Environment Canada Environnement Canada

Phenol, 4,4'-(1-methylethylidene) bis Bisphenol A

Chemical Abstracts Service Registry Number (CAS RN): 80-05-7

GUIDE FOR SAMPLING AND ANALYSIS OF BISPHENOL A (BPA) IN INDUSTRIAL EFFLUENT

Canada

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Environment Canada
November 2012

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Guide for Sampling and Analysis of Bisphenol A (BPA) in Industrial Effluent

1.0 INTRODUCTION

Bisphenol A (BPA) is an industrial chemical used in a wide variety of applications, including the investment-casting industry, the manufacture of polycarbonates, and as a lining for food cans. BPA was officially added to the List of Toxic Substances (Schedule 1 of the *Canadian Environmental Protection Act, 1999* [CEPA 1999]) in October 2010 (Environment Canada, 2010a).

On April 14, 2012, the Minister of the Environment published a *Notice Requiring the Preparation and Implementation of Pollution Prevention Plans with Respect to Bisphenol A in Industrial Effluents* under Part 4 of CEPA 1999 (www.ec.gc.ca/planp2-p2plan/default.asp?lang=En&n=6A389B0B-1) (Environment Canada 2010b).

This Pollution Prevention (P2) Planning Notice applies to any person or class of persons who owns or operates an industrial facility that:

(a) Manufactures BPA in a quantity greater than 100 kg and, as a result of manufacture, the effluent at the final discharge point of the facility contains BPA; or

(b) Uses BPA in a quantity greater than 100 kg and, as a result of use, the effluent at the final discharge point of the facility contains BPA; or

(c) Uses a mixture(s) containing BPA in a quantity greater than 100 kg and, as a result of use, the effluent at the final discharge point of the facility contains BPA.

The P2 Planning Notice outlines the requirements to prepare and implement pollution prevention plans, and includes the forms to be completed and submitted to the Minister within the required timelines by persons subject to the Notice. For more information on BPA P2 Planning notice, please visit: www.ec.gc.ca/planp2-p2plan/default.asp?lang=En&n=6A389B0B-1.

As part of the P2 Planning Notice, facilities must consider effluent monitoring activities including sampling and analysis as described below:

(a) Effluent samples are collected in such a way that they are representative of the effluent containing BPA release at the final discharge point under normal operating conditions;

(b) Effluent samples are collected and analyzed at a minimum of four times per year;

(c) Sampling and analysis of the samples should be performed in accordance with generally accepted standards of good scientific practice at the time of the analysis; and

(d) Analysis of the samples should be performed by a laboratory that is accredited by a Canadian accrediting body under the International Organization for Standardization standard ISO/IEC 17025, entitled *General Requirements for the Competence of Testing and Calibration Laboratories*, as amended from time to time.

Table 1 provides a summary of the substance information.

Table 1: Substance Information

Chemical Abstracts Service Registry Number (CAS RN)	80-05-7
Chemical name	Phenol, 4,4’-(1-methylethylidene)bis- 4,4’-isopropylidenediphenol
Chemical formula	$C_{15}H_{16}O_2$

BPA is toxic to aquatic organisms and can accumulate in biological tissue. BPA is expected to break down under aerobic conditions, but it has a long half-life under anoxic or anaerobic conditions.

1.1 Purpose

This guidance document is to provide practical advice to facility operators on the sampling and analysis of industrial effluents for BPA. The methods and procedures identified in this guide may also be useful in helping facilities understand process-specific BPA contributions to their final effluent as part of their P2 activities.

This guide should be relied upon for general information purposes only, and should not be interpreted as legal advice and may not necessarily reflect all legal requirements of the pollution prevention planning provisions of Part 4 of CEPA 1999. Should a discrepancy arise between this document and Part 4 of the Act, the latter shall prevail.

1.2 Scope

This guidance document applies to water and effluent sampling, including:

- Effluent at the final discharge point;
- Industrial process waters; and
- Cooling waters.

This guidance document does not apply to groundwater sampling. It also does not provide detailed guidance on the interpretation of data.

1.3 Intended Users

This guidance document is intended for any individual who samples industrial effluents for the purposes of detecting and measuring BPA, whether conducted by the facility personnel or a third party on behalf of the facility operator.

Facilities subject to the P2 Planning Notice must have a thorough understanding of where and when BPA is introduced to their effluent, in order to select the appropriate sampling method, as described in Section 4 of this guidance document. For instance, BPA may be introduced by one specific process, several processes, at various times during the day, all day, only during maintenance activities, or only during cleaning activities. These activities should be captured as part of the sampling plan.

2.0 PLANNING A SAMPLING EVENT

Planning and preparing for a sampling event is an important, time-saving step that typically reduces the number of obstacles that are encountered during sampling.

2.1 Logistics

The following basic steps are recommended to be used for planning sampling events. This guidance has been adapted from the Australian Environmental Protection Agency Guidelines Regulatory Monitoring and Testing: Water and Wastewater Sampling, June 2007, and has been modified based on recent BPA sampling experience.

During the planning stages, it is recommended that the individual collecting the samples undertake the following:

- Prepare a monitoring plan as discussed in Section 3, including the monitoring sites, sampling methods, number of samples required, and occupational health and safety issues;
- Identify all activities associated with the production, process, and release of BPA from the facility's effluent (e.g., during production, cleaning or maintenance activities);
- Coordinate with the analytical laboratory to discuss foreseeable problems with procedures, containers or limitations (high dissolved or suspended solids, temperature, etc.). Facilities should obtain appropriate sample containers (i.e., containers suitable for collecting samples for BPA analysis);
- Schedule the monitoring event, including planning how and when the samples will be transported back to the laboratory. It is important to ensure that the samples are delivered to the laboratory within the conditions and holding time recommended by the laboratory. The sampling schedules should also take into consideration the facility's activities, to ensure effluent content is representative of normal operating conditions associated with BPA;
- Organize and review site maps and locations to determine logistics of sampling. As discussed above, sampling may occur at several other locations outside of the scope of this guidance document. Facilities must be able to identify specific processes that contribute to the presence of BPA in their final discharge point;
- Obtain and prepare all of the required equipment (including sampling equipment and personal protective equipment [PPE]) for the sampling event. In addition, it is important to test all of the equipment prior to the sampling event to ensure that it is operational and calibrated; and
- Fill out as much paperwork as practical before the sampling event, such as the preparation of sample labels, to save time.

2.2 Occupational Health and Safety

A health and safety plan for the sampling event should be developed and included with the monitoring plan in order to mitigate the many hazards that can be associated with conducting fieldwork. The health and safety plan may include such elements as the following:

- Hazard identification and risk assessment:
  - exposure to hazardous substances (e.g., toxic gases);
  - temperature hazards (e.g., heat and cold stress);
  - working in high-traffic areas;
  - working adjacent to bodies of water; and
  - working in confined spaces.
- Actions undertaken to remove, mitigate or control risk; and
- Location of the nearest medical facility, and emergency procedures.

Due to the specific nature of the health and safety plans, a typical outline may include the following sections and/or pieces of important information:

- Purpose of the plan;
- Administrative information (project details, client information, project-specific health and safety personnel, etc.);
- Project description (site operations and physical description, type of fieldwork, scope, etc.);
- Primary responsibilities of project-specific health and safety personnel;
- Training requirements to carry out the fieldwork;
- Sign-in and sign-out procedure specific to the site;
- Preliminary assessment of potential hazards that may be encountered while working on-site (noise, moving equipment, traffic, etc.);
- PPE required while on-site;
- Emergency response procedure to follow while on-site;
- Map and directions to nearest hospital; and
- Health and safety plan approval information.

Please note that the above list does not represent a complete compilation of the information required for a specific site, but rather is meant to provide a general overview of typical requirements for guidance purposes.

3.0 MONITORING PLAN

In order to ensure that monitoring is specific, targeted and cost effective, a monitoring plan must be developed. The monitoring plan will detail the actions, responsibilities and time frames necessary for the monitoring objective to be met.

3.1 Objective

The P2 Planning Notice identifies the following Risk Management Objective (RMO):

- Achieve and maintain the lowest total BPA concentration that is economically and technically feasible below 1.75 µg/L in the effluent released at the final discharge point of the facility through methods other than dilution.

The objective of the monitoring plan is to understand the concentrations of BPA in the facility's effluent to ensure that they do not exceed the RMO identified in the P2 Planning Notice. A good understanding of the concentrations of BPA in the facility's effluent will enable the facility operators to know whether they are meeting the RMO or if they need to implement pollution prevention or pollution control processes to reduce the concentration of BPA in their effluent.

3.2 Preliminary Assessment

Prior to developing a sampling plan of the facility's effluent, it is important for the sample collector to understand the production process and effluent treatment process of the site. Once the sample collector has gained an understanding of the site's operating processes, a detailed sampling plan can be developed to meet the site's unique requirements. For example, a facility that only operates 8 hours each day will have a different effluent flow pattern than a facility that operates 24 hours each day.

Sampling should be representative of the effluent containing BPA released at the final discharge point under normal operating conditions. It is important to ensure that samples are collected from the last point where the facility has control over the quality of the effluent.

If sampling at this point is not possible, sampling can be taken earlier or later in the process (e.g., production, packaging or cleaning), provided that effluent at the sampling location is as close as possible to the expected concentration of BPA resulting from normal operating conditions or could lead, by using an estimation method, to the concentration of BPA at the final discharge point. Facilities should document the reasons for site selection and how estimates were determined.

Note: If there is more than one final discharge point, representative sampling should occur at each final discharge point.

3.3 Monitoring Plan Outline

A complete monitoring plan should include discussion of each of the following topics:

- Occupational health and safety equipment;
- Sampling equipment;
- Sampling type, method and location;
- Quality assurance and quality control;
- Laboratory analysis and analytical method; and
- Documentation and reporting.

4.0 SAMPLING TYPE

As discussed previously, the individual collecting the samples should be aware of production processes at the industrial facility to ensure that representative samples are collected.

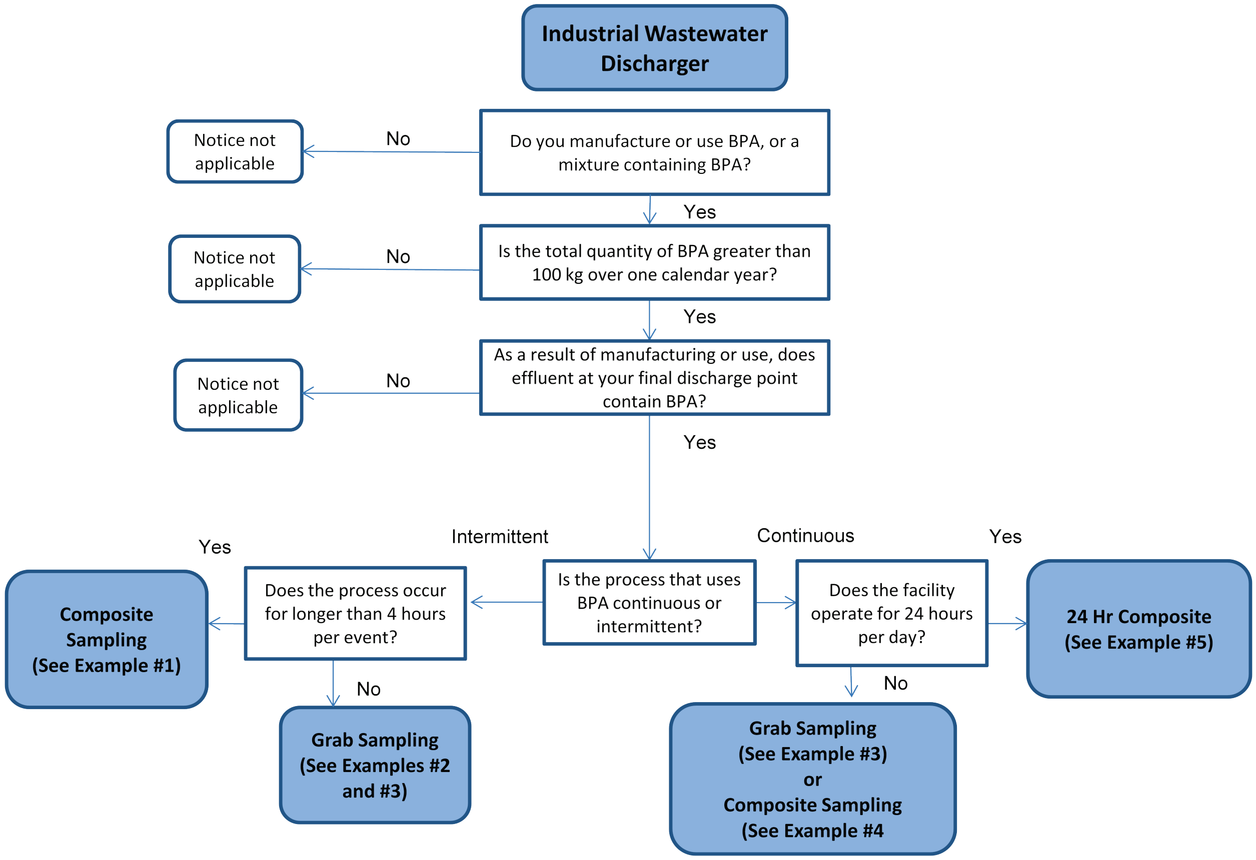
There are two basic collection techniques (grab sampling or composite sampling) that can be used when sampling industrial effluent containing BPA. It is imperative for facilities to determine their activities associated with the manufacture, use and release of BPA in order to identify whether a grab sample or composite samples will be required. Please refer to Figure 1 for a flow chart illustrating the appropriate sampling options.

Initially, the individual collecting the samples must know if the facility is continuously releasing BPA into effluent. If the BPA-contributing process is not continuous, the sample collector can treat it as an intermittent process and choose the appropriate sampling technique based on the duration of the BPA-contributing process.

The guidance below is recommended for BPA sampling under normal operating conditions. However, in some specific instances it may be acceptable to collect a grab sample of a facility's effluent when a composite sample would normally be required. This can occur if the facility collects all of the effluent prior to final discharge, such as in a retention or collection tank. Facilities may also use a composite sampling when the effluent content is highly variable, and use a grab sample when effluent content remains consistent during discharge. Also, if known, facilities can use grab samples at the precise moment when BPA releases are at their highest level at the final discharge point.

The individual collecting the samples should work with site contacts to understand and choose the best method to ensure that the samples are as representative as possible of BPA releases.

Figure 1: Sampling Decision Flowchart



4.1 Intermittent Process

Example #1 Composite Sample is appropriate for facilities that have an intermittent process which operates for more than four hours and contributes to the presence of BPA in the effluent. Composite sample at the final discharge point is recommended for the length of time that BPA is present in the effluent. Note: The facility may need to evaluate an appropriate lag time to ensure the BPA wastewater reaches the final discharge point prior to sampling.

Example #2 Grab Sample is appropriate for facilities that have an intermittent process which operates for less than four hours consecutively and contributes to the presence of BPA in the effluent. This situation may be experienced at a facility that uses a dry process, but which requires a cleaning or sanitation work shift. A grab sample of effluent at the facility's final discharge point is recommended during the four-hour cleaning or sanitation work shift.

Example #3 Grab Sample is appropriate for facilities that have an intermittent process which contributes to the presence of BPA in the effluent, but the wastewater is captured in a retaining tank prior to discharge. This situation may be experienced at a facility that captures wastewater for a few days prior to a discharge. It is recommended to collect a grab sample from the retaining tank prior to discharge and take a grab sample at the final discharge point after the retaining tank has been emptied to validate results. During tank sampling it is important to ensure that this tank is well mixed to ensure sample homogeneity and that no other effluent is released downstream from the final discharge point.

4.2 Continuous Process

Example #4 Composite Sample is appropriate for facilities that have a continuous process which operates for less than 24 hours per day and contributes the presence of BPA in the effluent. This situation may be experienced at a facility that operates during the day and has a sanitation work shift that washes equipment in contact with BPA. A composite sample is recommended for the duration of the facility's operation and the sanitation work shift.

Example #5 Composite Sample is appropriate for facilities that have a continuous process which operates for 24 hours per day and contributes to the presence of BPA in the effluent. This situation may be experienced at a facility that operates three production work shifts per day where BPA is processed or used for a full 24 hours. A 24-hour composite is recommended in this example.

5.0 EQUIPMENT

In order for a sampling event to be successful, the sample collector will need to ensure that the appropriate equipment is available. Appropriate equipment may fall into any of the general categories discussed below.

5.1 Sampling Equipment

When a sampling event involves sampling for trace analyses, as is typically expected with BPA sampling, it is very important that the sampling equipment be inert. Inert sampling equipment will not contaminate or interfere with the analytical results by imparting small concentrations of BPA into the sample. For example, organics (such as BPA) have a tendency to be absorbed by plastic sampling equipment (i.e., polyethylene, polypropylene and polycarbonate). Typically, it is recommended that stainless steel or Teflon® equipment (i.e., buckets and sampling rods) be used to collect the sample. The sample collector must ensure that any sampling equipment complies with the materials compatibility outlined above.

Under no circumstances should polycarbonate sampling equipment be used when collecting samples for BPA analysis. Polycarbonates have been found to leach BPA into water samples, especially at high temperatures.[1]

The following table provides a list of recommended equipment for various types of sampling events. Not all of these may be required for a particular sampling event, but they are included here for reference.

[1] Takao, Y. et al. 2002. Release of Bisphenol A from Food Can Lining Upon Heating. Journal of Health Science 48(4). p. 331–334.

Table 2: Suggested Equipment

Equipment	Grab Sample	Manual Composite Sample	Automatic Composite Sample
Autosampler			☑
Autosampler mounting hardware (for manhole installations)			☑
Teflon® suction tubing to fit autosampler suction fitting (usually 3/8” ID)			☑
Teflon®/stainless steel strainer			☑
Pick (to remove the manhole cover)	☑	☑	☑
Sledgehammer (in the event the manhole cover is difficult to open)	☑	☑	☑
Gear clamps (to clamp suction tubing in place around strainer and suction fitting for the pump)			☑
Nutdriver (to tighten the gear clamps)			☑
Graduated cylinder (to calibrate the autosampler)			☑
Rope			☑
Sandbag (if required – see Section 6)			☑
10-L glass composite sample jar or stainless steel container for use in the autosampler or manual composite sample		☑	☑
Knife or sharp scissors			☑
BPA-free gloves (i.e., nitrile gloves)	☑	☑	☑
BPA sample containers (i.e., 1-L amber glass bottle with a Teflon® lined lid)	☑	☑	☑
Deionized water	☑	☑	☑
Stainless steel bucket for equipment rinsing	☑	☑	☑
Stainless steel bucket for sampling of effluent from a pipe or similar outfall (the bucket must provide a low hydraulic retention time)			☑
Stainless steel sample rod with glass sample collection jar to collect grab samples from out-of-reach locations	☑	☑	
Waste bucket to collect rinse water	☑	☑	☑
Flashlight	☑	☑	☑
Measuring tape	☑	☑	☑
All required PPE (safety glasses, traffic cones, safety boots, hard hats, high-visibility vests, hearing protection, etc.)	☑	☑	☑
Camera	☑	☑	☑
Sample labels, Chain of Custody form, sampling data sheet and suitable marker/pen	☑	☑	☑
Cooler with ice/cold packs	☑	☑	☑
Thermometer	☑	☑	☑
pH meter	☑	☑	☑
Ice		☑	☑

5.2 Sample Containers

Given that organics such as BPA typically adsorb onto plastic surfaces, it is recommended that BPA samples be collected in a 1-L amber glass bottle with a Teflon®-lined lid. For automatic samplers, silicone tubing (preferably medical grade) fitted with a peristaltic pump is needed for sample collection. However, samples collected using this method should be accompanied by equipment blank samples (see section 7.2.1.).

5.3 Personal Protective Equipment

Prior to conducting a sampling event, the sample collector should, depending on the sampling location, identify the type of PPE required. The following list provides examples of the type of PPE that may be needed for sampling in the field:

- First aid kit;
- Drinking water;
- Mobile phone/communication equipment;
- Wet weather gear;
- Waders/rubber boots;
- Disposable coveralls;
- Hard hat;
- Safety glasses;
- Splash shield;
- Hearing protection;
- High-visibility vest;
- Traffic cones;
- Steel-toed boots;
- Warm clothing for cold weather work;
- Disposable gloves;
- Antiseptic hand wash;
- Lifejackets; and
- Emergency Position Indicating Radio Beacon (EPIRB).

5.4 Decontamination

Decontamination is the cleaning of sampling equipment to remove trace analyses and to avoid cross-contamination of samples. In order to minimize the chance and consequence of contamination, it is important to use good sampling design. When planning a sampling event, the individual collecting the samples should consider the following:

- Use dedicated sampling equipment (i.e., sampling equipment that is always used to sample effluent or for receiving-environment sampling) that is BPA-free;
- If possible, the individual collecting the samples should undertake tasks in a sterile laboratory environment rather than in the field;
- Eliminate the need for unnecessary equipment. Where possible, the sample collector should collect the sample directly in the sample container; and
- When multiple-use equipment is unpractical or may result in contamination, use disposable equipment that is BPA-free.

If multiple-use equipment is being used, it should be decontaminated prior to sampling and between collection of samples.

Since all sampling equipment presents a risk of cross-contamination, they must be thoroughly cleaned between sampling. When sampling for BPA, it is recommended that small sampling equipment be cleaned thoroughly using a laboratory-grade detergent solution and a scrubbing brush. Specifically, the equipment should be:

- Rinsed so that no soap residue is left;
- Triple-rinsed using laboratory-grade methanol;
- Triple-rinsed using deionized water; and
- Sealed in aluminum foil to prevent BPA contamination from the environment. For containers, ensure aluminum foil covers the opening.

It is important for the individual collecting the sample to consider the following:

- Do not decontaminate equipment near the sampling site. For example, plastic sheets can be used to contain the cleaning procedure and prevent contamination from ground material;
- Wear clean, sterile gloves and appropriate PPE while performing the decontamination process;
- Supply deionized water in glass containers to ensure that no BPA contamination is introduced from plastic sources; and
- Collect all waste rinse in a bucket and transport it back to the analytical laboratory for proper disposal.

6.0 SAMPLING METHODS

The following sections provide information regarding sampling methods for BPA.

Upon arrival at the sampling site the individual collecting the samples should document the following activities and observations, referred to collectively as “field notes”:

- Time, date, location, names of sampling team members and other pertinent project information;
- Major tasks completed or carried out;
- Field temperature and pH of the collected samples;
- Significant observations with respect to the samples themselves (e.g., suspended solids) or the sample location (e.g., end-of-pipe or earlier in the process); and
- Sample identification numbers and their corresponding locations.

6.1 Collection

Once the sampling procedure as outlined in Section 4 has been determined, the individual collecting the samples can use the information provided in this section to ensure that the samples are collected properly.

During sample collection in the field, the sample collector must take care to ensure sample homogeneity, as results may vary if the sample is not adequately mixed during collection. The sample collector should take note of whether the collected samples visually contain suspended solids, as they may have an impact on the amount of BPA contained in the sample.

Although only one composite or grab sample of effluent is required per sampling event, equipment blanks are also recommended at the start of each event to ensure BPA from the equipment is not affecting the analytical results. To contribute to sample quality assurance/quality control (QA/QC), at least one set of duplicate samples should be taken annually.

It is recommended that there be an initial data collection period in order for all facilities to familiarize themselves with the monitoring process and to gather data on the concentrations of BPA being released to the environment. This would involve an increased sampling frequency during the first year of the program (up to monthly samples) and a subsequent reduction during the following years (minimum of quarterly), provided that the effluent concentration has not increased over this time period.

In the event that the BPA effluent concentration remains high or has increased during a time period (e.g., increase in production), it is recommended to increase the sampling for the duration of the time period. However, if the BPA effluent concentration has decreased (e.g., below the RMO 1.75 µg/L), the facility may consider reducing its sampling frequency as long as BPA releases remain constant.

6.2 Sampling Location

Effluent samples should be collected at the final discharge point. A final discharge point is an identifiable discharge point beyond which the industrial facility owner or operator no longer exercises control over the quality of the effluent. If sampling at this point is not possible, sampling can be taken earlier or later in the process, provided that effluent at the sampling location is as close as possible to the expected concentration of BPA resulting from normal operating conditions or could lead, by using an estimation method, to the concentration of BPA at the final discharge point.

As part of their monitoring plan, facilities should record sampling site information such as identifying the sampling location, the rationale for the site location, and the predicted concentration of BPA at the final discharge point as a result of any removal or treatment of BPA by the industrial facility.

6.3 Manual Grab Sample

A grab sample is the collection of a representative sample from a particular location using a short time period. A grab sample is normally taken at the surface of the water. In order to avoid surface films during the collection, the sample container should be inserted vertically into the water with the neck facing downwards. Once the sample container is submerged, it should be slowly inverted to allow water to flow in. If there is a current within the water body, the mouth of the container should face into it. If there is no current within the water body, the container should be slowly moved forward to obtain a continuous uncontaminated sample.

In some cases, a sample point may be very difficult to safely reach in order to obtain a grab sample (i.e., sampling from a manhole). The individual collecting the samples should use a stainless steel sample rod to extend his/her reach in order to safely obtain a sample. The rod may also allow the sample collector to directly use the BPA sample container to collect the sample. If the BPA sample container cannot be used, a glass or Teflon® jar should be used, and the sample collector can pour the effluent sample from the glass jar into the appropriate BPA sample container.

6.4 Composite Sample

Composite samples consist of two or more grab samples mixed together in known proportions. These samples may be collected manually or by an automatic sampler.

There are two main types of composite samples for effluent sampling:

- Time-weighted samples: grab samples of equal volume taken at constant intervals during the sampling period; and
- Flow-weighted samples: grab samples are proportional to the effluent flow rate or volume during the sampling period. Flow-weighted samples can be taken at constant intervals during the sampling period but with varying sample volumes that are proportional to the flow at the sampling time, or a fixed sample volume can be taken every time a fixed amount of effluent has passed the sampling point.

Time-weighted samples are typically used if the sample collector is aware that the effluent flow through the sample point will remain relatively constant over the duration of the sampling event. If a particular facility experiences significant variations in the flow rate of their final discharge point over the duration of the sampling event, it is preferable to collect samples using a flow-weighted basis. Flow-weighted sampling requires an accurate flow meter to provide guidance on when a grab sample must be collected.

When using composite samples, it is recommended that composite samples be collected at the facility's final discharge point. This location is often in a manhole upstream of a municipal sewer connection; however, it may also consist of a discharge ditch or discharge pipeline. It is important to verify that the composite sampling event will incorporate all important plant activities so that representative effluent is collected (please refer to Section 5).

Automatic composite samples are prepared in much the same way as the manual composite samples. The main difference is that the sample collector must rely on an autosampler rather than collect the samples manually. It is recommended that sample collectors make use of an automatic sampler for any composite sampling events that are planned to occur over a period of 6 hours or longer, to ensure sampling consistency, accuracy and precision.

6.5 Detailed Sampling Collection and Recovery Procedures

Procedures for grab sampling, manual composite sampling and automatic sampling are described below.

6.5.1 Location Preparation

a) **If the final discharge point occurs in a manhole,** remove manhole lid using a pickaxe and assess the water flow through the manhole:

i) If there appears to be sufficient flow to keep the strainer completely submerged at all times, continue with sample collection procedures.

ii) If there is insufficient flow to take samples, the flow path needs to be partially obstructed using a sandbag to create a pool of water from which the sample can be taken. The pool of water created by the sandbag will allow for sampling during low effluent flows.

Note: The sandbag must not be allowed to block the manhole. Blocking the manhole discharge can cause the sewer line to become backed up and may flood the facility. When installing the sandbag, lower it into the flow path using rope and tie it to the top rung of the manhole access ladder, keeping the rope taut so the sandbag does not have any slack to move if the flow increases. The sandbag should be installed such that the flow channel retains a small pool of water, approximately halfway down the flow channel to ensure that pooled water can still flow around the sandbag and through the manhole discharge.

b) **If the final discharge point occurs at the discharge from a pipeline,** use a small stainless-steel bucket to provide a pool of sample water so that samples can easily be taken. The sample collector will need to use his/her judgment in the selection of the bucket size. For larger flow rates (> 10 L/min), a larger bucket (20 L) will be required to reduce splashing; for smaller flow rates (< 10 L/min), a smaller bucket (5 L) will be required to ensure adequate turnover of the collected effluent in the bucket.

c) **If the final discharge point occurs at a discharge ditch,** ensure that the flow through the ditch is sufficient to collect a sample at all times during the sampling event. Please refer to step a) ii) if the flow through the ditch appears too low to collect the samples.

6.5.2 Sample Collection Procedures

Manual grab sampling:

a) Collect a similar volume of deionized water using the chosen, cleaned sampling equipment and pour it into a BPA sample container for the equipment blank (please refer to Section 7.2.1 for more information); and

b) Take the sample using the sample container and the appropriate technique described in Section 6.3. It is important to ensure that the volumes of the grab samples can be accurately measured to ± 5%. Each sample must be of sufficient volume to fill the required 1-L sample containers.

Manual composite sampling:

a) Collect a similar volume of deionized water using the chosen, cleaned sampling equipment and pour it into a BPA sample container for the equipment blank (please refer to Section 7.2.1 for more information);

b) Take the sample using the sample container and the appropriate technique described in Section 6.4. It is important to ensure that the volumes of the samples are able to be accurately measured to ± 5%. Each sample must be of sufficient volume to result in enough composite samples at the end of the sampling event to fill the required 10-L sample jar;

c) Pour each sample into a clean and decontaminated glass composite sample jar with ice packed around it to keep the sample cool. It is important for the sample collector to immediately refrigerate collected samples or put them in a cooler with cold packs or ice, to reduce degradation of the sample; and

d) Continue collecting samples and adding them to the composite sampling jar every 20 minutes until the end of the sample event.

Automatic composite sampling:

a) Measure the approximate length of tubing required so that the autosampler strainer is completely submerged in effluent;

b) Attach a Teflon® and/or stainless steel strainer to one end of the suction tubing. Once the strainer is attached, ensure that it will not come off by tightening a gear clamp around the tubing/hose barb fitting on the strainer;

c) Attach the tubing to the suction fitting on the autosampler pump. Once the tubing is attached, ensure that it will not come off by tightening a gear clamp around the tubing/hose barb fitting on the suction end of the autosampler pump;

d) Submerge the strainer in deionized water and manually run the autosampler pump for 10 seconds to rinse the sample line, collecting the rinse water in the waste bucket;

e) Collect an equipment blank using an appropriate volume of deionized water and the manual pumping option (please refer to Section 7.2.1 for more information);

f) Using the autosampler interface, set up the sampling program. It is recommended that one sample be taken by the autosampler every 20 minutes for the duration of the sampling event. For example, the sampling program may be set up such that the autosampler would automatically collect at least 100 mL of effluent sample every 20 minutes for one 24-hour period (7.2 L of sample in total);

g) Calibrate the sample volume using deionized water and a graduated cylinder. Typically, this is done during the sampling program set-up and may involve inputting the length of tubing used or setting the pumping interval required to obtain the desired sample volume. It is important to ensure that the volumes of the samples are able to be accurately measured to ± 5%. Each sample must be of sufficient volume to result in enough composite samples at the end of the sampling event to fill the 10-L sample jar;

h) Place a clean and decontaminated glass or stainless-steel composite sample jar inside the autosampler and ensure that the discharge tubing from the pump is positioned such that the sample will enter the container;

i) Pack ice around the outside of the sample container to keep it in place and to reduce degradation of the sample. It is important for the sample collector to refrigerate collected samples immediately or put them in a cooler with cold packs or ice to prevent degradation of the sample;

j) Take care not to kink the sampler tubing and ensure that the strainer is fully submerged in effluent when the autosampler is put into operation. Manhole installation brackets should be used if installing an autosampler in a manhole for the sampling event; and

k) Verify that the autosampler is functioning and that the sample is being collected by observing the first sample collection performed by the autosampler.

6.5.3 Sample Recovery Procedure

Once sampling is complete, the following procedure should be followed to recover any type of sample:

a) Wearing nitrile gloves, take the temperature and pH (pH can also be measured by the laboratory) of the sample and note it in the field notes. Make note if the ice in the autosampler has melted;

b) Thoroughly mix the grab sample or composite sample to ensure that any particulate is re-suspended into the sample before collecting the samples;

c) To take samples, pour the effluent from the sample collection container directly into the sampling jar to avoid any contamination from intermediate equipment. Repeat this process until all of the BPA samples have been transferred to the sampling jar;

d) If required, due to the nature of the effluent (e.g., effluent has high bacterial concentration), add a preservative agent to the sampling jar (e.g., 10 mL per 1 L of 37% formalin). Please contact the laboratory to ensure the preservative is compatible with the analytical test method;

e) Immediately place filled sample jars in the cooler with ice/cold packs to minimize BPA degradation during transit;

f) Dispose of the remaining sample (if any is left) in the wastewater; and

g) Replace the manhole lid (if required) and clean up all equipment.

6.6 Sample Transportation and Delivery

After BPA samples are collected, it is important that they be delivered to the analytical laboratory as quickly as possible so that they can be properly stored in a refrigerator at the required holding temperature. The cooler with ice/cold packs should only be used as temporary storage during transportation to the laboratory. The recommended holding time is 28 days refrigerated between 0 and 4°C.[2]

It is important for the individual collecting the samples to specify the low BPA concentration analysis method for any equipment blanks rather than the regular BPA analysis method for effluent samples.

Prior to relinquishing custody of the BPA samples to the analytical laboratory, it is imperative that the Chain of Custody (COC) forms be completely filled out by the individual who performed the sampling and transported the samples to the lab. As discussed further in Section 9.4, COC forms demonstrate the integrity of the samples and instill confidence in the sample results. If responsibility for the samples needs to be transferred at any time, this information should also be captured on the COC.

[2] ASTM D7065 Standard Test Method for Determination of Nonylphenol, Bisphenol A, p-tert-Octylphenol, Nonylphenol Monoethoxylate and Nonylphenol Diethoxylate in Environmental Waters by Gas Chromatography Mass Spectrometry (www.astm.org/Standards/D7065.htm).

7.0 QUALITY

7.1 Quality Assurance

QA consists of the policies, actions and procedures established to provide and maintain a degree of confidence in data integrity and accuracy. In order to achieve consistent data collection during a sampling event, a QA system should be followed.

7.2 Quality Control

QC is a sample or procedure intended to verify the performance characteristics of a system. The goal of QC procedures is to identify any significant change in or contamination to the sample, due to containers, handling and transportation. Typical QC components include field equipment blanks and sample spikes as discussed here.

Data quality objectives are used to establish the type and number of QC samples that must be collected. The greater the number of QC samples, the greater the degree of confidence in the reliability of results.

7.2.1 Equipment Blanks

Contamination introduced to the sample through contact with the sampling equipment is detected and measured using an equipment blank. The equipment blank must be prepared by the sample collector prior to starting a sampling event, to illustrate that no BPA is being introduced to the sample from the sampling equipment. The individual collecting the samples should use the sampling equipment to collect a sample of deionized water for BPA analysis as described in Section 5. An equipment blank should be submitted once per sampling event.

If analysis of the blanks identifies elevated concentrations of target analytes, a thorough review of the portions of the sampling plan that may be introducing contamination should be initiated, as this will affect results and corresponding conclusions.

7.2.2 Sample Spiking

It may be prudent to prepare a spiked sample with a known amount of BPA at the sample location prior to transportation of the samples if the recommended holding time cannot be met. The spiked sample should be prepared using deionized water in an appropriate BPA sample container. The sample collector should spike the deionized water with a known amount of BPA at the same time as the sample is collected. BPA standard solution can be provided by the laboratory.

If the analysis of the spiked sample has a lower BPA result than the known spiked concentration, degradation of the BPA in the sample must be evaluated. Alternative methods of shipment for the samples should be investigated, as BPA degradation will affect results and corresponding conclusions.

8.0 LABORATORY ANALYSIS

It is recommended that the analytical test be performed by a laboratory that is accredited by a Canadian accrediting body under the International Organization for Standardization standard ISO/IEC 17025 entitled *General Requirements for the Competence of Testing and Calibration Laboratories*. It is also recommended that the analytical method used is accredited under Canadian Association for Laboratory Accreditation specifically for the analysis of BPA in water. The method should be able to report to a method detection level of 0.2 µg/L for clean water samples.

Since there can be so much variation in the chemical composition of industrial effluents, it can be challenging to predict what interferences could be present in a given effluent sample. However, a high concentration of dissolved solids (TDS) may interfere with the analysis, and one way to overcome this issue is through dilution of the sample. Typical method detection limits in clean water are on the order of 0.2 µg/L; if a sample requires dilution due to matrix interferences, the detection limit would be increased accordingly. In samples where high TDS may be an issue, it is recommended that the laboratory check the electrical conductivity, which is an indicator of the TDS level, prior to analysis. The laboratory can then use the appropriate dilutions based on this additional information.

During sample collection in the field, the sample collector should take note of whether the collected samples visually contain suspended solids, as they may have an impact on the amount of BPA contained in the sample. If the analytical method will require the sample to be filtered before analysis of BPA, the monitoring plan should include measurement of the suspended solids content in the sample.

In the event that hold times might be compromised because of geographic location of the facility in relation to the laboratory, a spiked sample should also be considered.

9.0 DOCUMENTATION AND REPORTING

9.1 Record Keeping

Facilities must keep their P2 Plan and any records pertaining to the Plan for a minimum of five years following the implementation of the Plan. Please refer to the *Notice Requiring the Preparation and Implementation of Pollution Prevention Plans with Respect to BPA in Industrial Effluents* published by the Minister of the Environment under Part 4 of CEPA 1999 for details on record-keeping requirements.

Facilities should keep all records up-to-date and accessible for inspections. Records pertinent to sampling and analysis may include:

- Monitoring plan;
- Date and time of sampling activities;
- Sample collection type (grab or composite) and sampling method;
- Sampling location;
- Identification of sampling staff;
- Malfunctions and corrective actions taken;
- Maintenance log, including the frequencies and types of maintenance performed;
- Calibration, cleaning and repair logs;
- Date that the samples were sent to the laboratory for analysis;
- Date that the analysis test was performed;
- Laboratory test method, including detection limit;
- Laboratory accreditation number;
- Laboratory address and phone number; and
- Any other relevant information.

9.2 Reporting

Facilities must submit the information required in the schedules of the *Notice Requiring the Preparation and Implementation of Pollution Prevention Plans with Respect to Bisphenol A in Industrial Effluents* published by the Minister of the Environment under Part 4 of CEPA 1999.

As part of the reporting requirements for sampling and analysis, facilities must submit the following information in order to complete Table 4.5.1 found in Schedules 1, 4 and 5 of the P2 Planning Notice:

- Temperature and pH of the effluent at the time of sampling;
- Concentration of BPA in the effluent following laboratory analysis;
- Date that the samples were collected and date that the analysis test was performed; and
- Name, address, phone number and accreditation number of the laboratory that performed the analysis.

Example: Table 4.5.1 in Schedules 1, 4 and 5.

Sample	Temperature (°C)	pH	Concentration of BPA at the final discharge point [µg/L]	Date of sampling	Date of laboratory analysis	Laboratory name, city and phone number	Laboratory accreditation number
No. 1							
No. 2							
No. 3							
No. 4							
Average							

Note: If sampling has occurred at a site other than the final discharge point, facilities should record and report sampling site location information such as location in relation to final discharge point, the rationale for the site location, and the predicted concentration of BPA at the final discharge point as a result of any removal or treatment of BPA by the industrial facility. This information should be reported under Part 8.0, “Factors to Consider,” subsection 4(6), of Schedules 1, 4 and 5 of the P2 Planning Notice.

9.3 Labelling and Identification

Samples should be labelled so that they can be readily identified at all times. Sample labels should be durable, and be able to stay on the sample container even when wet. The ink used to mark a sample container label should be insoluble in water.

Labelling on samples should contain as much information as possible. The labels should specify a clear and unique identifying code that can be cross-referenced to the monitoring location and time of sampling. Labels may also contain the following:

- Date and time of sampling;
- Location and name of sampling site;
- Job or project number;
- Name of the sample collector;
- Container pre-treatment and preservatives added; and
- Observations that may affect the method or results of analysis.

The information listed above should also be recorded on the sampling sheet and retained as a permanent record.

9.4 Chain of Custody

COC procedures and documentation give confidence that the sample integrity has not been compromised. The COC documentation is a record used to trace possession and handling of a sample from collection, analysis, reporting and disposal.

COC control is based on the principle that a sample is always in someone's custody and as such they are responsible for it. If the sample is far away from the location of the analytical laboratory, the sample collector may make use of a courier service to deliver the samples to the laboratory. The sample collector must ensure that the samples are not tampered with, by securing the lid of the sample cooler with tape so that it is obvious if the items have been tampered with. This will ensure the integrity of the COC. When the samples change custody, the new person who is responsible for them will sign and date the seal on the cooler so that the custody chain can be easily traced.

Prior to packing the samples, the sample collector should complete the COC form. The original form remains with the samples at all times to enable the completion of custody details at each stage of progression through transportation, analysis and reporting.

In order to confirm receipt and appropriate transfer and handling, a final copy of the COC form should be obtained from the laboratory. The laboratory should also include a copy of the completed COC form as part of their analytical report.

9.5 Data Review

It is important that the results of the sampling event analysis are reviewed prior to assessment and interpretation. Major issues in the quality of sampling or analysis can be highlighted via simple reviews. These reviews provide useful information on the accuracy and precision of sampling and analytical methods.

Compare duplicate samples results (if required): The variation between duplicate samples should be within the tolerances for the analytical procedure. Typically, differences between duplicates are quantified as a relative percentage difference (RPD), which is calculated using the following formula:

$$RPD = \left((R_1 - R_2) \div \frac{(R_1 + R_2)}{2} \right) \times 100$$

where R_1 is the result of sample and R_2 is the result of duplicate sample.

If the RPD is greater than 20%, an investigation into the cause should be initiated and documented.

Compare triplicate samples results (if required): The variation between triplicate samples should be within the tolerances for the analytical procedure. Typically, differences between triplicates are quantified as a percentage relative standard deviation (RSD), which is calculated using the following formula:

$$RSD = \left(\frac{\sigma}{\bar{x}} \right) \times 100$$

where σ is the standard deviation of the triplicate sample results and $\bar{x}$ is the average of the triplicate results.

Intra-laboratory precision is considered generally good if the RSD is less than 10%.[3] If the RSD is greater than 20%, an investigation into the cause should be initiated and documented.

Review blank samples results: The concentrations of analytes of concern in blank samples should be below the detection limit. If high concentrations are reported, the sampling event will be thoroughly reviewed to determine whether contamination occurred.

10.0 SAMPLING RESOURCES

For additional sampling information and best practices, the sample collector may wish to consult one or more of the following references:

- Municipal/Industrial Strategy for Abatement (MISA) Protocol for Sampling and Analysis of Industrial/Municipal Wastewater published by the Ministry of the Environment (MOE).
- Australian EPA Guidelines Regulatory monitoring and testing: Water and wastewater sampling, June 2007 (www.epa.sa.gov.au/xstd_files/Water/Guideline/guide_wws.pdf).
- Ort, C., M.G. Lawrence, J. Rieckermann, A. Joss. 2010. Sampling for pharmaceuticals and personal care products (PPCPs) and illicit drugs in wastewater systems: are your conclusions valid? A critical review. Environmental Science and Technology, 44, 6024–6035.

For all technical inquiries regarding the content of the P2 Planning Notice, please contact:

- Products Division
  Environment Canada
  Place Vincent Massey, 18th Floor
  351 St. Joseph Boulevard
  Gatineau QC K1A 0H3
  Telephone: 819-956-3775
  Email: products.produits@ec.gc.ca

For inquiries regarding reporting and pollution prevention practices, please contact:

- Regulatory Innovation and Management Systems
  c/o Innovative Measures Section
  Environment Canada
  351 St. Joseph Boulevard
  Gatineau QC K1A 0H3
  Telephone: 819-994-0186
  Fax: 819-953-7970
  Email: LCPEPlansP2-CEPAP2Plans@ec.gc.ca

3 Su, Y., and Hung, H., Inter-laboratory comparison study on measuring semi-volatile organic chemicals in standards and air samples, Environmental Pollution, Volume 158, Issue 11, November 2010, p. 3365–3371.

11.0 REFERENCES

- ASTM D7065 Standard Test Method for Determination of Nonylphenol, Bisphenol A, p-tert-Octylphenol, Nonylphenol Monoethoxylate and Nonylphenol Diethoxylate in Environmental Waters by Gas Chromatography Mass Spectrometry (www.astm.org/Standards/D7065.htm).
- Australian Environmental Protection Agency Guidelines Regulatory Monitoring and Testing: Water and Wastewater Sampling, June 2007 (www.epa.sa.gov.au/xstd_files/Water/Guideline/guide_wws.pdf).
- Environment Canada – 2010a, Order Adding a Toxic Substance to Schedule 1 to the *Canadian Environmental Protection Act, 1999*, Supplement *Canada Gazette*, Part I, Vol. 144, No. 41, October 13, 2010.
- Environment Canada – 2010b, Proposed Notice Requiring the Preparation and Implementation of Pollution Prevention Plans with Respect to Bisphenol A in Industrial Effluents, Supplement *Canada Gazette*, Part I, Vol. 144, No. 42, October 16, 2010.
- ISO 17025:2005 General requirements for the competence of testing and calibration laboratories (www.iso.org/iso/catalogue_detail.htm?csnumber=39883).
- Lee, H. et al. 2002. Endocrine-Disrupting Chemicals in Industrial Wastewater Samples in Toronto, Ontario. Water Qual. Res. J. Canada, Vol. 37, No. 2, p. 459–472.
- MISA Protocol for the Sampling and Analysis of Industrial/Municipal Wastewater, Ontario Ministry of Environment, January 1999.
- Ort, C., M.G. Lawrence, J. Rieckermann, A. Joss. 2010. Sampling for pharmaceuticals and personal care products (PPCPs) and illicit drugs in wastewater systems: are your conclusions valid? A critical review. Environmental Science and Technology, 44, 6024–6035.
- Su, Y., and Hung, H., Inter-laboratory comparison study on measuring semi-volatile organic chemicals in standards and air samples, Environmental Pollution, Volume 158, Issue 11, November 2010, p. 3365–3371.
- Takao, Y. et al. 2002. Release of Bisphenol A from Food Can Lining Upon Heating. Journal of Health Science, 48(4), p. 331–334.

www.ec.gc.ca

Additional information can be obtained at:

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TTY: 819-994-0736
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