



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

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**U.S. DEPARTMENT OF THE INTERIOR  
U.S. GEOLOGICAL SURVEY**

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## INTRODUCTION

This manual presents validated analytical methods used by the Mineral Resources Team, Geologic Division. The manual updates the methods manual edited by Belinda Arbogast, Open-File Report 96-525 published in 1996. This edition contains a few methods that have not changed significantly from the 1996 edition, a number of methods that are essentially the same but involve changes in instrumentation or minor changes in the procedure, and a number of new methods that were recently developed and approved.

This manual is intended primarily for use by laboratory scientists; but can also assist laboratory users to evaluate the data they receive. The analytical methods are written in a step by step approach so that they may be used as a training tool and provide detailed documentation of the procedures for quality assurance. This manual is also available on the Internet at <http://cpg.cr.usgs.gov/pub/publications.html>

## SAFETY POLICY<sup>1</sup>

Because the laboratory work area inherently contains potential hazards, laboratory safety and health is a top priority. All federal, state, and local regulations concerning worker and community safety are to be strictly followed. Included in this policy is the propagation and distribution of Chemical Hygiene Plans (*CHP*) and Material Safety Data Sheets (*MSDS*) for every laboratory procedure that involves hazardous or toxic chemicals. These regulations affect Team management, personnel, facilities, and activities. If violated, some of these regulations carry financial and criminal penalties.

<sup>1</sup> Sutley, 1994

## **ANALYTICAL METHOD FORMAT**

The written analytical methods contained in this volume reflect the procedures actually being used in the laboratory. Routine methods are written in the following standard format:

**TITLE**—contains the name(s) of the analyte and the measurement method

**PRINCIPLE**—brief discussion of the scientific basis

**INTERFERENCE**—physical or chemical conditions or processes which cause analytical error.

**SCOPE**—the range of analyte concentration and applicable sample matrices for which the method is useful, and an estimate of time required for analysis

**APPARATUS**—instruments and special equipment required

**REAGENTS**—chemical name, chemical symbol, purity, method of preparation, and shelf life if stability is a problem

**SAFETY PRECAUTIONS**—hazards peculiar to the method of analysis and handling procedures

**PROCEDURE**—describes a strict time sequence and the critical steps in the analysis

**CALCULATION**—equation(s) necessary to calculate the results of the analysis

**ASSIGNMENT OF UNCERTAINTY**—statistical summary table of the historical analytical results for selected reference materials, duplicate samples, and method blank. For a detailed discussion please refer to the *Analytical Performance Summary* section.

**BIBLIOGRAPHY**—references to the literature on which the method is based

## **METHOD VALIDATION**

Before any method is approved to generate analytical data under the QA program, the method is assigned a unique code and must be validated. If a method is provisional, two dashes (--) are entered for the approval date. Method validation includes:

1. A copy of the analytical method in standard written format
2. Research report of analytical data from testing the proposed method using reference materials, duplicate samples, and method blanks
3. Quality assurance review
4. Research section review
5. Operations section review

## DEFINITION OF TERMS

### Limit of Detection

The limit of detection (LOD) must refer to the entire analytical measurement process and is usually regarded as the lowest concentration level of the analyte that can be determined to be statistically different from the analytical blank.

According to the American Chemical Society (ACS, 1980) a confidence level of 3 sigma above the measured average blank is considered minimum since this implies the risk for 7 percent false positives (concluding the analyte is present when it is absent) and false negatives (the reverse). The 3 sigma value actually corresponds to a confidence level of about 90 percent as "a 99.6 percent confidence level applies only for a strictly one-sided Gaussian distribution. At low concentrations, non-Gaussian distributions are more likely" (International Union of Pure and Applied Chemistry, 1978).

### Lower Reporting Limit

The terms "lower reporting limit", "lower limits of determination" and "lower limits of quantification" are confusing in the literature, and are described as either 5 sigma to 10 sigma. In this report the terms will be used for concentrations expected to be at or above five times the standard deviation determined from the method blank or low analyte concentration samples. Because of the different definitions given for these terms in the literature, the method descriptions will give the information in tables as 3s and 5s numbers. Given the varied matrices submitted to the laboratory and diverse data quality needs, these tables of method-blank and reference material results are included to assist in appropriate use of laboratory data.

All submitted samples are initially run undiluted unless sample dilutions are required in order to reduce or eliminate known matrix/interference effects. When an analyte concentration exceeds the calibration or linear range, the sample is re-analyzed after appropriate dilution. The analyst will use the least dilution necessary to bring the analyte within range. In both cases, a loss of sensitivity is experienced. All sample dilutions result in an increase in the lower reporting limit by a factor equal to the dilution.

Assuming independent normally distributed measurements, confidence limits may be assigned from the mean and standard deviation (based on a relatively large number of observations, or by use of a significance test). "In order to detect bias equal in magnitude to the standard deviation, one needs at least 12 degrees of freedom (13 replicates)" (Currie, 1988).

### Limit of Quantitation

Ten sigma above the average blank is often suggested for the limit of quantitation or limit of determination. This is the lower limit for quantitative measurements (as opposed to qualitative measurements) and at this level the risk of false positives and negatives is decreased.



## ANALYTICAL PERFORMANCE SUMMARY

A table is included under the *Assignment of uncertainty* section in each method write-up and provides an estimate of the analytical method performance. The results of the analytical measurement process are estimates of general performance only, given the sample matrix and analyte concentration. Outliers are not rejected unless reasons are known why the results are unacceptable. Calculated results (i.e. percent recovery) may not appear to match initial numbers due to rounding-off.

The analytical performance summary table is arranged in three sections: (1) reference materials, (2) duplicates, and (3) method blank results.

### Reference Materials

Reference material (RM) samples are materials having one or more well established or certified concentrations or physical properties to be used for instrument calibration, method accuracy, or testing. The RM is used for evaluation of the analytical method bias expressed as percent recovery (% R). An attempt is made to test methods (if appropriate reference material is available) at the lower, mid-point, and upper end of the operating range with a number of varied matrices. Solid phase samples are reported on an as received basis. No corrections are made for moisture content unless noted in the method.

The first section of the table lists selected reference materials tested and associated results in rows. The table has column headings as follows:

**REFERENCE** – sample name of the geochemical reference material

**DESCRIPTION** – identification of the reference material

*n* – number of observed measurements or samples in a subgroup

**Mean** – arithmetic mean. Generally, the result is quoted with all digits which are certain, plus the first uncertain one. In order to compare some laboratory to proposed values and avoid the loss of information, whole numbers may not appear rounded-off. Less than symbol, “<” is used for qualified data below the lower reporting limit

*s* – standard deviation

*pv* – proposed value taken from the published reference material compositions of Potts and others (1992). Where the proposed value has an accompanying upper case letter, the corresponding reference is in the headnote. According to Potts the tabulated data are distinguished by:

**bold typeface** indicates precision better than 10 percent relative (two sigma), normally based on five or more results from two or more independent techniques

certified value from the distributor of reference materials is designated “*cv*”

plain typeface indicates other compiled data; distinguished by a {?} question mark if there is additional uncertainty (for example, fewer than 3 reported results, large disparity in reported results, and/or data derived from only one non-definitive technique)

*italic typeface* indicates data abstracted from individual schemes of analysis fully described in the literature

**%RSD** – percent relative standard deviation

**%R** – percent recovery = (determined value/*pv*) x 100

## Duplicate Samples

Duplicate samples are a second aliquot of a submitted sample (taken at the time of sample weighing) selected to evaluate laboratory variance (precision) expressed as percent relative standard deviation (% RSD). The aliquot is treated the same as the original sample through the analytical process. Duplicate samples take into account the analyte concentration and matrix of the sample of interest, i.e. samples submitted by ACSG customers.

The second section of the table deals with duplicate samples. The column headings are as follows:

$k$  – number of subgroups under consideration

$n-2$ , number of samples in the subgroup

*Mean* – arithmetic mean for duplicate measurements

$s$  – standard deviation for duplicate measurements

*%RSD* – relative standard deviation

*Concentration Range* – the minimum and maximum values reported of unqualified data (data that are greater than the lower reporting limit)

*No. of "<" (total)* – the number of values less than the lower reporting limit

*No. of "<" (pairs)* – the number of times the duplicates were both reported as less than values

## Method Blank

A method blank contains deionized water or other solutions processed through the entire analytical method with submitted samples. It is used as an indicator of possible contamination due to reagents or apparatus and sensitivity of the analytical method. The variability (standard deviation) of the method blank can be used for estimating the lower limits of detection or determination. Pure solutions, however, assume no matrix effects and tend to be normally distributed. In reality, matrix effects occur even in methods considered to be relatively free from interferences.

The last section of the table lists the results for the method blank. The column headings are as follows:

$n$  – number of observed measurements on completely independently prepared blanks

*Mean* – arithmetic mean

$s$  – standard deviation

$3s$  – three times the standard deviation (limit of detection)

$5s$  – five times the standard deviation (lower reporting limit)

If the chapter author thinks the reporting limits should not be the same as the  $3s$  and  $5s$  determinations on blanks, then a separate table of reporting limits will be included in that chapter.

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## **Chapter V**

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

*By P.M. Theodorakos, W.M. d'Angelo and W.H. Ficklin*

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

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# Fluoride, chloride, nitrate, and sulfate in aqueous solution utilizing AutoSuppression chemically suppressed Ion Chromatography

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Codes: I011  
T05

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## 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  $\mu$ l 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<sub>4</sub>. The sulfate may accumulate by adsorption on Fe precipitates, to be released in subsequent elutions, resulting in elevated SO<sub>4</sub> 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 CuSO<sub>4</sub>. 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°C 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<sup>-</sup> 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 Suppressor (Dionex ASRS-II)  
Conductivity Detector (Dionex DS4 Detection Stabilizer)  
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<sub>2</sub>CO<sub>3</sub> ACS reagent grade  
Sodium bicarbonate, NaHCO<sub>3</sub> ACS reagent grade

*Eluent:* 3.5 mM Na<sub>2</sub>CO<sub>3</sub>, 1.0 mM NaHCO<sub>3</sub>.

## 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 equilibrate 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 <sub>2</sub> CO <sub>3</sub> sodium carbonate
.....	1.0 mM NaHCO <sub>3</sub> 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, autocal 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 <sup>-</sup>	0.08	0.4	0.8	2.0	4.0
Cl <sup>-</sup>	0.08	0.4	0.8	2.0	4.0
NO <sub>3</sub> <sup>-</sup>	0.08	0.4	0.8	2.0	4.0
SO <sub>4</sub> <sup>2-</sup>	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:

$$AMTi = (K_1 \times Area) + K_0$$

Where:

- Amti = the amount of the component I in the sample
- Areai = the area of component I in the sample
- K<sub>1</sub> = the slope of the response line of component I
- K<sub>0</sub> = 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.

<i>Reference</i>	<i>Description</i>	<i>n</i>	<i>Mean</i>	<i>s</i>	<i>pv</i>	<i>% RSD</i>	<i>% R</i>
Fluoride, F <sup>-</sup>							
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 <sup>-</sup>							
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 <sub>3</sub> <sup>-</sup>							
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 <sub>4</sub> <sup>2-</sup>							
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 <	No. of <
								(totals)	(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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