METHOD #: 300.0 Recommended for Approval for NPDES (November 1991)

TITLE: The Determination Of Inorganic Anions In Water By Ion Chromatography

ANALYTE:

		CAS #
BrO_3	Bromate	
Br	Bromide	7726-95-6
ClO_3	Chlorate	
Cl	Chloride	7782-50-5
ClO_2	Chlorite	
F	Fluoride	7782-41-4
NO_3	Nitrate	
NO_2		
HPO_4	Phosphate	
SO_4	Sulfate	

INSTRUMENTATION: IC

1.0 Scope and Application

1.1 This method covers the determination of the following inorganic anions.

Method A.	Storet No. (Total)
Bromide	71870
Chloride	00940
Fluoride	00951
Nitrate-N	00620
Nitrite-N	00615
Ortho-Phosphate-P	70507
Sulfate	00945

Method B.	Storet No. (Total)
Chlorite	50074
Chlorate	
Bromate	

1.2 The matrices applicable to each method are shown below:

A. Drinking water, surface water, mixed domestic and industrial wastewaters, groundwater, reagent waters, solids (after extraction 2.3), leachates (when no acetic acid is used 2.4)

B. Drinking water and reagent waters.

1.3 The Single Laboratory Method Detection Limit (MDL, defined in Section 13) for the above analytes is listed in Tables 1A and 1B. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample.

1.4 Method A is recommended for drinking and waste waters. The multilaboratory range tested for each anion is as follows in mg/L:

Bromide	0.63 - 21.0
Chloride	0.78 - 26.0
Fluoride	0.26 - 8.49
Nitrate-N	0.42 - 14.0
Nitrite-N	0.36 - 12.0
Ortho-P	0.69 - 23.1
Sulfate	2.85 - 95.0

1.5 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatogram. Each analyst must demonstrate the ability to generate acceptable results with this method, using the procedure described in Section 10.2.

1.6 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of fortified sample matrix covering the anions of interest. The forttification procedure is described in Section 11.6.

2.0 Summary of Method

2.1 A small volume of sample, typically 2 to 3 mL, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, separator column, suppressor device, and conductivity detector.

2.2 The main differences between Method A and B are the separator columns, guard columns and eluents. Sections 6 and 7 will elicit the differences.

2.3 In order to use this method for solids an extraction procedure must be performed (See 11.7).

3.0 Definitions

3.1 Stock standard solution - a concentrated solution containing a single certified standard that is a method analyte. Stock standard solutions are used to prepare calibration standards.

3.2 Calibration standards (CAL) - a solution of analytes prepared in the laboratory from stock standard solutions and diluted as needed and used to calibrate the instrument response with respect to analytic concentration.

3.3 Quality control sample (QCS) - a solution containing known concentrations of analytes, prepared by a laboratory other than the laboratory performing the analysis. The analyzing laboratory uses this solution to demonstrate that it can obtain acceptable identifications and measurements with a method.

3.4 Performance evaluation sample (PE) - a solution of method analytes distributed by the Quality Assurance Research Division (QARD), Environmental Monitoring Systems Laboratory (EMSL-Cincinnati), USEPA, Cincinnati, Ohio, to multiple laboratories for analysis. A volume of the solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses used by the QARD to determine

statistically the accuracy and precision that can be expected when a method is performed by a competent analyst. Analyte true values are unknown to the analyst.

3.5 Laboratory performance check standards (LPC) - a solution of analytes prepared in the laboratory by adding appropriate volumes of the stock standard solutions to reagent water used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.6 Laboratory duplicates (LD) - two aliquots of the same sample that are treated exactly the same throughout laboratory analytical procedures. Analyses of laboratory duplicates indicate precision associated with laboratory procedures but not the sample collection, preservation, or storage procedures.

3.7 Field duplicates (FD) - two samples taken at the same time and placed under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.8 Laboratory fortified sample matrix (LFM) - An aliquot of an environmental sample to whkh known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.9 Laboratory fonified blank (LFB) An aliquot of reagent water to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements at the required method detection limit.

4.0 Interferences

4.1 Interferences can be caused by substances with retention times that are similar to and overlap those of the anion of interest. Large amounts of an anion can interfere with the peak resolution of an adjacent anion. Sample dilution and/or spiking can be used to solve most interference problems.

4.2 The water dip or negative peak that elutes near and can interfere with the fluoride peak can usually be eliminated by the addition of the equivalent of 1 mL of concentrated eluent (7.3 100X) to 100 mL of each standard and sample.

4.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

4.4 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.

4.5 Any anion that is not retained by the column or only slightly retained will elute in the area of fluoride and interfere. Known coelution is caused by carbonate and other small organic anions. At concentrations of fluoride above 1.5 mg/L this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.6 The acetate anion elutes early during the chromatographic run. The retention times 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 acetic acid is used for pH adjustment.

4.7 The quantitation of unretained peaks should be avoided, such as low molecular weight organic acids (formate, acetate, propionate, etc.) which are conductive and coelute with or near fluoride and would bias the fluoride quantitation in some drinking and most waste waters.

5.0 Safety

5.1 Normal, accepted laboratory safety practices should be followed during reagent preparation and instrument operation. No known carcinogenic materials are used in this method.

6.0 Apparatus and Materials

6.1 Balance - Analytical, capable of accurately weighinq to the nearest 0.0001 g.

6.2 Ion chromatograph - Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and detectors.

6.2.1 Anion guard column: A protector of the separator column. If omitted from the system the retention limes will be shorter. Usually packed with a substrate the same as that in the separator column.

6.2.2 Anion separator column: This column producos the separation shown in Fgures 1 and 2.

6.2.2.1 Anion separator column (Method A): The separation shown in Figure 1 was generated using a Dionex AS4A column (P/N 37041). An optional column may be used if comparable resolution of peaks is obtained, and the requirements of section 10.2 can be met.

6.2.2.2 Anion separator column (Method B). The separation shown in Figure 2 was generated using a Dionex AS9 column (P/N 42025). An optional column may be used if comparable resolution of peaks is obtained and the requirements of section 10.2 can be met.

6.2.3 Anion suppressor device: The data presented in this method was generated using a Dionex Anion MicroMembrane Suppressor (P/N 37106).

6.2.4 Detector - Conductivity cell: approximately 1.25 µL internal volume, (Dionex, or equivalent) capable of providing data as required in section 10.2.

6.3 The Dionex AI-450 Data Chromatography Software was used to generate all the data in the attached tables. Systems using a stripchart recorder and integrator or other computer based data system may achbve approximately the same MDL's but the user should demonstrate this by the procedure outlined in Section 10.2.

7.0 Reagents and Consumable Materials

7.1 Sample bottles: Glass or polyethylene of sufficient volume to allow replicate anaiyses of anions of interest.

7.2 Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.3 Eluent solution (Method A and Method B): Sodium bicarbonate (CAS RN 144-55-8) 1.7 mM, sodium carbonate (CAS RN 497-19-8) 1.8 mM. Dissolve 0.2856 g sodium bicarbonate ($NaHCO_3$) and 0.3816 g of sodium carbonate (Na_2CO_3) in reagent water (7.2) and dilute to 2 liters.

7.4 Regeneration solution (MicroMembrane Suppressor): Sulfuric acid (CAS RN-7664-93-9) 0.025N. Dilute 2.8 mL conc. sulfuric acid (H_2SO_4) to 4 liters with reagent water.

7.5 Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade materials (dried at 105°C for 30 min.) as listed below.

7.5.1 Bromide (Br) 1000 mg/L: Dissolve 1.2876 g sodium bromide (NaBr, CAS RN 7647-15-6) in reagent water and dilute to 1 liter.

7.5.2 Bromate (BrO_3^-) 1000 mg/L: Dissolve 1.3057 g of potassium bromate ($KBrO_3$, CAS RN 7758-01-2) in reagent water and dilute to 1 liter.

7.5.3 Chlorate (ClO_3^-) 1000 mg/L: Dissolve 1.2753 9g sodium chlorate ($NaClO_3$, CAS RN 7775-09-9) in reagent water and dilute to 1 liter.

7.5.4 Chloride (Cl^-) 1000 mg/L: Dissolve 1.6485 g sodium chloride (NaCl, CAS RN 7647-14-5) in reagent water and dilute to 1 liter.

7.5.5 Chlorite (ClO_2^-) 1000 mg/L: Dissolve 1.3410 g of sodium chlorite ($NaClO_2$, CAS RN 7758-19-2) in reagent water and dilute to 1 liter.

7.5.6 Fluoride (F^-) 1000 mg/L: Dissolve 2.2100 g sodium fluoride (NaF, CAS RN 7681-49-4) in reagent water and dilute to 1 liter.

7.5.7 Nitrate (NO_3^--N) 1000 mg/L: Dissolve 6.0679 g sodium nitrate ($NaNO_3$, CAS RN 7631-994) in reagent water and dilute to 1 liter.

7.5.8 Nitrite ($NO2^-$-N) 1000 mg/L: Dissolve 4.9257 g sodium nitrite ($NaNO_2$, CAS RN 7632-00-0) in reagent water and dilute to 1 liter.

7.5.9 Phosphate ($HPO_4^=$-P) 1000 mg/ L: Dissolve 4.3937 g potassium phosphate, monobasic (KH_2PO_4, CAS RN 7778-77-0) in reagent water and dilute to 1 liter.

7.5.10 Sulfate ($SO_4^=$) 1000 mg/L: Dissolve 1.8141 g potassium sulfate (K_2SO_4, CAS RN 7773-80-5) in reagent water and dilute to 1 liter.

Note: Stability of standards: Stock standards (7.5) are stable for at least one month when stored at 4°C. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate should be prepared fresh daily.

8.0 Sample Collection, Preservation and Storage

8.1 Samples should be collected in scrupubusly clean glass or polyethylene bottles.

8.2 Sample preservation and holding times for the anions that can be determined by this method are as follows.

Analyte	Preservation	Holding Time
Bromate	None required	28 days
Bromide	None required	28 days
Chlorate	None required	28 days
Chloride	None required	28 days
Chlorite	Cool to 4°C	immed.
Fluoride	None required	28 days
Nitrate-N chlorinated	Cool to 4°C	28 days
nonchlorinated pH < 2	conc. H_2SO_4	14 days
Nitrite-N	Cool to 4°C	48 hours
o-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

8.3 The method of preservation and the holding time for samples analyzed by this method are determined by the anions of interest. In a given sample, the anion that requires the most preservation treatment and the shortest holding time will determine the preservation treatment. It is recommended that all samples be cooled to 4°C and held no longer than 28 days for Method A and analyzed immediately for Method B.

9.0 Calibration and Standardization

9.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1A or 1B.

9.2 For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards (7.5) to a volumetric flask and diluting to volume with reagent water. If a sample analyte concentration exceeds the calibration range the sample may be diluted to fall within the ranse. H this is not possible then three new calibration concentrations must be chosen, two of which must bracket the concentration of the sample analyte of interest. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

9.3 Using injections of 0.1 to 1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

9.4 The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 20 samples. If the response or retention time for any analyte varies from the expected values by more than ± 10%, the test must be repeated, using fresh calibratbn standards. If the results are still more than ± 10%, a new calibration curve must be prepared for that analyte.

9.5 Non-linear response can result when the separator column capacity is exceeded (overloading). The response of the detector to the sample when diluted 1:1, and when not diluted, should be compared. If the calculated responses are the same, samples of this total anionic concentration need not be diluted.

10.0 Quality Control

10.1 Each laboratory using this method should have a formal quality control program. The minimum requirements of this program consist of an initial demonstration of laboratory capability (10.2) and the analysis of fortified samples as a continuing check on performance. The laboratory should maintain performance records to define and document the quality ot data that are generated.

10.1.1 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Section 10.2.

10.1.2 The laboratory should fortify and analyze a minimum of 10% of all samples to monitor continuing laboratory performance. A minimum of 10% of all samples should be run in duplicate.

10.2 Before performing any analyses, the analyst should demonstrate the ability to generate acceptable accuracy and precision with this method, using a laboratory performance standard.

10.2.1 Select a representative check concentration for each analyte to be measured. Using stock standards, prepare a laboratory performance check sample concentrate in reagent water 100 times more concentrated than the selected concentrations.

10.2.2 Using a pipet, add 1.00 mL ot the check sample concentrate (10.2.1) to each of a minimum of four 100-mL aliquots of reagent water. Analyze the aliquots according to the procedure in Section 11.

10.2.3 Calculate the average percent recovery, (R), and the standard deviation(s) of the percent recovery, for the results.

10.2.4 Using the appropriate data from Table 2, determine the recovery and single operator precision expected for the method, and compare these results to the values cakulated in Section 10.2.3. If the data are not comparable within control limits (10.3.1), review potential problem areas and repeat the test.

10.3 The analyst must calculate method performance criteria and define the performance of the laboratory for each spike concentration of analyte being measured.

10.3.1 Calculate upper and bwer control limits for method performance as follows:

Upper Control Limit (UCL) = R + 3s
Lower Control Limit (LCL) = R - 3s

where R and s are calculated as in Section 10.2.3. The UCL and LCL can be used to construct control charts that are useful in observing trends in performance.

10.4 The laboratory should develop and maintain separate accuracy statements of laboratory performance for each matrix being analyzed by the laboratory. An accuracy statement for the method is defined as R ± s. The accuracy statement should be developed by the analyses of four aliquots of water or wastewater, as described in Section 10.2.2, followed by the calculation of R and s.

10.5 Before processing any samples, the analyst must demonstrate through the

analysis of an aliquot of reagent water that all glassware and reagent interferences are under control. Each time there is a change in reagents, a laboratory reagent blank must be processed as a safeguard against laboratory contamination.

10.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Field duplicates may be analyzed to monitor the precision of the sampling technique. When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and fortification, must be used. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.

10.7 In order to verify that standards have been prepared conectly a reference standard check should be performed using a standard of known concentration prepared by an independent source.

10.8 With each batch of samples processed analyze a single laboratory fortified blank containing each analyte of concern at a concentration at or near those used in the reagent water data in Tables 2A or 2B. If more than 20 samples are run in a batch analyze one LFB for every 20 samples. Evaluate the accuracy by comparing to Tables 2A of 2B. If acceptable data cannot be obtained, locate the problem and correct it.

10.9 At least quarterly, replicates of LFBs should be analyzed to determine the precision of the laboratory measurements. Add these results to the ongoing control charts to document data quality.

10.10 When using Part B, the analyst should be aware of the purity of the reagents used to prepare standards. Allowances must be made when the solid materials are less than 99% pure.

11.0 Procedure

11.1 Tables 1A and 1B summarize the recommended operating conditions for the ion chromatograph. Included in this table are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Section 10.2 are met.

11.2 Check system calibration daily and, if required, recalibrate as described in Section 9.

11.3 Load and inject a fixed amount of well mixed sample. Flush injection loop thoroughly, using each new sample. Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

11.4 The width of the retentbn time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.5 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

11.6 If the resulting chromatogram fails to produce adequate resolution, or if

identification of specific anions is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

Note: Retention time is inversely proportional to concentration. Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases this peak migration may produce poor resolution or identification.

11.7 The following extraction should be used for solid materials. Add an amount of reagent water equal to ten times the weight of dry solid material taken as a sample. This slurry is mixed together for ten minutes using a magnetk stirring device. Filter the resulting slurry before injecting using a 0.45 µ membrane type filter. This can be the type that attaches directly to the end of the syringe. Care should be taken to show that good recovery and identification of peaks is obtained with the users matrix through the use of spikes.

12.0 Calculation

12.1 Prepare separate calibration curves for each anion of interest by plotting peak size in area, or peak height units of standards against concentration values. Compute sample concentration by comparing sample peak response with the standard curve.

12.2 Report results in mg/L.

12.3 Report
NO_2^- as N
NO_3^- as N
$HPO_4^=$ as P

13.0 Precision and Accuracy - Method Detection Limit

13.1 The method detection limit (MDL) is defined as the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero. The MDL concentrations listed in Table 1A and 1B were obtained using reagent waters.

13.2 Single operator accuracy and precision for reagent, drinking and surface water, and mixed domestic and industrial wastewater are listed in Table 2A and 2B.

13.3 Multiple laboratory accuracy and precision data for reagent, drinking and waste water using method A ue given for each anion in tables 3 through 9. Data from nineteen laboratories were used for this data.

13.4 Some of the bias statements, for example chloride and sulfate, may be misleading due to spiking small increments of the anion into large naturally occuring concentrations of the same anion.

14.0 References

14.1 "Determination of Inorganic Disinfection By-Products by Ion Chromatography", J. Pfaff, C. Brockhoff. J. Am. Water Works Assoc., Vol 82, NO. 4, p. 192.

14.2 Standard Methods for the Examination of Water and Wastewater, Method 4110B, "Anions by Ion Chromatography" proposed for the supplement 1 7th Edition of Standard Methods.

14.3 Dionex, System 4000 Operation and Maintenance Manual, Dionex Corp., Sunnyvale, California 94086. 1988.

14.4 Method Detection Limit (MDL) as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, page 1426, December 1981.

Table 1A. Chromatographic Conditions and Detection Limits In Reagent Water (Method A)

Analyte	Peak # (*)	Retention Time (min)	MDL (mg/L)
Fluoride	1	1.2	0.01
Chloride	2	1.7	0.02
Nitrite-N	3	2.0	0.004
Bromide	4	2.9	0.01
Nitrate-N	5	3.2	0.002
o-Phosphate-P	6	5.4	0.003
Sulfate	7	6.9	0.02

Standard Conditions:

Columns:	as specified in 6.2.2.1
Detector:	as specified in 6.2.4
Pump Rate:	2.0 mL/min.
Eluent:	as specified in 7.3.1
Sample Loop:	50 µL

MDL calculated from data system using a y-axis selection of 1000 ns and with a strip chart recorder with an attenuator setting of 1 µMHO full scale.

(*) See figure 1

Table 1B. Chromatographic Conditions and Detection Limits In Reagent Water (Method B)

Analyte	Peak # (*)	Retention Time (min)	MDL (mg/L)
Chlorite	1	2.8	0.01
Bromate	2	3.2	0.02
Chlorate	4	7.1	0.003

Standard Conditions:

Column:	as specified in 6.2.2.2
Detector:	as specified in 6.2.4
Pump Rate:	1.0 mL/min.
Eluent:	as specified in 7.3
Sample Loop:	50 µL
Attentuation:	1
y - axis:	500 ns

(*)See figure 2

Table 2A. Single Operator Accuracy and Precision of Standard Anions (Method A)

Analyte	Sample Type	Spike (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
Bromide	RW	5.0	7	99	0.08
	DW	5.0	7	105	0.10
	SW	5.0	7	95	0.13
	WW	5.0	7	105	0.34
	GW	5.0			
	SD	2.0	7	82	0.06
Chloride	RW	20.0	7	96	0.35
	DW	20.0	7	108	1.19
	SW	10.0	7	86	0.33
	WW	20.0	7	101	5.2
	GW	20.0	7	114	1.3
	SD	20.0	7	90	0.32
Fluoride	RW	2.0	7	91	0.05
	DW	1.0	7	92	0.06
	SW	1.0	7	73	0.05
	WW	1.0	7	87	0.07
	GW	0.4	7	95	0.07
	SD	5.0	7	101	0.35

Nitrate-N	RW	10.0	7	103	0.21
	DW	10.0	7	104	0.27
	SW	10 0	7	93	0.17
	WW	10.0	7	101	0.82
	GW	10.0	7	97	0.47
	SD	10.0	7	82	0.28
Nitrite-N	RW	10.0	7	97	0.14
	DW	10.0	7	121	0.25
	SW	5.0	7	92	0.14
	WW	5.0	7	91	0.50
	GW	10.0	7	96	0.35
	SD	2.0	7	98	0.08
o-Phosphate-P	RW	10.0	7	99	0.17
	DW	10.0	7	99	0.26
	SW	10.0	7	98	0.22
	WW	10.0	7	106	0.85
	GW	10.0	7	95	0.33
Sulfate	RW	20.0	7	99	0.40
	DW	50.0	7	105	3.35
	SW	40.0	7	95	1.7
	WW	40.0	7	102	6.4
	GW	40.0	7	112	3.2

RW = Reagent Water
DW = Drinking Water
SW = Surface Water
WW = Mixed Domestic and Industrial Wastewater
GW = Groundwater
SD = USEPA ac Solid (Shale)

Table 2B. Single-Operator Accuracy and precision of By-Products (Method B)

Analyte	Sample Type	Spike (mg/L)	Number of Replicates	Mean Recovery %	Standard Deviation (mg/L)
Bromate	RW	5.0	7	103	0.07
		1.0	7	98	0.04
		0.1	7	155	0.005
		0.05	7	122	0.01
	DW	5.0	7	95	0.04
		1.0	7	85	0.02
		0.1	7	98	0.005
		0.05	7	98	0.005
Chlorate	RW	5.0	7	101	0.06
		1.0	7	97	0.01
		0.1	7	100	0.01
		0.05	7	119	0.05
	DW	5.0	7	101	.04
		1.0	7	115	0.01
		0.1	7	121	0.005
		0.05	7	110	0.01
Chlorite	RW	5.0	7	100	0.04
		1.0	7	98	0.01
		0.1	7	86	0.01
		0.05	7	94	0.01
	DW	5.0	7	96	0.03
		1.0	7	100	0.02
		0.1	7	76	0.00
		0.05	7	96	0.01

RW = Reagent Water
DW = Drinking Water

Table 3. Determination of Bias for Fluoride

Water	Am't Added mg/L	Am't Found mg/L	S_t	S_o	Bias %
Reagent	0.26	0.25	0.08	0.11	-3.8
	0.34	0.29	0.11	-14.7	
	2.12	2.12	0.07	0.12	0.0
	2.55	2.48	0.14	-2.7	
	6.79	6.76	0.20	0.19	-0.4
	8.49	8.46	0.30	-0.4	
Drinking	0.26	0.24	0.08	0.05	-7.7
	0.34	0.34	0.11	0.0	
	2.12	2.09	0.18	0.06	-1.4
	2.55	2.55	0.16	0.0	
	6.79	6.84	0.54	0.25	+0.7
	8.49	8.37	0.75	-1.4	
Waste	0.26	0.25	0.15	0.06	-3.8
	0.34	0.32	0.08		-5.9
	2.12	2.13	0.22	0.15	+0.5
	2.55	2.48	0.16	-2.7	
	6.79	6.65	0.41	0.20	-2.1
	8.49	8.27	0.36	-2.6	

Table 4. Determination of Bias for Chloride

Water	Am't Added mg/L	Am't Found mg/L	S_t	S_o	Bias %
Reagent	0.78	0.79	0.17	0.29	+1.3
	1.04	1.12	0.46	+7.7	
	6.50	6.31	0.27	0.14	-2.9
	7.80	7.76	0.39	-0.5	
	20.8	20.7	0.54	0.62	-0.5
	26.0	25.9	0.58	-0.4	
Drinking	0.78	0.54	0.35	0.20	-30.8
	1.04	0.51	0.38	-51.0	
	6.50	5.24	1.35	1.48	-19.4
	7.80	6.02	1.90	-22.8	
	20.8	20.0	2.26	1.14	-3.8
	26.0	24.0	2.65	-7.7	
Waste	0.78	0.43	0.32	0.39	-44.9
	1.04	0.65	0.48	-37.5	
	6.50	4.59	1.82	0.83	-29.4
	7.80	5.45	2.02	-30.1	
	20.8	18.3	2.41	1.57	-11.8
	26.0	23.0	2.50	-11.5	

Table 5. Determination of Bias for Nitrite - Nitrogen

Water	Am't Added mg/L	Am't Found mg/L	S_t	S_o	Bias %
Reagent	0.36	0.37	0.04	0.04	+2.8
	0.48	0.48	0.06	0.0	
	3.00	3.18	0.12	0.06	+6.0
	3.60	3.83	0.12	+6.4	
	9.60	9.84	0.36	0.26	+2.5
	12.0	12.1	0.27	+0.6	
Drinking	0.36	0.30	0.13	0.03	-16.7
	0.48	0.40	0.14	-16.7	
	3.00	3.02	0.23	0.12	+0.7
		3.60	3.62	0.22	+0.6
	9.60	9.59	0.44	0.28	-0.1
	12.0	11.6	0.59	-3.1	
Waste	0.36	0.34	0.06	0.04	-5.6
	0.48	0.46	0.07	-4.2	
	3.00	3.18	0.13	0.10	+6.0
	3.60	3.76	0.18	+4.4	
	9.60	9.74	0.49	0.26	+1.5
	12.0	12.0	0.56	+0.3	

Table 6. Determination of Bias for Bromide

Water	Am't Added mg/L	Am't Found mg/L	S_t	S_o	Bias %
Reagent	0.63	0.69	0.11	0.05	+9.5
	0.84	0.85	0.12	+1.2	
	5.24	5.21	0.22	0.21	-0.6
	6.29	6.17	0.35	-1.9	
	16.8	17.1	0.70	0.36	+1.6
	21.0	21.3	0.93	+1.5	
Drinking	0.63	0.63	0.13	0.04	0.0
	0.84	0.81	0.13	-3.6	
	5.24	5.11	0.23	0.13	-2.5
	6.29	6.18	0.30	-1.7	
	16.8	17.0	0.55	0.57	+0.9
	21.0	20.9	0.65	-0.4	
Waste	0.63	0.63	0.15	0.09	0.0
	0.84	0.85	0.15	+1.2	
	5.24	5.23	0.36	0.11	-0.2
	6.29	6.27	0.46	-0.3	
	16.8	16.6	0.69	0.43	-1.0
	21.0	21.1	0.63	+0.3	

Table 7. Determination of Bias for Nitrite - Nitrogen

Water	Am't Added mg/L	Am't Found mg/L	S_t	S_o	Bias %
Reagent	0.42	0.42	0.04	0.02	0.0
	0.56	0.56	0.06	0.0	
	3.51	3.34	0.15	0.08	-4.8
	4.21	4.05	0.28	-3.8	
	11.2	11.1	0.47	0.34	-1.1
	14.0	14.4	0.61	+2.6	
Drinking	0.42	0.46	0.08	0.03	+9.5
	0.56	0.58	0.09	+3.6	
	3.51	3.45	0.27	0.10	-1.7
	4.21	4.21	0.38	0.0	
	11.2	11.5	0.50	0.48	+2.3
	14.0	14.2	0.70	+1.6	
Waste	0.42	0.36	0.07	0.06	-14.6
	0.56	0.40	0.16	-28.6	
	3.51	3.19	0.31	0.07	-9.1
	4.21	3.84	0.28	-8.8	
	11.2	10.9	0.35	0.51	-3.0
	14.0	14.1	0.74	+0.4	

Table 8. Determination of Bias for Ortho-Phosphate

Water	Am't Added mg/L	Am't Found mg/L	S_t	S_o	Bias %
Reagent	0.69	0.69	0.06	0.06	0.0
	0.92	0.98	0.15	+6.5	
	5.77	5.72	0.36	0.18	-0.9
	6.92	6.78	0.42	-2.0	
	18.4	18.8	1.04	0.63	+2.1
	23.1	23.2	0.35	+0.4	
Drinking	0.69	0.70	0.17	0.17	+1.4
	0.92	0.96	0.20	+4.3	
	5.77	5.43	0.52	0.40	-5.9
	6.92	6.29	0.72	-9.1	
	18.4	18.0	0.68	0.59	-2.2
	23.1	22.6	1.07	-2.0	
Waste	0.68	0.64	0.26	0.09	-7.2
	0.92	0.82	0.28	-10.9	
	5.77	5.18	0.66	0.34	-10.2
	6.92	6.24	0.74	-9.8	
	18.4	17.6	2.08	1.27	-4.1
	23.1	22.4	0.87	-3.0	

Table 9. Determination of Bias for Sulfate

Water	Am't Added mg/L	Am't Found mg/L	S_t	S_o	Bias %
Reagent	2.85	2.83	0.32	0.52	-0.7
	3.80	3.83	0.92	+0.8	
	23.8	24.0	1.67	0.68	+0.8
	28.5	28.5	1.56	-0.1	
	76.0	76.8	3.42	2.33	+1.1
	95.0	95.7	3.59	+0.7	
Drinking	2.85	1.12	0.37	0.41	-60.7
	3.80	2.26	0.97	-40.3	
	23.8	21.8	1.26	0.51	-8.4
	28.5	25.9	2.48	-9.1	
	76.0	74.5	4.63	2.70	-2.0
	95.0	92.3	5.19	-2.8	
Waste	2.85	1.89	0.37	0.24	-33.7
	3.80	2.10	1.25	-44.7	
	23.8	20.3	3.19	0.58	-14.7
	28.5	24.5	3.24	-14.0	
	76.0	71.4	5.65	3.39	-6.1
	95.0	90.3	6.80	-5.0	