Annex 1. Standard Operation Procedures (SOPs)

a. SOP for cleaning and preparation of sampling bottles

Sampling bottles are 65-mL amber glass bottles, equipped with open-top screw caps with Teflon-lined septa.
Sampling bottles cleaning - wash 65-mL amber glass bottles, equipped with open-top screw caps with Teflon-lined septa, by soaking in hot water with some liquid laboratory detergent for two hours. Rinse them four times with hot tap water, three times with Milli-Q water and invert them in a tray lined with paper towels to drip dry. Heat bottles on their sides in a 400°C muffle oven for 6 hours and allow them to cool overnight. Seal bottles with clean caps, with clean Teflon lined Tufbond liners.

Caps and Septa - wash in beakers by soaking them in hot soapy water, rinsing with tap water 5 times and 4 - with Milli-Q water. Dry them on trays covered with paper towels and large Kimwipes.

Attach a label generated according to Stats Can protocol to each bottle. Prior to shipping, add 1mL buffer solution (pH 4 - 4.3, prepared in-house) or 1 mL diluted hydrochloric acid (0.1 N) and 0.2 mL ascorbic acid solution (0.114 M) to each bottle.

b. SOP for shipping sampling bottles and samples

Place bottles in boxes and ship them to Stats Can field lab in coolers with ice packs to keep them at 4 to 10°C.

Prior to shipping, store all collected samples either in a refrigerator or a cooler with frozen ice packs to keep them at or below 10°C (to maintain proper temperature, replace ice packs regularly as they thaw). Do not allow samples to freeze.

Include one travel blank (bottle with a green dot, supplied by our lab) in each cooler of samples.

Pack shipping cooler as required to prevent bottle breakage / leakage and to maintain cool conditions: - place sample bottles and blanks into boxes they came in

- fill void space with packing paper

- insert sample boxes into supplied zip-lock bag and seal it to prevent water damage

- place the boxes with samples into a cooler, put two frozen ice packs and fill void space with crumpled packing paper until the boxes sit tightly (without any movement when shaking the cooler).

- make sure cold packs are completely frozen (if thawed, ice bags may be used but must be double bagged to prevent water leakage; we supply the bags)

- seal the coolers with a 3-inch packing tape, attach the labels and ship to Health Canada laboratory by Purolator or FedEx for next day 9 a.m. delivery.

c. SOP -sample chain-of-custody

Sampling bottles are prepared and packed by the EBD laboratory and sent to the site. Labels are attached and sampling bottles codes entered in the system. Sampling bottles are kept in the fridge at the site and distributed to the interviewers. Interviewers sample in the participant's homes and return the sample bottles to the site. Sample labels are entered into the system and samples are sent through overnight courier to EBD lab. Samples are unpacked and entered in the system at the lab. Samples that pass the rejection criteria are analysed by the lab and discarded afterwards at the lab.

d. SOP for receiving samples from the field and checking rejection criteria

Minimum volume requirement: in this case, the minimum volume requirement is replaced by a "full bottle requirement". Sample bottles have to be filled with no headspace left.

Shipping requirements: samples have to be kept at a temperature above freezing and below 10C.

Sample rejection criteria

Reject samples which are frozen, in broken bottles, have more than 3 mL head space, have septa with TEFLON side up, or if sample was collected in a bottle with "past due" date.

After chlorine and pH determination, reject samples with any detectable chlorine or with pH above 6.

When samples arrive in the lab, use cooler ID to verify samples received against CHMS tracking system receiving list (use Voyager CG laser scanner).

Sort samples according to the day of the week collected (use the colour of the dot on the bottle as a guide, each colour corresponding to a particular day of the week).

Scan bar codes into Lab data Sheet. Print.

Make a visual inspection of samples and make notes of any irregularities.

Reject samples which are frozen, in broken bottles, have more then 3 mL head space, have septa with TEFLON side up, or if sample was collected in a bottle with "past due" date. Record the numbers of rejected samples on Lab Data Sheet.

Start processing samples in the same order as collected. Process only 20 samples in a day, due to time requirement on the analytical instrument. Keep remaining samples at temperature of 4C.

Before processing, let water samples sit at ambient temperature for about 30 minutes (when too cold, condensation will interfere when measuring free chlorine).

Determine free chlorine of the first sample using HACH colorimeter (and DPD pouch) . Record the value on Data Sheet.

Immediately after, with a 10-mL graduated disposable pipette and pipette helper, take two 12-mL sample aliquots (duplicates A and B) and place them in SPME vials containing 1.2g of NaCl. Cap immediately. Take a 6-mL aliquot and place it in SPME vial containing 6 mL of pH-adjusted Labrador water and 1.2 g of NaCl (aliquot D). Cap. Aliquot D (diluted) will be analysed only if THM concentration of the duplicate A is over the linear range, and dilution is required.

Continue measuring chlorine and taking aliquots of all samples in this manner.

After all aliquots are taken, determine pH of every sample using EMD pH-indicator strips (pH 4.0-7.0). Record the values.

Reject any sample which is not properly quenched (free chlorine remaining) or with pH over 6.0.

Chemical Laboratory Safety.

As per usual safety laboratory operation procedures. MSDS sheets are available for all compounds mentioned in these SOP.

e. SOP for the analytical method for VOC analysis from drinking water.

Materials and instrumentation

Sample preparation materials and instrumentation.

Sample preparation is done automatically by a CombiPAL autosampler (CTC Analytics AG, Zwingen, CH) fitted with a PDMS 100 µm Solid Phase Micro Extraction fibre (SPME Fiber)-Sigma-Aldrich, St. Louis, Mo).

Solvents, reagents

Ascorbic acid solution. Prepare a 0.114M solution in purified water (0.50 mg per 25 mL).

Buffer solution - pH 4.3. Prepare 250 mL by adding 4.6mL of 0.2N NaOH and 63.5mL of 0.2M potassium hydrogen phthalate to a volumetric flask. Dilute with purified water. Determine actual pH with a pH-meter.

Hydrochloric acid solution 0.1 N.

Purified water is prepared by distillation of Milli-Q water over $KMnO_4$ and H_2SO_4 (0.38g of potassium permanganate and 6 mL of conc. sulfuric acid per 3L of Milli-Q water).

Labrador water. Adjusted to pH 4.5. Determine volume of 0.1 N HCl needed to adjust pH of 50 mL of Labrador water. Calculate the amount needed for 4 L and add this amount to a 4-L bottle of Labrador water.

Sodium Chloride (CAS 7647-14-5) - biological grade containing minimal bromide ion. Used as supplied.

Methanol (CAS 67-56-1) and Acetone (CAS-67-64-1), high purity solvents for gas chromatography.

Methyl-t-Butyl Ether (MTBE), preservative-free, 99.0% pure or better, demonstrated to be free of target DBPs and interferences.

Glassware and supplies/Sample bottle requirements

Volumetric flasks

20 ml SPME vials with metallic caps fitted with 1.5mm 'blue' Silicone/Teflon septa.

10 ml disposable graduated pipettes, used with Pipette Helper.

Hamilton micro syringes – 10ul and 25ul

Vortex for mixing solutions

Top Loading Balance – general purpose (0.01 g)

Sampling bottles are 65-mL amber glass bottles, equipped with open-top screw caps with Teflon-lined septa.

Specialized Glassware Preparation

Volumetric flasks - wash by soaking in Chromerge for 2 hours, rinse 4 times with tap water following 4 times rinse with Milli-Q water. Allow to drip dry and rinse with acetone. Allow to dry. Prior to use rinse with solvent again, dry with a stream of nitrogen.

Glass pipettes - before use, rinse the pipettes with solvent (MTBE) and allow them to dry in a fume hood, or dry with a stream of nitrogen

Analytical Instrumentation

A GC-MS triplequad (Bruker 450/300 GC/MS, from Brucker LTD, Freemont, CA) instrument equipped with a CombiPAL autosampler (CTC Analytics AG, Zwingen, CH) and a PDMS 100 SPME (Sigma-Aldrich, St. Louis, Mo) fibre is used to extract and analyse THM and BTEX from drinking water.

A Hach colorimeter (Hach ltd., Mississauga, ON) is used to determine chlorine concentration upon reception of samples.

Sample preparation procedure

Sample handling conditions

Volume/amount of test material is 65 mL of drinking water/household.

Storage of leftover sample

Drinking water samples can not be re-analysed. After opening the 65 mL bottle, water is transferred to 3 prepared vials: 2 X 12 mL samples (samples A and B) and 1X6mL sample D to be used when dilution is required. After analysis, samples are discarded. Drinking water samples can not be stored more than 14 days from the time of collection and can not be re-used after opening.

Step-by step instructions for sample preparation

Prepare 20ml SPME vials by adding 1.2g NaCl to each and cap.
Start processing samples in the same order as collected. Process only 20 samples in a day, due to time requirement on the analytical instrument. Keep remaining samples at temperature of 4C.
Before processing, let water samples sit at ambient temperature for about 30 minutes (when too cold, condensation will interfere when measuring free chlorine).
Determine free chlorine of the first sample using HACH colorimeter (and DPD pouch) . Record the value on Data Sheet.
Immediately after, with a 10-mL graduated disposable pipette and pipette helper, take two 12-mL sample aliquots (duplicates A and B) and place them in SPME vials containing 1.2g of NaCl. Cap immediately. Take a 6-mL aliquot and place it in SPME vial containing 6 mL of pH-adjusted Labrador water and 1.2 g of NaCl (aliquot D). Cap. - Aliquot D (diluted) will be analysed only if THM concentration of the duplicate A is over the linear range, and dilution is required.
Continue measuring chlorine and taking aliquots of all samples in this manner.
After all aliquots are taken, determine pH of every sample using EMD pH-indicator strips (pH 4.0-7.0). Record the values.
Reject any sample which is not properly quenched (free chlorine remaining) or with pH over 6.0.
Add Isotopic Standard to each vial, cap and vortex.
Run (A) samples with appropriate QA check standards every 10^{th} sample and store (B) and (D) samples at 4C to run next day. Use (D) samples only if (A) is out of linear range.

Instrumental analysis

Instrumental parameters/conditions

GC-MS/MS PREPARATION (daily)
Air/Water diagnostics to check for possible air leak
Change septum on front Injector (pre-bore the septum prior to use)
Create a Sample list for the day's batch
Run a BLK Fiber prior to running standards and samples
GC-MS/MS CONDITIONS as per method indicated by Health Canada technical authority.

Preparation of method blanks, QC samples, recovery checks, etc.
STANDARD PREPARATION (per daily use)
To 20 ml SPME vials add 1.2 g NaCl and 12ml of pH 4.5 adjusted Labrador Water, cap immediately.
Add appropriate amount of standard and isotopic standard to each SPME vial. Cap immediately after each addition and vortex **ONLY** after all standard/isotopic additions have been made.
Spike according to the chart provided by the HC technical authority.

f. Inorganic contaminants identified as CMP3 priorities in the Metals Database Project

The inorganic contaminants identified as CMP3 priorities for which exposure data are available from previous drinking water surveys and which will be introduced in this database in the first year (2014-2015) are: aluminum, antimony, bismuth, copper, uranium, lithium, molybdenum, silver, titanium, vanadium, zinc.

Other elements that are listed as miscellaneous but met categorization criteria (lower priority) for which data from previous surveys can be added in the second year (2015-2016) are: barium, beryllium, cadmium, iodine, nickel, platinum, manganese, tellurium, palladium.

Data for bromide, iodide and ammonium, as well as a number of water quality parameters and potential drinking water contaminants collected during previous surveys, will also be included in the database for future needs.