



# Practices for the Collection and Handling of Drinking Water Samples

Version 2.0

**April 1, 2009**



*Protecting our environment.*





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And Handling of  
Drinking Water Samples**

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**Laboratory Services Branch  
Ministry of the Environment**

**April 1, 2009**

## **Disclaimer**

Although efforts have been made to ensure the accuracy of the information in this guidance document, the Laboratory Services Branch (LaSB) of the Ontario Ministry of the Environment (MOE) does not assume liability for errors that may occur. The mention of trade names or commercial products in this document is for illustration purposes only and does not constitute endorsement or recommendation for use by the MOE.

This document has been produced as a guidance document for MOE staff submitting drinking water samples for analysis to LaSB. Sample container, preservative and holding time requirements are specific to analytical methods used by LaSB.

The sampling techniques may be used as guidance and an example of best practices for treatment plant owners/operators sampling to meet Ontario's environmental regulatory and approval requirements.

Laboratories are recommended to use this document as a guide to the required information they need to provide to their samplers, but should ensure that the sampling information corresponds to the requirements of their analytical methods.

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## **1.0 Introduction**

To ensure the provision of safe drinking water to the citizens of Ontario, regulatory requirements under the Safe Drinking Water Act, 2002 govern the sampling and testing of water provided by municipal and non-municipal communal water systems. The purpose of this document is to provide guidance for the collection, labelling, storage, transportation and chain-of-custody of all drinking water samples that fall under the Drinking Water Systems Regulation (Ontario Regulation 170/03), Transitional – Small Drinking Water Systems (O Reg 318/08), Small Drinking Water Systems (O Reg 319/08), and Schools, Private Schools and Day Nurseries Regulation (O Reg 243/07). Unless specifically indicated, the term “Regulations” will be used throughout the rest of this document to refer collectively to these four Ontario regulations, which may be amended from time to time.

This document is intended to provide sampling guidance for Ministry of the Environment (MOE) Provincial Officers sampling to verify the integrity of a drinking water system’s self-monitoring information or sampling in response to adverse water quality notifications. It also includes the necessary container, preservative, labelling, transportation and holding time requirements for drinking water samples being submitted to the ministry’s Laboratory Services Branch (LaSB) for analysis.

These practices may be used as guidance by treatment plant owners/operators sampling to meet Ontario’s environmental regulatory and approval requirements. Guidance for the sampling of plumbing for lead testing as applicable to O Reg 170/03 and O Reg 243/07 is also provided. The licensed drinking water testing laboratory may also use these procedures as a guide for developing their specific documents for the safe handling and storage of drinking water samples.

These practices provide the minimum level of quality assurance necessary to ensure that the samples analyzed continue to accurately reflect the quality of the raw, treated and distributed water supply. They comprise “front-end” quality assurance activities and are intended to supplement the analytical method quality assurance and control activities already in place. It is recognized that laboratories and drinking water systems may have their own standard operating procedures for the collection and handling of drinking water samples. Where they exist, these procedures must incorporate best practices for ensuring the integrity of the sample.

## **1.1 Limitations**

This document is intended to apply only to grab samples that are collected and transported to a licensed laboratory for the analysis of regulated parameters. Operational checks of the treatment process, which include the continuous in-line monitoring for parameters such as pH, turbidity, chlorine residual and fluoride, are beyond the scope of this document. It is expected that drinking water system operators can apply many of the quality assurance principles discussed here to the collection and analysis of discrete grab samples on-site by the operators for routine, non-regulated “process” parameters such as colour, residual aluminum, fluoride, iron, manganese, alkalinity and pH.

## **1.2 Why Have Standard Sample Collection and Handling Protocols?**

Chain-of-custody records and standard protocols for sample collection, labelling storage and transportation to the laboratory help to ensure the integrity of the analytical data. These protocols are equally applicable to samples taken by drinking water system owners/operators, provincial operators and laboratory staff. Standard protocols and best practices facilitate uniform compliance inspection program delivery throughout the province, and ensure the collection and monitoring of similar information for each sample. Such procedures also help maintain the integrity of the information stored in the provincial Drinking Water Information System (DWIS) database. This corporate database can then be used confidently by other branches of the ministry and other jurisdictions. The data can also be used in the MOE’s Drinking Water Surveillance Program (DWSP) to identify drinking water systems that have specific and unique optimization challenges.

Audit samples, taken to verify a drinking water system’s self-monitoring data and procedures, are more reliable when water system owner/operators and Provincial Officers use standardized sample collection and handling procedures. Accredited and licensed drinking water analytical methods can only produce reliable, high quality data when laboratory and field personnel use sample collection and handling best practices consistently.

## **2.0 Representative Samples and Representative Data**

The water sampling and analysis required by the Regulations are intended to ensure the provision of safe drinking water. Regulations are important components of the safety net established to ensure drinking water safety in Ontario. As such, sampling and analytical activities must be carried out in a manner that produces data that accurately describes and represents the quality of the water in the supply system.

A *representative* sample is one that reflects the same characteristics as, and can be considered an accurate subset of the material being measured. Representative samples taken in a similar manner at the same time and location have an equal probability of yielding the same result. The location, time and method of sample collection must adequately define and isolate the material of interest or concern. For example, when selecting the time and location of distribution system sampling, consideration must be given to peak usage periods and the isolation of the effects of reservoir or elevated tank storage, dead ends in the system, the extremities of the distribution system and residential plumbing, wherever possible. Simply put, the sampler must be cognisant of the conditions that the material sampled represents. Sampling points must be selected to address the intent of monitoring outlined in the Regulations. The choice of sample type (i.e., grab samples, composite samples or continuous in-line sampling) will depend on certain characteristics such as average, maximum or minimum concentrations of a contaminant. As well, the sample type selected must be fit for purpose so that the data gathered meets the monitoring objectives.

The integrity of the target analyte of interest must be maintained by taking steps to ensure that the physical, chemical and biological characteristics of the sample are not compromised. Sample collection and handling procedures are the key steps in ensuring that the sample remains representative. Temperature control and chemical preservation are two measures that may be taken to stabilize a sample after collection. The sample should also be protected from contamination by extraneous materials. Best practices must also be followed for recording sample information, maintaining chain-of-custody, and for sample labelling, transportation and storage procedures. In summary, a drinking water sample arriving at the laboratory must be traceable to its origin, and time and date of collection, and must continue to accurately reflect the concentration of target analyte at the location and time of sampling.

Storage duration is also a consideration; the lag time between sample collection and analysis should be geared towards minimising changes in analyte concentration. Testing must be performed in a manner and by a method with sufficient sensitivity, precision and accuracy to ensure that the result can be used confidently for comparison with the Ontario Drinking Water Quality Standards (ODWQS) (O Reg 169/03). Acceptable methods for drinking water testing are listed in the *Protocol for Accepted Drinking Water Testing Methods*, Version 1, March 17, 2008 (as amended from time to time).

### **3.0 Sampling**

The location and manner in which a sample is collected and handled in the field is the first step to ensuring representative and reliable analytical data. This

document recommends practices that the MOE, the Ontario Clean Water Agency and other leading jurisdictions have found to be the minimum requirements to ensuring a valid sample. However the document is not prescriptive. The sample handler or analyst may incorporate additional quality assurance activities into sampling designs and procedures, which will further improve the certainty of the analytical data. In specific cases, local conditions (geology, industry, etc.) will necessitate additional sampling and analysis over and above that required by regulation. Additional requirements may be listed in an approval issued to the drinking water system via a Certificate of Approval (C of A), licence, permit, an order (including an Ontario Water Resources Act order) or another directive. Best practices should also be followed for all samples collected to comply with approval and other control document requirements.

### **3.1 Sample Type**

In most environmental sampling situations, two types of samples are generally considered: *composite* samples and *grab* samples.

*Composite* samples are most appropriate in situations where the sampler is seeking to obtain information on the average value of a system in which a high degree of variability in the characteristics of the system or process being sampled is expected over time. An example of such a system is an industrial waste stream.

*Grab* samples consist of either a discrete sample or a series of samples collected over a period of time, generally not exceeding a total time period of 15 minutes. Grab samples represent the characteristics of the water sampled at a particular point in time. Sampling at the same point at a given frequency will allow the identification of trends through time and can provide a measure of variability over the long term. Grab sampling methods are used to fulfil the requirements of the Regulations. Sampling discussions in this document are restricted to grab samples. In addition to grab samples, the monitoring of treatment efficiency and effectiveness at large water treatment facilities requires continuous process control. This is achieved through the continuous measurement of the effectiveness of the coagulation/sedimentation/filtration and disinfection processes by in-line measurements of parameters such as total and free chlorine residual and turbidity. Best practices related to these types of sampling and analysis is beyond the scope of this document.

### **3.2 Sampling Design**

Environmental sampling strategies and designs generally fall into two groups: *directive* or *probabilistic*. Directive sampling strategies are based on instructions that are laid out in regulations, permits, approvals and other authorising

documents. This approach is used when there is an understanding of the system and its anticipated characteristics. In this situation, legislation or control documents are used to specify sampling locations and frequency of sampling. Sampling as required by the Drinking Water Systems Regulation (O Reg 170/03) is an example of directive sampling.

A *probabilistic* approach would be used in environmental investigations designed to determine the source and/or extent of possible contamination of an area. This approach relies on field experience, historical documentation and knowledge of the behaviour of the contaminant under specific environmental conditions.

### **3.3 Sampling Location**

The O Reg 170/03 requires the collection and testing of raw water, treated water and distribution system samples. The sampling locations must be carefully chosen to ensure that a sample accurately represents the quality of the water being sampled. As per the *Terms of Reference: Engineer's Report for Waterworks* (January 2001), the Engineer is responsible for recommending a site-specific monitoring program for the supply/treatment/storage works and the distribution system, in accordance with the ODWQS and O Reg 170/03.

The Schools, Private Schools and Day Nurseries (O Reg 243/07) regulation has specified the sampling points, sampling procedures and minimum frequency of sampling. Operators/owners of these facilities should check the current version of this regulation for any changes to sampling instructions.

The sampling points selected by a MOE Provincial Officer for collecting an audit sample should take into consideration the sampling points used by the facility owner/operator.

#### **3.3.1 Raw Water**

Raw water refers to the source water for the water supply system. Its characterization is necessary to decide on treatment requirements. Changes to the temperature, pH, alkalinity, colour, turbidity and biological quality of the source water will affect the efficiency of, and may necessitate alterations to, the treatment process. Raw water monitoring for microbiological contamination is required under O Reg 170/03 for certain types of systems. The current version of the regulation should be consulted to determine the requirements for a specific system. Raw water characterization with respect to all parameters listed in the ODWQS and O Reg 170/03 may be required in the preparation of an Engineering Evaluation Report (New or Altered System).

All raw water samples should be collected prior to any treatment process. For groundwater systems using more than one well supply, grab samples for microbiological testing are required from each well on the system. If many wells are used and the water is blended at or before the high lift pumps, samples of the raw water from each well before blending should be taken. Sample collection assumes the availability of in-line plumbing, including the presence of a tap prior to any treatment process. If this is not the case, it may be necessary to shut down the pump and open the sanitary seal. Ideally, samples should be collected from a tap located as close as possible to the well. Usually a tap in the pump house is used. Sometimes a continuously running tap is present and provides a fresh representative sample of the raw water. The waste from the tap, however, should not be allowed to drain back into the well. The raw water sample must be taken preferably before the water enters any storage/pressure tank and definitely before any treatment. If samples are taken after storage units, the unit should be purged to allow a complete exchange of water. If samples are taken before a storage unit, taps located after the storage tank should be opened to prevent back flow from the storage unit. If it is necessary to turn off the disinfection system to obtain a raw water sample, the resulting water must be wasted and not allowed to enter the distribution system.

In surface water systems, it can be difficult to collect samples at an intake that is located at a great distance from shore. Near shore samples are not recommended as they are subject to increased turbidity, algal blooms and bacteria and do not accurately represent the water quality at the intake. Moreover, high, intermediate and low level intakes mean that different levels in the water body can be used for treatment simultaneously or during different periods of the year. For these reasons, samples are generally taken after screening, pre-sedimentation, wet well storage and low lift pumping to the treatment facility. These samples will reflect any changes in source water quality resulting from these activities. To adequately characterize the raw water source it is recommended to take the sample prior to any aeration/oxidation and pre-chlorination which is performed. At some locations, however, it is necessary to pre-chlorinate at the intake for zebra mussel control. During certain months of the year it may not be possible to sample unchlorinated raw water at these locations. In these cases, the installation of a separate intake line with tap at the plant is advised to allow the collection of samples that have not received treatment. If multiple surface source waters or a blend of ground and surface sources are used, each raw water source should be sampled separately prior to blending.

### **3.3.2 Treated Water**

Treated water refers to all water which has undergone one or more treatment processes such as chemically assisted filtration, iron and manganese sequestering,

primary disinfection, corrosion control, softening, fluoridation, etc. Treated water sampling locations must be selected to ensure that the samples represent the treated water after all treatment processes are complete. The sampling location must be at the point of entry of the water to the distribution system, after the minimum disinfection contact time and before the first consumer. Samples must be taken prior to standpipe, elevated tank or reservoir storage.

### **3.3.3 Distribution System Water**

The term distribution system refers to the entire network of storage tanks, reservoirs, standpipes, pumping stations, pumps, valves, metres and service pipes that deliver the treated water leaving the drinking water system to consumers. Sampling of the distribution system is mandatory under the Drinking Water Systems regulation (O Reg 170/03) and the Transitional – Small Drinking Water System regulation (O Reg 318/08). The required number of samples collected depends on the size of the population served. The selected sampling locations should be points significantly beyond the point of entry to the distribution system. These locations should represent and cover the distribution system, especially locations where the degradation of water quality and disinfection residual are possible and the formation of disinfection by-products is likely. Sampling locations should address elevated storage tanks within the distribution grid, dead ends, ageing water mains, distribution loops, points with the potential for cross connection/back flow and extremities of the distribution system. In some cases, secondary disinfection is delivered in the distribution system (i.e., at a chlorine booster station). Samples should also be collected immediately after this secondary disinfection is delivered.

The objective is to measure the quality of water being supplied to the consumer. Whenever possible, samples should be taken at dedicated sampling stations within the distribution system. These stations should eliminate the effects of residential plumbing. If residences are used, cold water taps where drinking water is consumed should be sampled to eliminate the effects of deposits in the hot water tank. Samples must be taken prior to water softeners or other home-treatment devices, and should preferably be taken from taps located on a service pipe connected directly to the water main. Local plumbing problems such as line-breaches or illegal connection to cisterns that allow the entry of water that has not been disinfected into the system must be avoided. Sample taps that are used infrequently should be avoided as localized microbial growth and mineral crusts within the plumbing fixtures may affect the sample. Similarly, lines in which water pressure is not constant should be avoided because temporary changes in line pressure may break up and suspend biological growth and metal crusts that may be attached to walls of the lines. Leaking taps and taps where water tends to run up the side of the lip of the faucet should not be used.

### **3.3.4 Plumbing**

The term plumbing refers to the pipes and fixtures that distribute water within a building. Plumbing is considered to begin at the property line, where it is connected to the service pipe, which in turn is connected to the distribution system described in section 3.3.3. “Lead plumbing” and “lead service pipes” are defined as plumbing and service pipes with a lead content greater than eight percent. These types of plumbing and pipes are normally found only in areas constructed prior to the mid-1950s. Solder is the material used to connect pieces of plumbing. “Lead solder” means solder with a lead content greater than 0.2 per cent and was permitted for use on drinking water lines prior to January 1, 1990. Sampling points within the plumbing are specified within O Reg 170/03 and 243/07.

### **3.4 Sample Containers**

Sampling containers are usually provided by the laboratory that is conducting the testing. Generally, plastic or glass containers are recommended for inorganic and microbiological tests but most tests for organic compounds require glass bottles. Exceptions to the use of glass for organic compounds may include tests for the measurement of diquat, paraquat and glyphosate. If in doubt, the sample should be collected in a glass container. Amber glass containers are recommended for organic compounds that are light-sensitive. If this is not possible, the container should be wrapped in aluminum foil or kept stored in a light-proof case.

Certain tests have specific volume and container-cleaning requirements. Microbiology tests require sterile containers and many organic tests require 1-litre sample volumes. Other methods, such as one used for the measurement of volatile organic compounds, accommodate analysis directly from the sampling container. For these methods, the laboratory may recommend vials with Teflon™ septum caps. A summary of the MOE LaSB sampling containers and volume requirements for each regulated parameter analyzed by LaSB is provided in Table 1. Further information on containers is provided in the section entitled Sample Collection. It is very important to use the sampling container recommended by the laboratory conducting the testing.

### **3.5 Sample Collection**

The collection and handling of samples is crucial to obtaining valid data. Person(s) collecting regulatory samples should be properly trained, with respect to sample handling considerations, including aseptic procedures for the collection of samples for microbiological testing. Disposable gloves may be worn and care must be taken that the inside of the container and cap do not come into contact with anything other than the atmosphere. If the inside of the sampling container is touched, it

must be considered contaminated and should not be used. While the sample is being taken, the exterior of the cap should be held in the sampler's fingertips.

The collection of drinking water grab samples is generally done from taps located at the sampling points. Sampling taps should be free of aerators, hose attachments, strainers and mixing type faucets. The best method for collecting a grab sample is to collect the sample directly into the container provided by the laboratory. This eliminates the potential for sample contamination through the use of an intermediate container. This is especially important for analytes that are usually present in trace amounts (e.g., some metals, pesticides, dioxins/furans, etc.).

In some situations, such as when taps do not have enough clearance from the floor, it is not possible to collect the sample directly into the laboratory container. In these cases, it may be necessary to collect the sample in an intermediate vessel and subsequently transfer the sample to the laboratory container. Information on types and pre-cleaning methods for intermediate vessels is provided in the section, Intermediate Sampling Containers. Metal and plastic sampling equipment, other than tubing and the plumbing in place, should not come into contact with the collected samples. Teflon™ or stainless steel tubing is recommended for permanent sampling installations. **In the case of sampling for microbiological testing, phenols, sulphide, volatile organic compounds, hydrocarbons, and oil and grease (not regulated), the sample must always be collected directly into the laboratory sample container.**

Samplers should take care to avoid inadvertently contaminating the sample with the target analyte. This can occur in instances where the sample comes into contact with an unsuitable preservative that is not required to stabilize the analyte in the sample. Common examples include: potassium dichromate preservative causing chromium contamination in samples taken for metals analysis; residual nitric acid preservative on hands or gloves causing contamination in samples taken for nitrate analysis; or sodium thiosulphate preservative causing sodium contamination in samples taken for cation measurements.

Some sample containers are pre-charged with preservative; field personnel must not rinse these containers prior to sample collection. Also, sample containers for organic compound analysis should never be rinsed with the sample, as the organic compounds from the rinse may accumulate on the container walls and compromise the accuracy of the analytical results. Sample containers should be filled slowly to prevent overflowing when containers have been pre-charged with preservative, and to eliminate bubble formation. Specific sampling information for each regulated parameter in O Reg 170/03 or the ODWQS, when submitted for analysis

to LaSB, is provided in Table 1. This table is based on the MOE's practices and methods and can be used as a guide for other laboratories when providing information to their samplers.

The protocol for sample collection at communal wells sometimes requires purging of the well to achieve a stable pH and turbidity measurement, before sample collection. Purging is not required for communal wells in which the pump runs continually and where in-line plumbing is present. For these wells, flushing the lines for a minimum of two minutes prior to sample collection is sufficient. However, communal wells that are not currently used or that are used intermittently should be purged by flushing the lines with a volume of water equivalent to three to five times the volume of water standing in the well. (The volume will depend on the static level and the inside diameter of the well casing). For pumps that are operated intermittently, the purge volume must be calculated with respect to length of use and the size of storage/pressure tanks. If storage tanks are present, an adequate volume must be purged to ensure that the volume of water in the tank is completely exchanged.

In terms of chemistry, the United States Environmental Protection Agency (US EPA) recommends purging a well until pH and turbidity measurements stabilise and turbidity is less than 10 nephelometric turbidity units (NTU). For new, recently installed wells, purging is necessary to eliminate the effects of well installation. This document assumes that in-place plumbing and dedicated pumps can be used to facilitate purging. When this is not the case purging must be done with peristaltic, centrifugal or submersible pumps or with bailers. Discussion of these techniques and precautions for using these techniques is beyond the scope of this document and the reader is referred to reference #8 listed at the end of this document.

Samples in distribution systems must always be taken from a cold water tap. The lines should be flushed prior to sample collection to negate the effects of local residential plumbing. As a general practice, this can be achieved by flushing the system until the water reaches a constant temperature (usually between two and five minutes).

### **3.6 Specialized Sampling Techniques**

While sampling information based on MOE's methods of analysis is presented in Table 1, specialised sampling techniques for particular tests warrant further discussion.

### **3.6.1 Volatile Organic Compounds (VOCs)**

Volatile organic compounds are, as their name suggests, volatile and are easily vaporized from the sample. For this reason, some methods allow for sample collection in vials with septum (hole) screw caps, with Teflon™-lined silicone discs which can be placed directly in the auto-sampler of the analytical instrument. This eliminates the sample transfer step, which could induce a loss of volatile compounds to the atmosphere. If vials are not available, a glass bottle may be substituted provided that correct sampling techniques are used.

Samples should be collected in duplicate. Some laboratories may require triplicate samples. Laboratories may also recommend the use of a travelling blank that is opened at the sampling location for the duration of the sampling period, then closed and returned to the laboratory with the samples. The laboratory will provide direction on the collection of replicate samples and the use of travelling blanks (may also be called field blanks). Chlorinated water samples submitted to LaSB require a preservative to quench the reaction of sample analytes with any surplus chlorine, and thus keep the sample representative of the system at the time the sample was taken. The vials may be pre-charged with a sodium thiosulphate pellet or powder. If the containers are not pre-charged with sodium thiosulphate, two drops of 25% weight/volume sodium thiosulphate per 50 mL of sample should be added to the container first.

Aerators and strainers must be removed from taps during sample collection, and the water should be running slowly to prevent splashing. Extreme caution must be taken to eliminate turbulence. The vials or bottles should be filled slowly to the top rim of the container so that a dome or convex meniscus is present. A slight loss of sample may occur when the cap is applied. When capped, the cap or septum should be in contact with the sample so that no air is trapped in the sample container and when the vial or bottle is turned upside down no air bubble is present. The Teflon™ liner, not the silicone or rubber backing of the septum, must be in contact with the sample.

When raw water is collected for VOC analysis at LaSB, an alternate preservative is required to halt bacterial activity. Vials may be pre-charged with a 0.2 g sodium bisulfate monohydrate pellet, which will lower the pH and halt microbial activity. This will extend the holding time of the sample from 7 to 14 days.

### **3.6.2 Microbiological**

Aseptic techniques must be followed when handling the sterile sample bottles used for microbiological sample collection. Failure to do so will compromise the results. Aerators, hose attachments, filters and strainers may harbour bacteria and should be removed from taps when sampling for microbiological parameters.

There must be a clear pathway from the distribution line to the sample collection container.

Cold water taps must be used, as water stored in hot water heaters is exposed to environmental conditions not representative of the water being supplied by the drinking water system. The lines must be flushed prior to sampling. When sampling distribution system taps, it is advisable not to sample from an unprotected outside tap. Samplers should be aware that if raw surface water samples are taken from the near shore area instead of at the intake location, or if samples have been pre-chlorinated, the analytical results will not reflect the true bacteria count present at the raw water intake.

As it is especially important that the sterile bottles remain closed until the time of sampling, it is recommended that sample bottles for microbiological testing have caps with tamper-proof seals. If the seal is broken the bottle should be discarded. Appropriate care should be taken to ensure that only the outer surface of the cap and the bottle is touched/handled. The inside of the cap should not be allowed to come into contact with anything other than the atmosphere and the sample. After the sample is taken the bottle should be recapped immediately. When filling the bottle, the sampler should hold the bottle near the base and fill to the fill line on the label of the bottle (if indicated) or the shoulder of the bottle. The bottle should not be rinsed before taking the sample, as it is pre-charged with sodium thiosulphate. At least 120 mL of sample must be collected in containers submitted to LaSB. Sufficient headspace must be left in the bottle to allow for shaking before analysis. To prevent further bacterial growth in the sample after it has been collected, the sample should be refrigerated and transported to the laboratory on ice. Further detail is provided in the section Sample Storage and Transportation.

### **3.6.3 Dioxins/Furans**

Analysis for dioxins and furans involves ultra-trace analytical techniques and care must be taken not to contaminate sample containers. Samples must be collected in duplicate in 1-litre amber glass bottles with Teflon<sup>TM</sup>-lined caps. A duplicate travelling blank is required for each submission. Traveling blanks are prepared using high performance liquid chromatography (HPLC)-grade water or equivalent, provided by the laboratory doing the analytical testing. At the sampling location, the sampler must open the travelling blank bottles and transfer the HPLC-grade water from the supplier's container to the individual sample bottles and label them appropriately. The travelling blank bottles are left open while the drinking water samples are collected.

### **3.6.4 Lead in Plumbing**

Sampling for lead in plumbing, either for O Reg 170/03 or from facilities under O Reg 243/07, Schools, Private Schools and Day Nurseries have different requirements than for a routine metals scan under O Reg 170/03. Two, 1-litre samples are to be collected to reflect the cumulative effects of the plumbing system. Section 5 of O Reg. 243/07 and Schedules 15.1 and 15.2 of O Reg 170/03 specify the sampling locations within the building that are being tested, including the tap(s), the time of flushing before collecting the sample(s), the time between samples and the frequency of sampling. For these samples, if there is an aerator on the tap, it is left in place, unlike samples collected for other tests. A separate guidance document, *Flushing and Testing for Lead in Drinking Water* (reference #12) has been prepared to describe the specific steps to collect samples to test for lead in plumbing. Owners/operators should also consult the most recent version of the Regulations for any modifications to the frequency, locations and/or procedures for collecting these samples.

In all cases, a total volume of one litre must be collected for each required sample. A single container is preferred, but if a 1-litre container is not available, multiple containers can be used, but the time switching containers must be kept to a minimum. The laboratory receiving the samples for analysis must be notified if multiple containers were used to obtain the one litre of sample, as the laboratory must combine all of the containers prior to taking an aliquot for analysis.

### **3.6.5 Oil and Grease (Immiscible Liquids)**

Routine sampling for oil and grease are not required under O Reg 170/03 or in the approvals for drinking water systems. It is mentioned here, however, because there are often occasions when problems warrant sampling for oil and grease (e.g., spills in surface waters close to water supply intakes). Oil and grease will float on top of the water body or well and the sampler must take great care to ensure that the sample adequately addresses the presence of immiscible liquids. The best practice is to choose a sampling location in the area of greatest mixing to ensure that a representative sample is collected. The sample container should not be rinsed, as the hydrophobic nature of the oil and grease will cause it to coat the inside of the sampling container resulting in inflated results which are not representative of the water sampled.

### **3.7 Intermediate Sampling Equipment**

Although not recommended, the use of an intermediate sampling vessel is sometimes necessary. If an intermediate sampling container is used, it is best to contact the laboratory ahead of time for direction on the suitability of the container. In general, the preparation of sampling vessels should include hot

water, phosphate-free detergent and thorough rinsing with analyte-free (e.g., distilled) water. When sampling for organic compounds, an additional step of solvent rinsing should be incorporated into the cleaning regime (the laboratory will advise on the choice of solvent). A glass or stainless steel vessel is recommended for intermediate sampling to ensure that all tests (organic and inorganic) can be performed. If funnels or tubing are required, Teflon™ or stainless steel should be used, as these materials offer low friction surfaces that do not readily adsorb contaminants from water.

While it is recognized that pumps (e.g., well pumps, high and low lift pumps) form an integral part of a water system, it is recommended that auxiliary sampling pumps be avoided as they contain brass, plastic, rubber and other materials that can contaminate samples. Moreover, they contain pump oil that can sometimes infiltrate into the sample. This is an important consideration for trace organic compounds and metals analysis. If auxiliary sampling pumps must be used, the reader is recommended to consult reference #8 listed at the end of this document.

### **3.8 Sample Filtering**

Drinking water samples shall not be filtered in the field or at the laboratory prior to analysis. As it is not expected that the consumer filters their water prior to drinking it, unfiltered samples will provide a more representative sample of what the consumer is drinking. Unfiltered samples for the measurement of organic compounds and microbiological parameters are very important because many organic compounds adsorb to the particulate present in a water sample and membrane filtering will remove bacteria from the sample. Filtering is not permitted in order to compensate for poor sampling technique or the use of inappropriate methods of analysis.

### **3.9 Sample Preservation**

Preservation may be required to stabilize the analyte of interest in the sample prior to its transportation to the laboratory. The main types of preservation for drinking water samples are refrigeration and pH control. Sample preservation requirements for the MOE LaSB's methods of analysis for regulated parameters are presented in Table 1.

Containers that have been pre-charged with preservative should not be rinsed or allowed to overflow or the preservative will be diluted. When strong acid or alkali is used to preserve a sample taken in plastic sampling containers, the preservative must be added after taking the sample. If the strong acid/alkali is added first, it may corrode the plastic container releasing contaminants to the

sample. This is an important consideration in the preservation of samples with concentrated strong acid for trace metals analysis.

Preservatives should be stored separately to avoid cross contamination between preservatives, as this could result in inflated results for target analytes. An example of this is the contamination of nitric acid preservative by potassium dichromate preservative. When this occurs, the sample taken for metals analysis may show inflated results for chromium.

When preservatives are added to obtain a specific pH range, the sample should be swirled gently and left to equilibrate for two minutes. The pH should be checked with pH paper to ensure that the desired pH is reached. Different types of waters have different capacities for buffering (resisting a change in pH). The amount of preservative recommended in Table 1 is based on the majority of samples and should be used as a guide. It is recommended that the volume of preservative not exceed 1% of the sample. If this occurs, a note to this effect should be made on the sampling container label.

Refrigeration is also a form of preservation and is important to minimize chemical reactions and microbial growth in a sample. However, freezing a sample is not acceptable for some tests. In the case of microbiological testing, samples cannot be analyzed if they have been frozen. It is very important that samples for these tests are shipped to the laboratory as soon as possible after collection.

### **3.10 Sample Holding Times**

For certain tests, the sample must be received at the laboratory and analyzed within a short period of time. Examples of perishable parameters include turbidity, microbiological contaminants, volatile organic compounds and N-nitrosodimethylamine (NDMA). Table 1 lists suggested holding times for parameters listed in Schedules 1 and 2 of the ODWQS, as well as parameters sometimes identified in approvals, control orders or other directives issued by the MOE. Holding time is defined as the time between the collection of the sample and the start of analysis. For some tests, the sample may be stabilized by the first analytical process such as an extraction step. The extract may then be stored prior to instrumental analysis. These holding times are based on MOE's methods of analysis.

Preservation stabilizes the sample to differing degrees. For example, in the case of metals, preservation may extend the allowable storage time to weeks or even months. However, some reactions (e.g., changes in nitrogenous compounds) continue unabated and preservation to prevent these reactions without compromising the sample is not possible. Consequently, refrigeration and

transportation of all drinking water samples to the laboratory immediately after collection is encouraged to ensure that samples may be analyzed within the appropriate time frames.

### **3.11 Sample Labelling**

Accurate and complete labelling of samples ensures that the sample's identity is maintained. This is very important for sample tracking and data interpretation and is mandatory for sample data reporting and adverse water quality notification requirements under the Regulations. It is advisable to pre-label all sample containers prior to taking the sample or to label each container **immediately** after the sample is taken to prevent confusion. An indelible (permanent) marker or pen should be used and the material from which the label is comprised should be able to withstand water. In most cases, the laboratory conducting the analysis will supply the sampling container. Sample containers may have labels affixed to the container itself; alternatively the label or sample tag may be provided separately and attached to the container after the sample is collected. If the tags/labels are separate, the sampler should attach them prior to or immediately after taking the sample to prevent incorrect labelling.

When sample tags/labels are separate, a pre-printed sample identification number/code on the label may be available. This assigns a unique identification number/code to the sample in the field. If a pre-printed sample number is not assigned, it may be necessary for the sampler to create a field sample number. The sample ID generated should be simple and unique to the sampling set/batch collected. The following information should be recorded on either the sample label or on an accompanying sample information sheet.

1. Marking to indicate that this is a *regulated drinking water sample*.
2. Sample type: raw, treated or distribution
3. A unique sample identifier
4. The legal name of the water system (available in DWIS).
5. The waterworks number, if applicable
6. O Reg 243/07 facility registration number, if applicable (this is different than #5 and must be used for reporting lead exceedances)
7. The date and time of sample collection (critical for perishable tests)
8. The street address, if the sample is a distribution sample
9. Preservative(s) used
10. Pertinent field measurements (chlorine residual, turbidity, pH) (if room on the label/tag permits)
11. The initials of the sampler.

Much of this information can be put on the labels/tags in advance of sampling, either by the laboratory or the sampler. Pre-printed labels with the drinking

water system name, number, sample type, etc., are convenient, provide the necessary information for the lab analyst and help prevent mix-ups in labelling. In some cases sample tags used by laboratories have space to write the test requests. In other cases, a separate sample information sheet is used for this purpose and submitted to the laboratory with the samples.

If a separate sheet is used, some of the information need only be recorded on the sample information sheet. However, the sampler must ensure that information provided on the information sheet corresponds to information recorded on the sample bottle so that the laboratory staff can quickly match the information with the appropriate sample. The recorded sheet must also have the sampler's signature to fulfil chain-of-custody requirements (see Section 4). Correctly recording the sample identification is especially critical in the face of human health implications and in the event that a sample must be traceable for litigation purposes. Correct sample identification is also the key to ensuring the accurate reporting of adverse water quality results for regulatory purposes.

The rapid identification of samples at the laboratory helps to ensure that samples are analyzed promptly and that adverse water quality in treated and distribution drinking water samples are immediately reported. The MOE-LaSB affixes green labels bearing the words *Drinking Water Regulation Sample* to facilitate this rapid sample recognition. Laboratories testing drinking water samples may implement a similar system in place to quickly cull these samples.

### **3.12 Sample Storage and Transportation**

It is recommended that all samples be delivered to the laboratory as soon as possible after sampling. Samples should be kept cool (refrigerated) if immediate shipping is not possible. Samples should be packaged to avoid breakage during shipping. Samples must be shipped to arrive at the laboratory before the holding time for the samples has expired.

Samples for microbiological testing should be packed with ice packs or a suitable leak-proof container of ice and shipped in insulated boxes/coolers. Packing the sample with loose ice is not recommended as it may contaminate the sample. The ice should be encased in waterproof packaging or a sealed container. If possible, the sample should be chilled to below 10°C, but not frozen, prior to packing. Optimal temperatures conditions during transport are less than 10°C. The inclusion of maximum/minimum thermometers beside the sample(s) during shipment may provide further information on sample conditions during transport and may help to validate the integrity of the sample.

Although samples must be cool, it is important to ensure that samples for microbiological testing do not freeze during shipment. Some courier companies offer shipping in heated vehicles during the winter months.

The sample container should be sealed for shipping. Doing so will help make obvious any evidence of tampering. This may simply involve the use of a label or similar item that must be torn to open the box/case. The sample information sheet, if used, and the chain-of-custody record must be included in the shipping box/case. A written record of how the samples are shipped, the time, date, carrier and tracking numbers for the shipments should be kept by the sampler.

The laboratory generally provides instructions for sample delivery to the laboratory. If samples are shipped directly by bus, train or air without the use of a courier, the sampler should notify the laboratory and provide flight/bus numbers, expected arrival times, way bill numbers, etc. to ensure that the laboratory arranges sample pick-up from the airport or bus/train terminal.

Sample storage conditions at the laboratory should be secure and should inhibit sample degradation or chemical/biological changes to target analytes prior to analysis.

#### **4.0 Chain-of-Custody**

As previously mentioned, proper sample labelling is crucial to maintaining the identity of a sample. However, additional measures are then required to ensure a sample is traceable from the time of collection through to its analysis. These steps are referred to as a *chain-of-custody* and are used to ensure the integrity of the sample and resulting data. A sample or set of samples is considered to be “in custody” if it is in a custodian’s physical possession or view, if it was in the custodian’s physical possession and was then secured to prevent tampering, or if it is placed in a secured area. When samples are taken for litigation purposes, a chain-of-custody form provides an accurate written record that can be used to trace the possession, transfer and custody of a sample from the time of its collection through to its introduction into the analytical data set. Each person involved in the chain of possession must sign the custody form when a sample or set of samples is received or relinquished.

In the case of drinking water samples, a chain-of-custody form must accompany samples to the point of receipt by the laboratory. The intent of this form is to document the transfer of custody of the samples from the sample custodian (sampler) to any other person and to the laboratory. It is recommended that the fewest number of people as possible be responsible for sample collection and transfer to the laboratory. If common carriers are used, receipts should be kept

and, if packages are mailed, they should be registered and return receipts requested. These should be kept as part of the chain-of-custody documentation.

Once the samples have arrived at the laboratory, the chain-of-custody form must be signed off by an authorized person at the laboratory receiving the samples. The custodian should note either on the chain-of-custody form or on the sample information sheet provided with the samples, any samples that arrive in a condition unsuitable for analysis (e.g., broken, improperly preserved). This includes checking sampling dates recorded on containers and information sheets to make certain that holding times for the tests requested have not been exceeded. Samplers should be notified immediately of samples that cannot be analyzed so that a second sample can be taken. The laboratory staff should record the time and date that the sampler was contacted. It is not necessary that the chain-of-custody document accompany routine (non-litigation) drinking water samples to each analytical department as long as an electronic or hardcopy record of sample routing within the laboratory is maintained. This will ensure a traceable chain of possession.

Laboratory staff must check that the information provided on the sample container tag/label matches information recorded on other sample information sheets and/or chain-of-custody documents. Samples should be handled and managed within a secure environment. Temporary sample storage must be in a place that is clean, dry, lockable and environmentally-controlled to prevent analyte degradation prior to analysis. A record must be made of the date of analysis and the name of the analyst. The sample must be in the analyst's possession or view, or secured in an area accessible only to authorized personnel at all times while in the laboratory.

Samples may be discarded when sample holding times have expired, if the sample has deteriorated for other reasons or is exhausted, if the results have been approved and released to the customer or if it is certain that no further information is required (e.g., repeat analysis). Records of sample destruction should be kept.

## **5.0 Summary**

Continual verification that safe drinking water is supplied to the public can only be done when monitoring locations adequately represent all aspects of the water supply and samples taken accurately reflect the physical, chemical and biological attributes of the water sampled. Meeting both of the above conditions will result in the early detection and rapid resolution of water quality problems. The intent is for these recommended practices to be accompanied by analytical methods that are appropriate and fit for the purpose of analysing drinking water samples. The

reader is referred to the Drinking Water Testing Services Regulation (O Reg 248/03), and the companion document a *Protocol of Accepted Drinking Water Testing Methods*, Laboratory Services Branch, Ministry of the Environment, Version 1, March 17, 2008 (as amended from time to time) for further information regarding suitability of methods of analysis.

It is the duty of both the sampler and the laboratory to ensure the implementation and continued use of best practices and accepted testing methods for the collection and analysis of drinking water samples. The quality of the data produced can only be as good as the poorest level of quality assurance in the entire process of sampling and analysis.

## **6.0 References**

1. Ontario Ministry of the Environment (1993) *A Guide to the Collection and Submission of Samples for Laboratory Analysis*, Customer Services Unit, Laboratory Services Branch, December 1993.
2. Ontario Ministry of the Environment (2001). *Laboratory Services Guide to the Submission of Samples for Laboratory Analysis*.
3. Ontario Ministry of the Environment, Laboratory Services Branch. *Protocol of Accepted Drinking Water Testing Methods*. Version 1, March 17, 2008, (as amended from time to time).
4. Ontario Regulation 170/03, *Drinking Water Systems*, made under the Safe Drinking Water Act, S.O. 2002, Chapter 32.
5. Ontario Regulation 169/03, *Drinking Water Quality Standards*, made under the Safe Drinking Water Act, S.O. 2002, Chapter 32.
6. Ontario Regulation 248/03, *Drinking Water Testing Services*, made under the Safe Drinking Water Act, S.O. 2002, Chapter 32.
7. United States Environmental Protection Agency (1997). *Manual for the Certification of Laboratories Analyzing Drinking Water – Criteria and Procedures Quality Assurance*. Office of Ground Water and Drinking Water, Cincinnati, OH. EPA 815-B-97-001.
8. United States Environmental Protection Agency (1996) (includes 1997 revisions). *Environmental Investigations Standard Operating Procedures and Quality Assurance Manual*. U.S. Environmental Protection Agency, Athens, Georgia.

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9. Ontario Clean Water Agency (2003). Standard Operating Procedures, (microbiological sampling and general chemistry sampling).
10. Ontario Regulation 318/08, Transitional – Small Drinking Water Systems, made under the Health Protection and Promotion Act, R.S.O. 1990, Chapter H.7.
11. Ontario Regulation 243/07, Schools, Private Schools and Day Nurseries, made under the Safe Drinking Water Act, S.O. 2002, Chapter 32.
12. Ontario Ministry of the Environment (2007), *Flushing and Testing for Lead in Drinking Water*, PIBS 6530e, November 2007.
13. Ontario Regulation 319/08, Small Drinking Water Systems, made under the Health Protection and Promotion Act, R.S.O. 1990, Chapter H.7.

**TABLE 1. Sample Requirements for Ministry of the Environment Laboratory Services Branch Test Methods for Drinking Water Samples**

Note: The information provided in this table applies to analytical methods used by the Laboratory Services Branch (LaSB) and are valid at the time that this document is published. LaSB may amend these requirements from time to time and LaSB customers are notified. Laboratories that use other analytical methods from the *Protocol of Accepted Drinking Water Testing Methods* may have alternate sample specifications.

Parameter/Test Group	Sample Container	Minimum Volume	Preservative	Maximum Holding Time	Storage Conditions	Comments
Total Coliforms	Glass or plastic, sterile	250 mL	30 mg sodium thiosulphate	48 hours	4°C ± 3°C	Transport chilled, not frozen
<i>Escherichia coli</i> ( <i>E. coli</i> )	Glass or plastic, sterile	250 mL	30 mg sodium thiosulphate	48 hours	4°C ± 3°C	Transport chilled, not frozen
Heterotrophic plate count** or total coliform background count** by membrane filtration	Glass or plastic, sterile	250 mL	30 mg sodium thiosulphate	48 hours	4°C ± 3°C	Transport chilled, not frozen

\*\* Revoked from O Reg 169/03 by O Reg 248/06 but is part of operational testing and may be included in a site-specific C of A



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Parameter/Test Group	Sample Container	Minimum Volume	Preservative	Maximum Holding Time	Storage Conditions	Comments
<b>Metals (except mercury)</b> Aluminum* Antimony Arsenic Selenium Barium Boron Cadmium Chromium Copper* Iron* Lead Manganese* Selenium Uranium Zinc  * not part of O Reg 169/03 but may be part of a C of A	Plastic (PET) or High density polyethylene (HDPE)	100 mL	Nitric acid to pH < 2 done immediately upon collection or as soon as possible.  Samples may be preserved at the laboratory up to 14 days after collection.  Do NOT add acid to the container prior to sample collection.	60 days  Samples that are preserved at the laboratory must be held for 24 hours before analysis begins.	Room temperature for preserved samples	Bottles with aluminum-lined caps are unacceptable. Results should be flagged if the sample is preserved at the laboratory.

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Parameter/Test Group	Sample Container	Minimum Volume	Preservative	Maximum Holding Time	Storage Conditions	Comments
Lead in plumbing	Plastic (PET) or HDPE	1 L	Nitric acid to pH < 2 done immediately upon collection or as soon as possible.  Samples for Lead in Plumbing may be preserved at the laboratory up to 14 days after collection.  Do NOT add acid to the container prior to sample collection.	60 days  Samples that are preserved at the laboratory must be held for 24 hours before analysis begins.	Room temperature for preserved samples	Bottles with aluminum-lined caps are unacceptable. Results should be flagged if the sample is preserved at the laboratory.
Nitrate Nitrite Nitrate+Nitrite	Glass or plastic (PET)	75 mL	None	7 days	5°C ± 3°C	Samples may be frozen
Fluoride	Plastic (PET)	50 mL	None	30 days	5°C ± 3°C	
Nitrilotriacetic acid (NTA)	Plastic (PET)	50 mL	None	30 days	5°C ± 3°C	
Cyanide (free)	Glass or plastic (PET)	500 mL	Sodium hydroxide to pH ≥ 12	14 days for preserved samples	Room temperature for preserved samples	

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Parameter/Test Group	Sample Container	Minimum Volume	Preservative	Maximum Holding Time	Storage Conditions	Comments
Mercury	Glass	100 mL	0.5–1.0 mL concentrated nitric acid (minimum 20 drops per 250 mL) and approximately 5–10 drops of potassium dichromate solution per 250 mL, pH must be < 2 and sample must be yellow colour	14 days	Room temperature for preserved samples	
Bromate	Plastic (PET)	50 mL	See comments	28 days	5°C ± 3°C	Upon receipt at the lab, the sample should be sparged with N, He or Ar for 10 minutes and ethylenediamine preservative should be added to a concentration of 50 mg/L in the sample.
<b>Triazine Herbicides:</b> Atrazine Cyanazine Metolachor Metribuzin Simazine Alachlor Prometryne	1 L amber glass bottles with Teflon™-lined screw caps	1 L	None	20 days until extraction, 40 days after extraction	Dark 5°C ± 3°C	

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Parameter/Test Group	Sample Container	Minimum Volume	Preservative	Maximum Holding Time	Storage Conditions	Comments
<b>Carbamate Pesticides:</b> Bendiocarb Carbaryl Carbofuran Aldicarb Triallate	1 L amber glass bottles with Teflon™-lined screw caps	1 L	Preserve with 10 drops of 28% w/v sulphuric acid to pH3-4, per litre. Add 1 mL (~30 drops) per litre of 25% w/v sodium thiosulphate solution. Check pH after 30 minutes & add more acid if pH>4.	20 days until extraction, 40 days after extraction	Dark 5°C ± 3°C	
<b>Organochlorine Pesticides and Total PCBs</b> Trifluralin Aldrin + Dieldrin Chlordanes (Total) Heptachlor + Heptachlor epoxide Lindane DDT + metabolites: p,p' DDT o,p' DDT p,p' DDD p,p' DDE Methoxychlor PCB (Total)	1 L amber glass bottles with Teflon™-lined screw caps	1 L	None	20 days until extraction, 40 days after extraction	Dark 5°C ± 3°C	

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Parameter/Test Group	Sample Container	Minimum Volume	Preservative	Maximum Holding Time	Storage Conditions	Comments
<b>Organophosphorus Pesticides:</b> Azinphos-methyl Chlorpyrifos Diazinon Dimethoate Malathion Parathion Phorate Terbufos Temephos	1 L amber glass bottles with Teflon™-lined screw caps	1 L	Add 1 mL (~30 drops) per litre of 25% w/v sodium thiosulphate solution	14 days until extraction, 50 days after extraction	Dark 5°C ± 3°C	
<b>Phenoxyacetic Acid Herbicides and Chlorophenols:</b> 2,4,5-Trichlorophenoxyacetic acid (2,4,5-T) 2,4-Dichlorophenoxyacetic acid (2,4-D) Bromoxynil Dicamba Diclofop-methyl Dinoseb Picloram 2,3,4,6-Tetrachlorophenol 2,4,6-Trichlorophenol 2,4-Dichlorophenol Pentachlorophenol	1 L amber glass bottles with Teflon™-lined screw caps	1 L	Add 1 mL (~30 drops) per litre of 25% w/v sodium thiosulphate solution	20 days until extraction, 40 days after extraction	Dark 5°C ± 3°C	

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<b>Parameter/Test Group</b>	<b>Sample Container</b>	<b>Minimum Volume</b>	<b>Preservative</b>	<b>Maximum Holding Time</b>	<b>Storage Conditions</b>	<b>Comments</b>
Paraquat Diquat	Polypropylene, PET, or HDPE bottles	500 mL	Add 1 mL of (~30 drops) per litre of 25% w/v sodium thiosulphate solution	20 days until extraction, 36 days after extraction	5°C ± 3°C	
Glyphosate	Polypropylene, PET, or HDPE bottles	500 mL	Add 1 mL (~30 drops) per litre of 25% w/v sodium thiosulphate solution	20 days until extraction, 40 days after extraction	5°C ± 3°C	
Diuron	1 L amber glass bottles with Teflon™-lined screw caps	1 L	Add 1 mL (~30 drops) per litre of 25% w/v sodium thiosulphate solution	20 days until extraction, 40 days after extraction	Dark 5°C ± 3°C	
Benzo(a)pyrene	1 L amber glass bottles with Teflon™-lined screw caps	1 L	Add 1 mL (~30 drops) per litre of 25% w/v sodium thiosulphate solution	20 days until extraction, 40 days after extraction	Dark 5°C ± 3°C	
Dioxins and Furans – Total Toxic Equivalents (TEQ)	1 L amber glass bottles with Teflon™-lined screw caps	2 L per sample plus travelling blank; collect sample in duplicate (consult LaSB)	None	30 days until extraction, 1 year after extraction	5°C ± 3°C	Keep cool during shipment (8°C or less)

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Parameter/Test Group	Sample Container	Minimum Volume	Preservative	Maximum Holding Time	Storage Conditions	Comments
N-nitrosodimethylamine (NDMA)	1 L amber glass bottles with Teflon™-lined caps	1 L	None	10 days until extraction, 28 days after extraction	Dark 5°C ± 3°C	If non-amber bottles are used protect samples from light by wrapping in aluminum foil or place in a light-proof container
Microcystin-LR	1 L amber glass bottles with Teflon™-lined screw caps or PET	1 L	100 mg sodium thiosulphate (or 2 x 50 mg tablets) per 1 L. Samples may be preserved at the laboratory.	21 days until extraction, 28 days after extraction	Dark 5°C ± 3°C	Results should be flagged if the sample is preserved at the laboratory.
<b>Other Parameters Which May be Listed in Approvals and Orders (including OWRA Orders)</b>						
Alkalinity, pH	Plastic (PET)	100 mL	None	14 days	5°C ± 3°C	Avoid freezing
Ammonia	Glass or plastic (PET)	75 mL	None	7 days	5°C ± 3°C	Samples may be frozen
Chemical Oxygen Demand (COD)	Plastic (PET) or glass	50 mL	Can be preserved with sulphuric acid to pH >1.5 and <2.0	7 days	5°C ± 3°C	
Chloride	Plastic (PET) or glass	50 mL	None	30 days	5°C ± 3°C	
Colour	Plastic (PET) or glass	75 mL	None	14 days	5°C ± 3°C	
Dissolved Organic Carbon	Plastic (PET) or glass	50 mL	None	14 days	5°C ± 3°C	

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Parameter/Test Group	Sample Container	Minimum Volume	Preservative	Maximum Holding Time	Storage Conditions	Comments
<b>Haloacetic Acids</b> Monochloroacetic acid Dichloroacetic acid Trichloroacetic acid Monobromoacetic acid Bromochloroacetic acid Dibromoacetic acid Dalapon (2,2-dichloropropanoic acid)	Glass, 40 mL US EPA vial	2 x 40 mL	None	28 days	5°C ± 3°C	100 mg/L or 4 mg/40 mL of ammonium chloride as a quenching agent may be added to the sample to combine with any residual chlorine and halt the chlorination reaction.
Hexavalent Chromium	Glass	250 mL; fill to the top of the container	Do not add preservatives	5 days	5°C ± 3°C	
Ortho-phosphate	Glass or plastic (PET)	75 mL	None	7 days	5°C ± 3°C	Samples may be frozen
Phenolic compounds – Total (4AAP)	Glass with Teflon™ lids	180 mL	Sulphuric acid to pH >1.5 and <2.0	30 days	Dark 5°C ± 3°C	Samples in plastic containers or lids with metal liners are not acceptable
Silica	Plastic (PET)	50 mL	None	14 days	5°C ± 3°C	
Sulphate	Plastic (PET)	50 mL	None	30 days	5°C ± 3°C	

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Parameter/Test Group	Sample Container	Minimum Volume	Preservative	Maximum Holding Time	Storage Conditions	Comments
Sulphide	Glass	250 mL	2 mL zinc acetate per litre followed by the dropwise addition and mixing of 5% sodium carbonate solution until precipitation is complete.	30 days	5°C ± 3°C	The addition of too much Na <sub>2</sub> CO <sub>3</sub> to the sample can present a problem in re-dissolving the precipitate. Only sufficient Na <sub>2</sub> CO <sub>3</sub> should be added to completely precipitate all metals and raise the pH to 10.  Sample containers (glass or plastic) should be filled to the top to exclude air from the sample.
Sodium	Plastic (PET)	50 mL	None	30 days	5°C ± 3°C	
<b>Taste and Odour Compounds</b> Geosmin 2-Methylisoborneol 2-Isopropyl-3-methoxypyrazine 2-Isobutyl-3-methoxypyrazine 2,3,6-Trichloroanisole 2,4,6-Trichloroanisole	1 L amber glass bottles with Teflon™-lined screw caps	1 L; fill to the top with no headspace; cap must be tightly closed	None	10 days until extraction, 5 days after extraction	Dark 5°C ± 3°C	Containers should be filled to the top with no headspace.
Total Kjeldahl Nitrogen (TKN)	Glass or plastic (PET)	50 mL	None; can also be preserved with sulphuric acid	7 days	5°C ± 3°C	Samples may be frozen

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<b>Parameter/Test Group</b>	<b>Sample Container</b>	<b>Minimum Volume</b>	<b>Preservative</b>	<b>Maximum Holding Time</b>	<b>Storage Conditions</b>	<b>Comments</b>
Total Phosphorus	Glass or plastic (PET)	50 mL	None; can also be preserved with sulphuric acid	7 days	5°C ± 3°C	Samples may be frozen
Total Organic Carbon	Glass, 40 mL US EPA vial; Plastic (PET) or glass	2 x 40 mL	None	7 days	5°C ± 3°C	Sample can be transferred to vials at the laboratory.
Turbidity	Glass or plastic (PET)	100 mL	None	2 days Analyze as soon as possible	Dark 5°C ± 3°C	Avoid freezing. Analyze within 1 business day of receipt at laboratory.
Total Dissolved Solids	Plastic (PET) or glass	500 mL	None	14 days	5°C ± 3°C	The solids test should be performed as soon as possible.
<b>Additional Organic Analyses, including Emerging Complex Contaminants</b>						
Polybrominated Diphenyl Ethers	1 L amber glass bottles with Teflon™-lined screw caps	2 x 1 L	None	30 days until extraction, 1 year after extraction	Dark 5°C ± 3°C	
Characterization of Extractable Organic Compounds	1 L amber glass bottles with Teflon™-lined screw caps	1 L	Add ~20 drops per litre of 25% w/v sodium thiosulphate solution (167 mg)	14 days until extraction, 1 year after extraction	Dark 5°C ± 3°C	

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<b>Parameter/Test Group</b>	<b>Sample Container</b>	<b>Minimum Volume</b>	<b>Preservative</b>	<b>Maximum Holding Time</b>	<b>Storage Conditions</b>	<b>Comments</b>
Perfluorinated Alkyl Compounds	Polyethylene bottle and cap or PET bottle with polyethylene screw cap	500 mL	None	30 days until extraction, 1 year after extraction	Dark 5°C ± 3°C	

## 7.0 Acronyms

4AAP	4-aminoantipyrene
Ar	argon
C of A	Certificate of Approval (issued by the MOE)
DWIS	Drinking Water Information System
DWSP	Drinking Water Surveillance Program (Ontario)
HDPE	high density polyethylene
He	helium
L	litre
LaSB	Laboratory Services Branch
mL	millilitre
MOE	Ontario Ministry of the Environment
N	nitrogen
NTU	nephelometric turbidity units
ODWQS	Ontario Drinking Water Quality Standards (O Reg 169/03)
O Reg	Ontario Regulation
OWRA	Ontario Water Resources Act
o,p'-DDT	o,p'-dichlorodiphenyltrichloroethane
p,p'-DDD	p,p'-(dichlorodiphenyl)dichloroethane
p,p'-DDE	p,p'-(dichlorodiphenyl)dichloroethylene
p,p'-DDT	p,p'-dichlorodiphenyltrichloroethane
PCB	polychlorinated biphenyl
PET	polyethylene terephthalate
TEQ	toxic equivalent quantity
US EPA or EPA	United States Environmental Protection Agency
w/v	weight/volume
VOC	volatile organic compound

## 8.0 History of Changes

Version 2 – April 2009

- added Disclaimer at the front of the document
  - MOE does not endorse trade names
  - MOE does not assume liability for errors
  - Document is a guidance document for MOE staff submitting samples specifically to LaSB for analysis
  - Requirements are specific to LaSB analytical methods (this was also indicated throughout the document)
  - May be used as a guidance document for best practices by treatment plant owner/operators and other laboratories

## Practices for the Collection and Handling of Drinking Water Samples

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- added references to Transitional – Small Drinking Water Systems (O Reg 318/08), Small Drinking Water Systems (O Reg 319/08), and Schools, Private Schools and Day Nurseries (O Reg 243/07)
- added section 3.3.4, lead in plumbing to descriptions of sampling locations
- removed the term “spigot” throughout the document
- numbered the subsections in Section 3.6 specialized sampling techniques
- added preservative requirement for raw and untreated samples for VOCs in 3.6.1
- minor revisions to microbiological sampling in 3.6.2
- added section 3.6.3 for dioxins/furans
- added section 3.6.4 for lead in plumbing
- defined holding time in section 3.10
- removed reference to DWIS chain-of-custody form in section 4.0
- updated bibliography
- added list of acronyms
- added history of changes
- changes in Table 1:
  - added note that heterotrophic plate count and total coliform background have been revoked from O Reg 169/03 in 2006 but is part of operational testing and may be part of a site-specific C of A
  - added requirement that sample containers for microbiological samples be sterile
  - added requirement for VOC vials to have no headspace (sample volume)
  - added use of sodium bisulfate preservative for VOCs in untreated and raw water samples
  - clarified holding times for VOC samples, depending on use of preservatives
  - added container and preservative requirements for lead in plumbing separate from full list of metals
  - added high density polyethylene (HDPE) as an acceptable container material for some parameters
  - added “nitrate+nitrite” to parameter list in same group as nitrate and nitrite
  - increased minimum sample volume for nitrite/nitrate/nitrate+nitrite and removed polyethylene as type of acceptable plastic container
  - corrected preservative requirement for cyanide to pH greater than 12
  - lowered holding time for cyanide to 14 days; align with US EPA
  - added requirement to acidify sample for carbamate pesticides and instructions to check pH after 30 minutes
  - added p,p’ DDD and p,p’ DDE to list of metabolites that form the sum of DDT+metabolites
  - added requirement to add sodium thiosulphate to samples for phenoxyacid herbicides, chlorophenols, paraquat, diquat, and diuron

## *Practices for the Collection and Handling of Drinking Water Samples*

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- added option for polypropylene containers for paraquat, diquat and glyphosate
- removed option for smaller sample volume for dioxins and furans and clarified holding time to sample extraction
- added minimum sample volume required (1 L) to N-nitrosodimethylamine (NDMA) and removed note re presence of NDMA precursors reducing holding time to 2 days
- added regulated parameter microcystin-LR and applicable sample requirements
- added holding time for sample extracts to all applicable organic compounds
- added the following non-regulated parameters and parameter groups with the applicable sample requirements: ammonia, chemical oxygen demand (COD), haloacetic acids, hexavalent chromium, ortho-phosphate, total phenolic compounds (4AAP), silica, taste & odour compounds, total Kjeldahl nitrogen (TKN), total phosphorus and total organic carbon (TOC)
- revised storage conditions to room temperature for phenolic compounds – total (4AAP)
- increased holding time for colour to 14 days
- indicated that no preservative is required in samples for chloride, dissolved organic carbon, sulphate, sodium, and total dissolved solids
- reduced holding time for turbidity to 2 days, indicated that samples should be analyzed as soon as possible, and added comment that samples must be analyzed within 1 business day of receipt at laboratory
- increased holding time for total dissolved solids to 14 days
- added a new section for additional organic analyses, including emerging complex compounds with the applicable sample requirements: polybrominated diphenyl ethers, characterization of extractable organics, and perfluorinated alkyl compounds