

## TITLE: Iodine by ICP/MS

### 1.0 Scope

- 1.1 This method describes the procedure for the determination of total iodine in groundwater by inductively coupled argon plasma mass spectrometry.
- 1.2 This method is recommended for use only by or under the supervision of analysts experienced in the evaluation and correction of spectral, chemical, and physical interferences in inductively coupled argon plasma/mass spectroscopy (ICP/MS). Each analyst must demonstrate the ability to generate acceptable results with this method.

### 1.0 Principle

- 1.1 The method measures ions produced by a radio-frequency inductively coupled plasma. Iodine in an aqueous sample is nebulized and the resulting aerosol is transported by argon gas into the plasma torch. The ions produced are transported by the plasma gas and extracted through a differentially pumped vacuum interface to be separated on the basis of mass-to-charge ratio by a mass spectrometer. The ions transmitted through the mass spectrometer are quantified by a channel electron multiplier or Faraday detector and the ion information is processed by the instrument's data handling system. Interferences must be assessed and valid corrections applied or the data qualified to indicate problems. Interference correction must include compensation for background ions contributed by the plasma gas, reagents, and constituents of the sample matrix.
- 1.2 An aliquot of sample is filtered and placed into clean 10 mL tubes. Internal standard is added. The sample is ready for analysis.

### 2.0 Safety

- 2.1 Many metal salts are extremely toxic if inhaled or swallowed. Extreme care must be taken to ensure that samples and standards are handled properly and that all exhaust gases are properly vented. Wash hands thoroughly after handling.

### 3.0 Interferences

- 3.1 Samples with high concentrations of dissolved solids may cause clogging and poor replicate precision.
- 3.2 High-purity acids and reagents must be used to avoid interferences.

#### 4.0 Equipment

- 4.1 Perkin-Elmer Elan 9000 ICP/MS
- 4.2 Volumetric glassware and pipettes.
- 4.3 Clean 25 mL test tubes (glass or PTFE)

#### 5.0 Reagents

- 5.1 Certified Reference Material, Potassium Iodide Solution, Inorganic Ventures, 30 ppb.
- 5.2 Potassium Iodide Solution, Inorganic Ventures.
- 5.3 Water, LCMS Grade, VWR Optima Part number W6-4 or equivalent.
- 5.4 Rhodium, internal standard, 25 ppb.
- 5.5 Tuning solution,
- 5.6 Argon gas, 99.99% purity

#### 6.0 Preservation and Holding Times

- 6.1 Samples are collected in glass containers. If not analyzed immediately, store at <math>6^{\circ}\text{C}</math>. Analyze samples within 28 days of collection or as determined by the storage stability study performed as part of this method's validation.
- 6.2 Do not acidify samples.

#### 7.0 Calibration and Standardization.

- 7.1 Perkin-Elmer Elan 9000 Settings
  - 7.1.1 Spray Chamber: Cyclonic
  - 7.1.2 Nebulizer: Meinhard
  - 7.1.3 RF Power: 1100 W.
  - 7.1.4 Plasma Gas Flow: 15.
  - 7.1.5 Nebulizer Gas Flow: 0.93
  - 7.1.6 Dwell Time: 50.
  - 7.1.7 Sweeps: 25.
  - 7.1.8 Replicates: 3.
  - 7.1.9 Delay Time: 50.
  - 7.1.10 Wash Time: 80.
- 7.2 Tuning:
  - 7.2.1 Follow Perkin-Elmer Elan 9000 tuning procedures.
- 7.3 Calibration:
  - 7.3.1 Prepare all standards from 500 ppm Potassium Iodide Stock Solution.

- 7.3.2 Curve concentrations: 0 ppb, 5 ppb, 25 ppb, 50 ppb, 100 ppb.
- 7.3.3 Curve acceptance:  $r^2 \geq 0.995$
- 7.4 Continuing calibration.
  - 7.4.1 Initial Calibration Verification (ICV):
    - 7.4.1.1 50 ppb iodide, add internal standard. Use standard source different from calibration curve.
    - 7.4.1.2 Analyze immediately after calibration.
    - 7.4.1.3 Acceptance criteria: 90%-110% of expected value.
  - 7.4.2 Initial Calibration Blank (ICB):
    - 7.4.2.1 LCMS grade water with added internal standard.
    - 7.4.2.2 Analyze immediately after ICV.
    - 7.4.2.3 Acceptance criteria: < Reporting Limit (2 ug/L).
  - 7.4.3 Continuing Calibration Verification (CCV):
    - 7.4.3.1 50 ppb iodide, add internal standards.
    - 7.4.3.2 Analyze after every 10 analyses and end of run.
    - 7.4.3.3 Acceptance criteria: 90% -110% of expected value.
  - 7.4.4 Continuing Calibration Blank (CCB):
    - 7.4.4.1 Same as ICB.

## 8.0 Data Analysis and Calculations

- 8.1 Final concentration is calculated by multiplying the instrument read-out by any dilutions.

## 9.0 Quality Control

- 9.1 Method Detection Limits (MDL)
  - 9.1.1 Method Detection Limit (MDL) refers to the lowest concentration of the analyte that a method can detect reliably. To determine the MDL, 7 aliquots of LC/MS-grade water are spiked with 3 µg/L and processed through the entire method along with a blank. The standard deviation derived from the spiked sample recoveries was used to calculate the MDL for iodine using the following equation:

$$\text{MDL} = tS$$

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,  $t=3.143$ .

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

## 9.2 Reporting Limit (RL)

9.2.1 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 iodine is 2 µg/L.

## 9.3 Method Validation

9.3.1 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 iodine are shown in Appendix 2.

## 9.4 Control Charts and Limits

9.4.1 Control charts were generated using the data from the method validation for each analyte. 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.

## 9.5 Acceptance Criteria

9.5.1 Each set of samples will have a matrix blanks and a spiked matrix sample.

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

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

### 9.5.4 Method Blank.

9.5.4.1 Process 1 per batch.

9.5.4.2 Comprised of LCMS grade water with internal standard added.

9.5.4.3 Acceptance criteria:  $\leq$  Reporting Limit.

### 9.5.5 Laboratory control/SRM/CRM:

9.5.5.1 Process 1 per batch.

9.5.5.2 Comprised of a purchased certified reference material or LCMS grade water fortified with a known concentration of potassium iodide solution and internal standard. Calculate percent recovery.

9.5.5.3 Acceptance criteria: 89% - 107%.

- 9.5.5.4 Corrective action: evaluate impact of unacceptable recoveries on data.
- 9.5.6 Matrix spike/spike duplicate.
  - 9.5.6.1 Process 1 pair (MS/MSD) per batch.
  - 9.5.6.2 Comprised of 2 separate sample aliquots fortified with a known concentration of potassium iodide solution and internal standard.
  - 9.5.6.3 MS/MSD samples are spiked at 2 concentration levels: 5x the RL and 10x the RL. The sample spike with the concentration closest to 4-5x the native concentration is used to calculate recovery.
  - 9.5.6.4 Acceptance criteria: evaluate recoveries against the LCS/CRM for trends.
- 9.5.7 Duplicate.
  - 9.5.7.1 Process 1 per batch.
  - 9.5.7.2 Comprised of a second aliquot of a selected field sample with added internal standard.
  - 9.5.7.3 Acceptance criteria:  $\pm 25\%$  RPD.

## 10.0 Calculations

- 10.1 Quantitation is provided by the instrument software. A linear curve is used to calculate iodine concentration.

## 11.0 References.

- 11.1 EPA-NERL, "Method 200.8, Metals in Water by ICPMS."

## 12.0 Attachments

- 12.1 Appendix 1 MDL and RLs
- 12.2 Appendix 2 Method Validation Date and Control Limits.
- 12.3 Appendix 2 Storage Stability Study

**Appendix 1:**

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

Spike	Spike Amount, µg/L	Result, µg/L
MDL1	3	3.10
MDL2	3	2.84
MDL3	3	2.62
MDL4	3	2.80
MDL5	3	2.58
MDL6	3	2.74
MDL7	3	2.72
Standard Deviation		0.17
MDL		0.54
RL		2.00

**Appendix 2:**

Method Validation Data and Control Limits (LCMS water matrix)

Spike Level, µg/L	Set 1		Set 2		Set 3		Set 4		Recovery % Average
	µg/L	%R	µg/L	%R	µg/L	%R	µg/L	%R	
5	4.65	93%	4.56	91%	5.16	103%	5.10	103%	98%
10	9.49	95%	9.78	98%	10.2	102%	9.80	98%	
25	23.7	95%	24.0	96%	25	100%	24.20	97%	
50	48.5	97%	49.1	98%	51.2	102%	48.50	97%	
100	96.1	96%	96.0	96%	102	102%	99.0	99%	
Standard Deviation (SD)									
Upper Control Limit (Average + 3SD)									107
Upper Warning Limit (Average + 2SD)									104
Lower Warning Limit (Average -2SD)									92
Lower Control Limit (Average -3SD)									89

**Appendix 3:**

LCMS Water spiked with 10 µg/L

	Day 0 11/29/2011	Day 3 12/2/2011	Day 14 12/13/2011	Day 36 1/4/2012	Day 62 1/30/2012
Rep 1	9.9	7.82	8.22	10.5	8.88
Rep 2	10.2	7.22	8.11		
Rep 3		7.61	8.06		

**Auburn Well Water, unspiked**

	Day 0	Day 133	Day 144	Day 166
Rep 1	9.90	9.62	9.43	10.8
Rep 2	10.2	8.60	9.06	
		8.97	9.48	