerations in mind the chromatographic system was optimized in terms of separation and detection.

The optimum conditions are reported in table 4.

TABLE 2
ELUENT SYSTEMS STUDIED FOR THEIR EFFECTIVENESS ON THE SEPARATION AND QUANTITATIVE DETERMINATION OF THE EIGHT INORGANIC ANIONS EXAMINED IN THE PRESENT STUDY

Eluent system	Compound	Concentration (mM)	pH	Background conductivity ($\mu S \cdot cm^{-1}$)	Flow rate (ml/min)	Pressure (psi)
A	Potassium hydrogen phthalate	2.0	6.0	6.8	1.3	700
B	p-hydroxy-benzoic acid (pHBA)	4.0	9.0	12.75	1.3	625
C	phthalic acid	5.0	9.0	11.7	1.3	875
D	Sodium benzoate	2.0	9.0	4.15	1.0	625
E	pHBA Na benzoate	2.0 2.0	9.0	14.15	1.0	675
F	pHBA Na benzoate	2.0 1.0	9.0	11.5	1.0	775
G	pHBA Na benzoate	3.0 2.0	9.0	19.6	1.0	1125
H	pHBA Na benzoate	2.5 1.5	9.0	14.25	1.0	1150
I	pHBA Na benzoate	2.0 1.5	9.0	9.75	1.0	1075
J	pHBA Na benzoate	1.5 1.5	9.0	15.0	1.0	900
K	pHBA Na benzoate	1.5 2.0	9.0	17.1	1.0	875
L	pHBA Na benzoate	2.5 2.0	9.0	12.25	0.7	675

TABLE 3
INORGANIC ANION SEPARATION WITH DIFFERENT ELUENT SYSTEMS AS DESCRIBED IN TABLE 2

Anions	Retention Time with Different Eluent Systems (min)											
	A	B	C	D	E	F	G	H	I	J	K	L
F^-	2.53	1.26	NS	4.53	1.79	1.63	1.66	2.31	2.49	3.54	1.52	1.71
HCO_3^-	-	1.79	-	-	-	-	5.76	11.9	4.05	8.99	7.91	2.35
Cl^-	2.53	2.15	2.91	6.61	2.71	3.10	2.62	3.18	3.85	3.61	3.51	2.66
NO_2^-	3.12	2.81	4.14	7.18	3.17	3.57	2.97	3.61	4.44	4.15	3.91	3.01
Br^-	4.28	4.41	3.91	9.36	4.01	4.66	3.79	4.71	6.04	5.73	5.41	4.21
NO_3^-	5.26	5.31	4.21	10.3	4.41	5.22	4.16	5.21	6.83	6.49	6.13	4.76
$HPO_4^=$	-	5.21	10.1	12.8	5.61	6.91	4.51	6.71	11.31	11.51	10.6	6.88
$SO_4^=$	7.8	7.41	13.6	-	7.01	9.12	5.81	8.91	16.5	12.2	11.21	9.39

TABLE 4
OPTIMUM CONDITIONS FOR THE CHROMATOGRAPHIC SEPARATION OF INORGANIC ANIONS.

Operation	Parameter	Value
Separation	p-hydroxybenzoic acid	2.5 mM
	sodium benzoate	2.0 mM
	pH	9.0
	methanol	8%
	Flow rate	0.7 ml/min
	Inlet pressure observed	675 psi
Detection	Conductometric	
	Time constant	0.2 s
	Sensitivity	$0.5\ \mu S\cdot cm^{-1}FS$
	Temperature	35±0.1 °C

Figure 2 shows the chromatogram obtained during the separation of the eight inorganic anions by means of the chromatographic system developed at the present study.

The Rs values for the eight inorganic anions : fluoride, hydrogen carbonate, chloride, nitrite, bromide, nitrate, hydrogen phosphate and sulphate are 1.40, 0.25, 0.99, 2.15, 0.80, 2.24 and 1.99 respectively per couple of anions.

Performance characteristics of the proposed method.

The system described here was used for the simultaneous determination of eight inorganic anions: fluoride, hydrogen carbonate, chloride, nitrite, bromide, nitrate, hydrogen phosphate and sulphate.

Optimized chromatographic conditions were set and the following analytical characteristics were evaluated:

- Precision and accuracy.
- Working range and detectability.
- Analysis time.
- Calibration data.
- Real sample analysis.

Precision and Accuracy

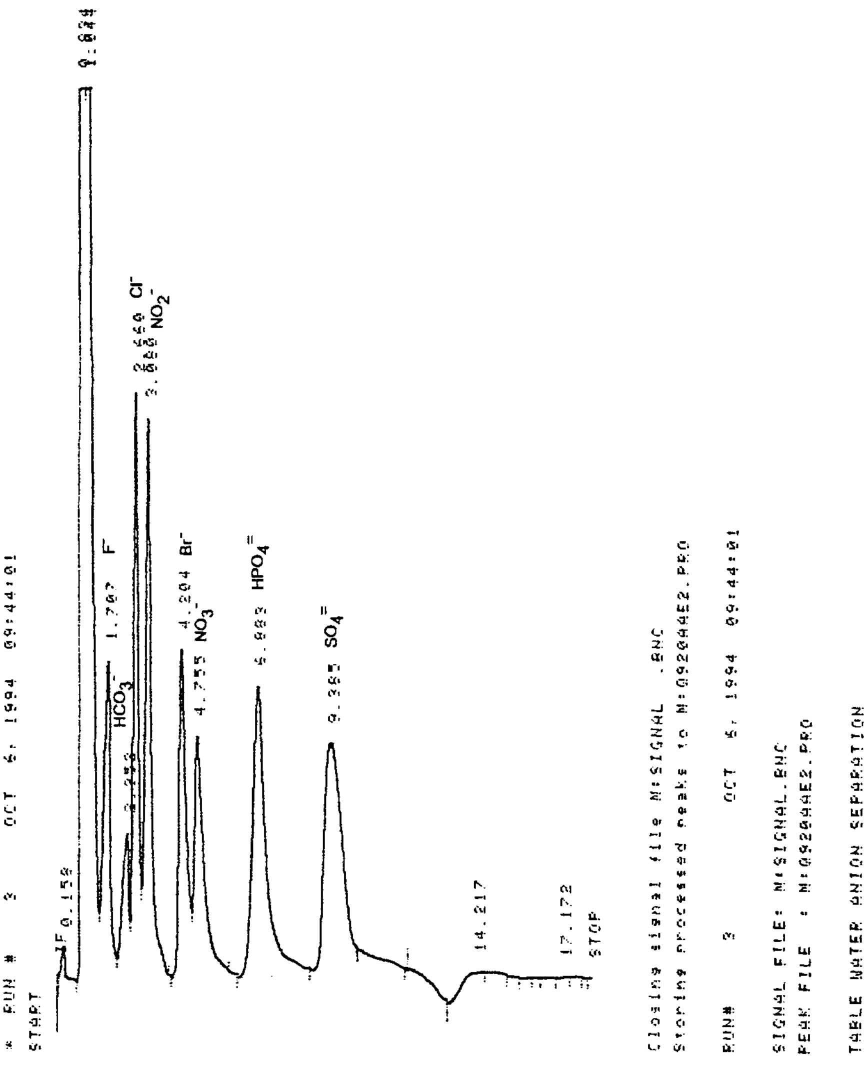
In order to verify the reproducibility, replicate injections of standard solutions at low and high concentration levels were made and peak areas were measured in comparison to the peak area of the internal standard.

Statistical evaluation revealed relative standard deviations at different values for eight injections. The results are shown in table 5.

Long term stability was examined during routine operation of the system over a period of ten consecutive days. Results are presented in table 6. The inter-day reproducibility was usually better than 10% even when the instrument was shut down during working breaks.

Working range and detectability

For the analysis of a multi anion solution it is found that the maximum concentration or amount that can be injected is limited by saturation of the



```
*  RUN #    3     OCT  6, 1994  09:44:01
START

Closing signal file M:SIGNAL  .BNC
Storing processed peaks to M:0920AAE2.PRO

RUN#     3          OCT  6, 1994  09:44:01

SIGNAL FILE: M:SIGNAL.BNC
PEAK FILE  : M:0920AAE2.PRO

TABLE WATER ANION SEPARATION
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Figure 2. Chromatographic separation of the eight inorganic anions examined in the present study. Conditions are described in text.

TABLE 5
INTRA-DAY CALIBRATION RESULTS (n=8)

Anions	Added (ppm)	Found (ppm)	SD	RSD (%)	Recovery (%)
F^-	1.77	1.69	0.25	14.79	95.48
	2.66	2.59	0.12	4.63	97.37
	4.40	4.52	0.36	7.96	102.73
	6.20	6.70	0.52	7.76	108.06
HCO_3^-	1.94	1.97	0.14	7.11	101.55
	3.88	3.62	0.23	6.35	93.30
	5.81	5.66	0.28	4.95	97.42
	7.75	7.99	0.42	5.26	103.10
Cl^-	2.69	2.31	0.22	9.52	85.87
	4.04	3.93	0.16	4.07	97.29
	6.70	6.65	0.35	5.26	99.25
	9.43	9.06	0.59	6.51	96.08
NO_2^-	2.44	2.35	0.22	9.36	96.31
	3.66	3.52	0.37	10.51	96.17
	6.10	6.18	0.47	7.61	101.31
	8.53	8.48	0.68	8.02	99.46
NO_3^-	1.90	1.85	0.21	11.35	97.37
	3.79	3.79	0.33	8.71	100.00
	5.69	5.45	0.46	8.44	95.78
	9.50	9.66	0.56	5.80	101.68
HPO_4^{2-}	1.69	1.84	0.22	11.96	108.88
	3.38	3.48	0.29	8.33	102.96
	5.08	5.17	0.24	4.64	101.77
	8.50	8.42	0.53	6.29	99.06
SO_4^{2-}	1.99	1.93	0.18	9.33	96.98
	3.97	3.96	0.24	6.06	99.75
	5.96	5.39	0.51	9.46	90.44
	9.90	10.07	0.73	7.25	101.74

capacity of the column, resulting in poor peak shapes. The term working range is therefore more appropriate than linear range.

Table 7 provides the maximum amounts of multi-anion solution that can be injected onto the analytical column. It should be noted that the upper limit reported for each anion assumes the co-existing concentration of the other anions at a similar level. For this reason higher concentrations could also be injected in case of absence of other anions.

Detection limits were not evaluated by statistical treatment of the data because they depend on the injection volume and to a considerable extent

TABLE 6
PRECISION AND ACCURACY OVER A PERIOD OF 10 CONSECUTIVE DAYS.

Anions	Added (ppm)	Found (ppm)	SD	RSD (%)	Recovery (%)
F^-	1.77	1.73	0.17	9.83	98.30
	2.66	2.67	0.11	4.12	100.38
	4.40	4.08	0.11	2.70	92.73
	6.20	6.17	0.26	4.21	99.52
HCO_3^-	1.94	1.89	0.09	4.76	97.42
	3.88	3.95	0.31	7.85	101.80
	5.81	5.94	0.21	3.54	102.24
	7.75	7.82	0.39	4.99	100.90
Cl^-	2.69	2.50	0.21	8.40	92.94
	4.04	3.92	0.14	3.57	97.03
	6.70	6.67	0.15	2.20	99.55
	9.43	9.53	0.11	1.19	101.06
NO_2^-	2.44	2.32	0.09	3.88	95.08
	3.66	3.49	0.25	7.16	95.36
	6.10	6.00	0.15	2.50	98.36
	8.53	8.70	0.12	1.38	101.99
NO_3^-	1.90	2.05	0.26	12.68	107.89
	3.79	3.84	0.11	2.86	101.32
	5.69	5.52	0.14	2.46	97.01
	9.50	9.55	0.34	3.56	100.53
HPO_4^{2-}	1.69	1.69	0.07	4.14	100.00
	3.38	3.40	0.20	5.88	100.59
	5.08	5.04	0.41	8.13	99.21
	8.50	8.48	0.61	7.19	99.76
SO_4^{2-}	1.99	2.05	0.21	10.24	103.02
	3.97	4.00	0.32	7.92	100.76
	5.96	5.96	0.14	2.35	100.00
	9.90	9.87	0.29	2.94	99.70

TABLE 7
WORKING RANGE AND DETECTION LIMITS

Anions	Upper limit (µg)	Detection limit (ng)
F^-	2.0	2.5
HCO_3^-	1.5	5.0
Cl^-	2.0	2.5
NO_2^-	2.0	2.5
Br^-	2.0	2.5
NO_3^-	2.0	2.5
$HPO_4^=$	2.0	2.5
$SO_4^=$	2.0	2.5

on the noise level of the detectors employed. In conductivity detection noise is mainly created by temperature fluctuations. The proper thermostating of the measuring cell and suitable design of the flow cell allows the detection of very small conductivity differences.

Detection limits calculated as a three-fold signal-to-noise ratio at the baseline (S/N=3) are shown in table 7.

Analysis time

The analysis time in the proposed method is determined solely by the retention time of the most strongly retained ion in the chromatographic separation due to the lack of system peak. As is evident from figure 2 the sample analysis time can be less than 10 minutes, as sulphate the last eluting anion has 9.385 min. retention time.

Calibration data

Calibration of the method was done by injection of mixed ion standards covering the entire working range. The sensitivity setting of the conductivity detector was adjusted to give almost fullscale deflection for the highest standard concentration. Each sample was injected five times.

Linear correlation (r>0.99148) between concentration and peak area ratio was obtained for all ions using bromide as internal standard at a concentration of 7.8 mg/l. Bromide was chosen as internal standard for being absent in drinking water samples.

The results of the statistical treatment of calibration data for the seven anions are summarized in table 8.

REAL SAMPLE ANALYSIS

Analysis of drinking water

In order to examine the suitability of the method for the determination of inorganic anions, several drinking water samples: tap, mineral and table water provided by the water supply oraganization and local market respectively were analysed. Results are presented in table 9.

Examples of chromatograms obtained are illustrated in figures 3 and 4.

TABLE 8
CALIBRATION DATA FOR SIMULTANEOUS DETERMINATION OF INORGANIC ANIONS (PEAK AREA RATIO MEASUREMENTS WITH 7.8 MG/L BROMIDE AS INTERNAL STANDARD -RT=4.204 MIN).

Parameter	Value	F^-	HCO_3^-	Cl^-	NO_2^-	NO_3^-	$HPO_4^=$	$SO_4^=$
Concentration range	mg/l	0.5-40	0.5-30	0.5-40	0.5-40	0.5-40	0.5-40	0.5-40
Slope	$\mu S \cdot l \cdot cm^{-1} \cdot mg^{-1}$	0.06677	0.223272	0.19937	0.18422	0.07792	0.14698	0.33396
Intercept		0.45798	-0.002325	0.44741	0.24753	0.45555	0.42848	0.35135
Correlation coefficient		0.99148	0.99615	0.99459	0.99915	0.99684	0.99478	0.99966
Retention time	min	1.707	2.352	2.660	3.080	4.755	6.883	9.385

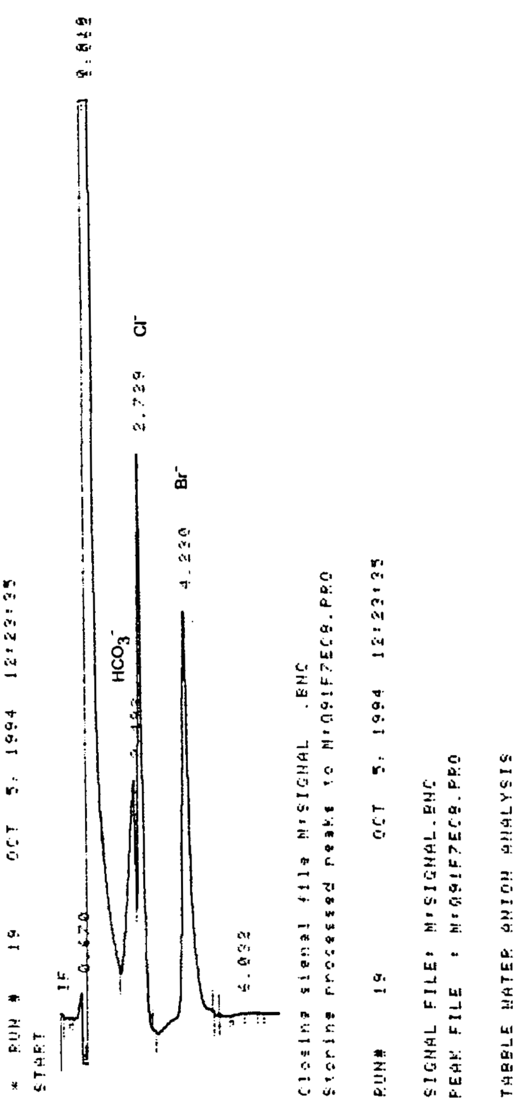
TABLE 9
SIMULTANEOUS DETERMINATION OF INORGANIC ANIONS IN DRINKING WATER SAMPLES.

Water sample	Anion	Label concentration (ppm)	Found[a] concentration (ppm)	RSD (%)
IVI (Mineral Water)	Cl^-	31.9	28.32±1.01	3.57
	NO_3^-	3.1	2.92±0.18	6.16
	SO_4^{2-}	5.8	5.74±0.26	4.52
	HCO_3^-	391.7	100.8±18.4	18.25
SOUROTI (Mineral Water)	Cl^-	69.1	67.70±3.62	5.34
	SO_4^{2-}	63.2	49.20±0.78	1.59
	F^-	0.3	ND	
	NO_3^-	0.4	ND	
	NO_2^-	0.005	ND	
	HCO_3^-	924.1	844.7±25.6	3.03
VIKOS (Mineral Water)	Cl^-	8.42	8.15±0.36	4.41
	NO_3^-	4.97	2.21±0.13	5.88
	NO_2^-	0.0	ND	
	SO_4^{2-}	2.40	2.01±0.09	4.47
	HCO_3^-	296.53	125.3±10.2	8.14
IRIS (Mineral Water)	Cl^-	28.4	20.03±1.83	9.13
	NO_3^-	-	ND	
	NO_2^-	-	ND	
	SO_4^{2-}	5.3	3.86±0.21	5.44
	HCO_3^-	388.1	94.9±12.6	13.28

a= Mean value n=6 ± SD
ND= Not detected.

TABLE 9 (CONT.)

NIGRITA **(Table water)**	Cl^-	17.10	14.41±0.62	4.30
	NO_3^-	5.70	4.35±0.15	3.45
	NO_2^-	-	ND	
	SO_4^{2-}	16.90	12.65±0.27	2.13
	PO_4^{3-}	0.08	ND	
	F^-	0.35	ND	
	HCO_3^-	398.5	136.2±21.4	15.71
AVRA **(Table water)**	Cl^-	10.2	8.56±1.31	12.84
	NO_3^-	28.6	28.0±2.9	10.36
	SO_4^{2-}	28.3	20.7±1.3	6.28
	HCO_3^-	146.4	68.5±9.4	13.72
SELI **(Mineral Water)**	Cl^-	3.5	3.06±0.32	10.46
	NO_3^-	0.6	0.2±0.01	5.00
	SO_4^{2-}	24.0	17.9±1.78	9.94
	HCO_3^-	231.9	127.2±21.2	16.67
ZAGORI **(Mineral Water)**	Cl^-	8.27	5.33±0.25	4.69
	NO_3^-	4.35	2.13±0.08	3.75
	SO_4^{2-}	7.85	4.12±0.48	11.65
	HCO_3^-	206.76	137.71±21.6	15.68
Municipal Water Supply Organisation	Cl^-	34-57	39.1±5.3	13.55
	NO_3^-	7-10	1.18±0.05	4.24
	SO_4^{2-}	14-23	12.2±0.5	4.10
	HCO_3^-		118.3±9.7	8.20
	F^-	0.13-0.16	ND	
	P_2O_5	0.032-0.055	ND	



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TABBLE WATER ANION ANALYSIS
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Figure 3. Simultaneous determination of inorganic anions in Mineral Water (IRIS). Conditions are described in text.

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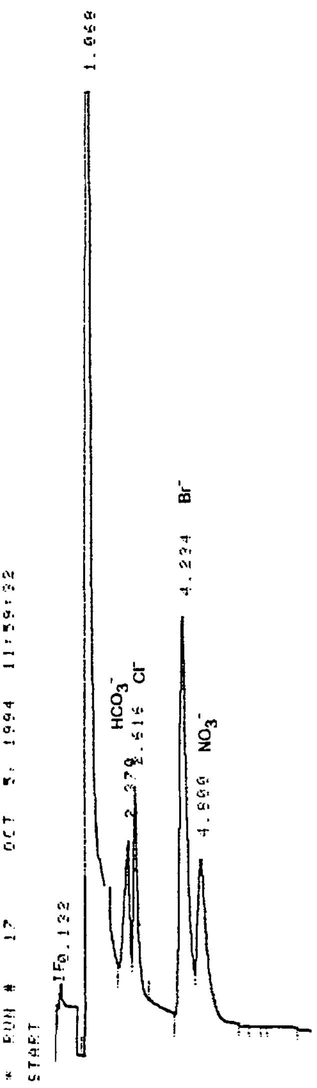

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TABBLE WATER ANION ANALYSIS
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Figure 4. Simultaneous determination of inorganic anions in Table Water (AVRA). Conditions are described in text.

CONCLUSIONS

Eight inorganic anions: fluoride, hydrogen carbonate, chloride, nitrite, bromide, nitrate, hydrogen phosphate and sulphate were separated and analysed by means of Single Column Ion Chromatography (SCIC) technique with conductometric detection.

The combination of p-hydroxybenzoic acid and sodium benzoate at concentrations 2.5 mM and 2.0 mM respectively provides the required anions for the displacement of the desired species from the low-capacity polymer-based anion exchange column, as well as the sufficiently low background conductivity for enhanced sensitivity. The pH value of the mobile phase is high enough so that the system peak often encountered in SCIC does not occur.

The day-to-day precision was tested for the analysed anions over 10 consecutive days, while the repeatability was investigated by performing intra-day calibration (n=8).

The applicability of the method was demonstrated on the analysis of several drinking water samples.

The developed method is characterised by high selectivity, sensitivity, high accuracy and precision, and low cost of operation, providing multi-anion analysis within ten minutes.

No suppressor column is required so that peak dispersion is less, resulting in a better resolution. Moreover no regeneration step has to be included and no special equipment is needed.

The separation can be achieved on any liquid chromatograph equipped with a conductometric detector.

Detection limits are within 5.0 ng range for 50 μl injected sample volume.

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