

# **Protocol of Accepted Drinking-Water Testing Methods**

**July 2003**

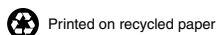
# Protocol of Accepted Drinking-Water Testing Methods

Report prepared by:  
Ministry of the Environment  
Laboratory Services Branch

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# 1. INTRODUCTION

This document sets out testing methods that may be used for the conduct of tests of Ontario Drinking Water. Under the *Safe Drinking Water Act, 2002*, only licensed laboratories located in Ontario and eligible out-of-province laboratories may conduct tests on samples of drinking-water. In addition, a laboratory must be accredited for the selected method by the Standards Council of Canada (SCC), by an accreditation body that, in the Director's opinion, is equivalent to the SCC, or the laboratory must be authorized by the Director to conduct a particular test without accreditation, in accordance with the provisions of the Act. In addition to these requirements, a laboratory must use validated methods for the parameters outlined in this document, to conduct drinking-water tests.

The methods that follow are derived from one of 4 sources:

1. Methods used by the Ministry of the Environment Laboratory Services Branch for the testing of drinking water for which the laboratory has been accredited through the Standards Council of Canada. These methods are indicated as **LSB Method**.
2. Methods as described in the reference "**Standard Methods for the Examination of Water and Wastewater**" 20<sup>th</sup> Edition, 1998, American Public Health Association, American Waterworks Association, Water Environmental Federation. These methods are indicated as **AWWA Method**.
3. Methods of the **United States Environmental Protection Agency** available through the National Services for Environmental Publications, Cincinnati, Ohio. These methods are indicated as **US EPA Method**.
4. Methods of the **American Society for Testing and Materials**, available through the International Library Service, Provo, Utah. These methods are indicated as **ASTM Method**.

A laboratory that uses a validated, accredited method derived from a source different from those above, must receive Ministry approval by the Director in accordance with the Act. The laboratory must provide a copy of the test procedure used, validation data for the method demonstrating that they meet or exceed the required Reporting Detection Limit, and any other documentation requested which demonstrates that the method is suitable and appropriate for use on drinking water matrices. If it is determined that the test is suitable and appropriate, the Director may add the test to this protocol as an accepted testing method, or may authorize a specific laboratory under its licence to conduct the test as permitted under the Act.

The methods are listed by the type of parameter for which each method may be used and grouped as listed in the Schedules of O. Reg. 169/03. Also listed are additional parameters that may be required under a Certificate of Approval, an Order or another directive issued by the Ministry of the Environment. The standard for each parameter, as set out in the Ontario Drinking-Water Quality Standards (ODWQS) (O. Reg. 169/03), is set out first, followed by the Reporting Detection Limit (RDL). The methods are grouped as follows: Schedule 1, Microbiological Parameters; Schedule 2, Chemical Parameters; Additional Parameters (Certificate of Approval or Ministry Orders).

**NOTE:** The units for the ODWQS are those listed in Ontario Regulation 169/03. The units for RDL are in the required reporting units for the Drinking Water Information System (DWIS).

## 2. SCHEDULE 1, MICROBIOLOGICAL PARAMETERS

### 2.1. Total Coliforms

PARAMETER	ODWQS		
	Methodology	Membrane Filtration	Most Probable Number
Total Coliforms	0 CFU/100 mL	0 MPN/100 mL	Absent/100 mL

Reporting units for Total Coliforms are dependant on the methodology used. The MAC values provided in the table above include the appropriate reporting unit for each methodology.

The following two LSB Methods apply to the testing of both Total Coliforms (this section) and *E. coli* (Section 4.1 below). They are repeated in both sections.

LSB Method: E3226 - The Detection of Coliform Bacteria Including *Escherichia coli* in Drinking Water by the Presence-Absence Procedure

Method Principle: The Ministry of Environment (MOE) Laboratory uses the Presence-Absence (P-A) Method for the detection and confirmation of coliform bacteria (including *Escherichia coli*) in treated drinking water. This method also allows for the optional opportunity to screen for other bacteriological indicators of deteriorating water quality (*Enterococcus faecalis*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Aeromonas hydrophila*).

This method is simple, cost-effective and enables the fast screening of a large number of treated drinking water samples. This method is not, however, designed for testing samples with high bacterial counts (water with high suspected levels of contamination, i.e. sewage). The growth of an abundance of bacteria may overwhelm the indicator system (bromocresol purple) resulting in a reduced sensitivity of the test.

The method described herein is a modification of the Method 9221D (Standard Methods for the Examination of Water and Wastewater) which is based on the Most Probable Number (MPN) procedure. The P-A Method is a qualitative procedure, which uses the Presence-Absence Broth. Coliforms, including *Escherichia coli*, ferment the available lactose in the broth causing a decrease in the pH. The lowering of the pH is identified by a change in colour of the broth, from purple to yellow (due to the indicator Bromocresol purple). This colour change (accompanied with or without the production of gas within 48 hours of incubation) is considered presumptive evidence of coliform bacteria. The presence of coliforms is unacceptable in drinking water (ODWS, 2000). Presumptive findings are confirmed with the use of specific bacteriological media and chemical tests (see MICSOP.10).

The P-A method can be used in conjunction with the membrane filtration method (E3407, see below) for the enumeration of Total Coliforms and *E. coli* on samples where there is a history of contamination, for repeat samples (special samples), or after the occurrence of a presumptive positive.

LSB Method: Method E3407 - Membrane Filtration Method Using DC Agar for the Simultaneous Detection of Total Coliforms and *Escherichia coli*

Method Principle: The method described below allows for the simultaneous detection and enumeration of Total Coliforms and *Escherichia coli* with a single filtration, on a single agar plate (using DC agar), incubated at one temperature ( $35\pm 0.5^{\circ}\text{C}$ ) for  $24\pm 2$  hours.

A vacuum is used to draw a measured volume of liquid through a 47 millimetre diameter,  $0.45\mu\text{m}$  pore size, white, gridded, cellulose ester (membrane) filter. The pore size of the membrane enables the capture of bacteria. After filtration, the filters are placed onto Differential Coliform (DC) agar plates which are then incubated at  $35\pm 0.5^{\circ}\text{C}$  for  $24\pm 2$  hours. The DC agar is specifically designed to enable the visual differentiation of coliforms from *E. coli* colonies. *E. coli* are blue, Coliforms are red, and non-targets are yellow. Upon completion of the incubation period, the number of coliforms and *E. coli* colony forming units (CFUs) are tabulated and reported as CFU per 100 mL of sample.

Some coliform bacteria are commonly isolated from the fecal material found in the intestines of humans and other warm-blooded animals (e.g. *E. coli*). Coliforms, in general, may also be isolated from plants, soil and sediments. The Total Coliform count, therefore, does not necessarily provide specific evidence of fecal contamination.

- AWWA Methods:<sup>1</sup>
- Method 9221 - Multiple-Tube Fermentation Technique for Members of the Coliform Group
  - Method 9222 - Membrane Filter Technique for Members of the Coliform Group
  - Method 9223 - Enzyme Substrate Coliform Test

## 2.2. *Escherichia coli* or Fecal\* Coliforms

PARAMETER	ODWQS		
	Membrane Filtration	Most Probable Number	Presence/Absence
<i>Escherichia coli</i> or Fecal* Coliforms	0 CFU/100 mL	0 MPN/100 mL	Absent/100 mL

\* Historically, methods for determining fecal coliforms were based on the ability of bacteria to grow at an elevated temperature of 44.5°C (thermotrophic). Other bacteria, however, can also grow at this temperature. Methods that are acceptable to MOE for use in determining either *E. coli* or fecal coliforms, therefore, cannot rely on this growth characteristic alone.

Reporting units for *E. coli* and Fecal Coliforms are dependant on the methodology used. The MAC values provided in the table above include the appropriate reporting unit for each methodology.

The following two LSB Methods apply to the testing of both Total Coliforms (Section 4.1 above) and *E. coli* (this section). They are repeated in both sections. This section also contains additional information specific to *E. coli*.

LSB Method: E3226 - The Detection of Coliform Bacteria Including *Escherichia coli* in Drinking Water by the Presence-Absence Procedure

Method Principle: The Ministry of Environment (MOE) Laboratory uses the Presence-Absence (P-A) Method for the detection and confirmation of coliform bacteria (including *Escherichia coli*) in treated drinking water. This method also allows for the optional opportunity to screen for other bacteriological indicators of deteriorating water quality (*Enterococcus faecalis*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Aeromonas hydrophila*).

This method is simple, cost-effective and enables the fast screening of a large number of treated drinking water samples. This method is not, however, designed for testing samples with high bacterial counts (water with high suspected levels of contamination, i.e. sewage). The growth of an abundance of bacteria may overwhelm the indicator system (bromocresol purple) resulting in a reduced sensitivity of the test.

The method described herein is a modification of the Method 9221D (Standard Methods for the Examination of Water and Wastewater) which is based on the Most Probable Number (MPN) procedure. The P-A Method is a qualitative procedure, which uses the Presence-Absence Broth. Coliforms, including *Escherichia coli*, ferment the available lactose in the broth causing a decrease in the pH. The lowering of the pH is identified by a change in colour of the broth, from purple to yellow (due to the indicator Bromocresol purple). This colour change (accompanied with or without the production of gas within 48 hours of incubation) is considered presumptive evidence of coliform bacteria. The

<sup>1</sup> (Standard Methods, 20th Ed.)

presence of coliforms is unacceptable in drinking water (ODWS, 2000). Presumptive findings are confirmed with the use of specific bacteriological media and chemical tests (see MICSOP.10).

The P-A method can be used in conjunction with the membrane filtration method (E3407, see below) for the enumeration of Total Coliforms and *E. coli* on samples where there is a history of contamination, for repeat samples (special samples), or after the occurrence of a presumptive positive.

LSB Method: Method E3407 - Membrane Filtration Method Using DC Agar for the Simultaneous Detection of Total Coliforms and *Escherichia coli*

Method Principle: The method described below allows for the simultaneous detection and enumeration of Total Coliforms and *Escherichia coli* with a single filtration, on a single agar plate (using DC agar), incubated at one temperature ( $35\pm 0.5^{\circ}\text{C}$ ) for  $24\pm 2$  hours.

A vacuum is used to draw a measured volume of liquid through a 47 millimetre diameter,  $0.45\mu\text{m}$  pore size, white, gridded, cellulose ester (membrane) filter. The pore size of the membrane enables the capture of bacteria. After filtration, the filters are placed onto Differential Coliform (DC) agar plates which are then incubated at  $35\pm 0.5^{\circ}\text{C}$  for  $24\pm 2$  hours. The DC agar is specifically designed to enable the visual differentiation of coliforms from *E. coli* colonies. *E. coli* are blue, Coliforms are red, and non-targets are yellow. Upon completion of the incubation period, the number of coliforms and *E. coli* colony forming units (CFUs) are tabulated and reported as CFU per 100 mL of sample.

*E. coli* are Gram-negative, facultatively anaerobic, non spore-forming, lactose-fermenting, rod-shaped bacteria which are oxidase negative. They produce indole from tryptophan and acids during the fermentation of sugars, giving a positive methyl red test. They do not, however, produce acetylmethylcarbinol as an end product of fermentation thus, giving a negative Vogues-Proskauer test. Furthermore, they cannot utilize citrate as the sole source of carbon for growth. In addition, most *E. coli* strains (approximately 95%) have the unique ability, among the lactose-fermenting members of the family Enterobacteriaceae, to produce the enzyme  $\beta$ -D-glucuronidase.

Historically, the presence of either or both *E. coli* and fecal coliforms has been described as an indication of sewage or fecal contamination as they are commonly isolated from the intestinal tract of warm-blood animals. Currently, *E. coli* is considered to be the most specific indicator of fecal contamination in the assessment of water quality for the following reasons:

1) *E. coli* isolates are normally present in the feces of warm-blooded animals (including humans) at higher densities ( $10^7$  to  $10^8$  cells per gram) than other lactose-fermenting members of the family Enterobacteriaceae.

2) *E. coli* isolates may persist for periods of time, once outside the human or warm-blooded animal intestine but they generally do not multiply in water or wastewater in temperate climates.

*E. coli* isolates have seldom been detected in environments which have not been contaminated by fecal wastes. In contrast, other thermotolerant organisms such as isolates of the genera *Klebsiella*, *Enterobacter* and *Citrobacter*, have been associated from both fecal material and other wastes including that from food and pulp and paper. These other thermotolerant organisms may also be included in methods for the determination of fecal coliforms.



AWWA Methods:<sup>2</sup> Method 9221 – Multiple-Tube Fermentation Technique for Members of the Coliform Group

Method 9222 - Membrane-Filter Technique for Members of the Coliform Group

ASTM Methods:<sup>3</sup> D5392-93, Standard Test Method for Isolation and Enumeration of *E. coli* in Water by the Two-Step Membrane Filtration Procedure

### 2.3. Heterotrophic Plate Count or Total Coliform Background Count by Membrane Filter Analysis

PARAMETER	ODWQS
Heterotrophic Bacteria Spread plate, Pour plate, or Membrane Filtration	<500cfu/mL
Total Coliform Background Count by Membrane Filter Analysis	<200cfu/mL

LSB Method: Method E3408 - The Spread Plate Method for the Enumeration of Aerobic, Heterotrophic Bacteria in Drinking Water

Method Principle: Plate count agar is inoculated with a volume of sample (0.1 mL). A turntable and spreader are then used to ensure consistent spreading of the inoculum over the entire surface of the agar plate. The plates are then inverted and incubated at 35±0.5°C for 48±3 hours.

Heterotrophic bacteria capable of growing in the presence of air, will produce colonies (CFU's) on the surface of the agar over the course of an incubation period of 48±3 hours at 35±0.5°C. All bacterial colonies which appear at the end of the 48±3 hour incubation period are counted. This count per plate represents the number of heterotrophic bacterial colony forming units per 0.1 mL of sample. The count is then divided by the volume of the inoculum (0.1 mL) to obtain the number of colony forming units (bacterial count) per mL.

AWWA Methods:<sup>4</sup> Method 9215 - Heterotrophic Plate Count

## 3. SCHEDULE 2, CHEMICAL PARAMETERS

### 3.1. Volatile Organics

PARAMETER	ODWQS mg/L	RDL µg/L
1,1-Dichloroethylene	0.014	1.4
1,2-Dichlorobenzene	0.2	20
1,2-Dichloroethane	0.005	0.5
1,4-Dichlorobenzene	0.005	0.5
Benzene	0.005	0.5
Carbon Tetrachloride	0.005	0.5
Dichloromethane	0.05	5
Ethylbenzene *	0.0024 *	1.2
Monochlorobenzene	0.08	8
Tetrachloroethylene	0.03	3

<sup>2</sup> (Standard Methods, 20th Ed.)

<sup>3</sup> Vol. 11.02, 2000

<sup>4</sup> (Standard Methods, 20th Ed.)

PARAMETER	ODWQS mg/L	RDL µg/L
Toluene *	0.024 *	2.4
Trichloroethylene	0.05	5
Trihalomethanes: Bromoform	0.1	10
Trihalomethanes: Bromodichloromethane	0.1	10
Trihalomethanes: Chloroform	0.1	10
Trihalomethanes: Chlorodibromomethane	0.1	10
Xylene, Total	0.3	150
Xylene, - ortho *		0.5
Xylene, - m/p *		0.5
Vinyl Chloride	0.002	0.2

\* These parameters are not part of Schedule 2 in O. Reg 169/03, but may be found in individual Certificates of Approval or Ministry Orders. The methods for analysis for these parameters fall into the same category as those Volatile Organics listed in Schedule 2.

LSB Method: E3144 - The Determination of Volatile Organic Compounds in Raw and Treated Drinking Water by Purge and Trap Capillary Gas Chromatography-Flame Ionization Detection/Mass Selective Detection (GC-FID/MSD)

Method Principle: Volatile Organic Compounds (VOCs) in water are determined by purge-and-trap technique, followed by capillary gas chromatography (GC) with simultaneous flame ionization and quadrupole mass spectral detection (MSD). The VOCs are purged from the sample with a stream of helium at ambient temperature onto an adsorbent trap. They are then thermally desorbed and, prior to being introduced into the oven of the GC, are cryo-focused with liquid nitrogen at the head of the capillary column. Target compounds are quantified by a linear, dual point, external standard primary FID method and secondary target ion MSD method and identified on the basis of retention time conformity and the presence of MS qualifier peaks of selected m/z values.

US-EPA Methods: Method 502.2, Rev 2.1, VOCs by Purge and Trap Capillary GC with Photoionization and Electrolytic Conductivity Detectors in Series

Method 524.2, Rev 4.1, Purgeable Organic Compounds by Capillary Column GC/Mass Spectrometry

Method 551.1, Rev 1.0, Chlorinated Disinfection By-Products and Chlorinated Solvents by Liquid-Liquid Extraction and GC with an Electron Capture Detector

### 3.2. Trace Metals

PARAMETER	ODWQS mg/L	RDL µg/L
Aluminum (Al)*	1.0	500
Antimony (Sb)	0.006	0.6
Arsenic (As)	0.025	2.5
Barium (Ba)	1.0	100
Boron (B)	5.0	500
Cadmium (Cd)	0.005	0.5
Chromium (Cr)	0.05	5
Copper (Cu)*	1	500
Iron (Fe)*	0.3	150
Lead (Pb)	0.01	1

PARAMETER	ODWQS mg/L	RDL µg/L
Manganese (Mn)*	0.05	25
Selenium (Se)	0.01	5
Uranium (U)	0.02	2
Zinc (Zn)*	5	2500

\* These parameters are not part of Schedule 2 in O. Reg 169/03, but may be found in individual Certificates of Approval or Ministry Orders. The methods for analysis for these parameters fall into the same category as those Trace Elements listed in Schedule 2.

LSB Method: E3051 -The Determination of Trace Metals in Potable Waters by Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS)

Method Principle: Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) is used for the detection of trace metals in drinking water samples. An inductively coupled argon plasma (ICAP or ICP) is used as an ion source to directly aspirate an aliquot of sample. A quadrupole mass spectrometer measures the number of ions on the basis of their respective mass to charge ratios (m/z).

Other Methods:

The following methods have been developed by the US-EPA, APHA/AWWA/WEF, and ASTM for the analysis of various trace elements in drinking water. To be acceptable to MOE for the analysis of Ontario drinking water samples, the laboratory must demonstrate that the method used meets or exceeds the applicable RDL listed in the table above.

Method	Al	Sb	As	Ba	B	Cd	Cr	Cu	Fe	Pb	Mn	Se	U	Zn
US-EPA - 200.7	√		√	√		√	√	√	√		√			√
US-EPA – 200.8	√	√	√	√		√	√	√		√	√	√		√
US-EPA - 200.9	√	√	√			√	√	√	√	√	√	√		
Standard Methods 20 <sup>th</sup> Ed. - 3120B	√		√	√	‡	‡	√	√	√	‡	√	‡		√
Standard Methods 20 <sup>th</sup> Ed. - 3111B						‡	‡	√	√	‡	√			√
Standard Methods 20 <sup>th</sup> Ed. - 3111D	√			√										
Standard Methods 20 <sup>th</sup> Ed. - 3113B	√	√	√	√		√	√	√	√	√	√	√		
Standard Methods 20 <sup>th</sup> Ed. - 3114B			√									√		
Standard Methods 20 <sup>th</sup> Ed. - 3125B	‡		‡	‡		‡	‡	‡		‡	‡	‡	‡	‡
Standard Methods 20 <sup>th</sup> Ed. - 4500B					‡									
Standard Methods 20 <sup>th</sup> Ed. - 4500C					‡									
ASTM – D857-95	‡													
ASTM – D858-95											‡			
ASTM - D1068-96									‡					
ASTM - D1687-92 (1996)							‡							
ASTM - D1688-95A								√						
ASTM - D1688-95C								√						
ASTM – 1691-95A														‡
ASTM - D1976-96	‡		‡		‡	‡	‡	‡	‡	‡	‡	‡		‡
ASTM - D2972-97B			√											
ASTM - D2972-97C			√											
ASTM – D3082-92 (1996)					‡									
ASTM – D3557-95						‡								
ASTM - D3559-96D										√				

Method	Al	Sb	As	Ba	B	Cd	Cr	Cu	Fe	Pb	Mn	Se	U	Zn
ASTM – D3697 – 92 (1996)		√												
ASTM - D3859-98A												√		
ASTM - D3859-98B												√		
ASTM – D3919-99			‡		‡	‡	‡	‡	‡	‡	‡	‡		
ASTM - D4382-95				‡										
ASTM – D5673 – 96	‡	‡	‡	‡		‡	‡	‡		‡	‡	‡	‡	‡

Legend: √ - Recommended by US-EPA ‡ - Available in Standard Methods 20<sup>th</sup> Ed. or from ASTM

- US-EPA Methods: Method 200.7 Rev 4.4, Metals and Trace Elements by ICP/Atomic Emission Spectrometry
- Method 200.8 Rev 5.3, Trace Metals by ICP/Mass Spectrometry
- Method 200.9 Rev 2.2, Trace Elements by Stabilized Temperature Graphite Furnace AA Spectrometry
- AWWA Methods:<sup>5</sup>
- Method 3111 B - Metals by Flame Atomic Absorption Spectrometry - Direct Air-Acetylene Flame Method
- Method 3111 B - Metals by Flame Atomic Absorption Spectrometry - Extraction/Nitrous Oxide-Acetylene Flame Method
- Method 3113 B - Metals by Electrothermal Atomic Absorption Spectrometric Method
- Method 3114 B - Arsenic and Selenium by Hydride Generation/Atomic Absorption Spectrometry - Manual Method
- Method 3120 B - Metals by Plasma Emission Spectroscopy - Inductively Coupled Plasma (ICP) Method
- Method 3125 B - Metals by Inductively Coupled Plasma/Mass Spectrometry (ICP/MS) Method
- Method 4500-B B - Boron - Curcumin Method
- Method 4500-B C - Boron - Carmine Method
- ASTM Methods:<sup>6</sup>
- D857-95, Standard Test Method for Aluminum in Water
- D858-95, Standard Test Method for Manganese in Water
- D1068-96, Standard Test Method for Iron in Water
- D1687-92 (1996), Standard Test Method for Chromium in Water
- D1688-95A, Standard Test Method for Copper in Water, Atomic Absorption, Direct
- D1688-95C, Standard Test Method for Copper in Water, Atomic Absorption, Graphite Furnace

<sup>5</sup> (Standard Methods, 20th Ed.)

<sup>6</sup> Vol. 11.01, 2000

D1691-95A, Standard Test Method for Zinc in Water, Atomic Absorption, Direct

D1976-96, Standard Test Method for Elements in Water by ICP-AES

D2972-97B, Standard Test Method for Arsenic in Water, Atomic Absorption, Hydride Generation

D2972-97C, Standard Test Method for Arsenic in Water, Atomic Absorption, Graphite Furnace

D3082-92 (1996), Standard Test Method for Boron in Water

D3557-95, Standard Test Method for Cadmium in Water

D3559-96D, Standard Test Method for Lead in Water, Atomic Absorption, Graphite Furnace

D3697-92 (1996), Standard Test Method for Antimony in Water

D3859-98A, Standard Test Method for Selenium in Water, Gaseous Hydride AAS

D3859-98B, Standard Test Method for Selenium in Water, Graphite Furnace AAS

D3919-99, Standard Practice for Measuring Trace Elements in Water by Graphite Furnace Atomic Absorption Spectrophotometry

D4382-95, Standard Test Method for Barium in Water, Graphite Furnace AAS

D5673-96, Standard Test Method for Elements in Water by Inductively Coupled Plasma-Mass Spectrometry

### 3.3. Mercury

PARAMETER	ODWQS mg/L	RDL µg/L
Mercury	0.001	0.1

LSB Method: E3060- The Determination of Mercury in Water by Cold Vapour-Flameless Atomic Absorption Spectrophotometry (CV-FAAS)

Method Principle: Mercury in the water sample is oxidized to its divalent ion form ( $Hg^{+2}$ ) by an acid digestion procedure. It is then reduced by a Stannous Chloride Solution to its elemental form. An air (or argon) stream carries the mercury vapour into a flow-through absorption cell positioned between a light source, set at 253.7 nm wavelength and a detector. The amount of light absorption is proportional to the concentration of mercury in the sample.

US-EPA Methods: Method 245.1 Rev 3.0, Mercury by Cold Vapor AA Spectrometry - Manual  
 Method 245.2, Mercury by Cold Vapor AA Spectrometry - Automated  
 Method 200.8 Rev 5.3, Trace Metals by ICP/Mass Spectrometry

AWWA Methods:<sup>7</sup> Method 3112 B - Metals by Cold-Vapor Atomic Absorption Spectrometry

<sup>7</sup> (Standard Methods, 20th Ed.)

ASTM Method:<sup>8</sup>

Method D3223-95, Standard Test for Mercury in Water

### 3.4. Nitrite, Nitrate, and Nitrate + Nitrite

PARAMETER	ODWQS mg/L	RDL mg/L
Nitrate	10	1
Nitrate +Nitrite	10	1
Nitrite	1	0.1

LSB Method:

E3364 - The Determination of Ammonia Nitrogen, Nitrite Nitrogen, Nitrite plus Nitrate Nitrogen and Reactive Ortho-Phosphate in Surface Water, Drinking Waters and Ground Waters by Colourimetry.

Method Principle:

Nitrite is determined as one of four automated nutrient tests performed simultaneously on the same aliquot of sample. Nitrite forms a diazotization product with sulphanilamide which is then coupled with N(1-naphthyl) ethylenediamine dihydrochloride at pH 1 ±0.1. A light red colour is produced. The absorbance of the solution is measured at 520 nm and the concentration of nitrite is determined by comparison with a known set of standards.

For Nitrite plus Nitrate, samples are analyzed via an automated colourimetric procedure, which entails converting nitrate to nitrite, and then analyzing the sample for nitrite; the original nitrite concentration is included in the result because nitrite anions are not affected by the preliminary reduction step. Nitrate is reduced to nitrite by heating (37°C) an aliquot of sample with hydrazine in alkaline media; this reaction is catalyzed by the addition of cupric ion. Subsequently, an azo dye is formed in acid media by diazotizing sulphanilamide with nitrite and coupling the product with N (1-naphthyl) ethylenediamine dihydrochloride. The absorbance of the light red azo dye is measured at 520 nm and the concentration of nitrate nitrogen plus nitrite nitrogen is determined by comparison with a similarly treated series of mixed Standards.

Nitrate may be calculated by subtracting the Nitrite result from the Nitrite plus Nitrate result.

US-EPA Methods:

Method 300.0 Rev 2.1, Inorganic Anions by Ion Chromatography

Method 300.1 Rev 1.0, Determination of Inorganic Anions in Drinking Water by Ion Chromatography

Method 353.2 Rev 2.0, Nitrate-Nitrite by Automated Colorimetry

AWWA Methods:<sup>9</sup>

Method 4110 B - Determination of Anions by Ion Chromatography with Chemical Suppression of Eluent Conductivity

Method 4500-NO<sub>2</sub><sup>-</sup> B - Colorimetric Method

Method 4500-NO<sub>3</sub><sup>-</sup> D - Nitrate Electrode Method

Method 4500-NO<sub>3</sub><sup>-</sup> E - Cadmium Reduction Method

Method 4500-NO<sub>3</sub><sup>-</sup> F - Automated Cadmium Reduction Method

<sup>8</sup> Vol. 11.01, 2000

<sup>9</sup> (Standard Methods, 20th Ed.)

ASTM Method:<sup>10</sup> Method D4327-97, Standard Test Method for Anions in Water by Chemically Suppressed Ion Chromatography

Method D3867-99A, Standard Test Method for Nitrite-Nitrate in Water, Automated Cadmium Reduction

Method D3867-99B, Standard Test Method for Nitrite-Nitrate in Water, Manual Cadmium Reduction

### 3.5. Triazines

PARAMETER	ODWQS mg/L	RDL µg/L
Alachlor	0.005	5
Atrazine + N-dealkylated metabolites	0.005	1
Cyanazine	0.01	1
Metolachlor	0.05	5
Metribuzin	0.08	8
Prometryne	0.001	0.25
Simazine	0.01	0.5

LSB Method: E3121 - The Determination of Triazine Herbicides in Water, Soils, Vegetation, and TCLP Leachate by Gas Chromatography/Mass Spectrometry (GC/MS).

Method Principle: Samples are made basic (pH > 12) and solvent-extracted. The sample extract is passed through sodium sulphate to remove excess water, evaporated to dryness and re-constituted in a measured amount of solvent prior to analysis by capillary gas chromatography/mass -spectrometry (GC/MS) for these target compounds.

US-EPA Methods: Method 505 Rev 2.1, Organohalide Pesticides and PCBs by Microextraction and GC  
 Method 507 Rev 2.1, Nitrogen- and Phosphorus-Containing Pesticides by GC with a Nitrogen Phosphorus Detector  
 Method 508.1 Rev 2.0, Chlorinated Pesticides, Herbicides and Organohalides by Liquid-Solid Extraction and GC with an Electron Capture Detector  
 Method 525.2 Rev 2.0, Organic Compounds by Liquid-Solid Extraction and Capillary Column GC/Mass Spectrometry

ASTM Method:<sup>11</sup> Method D5475-93 (1997), Standard Test Method for Nitrogen- and Phosphorus-Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorus Detector

<sup>10</sup> Vol. 11.01, 2000

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### 3.6. Carbamates

PARAMETER	ODWQS mg/L	RDL µg/L
Aldicarb	0.009	0.9
Bendiocarb	0.04	7.5
Carbaryl	0.09	9
Carbofuran	0.09	12.5
Triallate	0.23	23

LSB Method: E3158 - The Determination of Carbamates in Water by High Pressure Liquid Chromatography - Ultraviolet (HPLC-UV) Detection. (2000)

Method Principle: Samples are solvent-extracted. The sample extract is passed through sodium sulphate to remove excess water, evaporated to dryness and re-constituted in a measured amount of solvent prior to analysis by high performance liquid chromatography with a UV detector.

LSB Method: E3438 - The Determination of Carbamates in Water and Leachate by High Performance Liquid Chromatography and Mass Spectrometry-Mass Spectrometry (LC-MS-MS) Analysis (2003)

Method Principle: Samples can be extracted by using either a liquid-liquid or a solid phase extraction method. The sample extract is condensed to a pre-determined amount using roto-evaporating or nitrogen blow-down technique prior to analysis by high performance liquid chromatography (LC) with either an ultraviolet (UV) detector or a triple stage quadrupole mass spectrometry detector (MS/MS).

MS-MS analysis is done by using an electrospray ionization source (ESI) in positive ionization mode. The mass spectrometer is run in a Product Ion scan in which the first mass filter (quadrupole 1, Q1) separates or filters ions according to their m/z ratio (usually the molecular ion) and allows only ions with specific m/z ratio to enter the collision cell (quadrupole 2, Q2). The  $[M+H]^+$  ion enters Q2 where it is fragmented by collision with neutral gas molecules ( $N_2$  is used at this laboratory) in a process referred to as Collisionally Activated Dissociation (CAD). The fragmented ions generated are then passed into quadrupole 3 (Q3) and filtered to provide a spectrum. The ions created by the source (Q1) are referred to as precursor ions, the collision products are referred to as product or fragment ions. The most abundant product ion is chosen for using in MRM analysis later.

Identification of the target compound is done by using the LC retention time (RT) obtained from a reconstructed LC-MS-MS extracted ion chromatogram (XIC). The XIC is obtained from the Multiple Reaction Monitoring (MRM) and MS-MS identification of that specific peak. The MS-MS identification is done by using a precursor ion (usually the molecular ion obtained from the Q1) and a product ion produced by the CAD process and analyzed by Q3. This MS-MS identification process is also known as MRM. Upon positive identification of the target compound, quantification of the compound is done by the integrated area of that specific peak of the MRM chromatogram using internal standard calibration protocols and d7-carbaryl as an internal standard.

Taking advantage of the MS-MS instrumentation and to enhance operation efficiency, samples are first screened, semi-quantitatively, by using a short column LC-MS-MS analysis (< 5 min./sample) and, in the presence of target compounds, followed by a quantitative analysis (about 15 min./sample).



The ability of MS-MS detection allows the use of an isotope-labelled compound as an internal standard during the sample preparation and quantitative analysis to enhance data quality further. Therefore, deuterium labelled carbaryl (d7-Carbaryl) is added to the samples and the calibration standard as an internal standard.

- US EPA Methods: Method 531.1 Rev 3.1, N-Methylcarbamoyloximes and N-Methylcarbamates by HPLC with Post Column Derivatization
- AWWA Methods:<sup>12</sup> Method 6610 B - Carbamate Pesticides, High-Performance Liquid Chromatographic Method
- ASTM Method:<sup>13</sup> D5315-92 (1998), Standard Test Method for N-Methyl-Carbamoyloximes and N-Methylcarbamates in Water by Direct Aqueous Injection High-Performance Liquid Chromatography with Post-Column Derivatization

### 3.7. Organochlorine Pesticides and PCBs

PARAMETER	ODWQS mg/L	RDL µg/L
Aldrin + Dieldrin	0.0007	0.07
Chlordane (Total): Oxychlordane	0.007	0.7
Chlordane (Total): a-Chlordane	0.007	0.7
Chlordane (Total): g-Chlordane	0.007	0.7
Heptachlor+Heptachlor epoxide	0.003	0.3
DDT+metabolites : p,p-DDE	0.03	3
DDT+metabolites : p,p-DDE	0.03	3
DDT+metabolites : o,p-DDT	0.03	3
DDT+metabolites : p,p-DDT	0.03	3
Lindane	0.004	0.4
Methoxychlor	0.9	90
PCB (Total)	0.003	0.3
Trifluralin	0.045	4.5

LSB Method: E3400 - the Determination of Organochlorine Pesticides, Chlorobenzenes, Aroclors, and Toxaphenes in Water, Effluent, and Waste Water by Hexane Microextraction and Gas Chromatography-Mass Spectrometry (GC- MS)

Method Principle: An approximately 800 mL water sample is extracted with 5 mL hexane. The extract is concentrated, reconstituted in toluene, and analyzed by Gas Chromatography-Mass Spectrometry (GC/MS) for target compounds.

Qualitative identification of target compounds is achieved by comparison of target compound retention times (RT), intensities and ratios of target and qualifier ions with that of a Calibration Standard mixture. Quantitation of the target compounds as detected in a field sample is achieved by comparison of the target ion abundance with that from a Calibration Standard Mix prepared in the Laboratory. Retention times, target ions, and qualifier ions used for the analysis of the OC/CB, PCB Aroclors, Toxaphene and Pyrethrins targets are listed in the method. This method uses d<sub>10</sub>-Fluoranthene as an internal standard. The d<sub>12</sub>-Perylene, and 1,3,5-Tribromobenzene are used as surrogates to monitor method performance.

US-EPA Methods: Method 505 Rev 2.1, Organohalide Pesticides and PCBs by Microextraction and GC

<sup>12</sup> (Standard Methods, 20th Ed.)

<sup>13</sup> Vol. 11.02, 2000

Method 508, Rev 3.1, Chlorinated Pesticides by GC with an Electron Capture Detector

Method 508.1 Rev 2.0, Chlorinated Pesticides, Herbicides and Organohalides by Liquid-Solid Extraction and GC with an Electron Capture Detector

Method 525.2 Rev 2.0, Organic Compounds by Liquid-Solid Extraction and Capillary Column GC/Mass Spectrometry

ASTM Method:<sup>14</sup>

Method D5175-91 (1996), Standard Test Method for Organohalide Pesticides and Polychlorinated Biphenyls in Water by Microextraction and Gas Chromatography

### 3.8. Organophosphorus Pesticides

PARAMETER	ODWQS mg/L	RDL µg/L
Azinphos-methyl	0.02	2
Chlorpyrifos	0.09	9
Diazinon	0.02	2
Dimethoate	0.02	2.5
Malathion	0.19	19
Parathion	0.05	5
Phorate	0.002	0.5
Temephos	0.28	28
Terbufos	0.001	1

LSB Method: E3389 - The Determination of Organophosphorus Pesticides in Water by High Performance Liquid Chromatography - Ultraviolet (HPLC-UV) Detection (2000)

Method Principle: Samples are passed through pre-conditioned solid phase extraction (SPE) cartridges. Target analytes are eluted from the cartridge using ethyl acetate. The sample extract is evaporated to dryness and reconstituted in 1.0 mL acetonitrile prior to analysis by HPLC with UV detection.

LSB Method: E3437 - The Determination of Organophosphorus Pesticides in Water and Leachate by High Performance Liquid Chromatography and Mass Spectrometry-Mass Spectrometry (LC-MS-MS) Analysis (2003)

Method Principle: Samples can be extracted by using either a liquid-liquid or a solid phase extraction method. The sample extract is condensed to a pre-determined amount using a roto-evaporating or nitrogen blow-down technique prior to analysis by high performance liquid chromatography (LC) with either an ultraviolet (UV) detector or a triple stage quadrupole mass spectrometry detector (MS/MS).

MS-MS analysis is done by using an electrospray ionization source (ESI) in positive ionization mode. The mass spectrometer is run in a Product Ion scan in which the first mass filter (quadrupole 1, Q1) separates or filters ions according to their m/z ratio (usually the molecular ion) and allows only ions with specific m/z ratio to enter the collision cell (quadrupole 2, Q2). The  $[M+H]^+$  ion enters Q2 where it is fragmented by collision with neutral gas molecules ( $N_2$  is used at this laboratory) in a process referred to as Collisionally Activated Dissociation (CAD). The fragment ions generated are then passed into quadrupole 3 (Q3) and filtered to provide a spectrum. The ions created by the source (Q1) are referred to as precursor ions, the collision products are referred to as

<sup>14</sup> Vol. 11.02, 2000

product or fragment ions. The most abundant product ion is chosen for using in MRM analysis later.

Identification of the target compound is done by using the LC retention time (RT) obtained from a reconstructed LC-MS-MS extracted ion chromatogram (XIC). The XIC is obtained from the Multiple Reaction Monitoring (MRM) and MS-MS identification of that specific peak. The MS-MS identification is done by using a precursor ion (usually the molecular ion obtained from the Q1) and a product ion produced by the CAD process and analyzed by Q3. This MS-MS identification process is also known as MRM. Upon positive identification of the target compound, quantification of the compound is done by the integrated area of that specific peak of the MRM chromatogram using internal standard calibration protocols and d6-Dichlorovos as an internal standard.

Taking advantage of the MS-MS instrumentation and to enhance operation efficiency, samples are first screened, semi-quantitatively, by using a short column LC-MS-MS analysis (< 5 min./sample) and, in the presence of target compounds, followed by a quantitative analysis (about 15min./sample).

The ability of MS-MS detection allows the use of an isotope-labelled compound as an internal standard during the sample preparation and quantitative analysis to enhance data quality further. Deuterium labelled d6-Dichlorovos is added into the sample and the calibration standard to serve for this purpose.

US-EPA Method: Method 507 Rev 2.1, Nitrogen- and Phosphorus-Containing Pesticides by GC with a Nitrogen Phosphorus Detector

ASTM Method:<sup>15</sup> Method D5475-93 (1997), Standard Test Method for Nitrogen- and Phosphorus-Containing Pesticides in Water by Gas Chromatography with a Nitrogen-Phosphorus Detector

### 3.9. Chlorophenols (CPs) & Phenoxy Acids (PAs)

PARAMETER	ODWQS mg/L	RDL mg/L
2,4,5-Trichlorophenoxyacetic Acid (2,4,5-T)	0.28	28
2,4-Dichlorophenoxyacetic acid (2,4-D)	0.1	10
Bromoxynil	0.005	0.5
Dicamba	0.12	12
Diclofop-methyl	0.009	0.9
Dinoseb	0.01	1
Picloram	0.19	19
2,3,4,6-Tetrachlorophenol	0.1	10
2,4,6-Trichlorophenol	0.005	0.5
2,4-Dichlorophenol	0.9	90
Pentachlorophenol	0.06	6

LSB Method: E3119 - The Determination of Chlorophenols and Phenoxyacid Herbicides in Water by Solid Phase Extraction (SPE) and Gas Chromatography-Mass Spectrometry (GC/MS)

Method Principle: Water samples are acidified (pH ≤ 2) and passed through pre-conditioned C<sub>18</sub> solid phase extraction (SPE) cartridges. SPE cartridges are then dried and target compounds eluted using a small volume of solvent. The column elute is treated with diazomethane (to methylate target compounds), evaporated and finally diluted with solvent to 1.0 mL. This

<sup>15</sup> Vol. 11.02, 2000

extract is analyzed by gas chromatography with a mass spectrometer (GC/MS). CPs and PAs are quantified as their corresponding anisoles and methyl esters, respectively.

- US-EPA Methods:<sup>16</sup> Method 515.2 Rev 1.1 - Chlorinated Acids using Liquid-Solid Extraction and GC with and Electron Capture Detector
- Method 515.1 Rev 4.0 - Chlorinated Acids by GC with an Electron Capture Detector
- Method 515.3, Determination of Chlorinated Acids in Drinking Water by Liquid-Liquid Extraction, Derivatization and Gas Chromatography with Electron Capture Detection
- Method 555 Rev 1.0 - Chlorinated Acids by HPLC with a Photodiode Array Ultraviolet Detector
- US-EPA Methods:<sup>17</sup> Method 525.2 Rev 2.0 - Organic Compounds by Liquid-Solid Extraction and Capillary Column GC/Mass Spectrometry
- ASTM Method:<sup>18</sup> Method D5317-98, Standard Test Method for Determination of Chlorinated Organic Acid Compounds in Water by Gas Chromatography with an Electron Capture Detector

### 3.10. Quaternary Ammonium Compounds

PARAMETER	ODWQS mg/L	RDL µg/L
Diquat	0.07	7
Paraquat	0.01	1

- LSB Method: E3417 - The Determination of Diquat and Paraquat in Water and Vegetation Environmental Matrices by High Performance Liquid Chromatography (HPLC) and Electro-spray Isotope Dilution Mass Spectrometry Detection (IDMS)
- Method Principle: Water samples are extracted using mixed-mode, polymer SPE cartridges, with no pH modification. The SPE cartridge is pre-conditioned with water and methanol. Analytes are eluted using 1M ammonium chloride in an aqueous solution of 50% methanol. Sample extracts are analysed by LC-MS.
- Deuterated paraquat and diquat are used as method surrogates. With the incorporation of isotope labelled paraquat and diquat, the method is adapted to an isotope dilution MS procedure using LC/ESI-MS.
- This method provides a sample preparation procedure in which, electro-spray ionization mass (ESI-MS) detection may be used for the identification and quantitation of the compounds.
- US-EPA Method: Method 549.2 Rev 1.0, Diquat and Paraquat by Liquid-Solid Extraction and HPLC with a Photodiode Array UV Detector

### 3.11. Urea Derivative

PARAMETER	ODWQS mg/L	RDL µg/L
Diuron	0.15	15

<sup>16</sup> (PAs)  
<sup>17</sup> (CPs)  
<sup>18</sup> Vol. 11.02, 2000

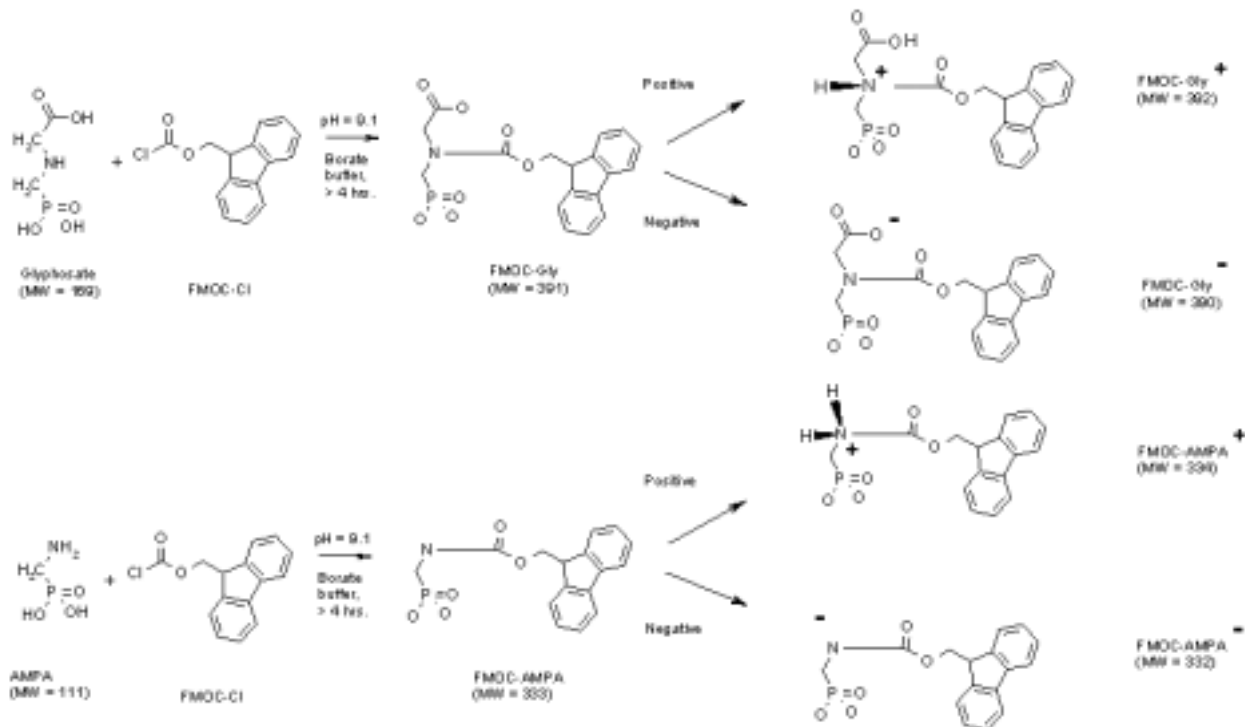
LSB Method:	E3230 - The Determination of Phenyl Ureas in Water by High Performance Liquid Chromatography-Ultraviolet (HPLC-UV) Detection. (2000)
Method Principle:	Samples are solvent-extracted. The sample extract is passed through sodium sulphate to remove excess water, evaporated to dryness and re-constituted in a measured amount of solvent prior to analysis by high performance liquid chromatography with UV detector.
LSB Method:	The Determination of Phenyl Ureas in Water and Leachate by High Performance Liquid Chromatography and Mass Spectrometry-Mass Spectrometry (LC-MS-MS) Analysis (2003)
Method Principle:	<p>Samples can be extracted by using either a liquid-liquid or a solid phase extraction method. The sample extract is condensed to a pre-determined amount using roto-evaporating or nitrogen blow-down technique prior to analysis by high performance liquid chromatography (LC) with either an ultraviolet (UV) detector or a triple stage quadropole mass spectrometry detector (MS/MS).</p> <p>MS-MS analysis is done by using an electrospray ionization source (ESI) in positive ionization mode. The mass spectrometer is run in a Product Ion scan in which the first mass filter (quadropole 1, Q1) separates or filters ions according to their m/z ratio (usually the molecular ion) and allows only ions with specific m/z ratio to enter the collision cell (quadropole 2, Q2). The <math>[M+H]^+</math> ion enters Q2 where it is fragmented by collision with neutral gas molecules (<math>N_2</math> is used at this laboratory) in a process referred to as Collisionally Activated Dissociation (CAD). The fragment ions generated are then passed into quadropole 3 (Q3) and filtered to provide a spectrum. The ions created by the source (Q1) are referred to as precursor ions, the collision products are referred to as product or fragment ions. The most abundant product ion is chosen for using in MRM analysis later.</p> <p>Identification of the target compound is done by using the LC retention time (RT) obtained from a reconstructed LC-MS-MS extracted ion chromatogram (XIC). The XIC is obtained from the Multiple Reaction Monitoring (MRM) and MS-MS identification of that specific peak. The MS-MS identification is done by using a precursor ion (usually the molecular ion obtained from the Q1) and a product ion produced by the CAD process and analyzed by Q3. This MS-MS identification process is also known as MRM. Upon positive identification of the target compound, quantification of the compound is done by the integrated area of that specific peak of the MRM chromatogram using internal standard calibration protocols and d6-Diuron as an internal standard.</p> <p>Taking advantage of the MS-MS instrumentation and to enhance operation efficiency, samples are first screened, semi-quantitatively, by using a short column LC-MS-MS analysis (&lt; 5 min./sample) and, in the presence of target compounds, followed by a quantitative analysis (about 15 min./sample).</p> <p>The ability of MS-MS detection allows the use of an isotope-labelled compound as an internal standard during the sample preparation and quantitative analysis to enhance data quality further. Deuterium labeled diuron (d6-Diuron) is added into the sample and the calibration standard to serve for this purpose.</p>
US-EPA Method:	Method 532 Rev 1.0, Determination of Phenylurea Compounds in Drinking Water by Solid Phase Extraction and High Performance Liquid Chromatography with UV Detection

### 3.12. Glyphosate

PARAMETER	ODWQS mg/L	RDL $\mu\text{g/L}$
Glyphosate	0.28	28

LSB Method: E3415 - The Determination of Glyphosate and Aminomethyl-phosphonic Acid in Water and Vegetation by High Performance Liquid Chromatography - Electro Spray Ionization - Mass Spectrometry (HPLC-ESI-MS)

Method Principle: Neutral sample conditions are used for extraction of water samples.



This method uses the derivatization of glyphosate with 9-fluorenyl methoxycarbonyl chloride (FMOC-Cl), Figure 1, prior to HPLC analysis to enhance the separation and bring these targets from the void volume using a bonded phase C-18 reversed phase column. This has greatly enhanced the efficiency of analytical procedures and data quality. Analysis of AMPA is achieved by the disassociation of one hydrogen atom from the AMPA, and the direct analysis of AMPA<sup>-</sup> ion directly (Figure 1).

**Figure 1: Reaction Scheme for Glyphosate with FMOC-Cl Detection Scheme for AMPA**

The identification is achieved by the HPLC retention time (within 0.2 minutes of established retention time), the molecular ion of the reaction product (FMOCCl-Gly m/z 390) and AMPA (m/z 110), respectively, in negative ESI-MS (see the reaction scheme listed in Figure 1). A confirmation ion of m/z 168 for the glyphosate is also used.

FMOCCl-Gly is not available commercially and is prepared in-house. The quantitation of glyphosate and AMPA in water, is done by using a standard prepared in de-ionized water and reacted with FMOC-Cl and borate buffer.

Isotope dilution is used for glyphosate analysis. Quantitation of AMPA is done through the external standard method as there is no correlation between the AMPA and <sup>13</sup>C<sub>2</sub><sup>15</sup>N-glyphosate.

US-EPA Methods: Method 547, Determination of Glyphosate by HPLC, Post Column Derivatization, and Fluorescence Detector

AWWA Methods:<sup>19</sup> Method 6651 - Glyphosate Herbicide by Liquid Chromatographic Post-Column Fluorescence Method.

### 3.13. Fluoride

PARAMETER	ODWQS mg/L	RDL mg/L
Fluoride	1.5	0.15

LSB Method: E3172 - The Determination of Fluoride and Sulphate in Water, Leachates and Effluents by Automated Ion Chromatography

Method Principle: Via Ion Chromatography (IC), fluoride is separated from other anions by using columns packed with ion exchange resin, and an eluent solution of sodium carbonate/sodium bicarbonate.

The sample is injected into the eluent stream and passes through a pre-column (AG-14). The pre-column removes any foreign matter entering the analytical system, which extends the life of the analytical column (AS-14). After separation, the anions are converted to their acid forms by ion exchange using a micro membrane suppressor, and their concentrations are determined from the conductivity of the fluoride produced. A conductivity meter measures the conductivity of each anionic species compared to the water background. Identities of the analytes are determined by their retention times.

US-EPA Methods: Method 300.0 Rev 2.1, Determination of Inorganic Anions by Ion Chromatography  
Method 300.1 Rev 1.0, Determination of Inorganic Anions in Drinking Water by Ion Chromatography

AWWA Methods:<sup>20</sup> Method 4500\_F<sup>-</sup> B - Preliminary Distillation Step  
Method 4500\_F<sup>-</sup> C - Ion-Selective Electrode Method  
Method 4500\_F<sup>-</sup> D - SPADNS Method  
Method 4500\_F<sup>-</sup> E - Complexone Method (Automated Alizarin)

Method 4110 B - Determination of Anions by Ion Chromatography with Chemical Suppression of Eluent Conductivity

ASTM Method:<sup>21</sup> Method D4327-97, Standard Test Method for Anions in Water by Chemically Suppressed Ion Chromatography

<sup>19</sup> (Standard Methods, 20th Ed.)

<sup>20</sup> (Standard Methods, 20th Ed.)

<sup>21</sup> Vol. 11.01, 2000

### 3.14. Benzo(a)pyrene {tc "4.18 Benzo(a)pyrene " \ 2}

PARAMETER	ODWQS mg/L	RDL µg/L
Benzo(a)pyrene	0.00001	0.01

LSB Method: E3399 - The Determination of Polycyclic Hydrocarbons (PAH) in Aqueous Matrices by Liquid-Liquid Micro-Extraction (LLME) and Gas Chromatography-Mass Spectrometry (GC/MS)

Method Principle: Six deuterated PAH internal standards are added to an 800 mL water sample which is extracted with 5 mL toluene using a liquid/liquid microextraction technique. The extract is concentrated and analyzed by Gas Chromatography/ Mass Spectrometry (GC/MS) for the target compounds.

Qualitative identification of target compounds is achieved by comparison of target compound retention times (RT), intensities and ratios of target and qualifier ions with that of a Calibration Standard mixture. Quantitation of the target compounds as detected in a field sample is achieved by comparison of the target ion abundance with that from a Calibration Standard Mix prepared in the Laboratory. The following compounds are used as Internal standards for this method: d<sub>10</sub>-Phenanthrene, d<sub>10</sub>-Fluoranthene, d<sub>12</sub>-Chrysene, d<sub>12</sub>-Benzo(a)pyrene, d<sub>12</sub>-Benzo(a)anthracene, and d<sub>14</sub>-Dibenzo(a,h)anthracene.

US-EPA Methods: Method 525.2 Rev 2.0 - Organic Compounds by Liquid-Solid Extraction and Capillary Column GC/Mass Spectrometry

Method 550, Polycyclic Aromatic Hydrocarbons (PAHs) by Liquid-Solid Extraction and HPLC with Coupled UV and Fluorescence Detection

Method 550.1, Polycyclic Aromatic Hydrocarbons (PAHs) by Liquid-Solid Extraction and HPLC with Coupled UV and Fluorescence Detection

ASTM Method:<sup>22</sup> Method D4657-92 (1998), Standard Test Method for Polycyclic Aromatic Hydrocarbons in Water

### 3.15. Cyanide

PARAMETER	ODWQS mg/L	RDL mg/L
Cyanide (free)	0.2	0.02

LSB Method: E3015 - The Determination of Free and Total Cyanide in Environmental Samples by Colourimetry.

Method Principle: Total cyanide includes the free simple cyanides (such as HCN and KCN), and weakly bound cyanides (such as Ni(CN)<sub>4</sub>), as well as those complexed cyanides that decompose to form free cyanides that distill out as HCN in an acidic environment. Aqueous samples are introduced directly to the continuous flow system from an autosampler. The distillation step isolates HCN under specific acidic conditions. The sequential combination of UV digestion plus distillation yields the measurement of "total cyanide". Interferences from thiocyanate are removed using a borosilicate glass coil in a UV-B

<sup>22</sup> Vol. 11.02, 2000



chamber (wavelengths above 290 nM). When thiocyanate is not dissociated during UV digestion, it does not carry over in the distillation step. Cyanide is determined colourimetrically by the reaction of cyanide with chloramine-T to form cyanogen chloride which further reacts with a combination of barbituric acid and isonicotinic acid to form a highly coloured coupling product, which is measured at 600 nM.

Free cyanides are the simple and weakly dissociable cyanides that form HCN upon acidification to pH 4.0. Free cyanide is determined as above, but with two changes; the elimination of the UV digestion, which avoids the conversion of the complexed cyanides to free cyanide and the replacement of the Pure-DW water reagent with a 10 mg/L zinc sulphate solution, for the elimination of interference from complexed iron cyanides

US-EPA Methods: Method 335.1 Rev 1.0, Determination of Cyanides Amenable to Chlorination, Titrimetric

AWWA Methods:<sup>23</sup> Method 4500-CN<sup>-</sup> G – Cyanides Amenable to Chlorination after Distillation

Method 4500-CN<sup>-</sup> H - Cyanides Amenable to Chlorination without Distillation (Short-Cut Method)

ASTM Method:<sup>24</sup> Method D2036-98 B, Standard Test Method for Cyanides in Water, Cyanides Amenable to Chlorination by Difference

### 3.16. Dioxins and Furans - Toxic Equivalent Quantity

PARAMETER	ODWQS mg/L	RDL TEQ 2378TCDD
Dioxin and Furan	0.000000015	0.000000075

LSB Method: E3418 - The Determination of Polychlorinated Dibenzo-p-dioxins (PCDD), Polychlorinated Dibenzofurans (PCDF) and Dioxin-like Polychlorinated Biphenyls (DLPCBs) in Environmental Matrices by Gas Chromatography-Mass Spectrometry (GC/MS).

Method Principle: Drinking water sample volumes are measured and recorded. If any of the samples contain particulate then the samples must be extracted using the Groundwater/Effluent Empore Disk Method. Samples are liquid/liquid extracted with pentane. A 2-stage chromatographic clean-up procedure is used to remove potential chemical interferences.

This analytical method is used to determine the concentrations of PCDDs, PCDFs and DLPCBs in a variety of matrices using isotope dilution with mass spectrometric detection. All samples are fortified prior to sample extraction, digestion or elution with known amounts of [<sup>13</sup>C<sub>12</sub> -] isotopically labelled PCDDs/PCDFs and/or DLPCBs. All PCDDs/PCDFs and DLPCBs are quantified against these labelled standards. Sample extracts are cleaned using a 2-stage column (silica/alumina) when PCDDs/PCDFs only are requested or no interferences such as polychlorinated diphenyl ethers(PCDPEs) are expected in the sample. If PCDDs/PCDFs and DLPCBs are requested or if a sample is highly contaminated with bulk interferences, a carbon cleanup procedure must be incorporated (3-stage).

US-EPA Method: Method 1613B, Chlorinated Dioxins by Isotope Dilution High Resolution Gas Chromatography/High Resolution Mass Spectrometry

<sup>23</sup> (Standard Methods, 20th Ed.)

<sup>24</sup> Vol. 11.02, 2000

### 3.16.1 Dioxins and Furans – Calculation of Toxic Equivalent Quantity

There are a total of 210 dioxins and furans. Only 17 are toxic (2,3,7,8-substituted congeners) and their toxicity is normalized to 2378-TCDD (the most toxic). The TEQ is determined (as shown in the following example) by multiplying the concentration of each detected 2,3,7,8-substituted congener by its respective TEF (toxic equivalent factor) to determine its toxic equivalence (TE). For the 2,3,7,8-substituted congeners that are not detected, ½ of the detection limit is multiplied by the TEF to determine the TE for that congener. This converts each of the congeners to 2378-TCDD toxic equivalents. The sum of the 17 toxic equivalents (TEs) gives the TEQ (Toxic Equivalent Quantity) for the sample normalized to 2378-TCDD. The result is 1.5 pg/L, which is well below the 15 pg/L IMAC.

#### TEQ EXAMPLE

Compound	Conc. Pg/L	EDL pg/L	TEF pg/L	TE /congener pg/L
2,3,7,8-TCDD	ND	1.1	1	0.55
1,2,3,7,8-PeCDD	ND	1	0.5	0.25
1,2,3,4,7,8-HxCDD	ND	1.2	0.1	0.06
1,2,3,6,7,8-HxCDD	ND	0.89	0.1	0.045
1,2,3,7,8,9-HxCDD	ND	1	0.1	0.05
1,2,3,4,6,7,8-HpCDD	ND	1.1	0.01	0.0055
OCDD	3.4		0.001	0.0034
2,3,7,8-TCDF	ND	1	0.1	0.05
1,2,3,7,8-PeCDF	ND	1	0.05	0.025
2,3,4,7,8-PeCDF	ND	1	0.5	0.25
1,2,3,4,7,8-HxCDF	ND	0.82	0.1	0.041
1,2,3,6,7,8-HxCDF	ND	1.1	0.1	0.055
2,3,4,6,7,8-HxCDF	ND	1.1	0.1	0.055
1,2,3,7,8,9-HxCDF	ND	1.2	0.1	0.06
1,2,3,4,6,7,8-HpCDF	ND	0.95	0.01	0.0048
1,2,3,4,7,8,9-HpCDF	ND	1	0.01	0.005
OCDF	1.8		0.001	0.0018
<b>TOTAL TEQ 2,3,7,8-TCDD (0.5 DL) = 1.5 pg/L</b>				

TEQ = Toxic Equivalent Quantity = sum of individual TE/congener  
 EDL = Estimated Detection Limit  
 TEF = Toxic Equivalent Factor  
 TE/congener = Toxic Equivalence / congener

### 3.17. Nitrotriactic Acid (NTA)

PARAMETER	ODWQS mg/L	RDL mg/L
Nitroloacetic Acid (NTA)	0.4	0.05

LSB Method: E3406 - The Determination of Nitrotriactic Acid (NTA) in Aqueous Samples by Automated Ion Chromatography (IC).

Method Principle: Using ion chromatography (IC), nitrotriactic acid (NTA) is separated from other anions using columns packed with ion exchange resin and an eluent solution of sodium hydroxide. The eluent is passed through an anion trap column (ATC-1) to remove impurities which may be present in the working eluent solution.

The sample is passed through a cation trap column (in house design) made of Amberlite IR-120(H) resin to remove calcium, magnesium and iron from the sample matrix before analysis. The sample is then injected into the eluent stream and passes through a pre-column (AG-11). The pre-column removes any foreign matter entering the analytical system, extending the life of the separator column (AS-11). After separation, the anions are converted to their acid forms by ion exchange using a micromembrane suppressor and their concentrations are determined from the conductivity of the NTA produced. A conductivity meter measures the conductivity of each anionic species against the water background. The identities of the species are determined by their retention times.

### 3.18. N-nitrosodimethylamine (NDMA)

PARAMETER	ODWQS mg/L	RDL µg/L
N-Nitrosodimethylamine (NDMA)	0.000009	0.00099

LSB Method: E3291 - The Determination of N-nitrosodimethylamine (NDMA) in Water by Gas Chromatography-High Resolution Mass Spectrometry (GC-HRMS)

Method Principle: This method is designed to identify and quantify N-nitrosodimethylamine (NDMA) in water by adsorption onto Ambersorb 572, elution into an organic solvent and analysis by gas chromatography-high resolution mass spectrometry (GC-HRMS). The designation “GC” refers to high resolution (capillary column) GC.

The internal standard, d<sub>6</sub>-NDMA, is added to the leachate. After the addition of Ambersorb 572, the bottle is rolled at 50 rpm on a roller apparatus for 1 hour. The granular adsorbent is isolated by filtration on filter paper and allowed to air dry for 1 hour, minimum. The Ambersorb 572 is transferred to a 2mL autosampler vial and 400 µL of dichloromethane are added. The vial is capped and the contents are analyzed by GC-HRMS. NDMA is quantified by isotope dilution with d<sub>6</sub>-NDMA.

### 3.19. Bromate

PARAMETER	ODWQS mg/L	RDL mg/L
Bromate	0.01	0.001

LSB Method: E3434 - The Determination of Bromide in Source Water by Ion Chromatography/Electrochemical Detection and Trace Levels of Bromate in Ozonated Drinking Water with the Addition of Postcolumn Reagent and a UV/Visible Detector

Method Principle: Using ion chromatography (IC), bromate and bromide are separated from other anions using columns packed with ion exchange resin and an eluent solution of sodium carbonate.

The sample is introduced into an ion chromatograph. The ions of interest are separated using a guard column, analytical column, suppressor device, electrochemical detector, a postcolumn delivery system (pneumatically controlled), a heated postcolumn reaction coil and an Ultraviolet/visible (UV/VIS) absorbance detector.

US-EPA Methods: Method 317.0 Rev 2.0, Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water Using Ion Chromatography with the Addition of a Postcolumn reagent for Trace Bromate Analysis.

Method 326.0, Determination of Inorganic Oxyhalide Disinfection By-Products in Drinking Water Using Ion Chromatography Incorporating the Addition of a Suppressor Acidified Postcolumn Reagent for Trace Bromate Analysis.

Method 300.1, Determination of Inorganic Anions in Drinking Water by Ion Chromatography.

## 4. ADDITIONAL PARAMETERS (CERTIFICATE OF APPROVAL OR MINISTRY ORDERS)

### 4.1. Alkalinity

PARAMETER	Standard mg/L as CaCO <sub>3</sub>	RDL mg/L as CaCO <sub>3</sub>
Alkalinity	30 – 500	

LSB Method: E3218 - The Determination of Conductivity, pH, and Alkalinity in Water and Effluents by Potentiometry

Method Principle: Alkalinity is defined as the capacity of a solution to neutralize acid, and is measured by titrimetry. Historically, alkalinity titration to the end-point of pH 4.5 is known as total fixed end-point (TFE) alkalinity. Any ion entering into a neutralization reaction with strong acid contributes to TFE alkalinity as long as the reaction takes place above pH 4.5.

An aliquot of the sample is titrated with sulphuric acid of known concentration. The delivery rate of the titrant is determined from the slope of the titration curve and the stability of the pH reading following the addition of each aliquot of the titrant.

AWWA Method:<sup>25</sup> Method 2320 - Alkalinity by Titration Method

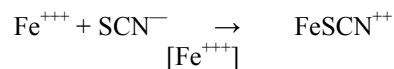
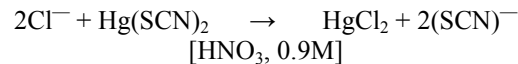
ASTM Method:<sup>26</sup> Method D1067-92 B (1996), Standard Test Method for Alkalinity of Water

### 4.2. Chloride

PARAMETER	Standard mg/L	RDL mg/L
Chloride	250	

LSB Method: E3016 - The Determination of Chloride In Drinking Water, Surface Water, Sewage, And Industrial Waste By Colourimetry

Method Principle: Chloride ions combine with mercuric thiocyanate to form an undissociated salt, mercuric chloride, and release thiocyanate ions which then complex with ferric ion to produce a coloured solution. The absorbance of the coloured solution is proportional to the original concentration of chloride ion in the sample.



<sup>25</sup> (Standard Methods, 20th Ed.)

<sup>26</sup> Vol. 11.02, 2000

US-EPA Methods: Method 300.0 Rev 2.1, Determination of Inorganic Anions by Ion Chromatography  
 Method 300.1 Rev 1.0, Determination of Inorganic Anions in Drinking Water by Ion Chromatography

AWWA Methods:<sup>27</sup> Method 4500<sub>Cl<sup>-</sup></sub> B – Argentometric Method  
 Method 4500<sub>Cl<sup>-</sup></sub> C – Mercuric Nitrate Method  
 Method 4500<sub>Cl<sup>-</sup></sub> D – Potentiometric Method  
 Method 4500<sub>Cl<sup>-</sup></sub> E – Automated Ferricyanide Method  
 Method 4110 B - Determination of Anions by Ion Chromatography with Chemical Suppression of Eluent Conductivity

ASTM Method:<sup>28</sup> Method D4327-97, Standard Test Method for Anions in Water by Chemically Suppressed Ion Chromatography  
 Method D512-89 (1999), Standard Test Methods for Chloride Ion in Water

### 4.3. Colour

PARAMETER	Standard TCU	RDL TCU
Colour	5	2.5

LSB Method: E3219 - The Determination of True Colour in Water, Effluents and Industrial Wastes by Colourimetry

Method Principle: An Auto-Analyzer system, which includes a reference stream, is designed to measure true colour of the supernatant of settled samples. The purpose of the reference stream is to eliminate the effect of non-settleable solids on colour measurements. Klett Summerson broad band filters were adapted to fit the filter holders of the Technicon AAI colourimeter. The broad band filter, with transmission limits of 405 to 450 nm, is suitable for true colour measurements while the filter with transmission limits of 660 to 740 nm, gave a turbidity/particulate only measurement. To obtain an appropriate correction for non-settleable solids at the required wavelengths (405 to 450 nm), the path lengths of the flow cells are 3.0 cm for the colour stream and 5 cm for the reference stream. This imbalance in cell length is designed to handle the relationship between light scattering and wavelength: the effect of particulates on absorbency measurements increases as the wavelength decreases.

US-EPA Methods: Method 110.0, Determination of Color by Colorimetry, ADMI  
 Method 110.1, Determination of Color by Colorimetry, Platinum-Cobalt

AWWA Methods:<sup>29</sup> Method 2120 B – Visual Comparison Method  
 Method 2120 C - Spectrophotometric Method

<sup>27</sup> (Standard Methods, 20th Ed.)

<sup>28</sup> Vol. 11.01, 2000

<sup>29</sup> (Standard Methods, 20th Ed.)

Method 2120 D – Tristimulus Filter Method

Method 2120 E – ADMI Tristimulus Filter Method

#### 4.4. Dissolved Organic Carbon (DOC)

PARAMETER	Standard mg/L	RDL mg/L
Dissolved Organic Carbon (DOC)	5	

LSB Method: E3370 - The Determination of Molybdate Reactive Silicates and Dissolved Carbon in Water, Industrial Waste, Soil Extracts and Precipitation by Colourimetry

Method Principle: Organic carbon is measured when the supernatant of a settled sample is introduced into an AutoAnalyzer System where it is acidified and flushed with nitrogen at 500 mL/minute to remove inorganic carbon. The sample is then oxidized with a UV digester in an acid-persulphate medium. The carbon is converted to carbon dioxide and, following dialysis, is measured by determining the loss in absorbance of a weakly buffered alkaline Phenolphthalein Solution using an AAI Colourimeter operating in the inverse mode.

AWWA Method:<sup>30</sup> Method 5310 C – Persulfate-Ultraviolet or Heated-Persulfate Oxidation Method

#### 4.5. Hardness

PARAMETER	Standard mg/L as CaCO <sub>3</sub>	RDL mg/ L as CaCO <sub>3</sub>
Hardness	80 – 100	

LSB Method: E3217 - The Determination of Cations in Water, Sewage, Health Samples, Industrial Waste, Leachates and Landfills by Atomic Absorption Spectrophotometry (AAS)

Method Principle: An automated atomic absorption method is used to measure the concentration of calcium, magnesium, sodium and potassium ions. A microcomputer controls the flow injection Atomic Absorption Spectrophotometry (AAS) system. Prior to sample aspiration as a fine mist into the air-acetylene flame of the AAS, the sample is automatically mixed with either lanthanum chloride, a releasing agent for calcium and magnesium analysis, or caesium chloride, an ionization suppressant, for the analysis of sodium and potassium. Light is emitted from a hollow cathode lamp and is directed through a flame into a monochromator and onto a detector that is set at a characteristic wavelength for each of the parameters (Ca 422.7 nm, Mg 285.2 nm, Na 589.0 nm, K 766.5 nm). The atoms of interest are heated in the flame, absorb the light at its particular wavelength and the detector measures the decreased intensity of the resulting beam. The amount of light absorbed is directly proportional to the concentration of the parameter in the sample. By comparing the sample with known standards, the sample concentration can be calculated.

Hardness is a calculated value based on the calcium and magnesium content and is expressed in terms of CaCO<sub>3</sub>. The formula is as follows:

$$\text{Hardness mg/L as CaCO}_3 = (\text{Ca}^{++} \text{ mg/L} * 2.497) + (\text{Mg}^{++} \text{ mg/L} * 4.116)$$

US-EPA Method: Method 200.7 Rev 4.4, Metals and Trace Elements by ICP/Atomic Emission Spectrometry

<sup>30</sup> (Standard Methods, 20th Ed.)

Method 130.2, Determination of Total Hardness by EDTA Titration

AWWA Methods:<sup>31</sup>

Method 3111 B - Metals by Flame Atomic Absorption Spectrometry - Direct Air-Acetylene Flame Method

Method 3120 B - Metals by Plasma Emission Spectroscopy - Inductively Coupled Plasma (ICP) Method

Method 2340 C – Hardness by EDTA Titrimetric Method

ASTM Methods:<sup>32</sup>

ASTM – D511-93A (1998), Standard Test Method for Calcium and Magnesium in Water by Complexometric Titration

ASTM – D511-93B (1998), Standard Test Method for Calcium and Magnesium in Water by Atomic Absorption Spectrophotometry

## 4.6. pH

PARAMETER	Standard	RDL
PH	6.5 – 8.5	

LSB Method:

E3218 - The Determination of Conductivity, pH, and Alkalinity in Water and Effluents by Potentiometry

Method Principle:

pH, a measurement of the hydrogen ion activity, is defined as the negative logarithm of the hydrogen ion activity, and is expressed in logarithmic units. Hence, it is important to realize that a pH change of one unit constitutes a tenfold change in hydrogen ion concentration. pH is determined using a calibrated potentiometric system consisting of a pH meter and a combination glass electrode with a reference cell. The electromotive force produced in the glass electrode system varies linearly with pH. Analysis requires immersion of the combination electrode in the sample, and recording the reading of the pH meter.

US-EPA Method:

Method 150.1, Determination of pH by Electrometric

AWWA Methods:<sup>33</sup>

Method 4500\_H<sup>+</sup> - pH Value

ASTM Method:<sup>34</sup>

Method D1293-95, Standard Test Methods for pH in Water

## 4.7. Sodium

PARAMETER	Standard mg/L	RDL mg/L
Sodium	20	2

LSB Method:

E3217 - The Determination of Cations in Water, Sewage, Health Samples, Industrial Waste, Leachates and Landfills by Atomic Absorption Spectrophotometry (AAS)

Method Principle:

An automated atomic absorption method is used to measure the concentration of calcium, magnesium, sodium and potassium ions. A microcomputer controls the flow injection

<sup>31</sup> (Standard Methods, 20th Ed.)

<sup>32</sup> Vol. 11.01, 2000

<sup>33</sup> (Standard Methods, 20th Ed.)

<sup>34</sup> Vol. 11.02, 2000

Atomic Absorption Spectrophotometry (AAS) system. Prior to sample aspiration as a fine mist into the air-acetylene flame of the AAS, the sample is automatically mixed with either lanthanum chloride, a releasing agent for calcium and magnesium analysis, or caesium chloride, an ionization suppressant, for the analysis of sodium and potassium. Light is emitted from a hollow cathode lamp and is directed through a flame into a monochromator and onto a detector that is set at a characteristic wavelength for each of the elements (Ca 422.7 nm, Mg 285.2 nm, Na 589.0 nm, K 766.5 nm). The atoms of interest are heated in the flame, and absorb the light at the wavelength specific to the element. The detector measures the decreased intensity of the resulting beam at each wavelength. The amount of light absorbed is directly proportional to the concentration of the element in the sample. By comparing the sample with known standards, the sample concentration can be calculated.

- ES-EPA Method: Method 200.7 Rev 4.4, Metals and Trace Elements by ICP/Atomic Emission Spectrometry
- AWWA Methods:<sup>35</sup> Method 3111 B - Metals by Flame Atomic Absorption Spectrometry - Direct Air-Acetylene Flame Method
- Method 3500 B – Sodium by Flame Emission Photometric Method
- Method 3120 B - Metals by Plasma Emission Spectroscopy - Inductively Coupled Plasma (ICP) Method
- ASTM Methods:<sup>36</sup> ASTM – D4191-93, Standard Test Method for Sodium in Water by Atomic Absorption Spectrophotometry

#### 4.8. Sulphate

PARAMETER	Standard mg/L	RDL mg/L
Sulphate	500	

- LSB Method: E3172 - The Determination of Fluoride and Sulphate in Water, Leachates and Effluents by Automated Ion Chromatography
- Method Principle: Via Ion Chromatography (IC), sulphate is separated from other anions by using columns packed with ion exchange resin, and an eluent solution of sodium carbonate/sodium bicarbonate.
- The sample is injected into the eluent stream and passes through a pre-column (AG-14). The pre-column removes any foreign matter entering the analytical system, which extends the life of the analytical column (AS-14). After separation, the anions are converted to their acid forms by ion exchange using a micro membrane suppressor, and their concentrations are determined from the conductivity of the fluoride produced. A conductivity meter measures the conductivity of each anionic species compared to the water background. Identities of the analytes are determined by their retention times.
- US-EPA Methods: Method 300.0 Rev 2.1, Determination of Inorganic Anions by Ion Chromatography
- Method 300.1 Rev 1.0, Determination of Inorganic Anions in Drinking Water by Ion Chromatography

<sup>35</sup> (Standard Methods, 20th Ed.)

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Method 375.2, Rev. 2.0, Determination of Sulfate by Automated Colorimetry

AWWA Methods:<sup>37</sup>

Method 4500<sub>SO<sub>4</sub><sup>2-</sup></sub> C – Gravimetric Method with Ignition of Residue

Method 4500<sub>SO<sub>4</sub><sup>2-</sup></sub> D - Gravimetric Method with Drying of Residue

Method 4500<sub>SO<sub>4</sub><sup>2-</sup></sub> F – Automated Methylthymol Blue Method

Method 4110 B - Determination of Anions by Ion Chromatography with Chemical Suppression of Eluent Conductivity

ASTM Method:<sup>38</sup>

Method D4327-97, Standard Test Method for Anions in Water by Chemically Suppressed Ion Chromatography

Method D516-90 (1995), Standard Test Method for Sulfate Ion in Water

#### 4.9. Sulphide

PARAMETER	Standard mg/L	RDL mg/L
Sulphide	0.05	

LSB Method:

E3100 - The Determination of Total Sulphide in Water, Sewage and Industrial Wastes by Colourimetry

Method Principle:

This method is used to determine Total Sulphide (S<sup>2-</sup>) which includes hydrogen sulphide H<sub>2</sub>S and HS<sup>-</sup> (both of which will have been precipitated as ZnS during sample preservation), and any acid soluble metal sulphides. The addition of acid to the sample releases the precipitated sulphides as hydrogen sulphide, which is then stripped from the sample by nitrogen gas in a continuous flow system. The hydrogen sulphide is then trapped in an alkaline absorbing solution of sodium carboxymethyl cellulose and cadmium sulphate and reacted with N,N-dimethyl-p-phenylenediamine dihydrochloride and ferric chloride to form methylene blue. The intensity of the methylene blue is measured at 660 nm, and compared to standards treated in the same manner.

US-EPA Methods:

Method 376.2, Determination of Sulfide by Colorimetry, Methylene Blue

AWWA Methods:<sup>39</sup>

Method 4500<sub>S<sup>2-</sup></sub> D – Methylene Blue Method

ASTM Method:<sup>40</sup>

Method D4658-92 (1996), Standard Test Method for Sulfide Ion in Water

#### 4.10. Total Dissolved Solids

PARAMETER	Standard mg/L	RDL mg/L
Total Dissolved Solids	500	

Note: The LSB method dries samples for Total Dissolved Solids at 103 °C. This temperature was included in Standard Methods up to the 15<sup>th</sup> edition (1980), but was discontinued in the 16<sup>th</sup> edition (1985). In subsequent editions of Standard Methods, and in the current edition of ASTM, samples for Total Dissolved Solids are dried at

<sup>37</sup> (Standard Methods, 20th Ed.)

<sup>38</sup> Vol. 11.01, 2000

<sup>39</sup> (Standard Methods, 20th Ed.)

<sup>40</sup> Vol. 11.01, 2000

180°C. Either temperature may be used for Ontario drinking water samples, as long as the laboratory specifies the temperature used.

LSB Method: E3188 - The Determination of Solids in Liquid Matrices by Gravimetry

Method Principle: Dissolved Solids refers to the material (residue, filtrate) which remains in solution when a well-mixed sample is filtered through a 1.5 to 2.0 µm glass fibre filter. An aliquot of the filtrate (50 or 100 mL) is transferred, using a transfer pipette, into a tared dish and evaporated to dryness (20 hours minimum), at 103 ±2°C.

Dissolved Solids is calculated after weighing the dried material (residue) using the following equation:

$$\text{Dissolved Solids (mg/L)} = \frac{(C - D) \times 10^6}{V}$$

where:

C = the weight (g) of the dish plus residue  
 D = the weight (g) of the dish  
 V = the volume (mL) of sample

For drinking water and surface water samples, Dissolved Solids (assuming that the Dissolved Solids arise solely from ionic species in natural Ontario waters and surface waters) may be calculated from the conductivity provided that the **conductivity is less than 800 µS/cm**, using the following calculation:

$$\text{Dissolved Solids (mg/L)} = \text{Conductivity} \times 0.65$$

A calculated result for Total Dissolved Solids is reported with a data qualifier indicating a calculated result.

AWWA Methods:<sup>41</sup> Method 2540 C – Total Dissolved Solids Dried at 180°C

ASTM Method:<sup>42</sup> Method D5907-96a, Standard Test Method for Filterable and Nonfilterable Matter in Water

#### 4.11. Turbidity

PARAMETER	Standard NTU	MDL NTU
Turbidity	1	0.1

LSB Method: E3311 - The Determination of Turbidity in Water by Nephelometry under Robotic Control

Method Principle: To accommodate low turbidity levels, the light scattering of the sample is measured at 90° ±30° using a nephelometer calibrated with Formazin Turbidity Standards. No instrument has been devised which exactly duplicates the results obtained on the Jackson candle turbidimeter for all samples, since there is no direct relationship between Jackson candle turbidity and the light intensity scattered at 90°. However, standards agree at 40 JTU and 40 FTU.

<sup>41</sup> (Standard Methods, 20th Ed.)

<sup>42</sup> Vol. 11.01, 2000

The turbidity test is therefore defined by the instrument and standards used as well as by the optical phenomenon being measured. Results are reported as FTU (Formazin Turbidity Units) rather than JTU (Jackson Turbidity Units). When formazin is used as a standard, FTU are equivalent to NTU (Nephelometric Turbidity Units).

US-EPA Methods: Method 180.1 Rev 2.0, Determination of Turbidity by Nephelometry

AWWA Methods:<sup>43</sup> Method 2130 B - Turbidity Nephelometric Method

ASTM Method:<sup>44</sup> Method D1889-94, Standard Test Method for Turbidity in Water

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<sup>43</sup> (*Standard Methods, 20th Ed.*)

<sup>44</sup> Vol. 11.01, 2000