Chapter V

Fluoride, chloride, nitrate, and sulfate in aqueous solution utilizing AutoSuppression chemically suppressed ion chromatography

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U.S. Geological Survey Open File Report 02-223-V

Analytical methods for chemical analysis of geologic and other materials, U.S. Geological Survey

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Codes: I011
T05

Accepted: 4/21/94
Revised: 1/15/02

Principle

Four common anions: fluoride, chloride, nitrate, and sulfate are determined in aqueous solutions by ion chromatography (IC). The anions are separated based on their differential affinity for a low capacity, strongly basic anion exchange resin (Small and others, 1975). Each anion elutes from the AS-14 analytical column with a characteristic retention time in the order fluoride, chloride, nitrate, and sulfate when using the conditions described below.

Chemically suppressed ion chromatography is achieved by employing AutoSuppression technology with the Anion Self-Regenerating Suppressor (ASRS-II) to enhance analyte conductivity while decreasing eluent conductivity. The AutoSuppression Recycle Mode uses the neutralized conductivity cell effluent as the source of water for the regenerant chamber water. This is the preferable method of operation for the ASRS-II. As the eluent passes through the ASRS-II, it is neutralized to form its weakly ionized form. After passing through the conductivity cell, the effluent is redirected to the regenerant inlet on the ASRS-II, thus supplying it with a source of water containing minute amounts of dilute analyte. This eliminates the need for chemical regenerants and regenerant cartridges (Dionex 1997b).

Interferences

The following discussion on interferences is taken directly from Pfaff and others (1991): "Interference can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or fortification can be used to solve most interference problems."

The water dip or negative peak that elutes near the fluoride peak can cause interference. This can usually be eliminated by the addition of the equivalent of 1 µl of concentrated (100x) eluent to 5 ml of each standard and sample or choosing the "void negative volume treatment for this peak" statement in the data events.

Method interference may be caused by contamination in the reagent water, reagents, glassware, and other sample processing apparatus that leads to discrete artifacts or elevated baseline in the ion chromatograms.

Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known co-elution is caused by carbonate and other small organic anions. Using the AS-14 analytical column with the advantages of improved retention and excellent resolution of fluoride this interference should not be significant. It is the responsibility of the user to generate precision and accuracy in the analysis in each sample matrix.

The acetate anion elutes early during the chromatographic run. The retention time of the anions also seem to differ when large amounts of acetate are present. Therefore, this method is not recommended for leachates of solid samples when acetate is used for pH adjustments.

In addition to these problems described by Pfaff and others (1991), another problem may arise from analysis of a large number of samples of low pH containing Fe and SO_4. The sulfate may accumulate by adsorption on Fe precipitates, to be released in subsequent elutions, resulting in elevated SO_4 concentrations. This problem can be solved by adding 100 µl of concentrated (100x) eluent to 5ml of sample to raise the pH >4.5. The solution is covered and allowed to sit over night, decanted and filtered through a .45 µm filter prior to running.

Interference can also be caused by metal contamination on the columns. This was experienced when running samples containing 500 ppm CuSO4. The problem was not recognized until check standards were run at the end of the job. Washing the columns with 500 ml of .01M oxalic acid solution followed by 500ml DI water removed the contamination.

Scope

This method is applicable to the analysis of natural waters and leachate solutions that do not contain acetate. It can be extended to include the analysis of water leachates of solid samples. Liquid samples should be refrigerated at 4^oC and stored no longer than 28 days when sulfate and nitrate are to be analyzed. For fluoride, chloride, and bromide no refrigeration is required. If nitrite and/or phosphate are to be analyzed, the samples must be refrigerated and analyzed within 48 hours. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment (Pfaff and others, 1991).

Using the DX-120 ion chromatograph, PeakNet workstation, and the AS40 automated sampler, an operator can analyze about 32 samples, including blank, calibration standards and reference sample solutions, in a normal 8 hour day. An additional 66 samples can be analyzed overnight. Fluoride is generally determined from .08 to 4 mg/L, chloride from 0.08 to 4 mg/L, nitrate from 0.08 to 4 mg/L, and sulfate from 1.2 to 80 mg/L. Solutions with higher concentrations can be diluted to the appropriate calibration range. If the majority of samples in the job have consistently high chloride values (>20 ppm) they are analyzed using a method for determining higher concentrations of chloride and nitrate while fluoride and sulfate concentration ranges remain as stated above. If the higher Cl^- concentration method is used, the lower level of determination for both chloride and nitrate is higher than in the procedure normally used.

Apparatus

Ion Chromatograph (Dionex Model DX-120)
Guard column (Dionex AG-14)
Analytical column (Dionex AS-14)
Anion Self-Regenerating Suppresser (Dionex ASRS-II)
Conductivity Detector (Dionex DS4 Detection Stablizer)
Automated sampler (AS40)
PeakNet Workstation (computer, printer, monitor, mouse, DX LAN card, AS40 serial port, and an operating environment supported by MS-DOS and Windows 3.1 or newer and PeakNet software.)

PeakNet Software

PeakNet software controls the instrumentation; automatically collects, processes, and reports data; and provides utilities that interpret analytical results. (Dionex, 1996).

Reagents

Deionized water with a resistivity of 17.8 mega-ohms or greater
Sodium carbonate, Na_2CO_3 ACS reagent grade
Sodium bicarbonate, $NaHCO_3$ ACS reagent grade

Eluent: 3.5 mM Na_2CO_3, 1.0 mM $NaHCO_3$.

Safety precautions

Normal laboratory safety procedures should be followed. The operator should take care when analyzing samples of an unknown nature. Refer to the CHP and MSDS for specific precautions, effects of overexposures, and first-aid treatment for reagents used in this method.

Running under PeakNet Control

When the DX-120 is connected to a PeakNet workstation via the DX LAN interface, PeakNet software (Release 4.30 or later) can monitor DX-120 status and control the following functions. Select the position of the injection and column selection valves, turn on the pump flow, SRS power, eluent pressure on and off, perform an auto offset, select the pressure units displayed on the screen (Mpa or psi), control TTL1 and TTL2 output signals, and control the auxiliary AC outlet (Dionex, 1996).

Procedure

Refer to the Dionex manual (Dionex 1994, 1996) for the proper procedure for operating the instrument. Allow the system to equilibate for 15 to 20 minutes prior to any sample or standard injection. The background conductivity should be between 15 and 17 microsiemens (μs). Instrumental operating conditions are summarized in table 1.

Table 1.---DX 120 Operating conditions for determination of selected anions by IC

Columns …… AG-14 (4x50mm) guard column
…… …… AS-14 (4x250mm) analytical column
Suppresser ……. ASRS II Anion self-regenerating suppresser
Eluent ……. 3.5 mM Na_2CO_3 sodium carbonate
……. 1.0 mM $NaHCO_3$ sodium bicarbonate
Flow Rate …….. eluent: 1.2 ml/min
Detector Cell …….. CDM-3 or DS4 Detection Stabilizer
Sample loop …… 25 μl
Sampler …….. AS40 Automated Sampler

The samples are prepared in 5 ml PolyVials with filtercap and placed in sample cassettes. The AS40 can take a maximum of 11 cassettes of 6 samples each, which are placed in the input tray ahead of the spring-loaded pusher.

Calibration is accomplished by injection of multi-element anion standards containing the anions of interest. For multi-level calibrations, several calibration standards covering the expected concentration range must be injected. A calibration curve for each component is determined from the data acquired for each different calibration level. Correlation coefficients of "r" value 0.995 or better should be obtained before proceeding with sample analysis. When typing the schedule use the special sample name AUTOCAL x, where x is the calibration level (1-10), only if the sample is a calibration standard. AUTOCAL x causes the Run program to use the current peak areas to update the Method Component Table. After the first sample of deionized water is run as a system flush, autocals 1-5 are run to establish a calibration curve for each anion of interest, plotting peak area vs. concentration. This calibration sequence is followed by a WRD anion standard to check precision and accuracy. After the WRD standard is run, samples 1-20, a duplicate, and a second WRD standard are run. This calibration sequence is repeated every 20 samples to compensate for drift in the system. Peak area for each anion detected is plugged into the individual quantitation equations established from the calibration curve for that specific anion and used to determine their concentration. The calibration standards and their concentrations are listed in table 2.

Table 2.-- Anion Calibration standards (ppm) for DX-120 IC Analysis

Anion	Autocal 1	Autocal 2	Autocal 3	Autocal 4	Autocal5
F^-	0.08	0.4	0.8	2.0	4.0
Cl^-	0.08	0.4	0.8	2.0	4.0
NO_3^-	0.08	0.4	0.8	2.0	4.0
SO_4^{2-}	1.6	8.0	16	40	80

Calculations

A calibration curve for each component is determined from the data acquired from each calibration level (table 2), using either a linear, quadratic, cubic, or point to point interpolation. A linear fit is used most often in this method and is determined by a least-squares calculation to fit a line through the calibration points. When the analyte concentration, for a specific component approaches the end of the calibration range and the detector response is known to "flatten out" toward one extreme or the other, a quadratic fitting may be used.

Linear Fit Calculation:

$$AMTi = (K_1 \times Area) + Ko$$

Where:

Amti = the amount of the component I in the sample

Areai = the area of component I in the sample

K_1 = the slope of the response line of component I

Ko = the Y-axis intercept of the component I calibration curve

Assignment of Uncertainty

Table 3. -- Analytical performance summary for selected anions (ppm) by IC

Reference materials are water samples with pv from Water Resources Division, (USGS OPF 95-395, 96-138, 97-20, 00-227, 00-398, and 01-137). See page ix of the introduction to this Methods Manual for an explanation of the abbreviations used in the analytical performance summary tables.

Reference	*Description*	*n*	*Mean*	*s*	*pv*	*% RSD*	*% R*
Fluoride, F^-							
P-25	major constituents	28	0.150	0.019	0.139	12.7	92.7
M-134	major constituents	18	0.563	0.033	0.561	5.81	99.6
M-140	major constituents	19	0.573	0.031	0.530	5.47	92.6
M-130	major constituents	30	1.115	0.186	1.23	16.7	110
Chloride, Cl^-							
P-25	major constituents	28	1.235	0.035	1.30	2.84	106
M-130	major constituents	30	22.083	0.750	21.4	3.40	96.9
M-140	major constituents	19	25.735	0.830	25.8	3.22	100
M-134	major constituents	18	66.502	0.673	65.0	1.01	97.7
Nitrate, NO_3^-							
N-63	major constituents	28	0.366	0.029	0.37	8.00	101
N-66	major constituents	28	4.135	0.076	4.12	1.85	99.6
N-64	major constituents	28	6.556	0.082	5.58	1.25	85.1
N-68	major constituents	28	7.484	0.100	7.44	1.33	99.4

[+]Values for nitrate were calculated from the nitrogen proposed values by multiplying by a 4.42680 gravimetric factor.

Sulfate, SO_4^{2-}							
P-25	major constituents	28	2.435	0.224	2.34	9.19	96.1
M-130	major constituents	30	55.883	0.903	58.0	1.62	104
M-134	major constituents	18	78.071	1.347	78.0	1.72	99.9
M-140	major constituents	19	149.89	4.559	150.0	3.22	100

Table 3.—Continued—Duplicate samples results

Duplicate samples	k	n	Mean	s	% RSD	Concentration Range			No. of < (totals)	No. of < (pairs)
Fluoride	30	2	0.58	0.03	5.867	0.08	to	4.0	0	0
Chloride	30	2	6.46	0.161	0.05	0.08	to	60	0	0
Nitrate	30	2	14.36	0.13	0.923	0.08	to	18	0	0
Sulfate	30	2	127.67	1.40	1.097	1.6	to	80	0	0

Table 3.—Continued—Method blank results 3s values are considered the lower limit of detection (LOD), and 5s values are considered the lower limit of determination (LLD)

Method blank	n	Mean	s	3s	5s
Chloride	30	0.03	0.01	0.04	0.05
Nitrate	30	0.04	0.02	0.06	0.1
Sulfate	30	0.04	0.01	0.02	0.05
Fluoride*	30	0.007	0.002	0.007	0.01

*Fluoride blank values determined using a low standard (0.005 ppm) 3s values are considered the lower limit of detection (LOD), and 5s values are considered the lower limits of determination (LLD)

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