TITLE: Iodide Anion by Ion Chromatography, EPA Method 300.

1.0 Scope

1.1 This method provides a procedure for the analysis of iodide by ion chromatography with ion suppression and a conductivity detector.

1.2 This method is applicable to the determination of iodide in ground waters with low sulfate and chloride concentrations.

1.3 The WPCL Method Detection Limit (MDL) for the above analytes is listed in Appendix 1. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample. MDLs and reporting limits are adjusted when samples are diluted.

1.4 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.

1.5 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 fortification procedure is described in Section 9.2.5.

2.0 Principle.

2.1 A small volume of sample, typically 2 to 3 mL, is introduced into the ion chromatograph. Sodium hydroxide (NaOH) is used as the eluent. Iodide is separated and measured, using a system comprised of a guard column, separator column, suppressor device, and conductivity detector.

3.0 Safety

3.1 Wear gloves, lab coats, and safety glasses when handling samples and reagents.

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 fortification can be used to solve most interference problems.

4.2 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.

5.0 Apparatus and Equipment

5.1 Ion chromatograph - Analytical system complete with ion chromatograph and all required accessories including auto-sampler, analytical column, guard columns, compressed helium gas, detectors and data system. The current system is the Dionex ICS-1000, S/n 04090303, purchased In October 2004.

5.1.1 Anion guard column: A protector of the separator or analytical column. If omitted from the system the retention times will be shorter. Usually packed with a substrate the same as that in the analytical column. See Table 1 for guard column information.

5.1.2 Anion separator (analytical) column: See Table 1 for analytical column information.

5.1.3 Anion suppressor device: The Dionex ASRS-Ultra Anion Suppressor is used for this system (P/N 064555).

5.1.4 Detector – 35^{o}C Heated Conductivity cell: See Table 1 for sample loop sizes.

5.1.5 Dionex Chromeleon DC36R051 Data Chromatography Software used to generate the data.

5.1.6 The Dionex AS-40 Autosampler.

6.0 Reagents and Supplies

6.1 Sample bottles: Glass or polyethylene of sufficient volume to allow replicate analyses of iodide.

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

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6.3 Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions may be purchased as certified solutions from Environmental Resource Associates or Inorganic Ventures.

6.3.1 Iodide (I^-) 1000 mg/L: Use purchased ERA certified stock standard.

6.3.2 Iodide Certified Reference Material, Inorganic Ventures, 30 ppb.

6.4 Stability of standards: Stock standards are stable for at least one month when stored at room temperature.

6.5 Dilute working standards should be prepared at 28 day intervals.

7.0 Sample Preservation and Storage

7.1 Samples should be collected in scrupulously clean glass or polyethylene bottles.

7.2 All samples must be cooled to <6^{o}C. Analysis of preserved analytes must be completed within 28 days of collection.

8.0 Calibration and Standardization/Instrument Set Up.

8.1 Instrument Operating Conditions: Instrument operating conditions are controlled by the Data System and a copy of the instrument operating parameters is presented in the Dionex Operator's Manual.

8.2 Calibration

8.2.1 Ion chromatographic operating parameters should be established which are equivalent to parameters in the Manual.

8.2.2 Prepare iodide calibration standards at six concentration levels consisting of a blank, and five standards ranging from the reporting limit to the established upper limit. Each attenuation range of the instrument used to analyze a sample must be calibrated individually.

8.2.3 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 also be recorded. These steps are done by the Data System which displays the peak height and area, the calibration curves and the linearity of the calibrations at the different concentrations.

8.2.4 The calibration curve must be verified on each working day, or whenever the anion eluent is changed, and after every 10 samples. A certified reference standard at a concentration near the mid-range of the curve must be used to verify the calibration curve. The standard must be purchased from a different vendor than the working standard. If the response or retention time for any analyte varies from the expected values by more than $\pm$20%, the test must be repeated, using fresh calibration standards. If the results are still more than $\pm$20%, a new calibration curve must be prepared for iodide.

8.2.5 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 undiluted, should be compared. If the calculated responses are the same, samples of this total anionic concentration need not be diluted.

9.0 Procedure

9.1 Sample Preparation.

9.1.1 If “dissolved” anions are requested, filter water samples through a 0.45 um filter prior to analysis. The samples are poured into the autosampler vials and the plug/filter is placed on the top of the vial and is forced into the vial using the tool supplied by Dionex. The plug filter is optional.

9.2 Analysis sequence.

9.2.1 Table 1 summarizes the operating conditions stored under the file name AS14A in the data system Program section. Included in the Analysis table are the estimated retention times of the anions of interest established under the conditions of this method.

9.2.2 Check system calibration daily, if required, recalibrate as described in Table 2.

9.2.3 Load standards, blanks, and samples by filling polyethylene autosampler vials and inserting cap/filter into the vial with the tool supplied by Dionex. Load autosampler holders with the ridges facing the front of the autosampler.

9.2.4 Begin analysis.

9.2.4.1 Turn gas on. Adjust helium to 20 psi.

9.2.4.2 Switch eluent degas module on and set pressure to 50 psi.

9.2.4.3 If the eluent is freshly prepared, prime the pump by opening the priming valve one-quarter to one-half turn counterclockwise. On the Chromeleon Control Panel click Pump Settings and then click **Eluent Flow Valve Open**. Place a 10 ml syringe in the hole of the priming valve and draw back about 3-4 syringes of eluent to eliminate air bubbles from the system.

9.2.4.4 After priming the lines thoroughly, close the priming valve. Close the eluent valve by clicking **Eluent Flow Valve Closed** on the control panel. Open the waste valve in the secondary pump

head by turning the knob one-quarter to one–half turn counterclockwise. Click **Prime on the Control Panel** and continue until no air bubbles are exiting the waste pump line. Press **Pump Off** and close the waste valve.

9.2.4.5 Press **startup** to begin the pump and **control acquisition on** to view the baseline. If the instrument does not begin, make sure the connected boxes are checked in the ICS-1000_Panel_1.pan.

9.2.4.6 The pump setting and eluent flow valve icons should be green.

9.2.4.7 Create a schedule or call up an existing one and modify it in the sequence folder. The calibration curve may be saved as raw data to use it in the current schedule.

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

9.2.5 If the resulting chromatogram fails to produce adequate resolution, or if identification is questionable, fortify the sample with an appropriate amount of standard and reanalyze.

9.2.6 **Note:** Retention time is inversely proportional to concentration. In some cases this peak migration may produce poor resolution or identification.

10.0 Quality Control

10.1 Method Detection Limits (MDL)

10.1.1 Method Detection Limit (MDL) refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, 7 lab Milli-Q water samples are spiked at 25 ug/L and processed through the entire method along with a blank. The standard deviation derived from the spiked sample recoveries were used to calculate the MDL for each analyte using the following equation:

$$MDL = tS$$

Where t is the Student t test value for the 99% confidence level with n-1 degrees of freedom and S denotes the standard deviation obtained from n replicate analyses. For the n=7 replicates used to determine the MDL, t=3.143.

10.1.2 The results for the standard deviations and MDL are in Appendix 1.

10.2 Reporting Limit (RL).

10.2.1 Reporting limit (RL) refers to a level at which reliable quantitative results may be obtained. The MDL is used as a guide to determine the RL. The RL is chosen in a range 1-5 times the MDL as per client agreement. The reporting limit for iodide by ion chromatography is 25 ug/L.

10.3 Method Validation

10.3.1 The method validation consisted of three sample sets. Each set included four levels of fortification and a method blank. All spikes and method blanks were processed through the entire analytical method. Spike levels and recoveries for iodide are shown in Appendix 2.

10.4 Control Charts and Limits

10.4.1 Control charts were generated using the data from the method validation for iodide. The upper and lower warning and control limits are set at $\pm$ 2 and 3 standard deviations of the average percent recovery, respectively, shown in Appendix 2.

10.5 Acceptance Criteria

10.5.1 Each set of samples will have a matrix blank and a spiked matrix sample.

10.5.2 The retention time should be within the retention time window.

10.5.3 The recoveries of the matrix spikes shall be within the control limits.

10.5.4 The sample shall be diluted if results fall outside of the calibration curve.

10.6 A certified reference material (CRM) is a commercially available solution accompanied by a vendor certificate of analysis, analyte true values, and sometimes acceptance control limits. The CRM is used to document an acceptable analysis and to check standards preparation by comparing recovered concentrations to certified values. The CRM is from a source different from the standards used to prepare the calibration curve and may also be used as the initial calibration verification (ICV).

10.7 When doubt exists over the identification of a peak in the chromatogram, confirmatory techniques such as sample dilution and fortification, must be used.

11.0 Calculations

11.1 After the standards have been analyzed review the calibration curves using the data system. The calibration curves for each anion should be reviewed for response and linearity ($r \geq 0.995$). If a problem is observed the run should be stopped and

corrective action should be taken prior to restarting the run. The standards may need to be prepared and analyzed again.

11.2 For the blank, a response less than the desired reporting limit (or MDL for compliance testing) should be observed. If there is a positive response for the blank the run should be stopped and corrective action should be taken prior to restarting the run. The blank should be prepared again and reanalyzed. Any affected samples must be reanalyzed.

11.3 Iodide should be reported in ug/L.

11.4 Concentration from linear calibration curves are calculated:

11.4.1 Concentration, mg/L = (y-b)/m

Where : m = slope of the curve.
y = area of iodide in sample.
B = y-intercept.

11.5 All results will be reported using three significant figures. If iodide is detected between the MDL and the RL, the result will be reported as detected not quantified (DNQ) and if the result is detected below the MDL the result will be reported as ND (not detected) and be followed by the MDL value.

12.0 Reporting

12.1 Sample results and quality control results are reported out according to the client's analytical specification sheets.

13.0 References

13.1 U.S. Environmental Protection Agency, *The Determination of Inorganic Anions in Water by Ion Chromatography,* Method 300.0. August 1991. Environmental Monitoring and Systems Laboratory, Cincinnati, OH 45268.

13.2 Dionex Corporation, Document No. 031879, ICS -1000, *Ion Chromatography System Operator's Manual.*

14.0 Attachments

14.1 Appendix 1: Method Detection Limit and Reporting limits).

14.2 Appendix 2: Method Validation and Control Limits

14.3 Appendix 3: Storage Stability Study

14.4 Table 1: IC Summary Sheet

14.5 Figure 1: Sodium Hydroxide Eluent Preparation

14.6 Table 2: Corrective Actions.

Appendix 1:

The Determination of Method Detection Limit (MDL) and Reporting Limit (RL).

Spike	Spike Concentration, µg/L	Iodide, µg/L
MDL1	25	24
MDL2	25	25
MDL3	25	20
MDL4	25	28
MDL5	25	23
MDL6	25	24
MDL7	25	23
Average		23.9
Standard Deviation (SD)		2.41
t-value (n-1)		3.143
MDL		7.58 (not detectable).
RL		25

Appendix 2:

Method Validation Data and Control Limits

	25 ug/L	50 ug/L	100 ug/L	150 ug/L	200 ug/L
Set 1	25.5	45.0	97.5	157.6	196.7
%R	102.0	90.0	97.5	105.1	98.4
Set 2	26.2	52.9	96.0	153.9	198.2
%R	104.8	105.8	96.0	102.6	99.1
Set 3	22.7	46.2	93.7	149.9	204.5
%R	90.8	92.4	93.7	99.9	102.3
Set 4	19.5	44.5	90.6	143.9	211.3
%R	78.0	89.0	90.6	95.9	105.7
Set 5	21.7	46.1	82.8	150.3	209.7
%R	86.8	92.2	82.8	100.2	104.9
Average of all %R	**Std Dev of all %R:**	**Upper CL**	**Upper WL**	**Lower WL**	**Lower CL**
96.3	7.5	118.8	111.3	81.3	73.8

Appendix 3 – Storage Stability Project
Matrix: Auburn Well Water.
Storage: 5 liter carboy, plastic, 4°C.

Storage Day	Replicate #	Spiked Concentration, µg/L	Sample Concentration, µg/L	Average % Recovery
0	1	100	92.5	98.8
	2	100	96.0	
	3	100	107.9	
2	1	100	116.6	99.9
	2	100	92.8	
	3	100	90.4	
4	1	100	86.6	88.9
	2	100	94.2	
	3	100	85.9	
7	1	100	94.2	95.9
	2	100	99.6	
	3	100	93.9	
14	1	100	94.0	98.9
	2	100	101.8	
	3	100	100.8	
28	1	100	119.3	104
	2	100	102.4	
	3	100	91.2	
56	1	100	97.7	92.7
	2	100	95.7	
	3	100	85	

Table 1: IC Summary Sheet

Analyte	Analytical/ Guard Column	Sample Loop	Current	Eluent	Preparation/ Preservation	Holding Times	Comments
Iodide	AS 20(P/N 063065) AG 20 (P/N 063066)	10uL (042949)	100 mA	35mM KOH (see Figure 1)	Don't Filter. Let settle if there is particles in it.	28 days	Prime for 30 min when column has just been put on

Figure 1: Sodium Hydroxide Eluent Preparation

5.2 Eluent Preparation

Sodium Hydroxide Eluent Concentration

Weight Method

When formulating eluents from 50% sodium hydroxide, DIONEX recommends weighing out the required amount of 50% sodium hydroxide.

Example: To make 1 L of 38 mM NaOH use 3.04 g of 50% sodium hydroxide:
(as used in Section 5.3, "Production Test Chromatogram")

For 38 mM: $\frac{0.038 \text{ mole/L} \times 40.01 \text{ g/mole}}{50\%}$ = 3.04 g diluted to 1 L

Volume Method

Although it is more difficult to make precise carbonate-free eluents for gradient analysis volumetrically, you may choose to use the following formula to determine the correct volume of 50% sodium hydroxide to be diluted.

$$g = dvr$$

Where: g = weight of sodium hydroxide required (g)
d = density of the concentrated solution (g/mL)
v = volume of the 50% sodium hydroxide required (mL)
r = % purity of the concentrated solution

Example: To make 1 L of 38 mM NaOH, use 1.99 mL of 50% sodium hydroxide:
(as used in Section 5.3, "Production Test Chromatogram")

For 38 mM: $\frac{0.038 \text{ mole/L} \times 40.01 \text{ g/mole}}{50\% \times 1.53 \text{ g/mL}}$ = 1.99 mL diluted to 1 L

* This density applies to 50% NaOH. If the concentration of the NaOH solution is significantly different from 50%, the upper (weight method) calculation should be used instead.

Sodium Hydroxide Eluents

Dilute the amount of 50% (w/w) NaOH (in water) specified in Table 6, "Dilution of 50% (w/w) NaOH to Make Standard AS15 Eluents" with degassed, deionized water having a specific resistance of 18.2 megohm-cm to a final volume of 1,000 mL using a volumetric flask. Avoid the introduction of carbon dioxide from the air into the aliquot of 50% (w/w) NaOH or the deionized water being used to make the eluent. Do not shake the 50% (w/w) NaOH or pipette the required aliquot from the top of the solution where sodium carbonate may have formed.

Table 6
Dilution of 50% (w/w) NaOH to Make Standard AS15 Eluents

50% (w/w) NaOH g (mL)	Concentration of NaOH Eluent (mM)
0.80 (0.52)	10
2.72 (1.78)	34
3.04 (1.99)	38
3.20 (2.09)	40
8.00 (5.25)	100
16.00 (10.5)	200

Table 2: **Calibration and QC Summary**

QC Type	Frequency	Criteria	Corrective Actions	Comments
Method Blank	Per batch per matrix, up to 20 samples.	≤ Reporting Limit (RL)	• Reanalyze to verify. • Assess impact on samples. • Re-prepare affected samples and QC.	Report DNQ (MDL to RL).
Lab control Sample (LCS)	Per batch, up to 20 samples.	80-120%	• Reanalyze to verify. • Re-prep associated samples and QC.	Spike preparation check
MS/MSD	Per batch, up to 20 samples.	80-120% RPD ±25%	• Reanalyze to verify. • Compare to LCS to assess matrix effects.	
Sample Duplicate	Per batch, up to 20 samples	0-25%	• Reanalyze to verify.	
Initial calibration	Daily or changes in system failure of ICV, CCV, initial calibration.	Minimum 6 points (including blank). $R^2 \geq 0.995$	• Review curve. • Reprepare standards and recalibrate.	
SRM/CRM=ICV (conc. between stds. bracketing mid-point)	Prepare one per batch up to 20 samples. Analyze immediately after multipoint calibration	80-120%	• Reanalyze. • Recalibrate.	.
ICB	Immediately after ICV.	≤ RL	• Reanalyze. • Recalibrate if drift suspected.	.
RL check	After calibration and prior to sample analysis.	± 30% of expected value.	• Reanalyze. • Review curve.	
CCV	After every 10 injections and end of run. Use midpoint standard.	80-120%	• Reanalyze samples back to the last acceptable CCV.	
CCB	Immediately after CCV.	≤ RL	• Reanalyze samples back to the last acceptable CCB.	
Sample concentration higher than highest standard.	Each sample	Exceeds highest standard.	• Dilute and reanalyze. • Apply dilution to MDL and RL.	