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NEWFOUNDLAND AND LABRADOR

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# GUIDANCE DOCUMENT

**Title:** **Sampling of Water and Wastewater – Industrial Effluent Applications**

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## *Table of Contents*



## *Important*

**Information contained in this document is meant to serve as a guideline for conducting water and wastewater sampling at industrial sites. Sampling methods and procedures may vary depending on sampling locations, media and industry requirements. Details specific to individual industries will be clearly outlined in the CofA and CofA's that include water and wastewater monitoring clauses should reference this guidance document.**

## *1.0 Subject*

Procedures for sampling of water and wastewater from sites with industrial applications.

## *2.0 Objective*

To outline the steps for the preparation, collection and shipping/delivery of water samples for laboratory analysis.

## *3.0 Definitions*

**ALT (acute lethality test)** means a test conducted as per Environment Canada's Environmental Protection Service reference method EPS/1/RM-13 Section 5 or 6.

**CofA** means Certificate of Approval issued under Part XI of the *Environmental Protection Act* SNL2002 Chapter E-14.2.

**Composite Sample** means a quantity of undiluted effluent collected continually at an equal rate or at a rate proportionate to flow over a designated sampling period.

**Department** means the Department of Environment and Conservation and its successors.

**DOC** means dissolved organic carbon.

**EEM** means Environmental Effects Monitoring.

**Environment** includes

i) air, land and water,
ii) plant and animal life, including human life,
iii) the social, economic, recreational, cultural and aesthetic conditions and factors that influence the life of humans or a community,
iv) a building, structure, machine or other device or thing made by humans,
v) a solid, liquid, gas, odour, heat, sound, vibration or radiation resulting directly or indirectly from the activities of humans, or
vi) a part or a combination of those things referred to in subparagraphs (i) to (v) and the interrelationships between 2 or more of them.

**Grab Sample** means a quantity of undiluted sample collected at any given time.

**Leachate** means a liquid that has percolated through solid waste and has extracted dissolved or suspended materials.

**MSDS** means Material Safety Data Sheet.

**QA/QC** means Quality Assurance/Quality Control.

**Recognized Form of Laboratory Accreditation** means accreditation obtained from an accreditation body that is a signatory to the International Laboratory Accreditation Cooperation (ILAC) Agreement and based on ISO 17025.

**TDS** means total dissolved solids.

**TPH** means total petroleum hydrocarbons, as measured by the Atlantic PIRI method.

**Treat** means to apply a method, technique or process, including neutralization, stabilization, filtration and settling that is designed to change the physical, chemical or biological concentration, character or composition of a substance.

**Treatment** means any physical, thermal, chemical or biological process, including sorting, that changes the characteristics of the waste in order to reduce its volume or hazardous nature, facilitates its handling or enhances its recovery.

**TSS** means total suspended solids.

**WHMIS** means Workplace Hazardous Material Information System

## *4.0 Background*

Water monitoring is a typical requirement outlined in an industry's CofA. Water monitoring is conducted to ensure that industries are operating within compliance of legislation and to ensure there are no adverse effects on the environment. The validity and confidence in the monitoring is contingent on the sample. The ultimate goal is to collect a sample that meets the requirements in the CofA in terms of location and frequency, and to prevent the deterioration and contamination of the sample before it is analyzed.

## *5.0 Quality Assurance/Quality Control*

Sample analysis must be conducted at a laboratory with a recognized form of accreditation. The laboratory may have specific sampling instructions and it is the responsibility of the sampler to become familiar with the requirements of the laboratory conducting the analysis. For more information on laboratory accreditation, please see the Department of Environment and Conservation's Policy Directive PD: PP2001-01.2. Note that some analyses are performed at industrial laboratories. These laboratories meet the requirements of the accredited laboratory policy. For the purpose of this guidance document these laboratories are considered to have a recognized form of laboratory accreditation.

Strict measures must be taken to avoid contamination and to maintain the integrity of the sample. Samples must be kept cool during storage at approximately 4°C, but samples must not be allowed to freeze. Samples are to be shipped to the laboratory in a timely fashion and the sampler must be aware of specific holding times that may be associated

with the specific analyses expected to be carried out on the sample.

If sampling protocol requires field measurements such as pH, conductivity, specific ions or other parameters to be obtained, then the field instrumentation utilized for such measurements must be stored and calibrated as per the respective instrument operating manuals. Probes, where applicable, must be stored in electrode storage solution and/or protective cases when not in use. Calibration of field equipment, utilizing certified calibration standards, must be performed just prior to and just after field measurements to ensure validity and accuracy of acquired data. If temperature-sensitive parameters are being determined, calibration standards must be equilibrated to sample/ambient temperature prior to the performance of instrument calibration and field measurements.

### 5.1 *Trip Blanks/Field Blanks*

Trip blanks are used to detect any contamination resulting from the sampling containers and/or preservatives during transport and storage. Typically trip blanks are prepared by filling each type of sampling bottle with de-ionized water and preserving them in the same manner as the samples that will be collected. These blanks are transported to the field with the regular sampling bottles, but they remain unopened throughout the duration of the trip. They are then submitted with the field samples for analysis.

Field blanks are used to detect any contamination that may result from the handling techniques and/or exposure to the sampling environment. They are prepared using de-ionized water in each type of sampling bottle that will be used for analysis. If the field blanks are prepared in the laboratory, then the bottle is to be opened while in the field and exposed to the environment for approximately the same amount of time it takes to collect a field sample. If the field blanks are prepared in the field, then de-ionized water is poured into the sampling bottles, capped and labeled. Filtration and/or preservation, if required, must be done in the field as well. This simulates sample collection. It must be documented whether the blank was laboratory prepared or field prepared.

Requirements for trip or field blanks would be directed by the laboratory performing the analysis or as a component to a specific monitoring event such as EEM.

### 5.2 *Duplicates*

Field duplicates are two or more samples collected as close as possible in location and time. These samples can be useful in documenting the precision of the entire sampling and analytical (laboratory) process.

Laboratory duplicates are conducted by the laboratory performing the analytical testing. Typically a sample is selected at random and is sub-sampled, with the required analysis being run on both sub-samples. This is useful for testing the level of accuracy of the laboratory instrumentation

Requirements for duplicates would be directed specifically to address QA/QC procedures

of the laboratory conducting the analysis.

## *6.0 Industrial Wastewater Sampling: Typical Parameters*

Wastewater discharges must be sampled at each final discharge point for the purpose of determining compliance. Effluent discharge criteria typically include but is not limited to the parameters listed in Table 1. The sampling schedule, locations, parameters and frequency will be outlined in the industry's CofA.

| **Table 1: Effluent Discharge Criteria** | | | | |
|---|---|---|---|---|
| ammonia | cadmium | lead | zinc | TPH |
| arsenic | chromium | mercury | TSS | flow rate |
| barium | copper | nickel | TDS | temperature |
| boron | iron | nitrate | pH | ALT |

General water chemistry analysis is typically required four times per calendar year, and includes but is not limited to the parameters listed in Table 2. Again, the sampling schedule, locations, parameters and frequency will be outlined in the industry's CofA. General water chemistry suites are performed on effluent discharges, receiving water bodies and background water bodies. These analyses help determine changes in the effluent and effects on the environment as a result of the industrial activity being undertaken.

| **Table 2: Water Chemistry Analysis** | | | | |
|---|---|---|---|---|
| **General Parameters** | | | | |
| nitrate + nitrite | color | magnesium | reactive silica | TDS (calculated) |
| nitrate | sodium | alkalinity | orthophosphate | phenolics |
| nitrite | potassium | sulphate | phosphorus | carbonate($CaCO_3$) |
| ammonia | calcium | chloride | DOC | hardness($CaCO_3$) |
| pH | sulphide | turbidity | conductance | bicarbonate($CaCO_3$) |
| **Metal Scan** | | | | |
| aluminum | boron | iron | nickel | tin |
| antimony | cadmium | lead | selenium | titanium |
| arsenic | chromium | manganese | silver | uranium |
| barium | cobalt | molybdenum | strontium | vanadium |
| beryllium | copper | mercury | thallium | zinc |
| bismuth | | | | |

## *7.0 Preparation for Sample Collection*

Often sampling is required in remote areas. The following is a list of items that may be necessary to take along when collecting samples in the field:

- All required sample bottles, requisition forms, labels and preservatives that are needed for specific laboratory analyses. The laboratory conducting the analysis typically provides these materials and specific directions.
- Instrumentation for any field measures that are to be collected (eg. pH,

temperature, etc.).
- Storage and transport materials (eg. Coolers, icepacks, etc.).
- Logbook or notebook, to document any field measurements, observations, deviations from standard protocol or unusual occurrences.
- Personal Gear (waterproof clothing, insulated clothing, rubber or steel toe boots, etc.) and Personal Protective Equipment (PPE) where required.
- First Aid Kit
- Equipment (eg. GPS, camera).
- Clean sample containers for collection if required, as some samples may need to be poured into the actual sample container.

## *8.0 Sample Collection*

Samples must be collected at the same location during each round of sampling. If it is unsafe to take a sample in a preselected location or circumstances prevent sample collection at that point, then choose an alternative location nearby or do not collect the sample. If an alternative location is chosen, make sure to log all information relevant to the new location and document the reasons for selecting a new location. If sample collection is not possible (eg. no flow, poor weather conditions, not enough water present to provide a representative sample), this information must be documented and included with the final sampling report and reported to the Department.

Laboratories have their own requirements for sample size, preservative, and bottle type. Sample containers must be obtained from the laboratory that will be doing the analysis to ensure that sample requirements are met.

Many preservatives are considered hazardous material and fall under the regulations outlined by WHMIS. It is important for the sampler to have the WHMIS MSDS for reference in the event that it is required. The shorter the elapsed time between sample collection and analysis, the more reliable the analytical results. When preserving the sample, be careful to avoid contact of the preservative vial with the sample and minimize the time the sample is exposed to the atmosphere.

If labels are affixed to the bottles prior to sampling, ensure that the sample labels are still intact and the information on the labels is clearly legible after sample collection.

### 8.1 *Sampling Types*

Grab samples are generally specified when:
- the concentration of a parameter under consideration is not expected to vary significantly with time
- values associated with extreme events are desired
- the analyte is such that the procedure of compositing would destroy the sample integrity.

Composite samples are generally specified when the concentration of the parameter

under consideration is expected to vary with time or location. The individual samples that make up the composite may be of equal volume or be proportional to the flow at the time of sampling. The composite time is defined according to the terms of the CofA (eg. Daily, 3-hour period, etc.). Automatic sampling devices are often used for composite sampling. However, they can be collected manually with the quantity to be collected each time previously calculated. Samples must be kept cool throughout the collection process and records must be maintained including sampling time and volume.

### 8.2 *Surface Water and Effluent Sampling*

Water samples are collected by filling the sampling containers by holding them just beneath the surface of the water, or under a flow at an outfall. If the sample bottle already contains a required preservative, then the sample must be collected in a clean sampling container and poured into the appropriate bottles. This will reduce the risk of losing the preservative or having it wash out of the sample bottles during the collection process. There are special samplers for taking samples under the surface at certain depths in a water body; these methods will not be covered here.

Sample bottles provided by a laboratory with a recognized form of accreditation are typically pre-cleaned, and therefore rinsing of the sample containers before sample collection is not necessary.

Sample Collection:

- Remove the lid of the sample container.
- Hold the bottle beneath the surface of the water until it is full. It is important to note that some sample containers have predetermined fill lines.
- Recap immediately.
- Note: sample filtration and/or preservation must be done as soon as possible after the samples are collected.
- If any of the sample bottles already contain preservative, another pre-cleaned container can be used to collect the sample from the water body and then poured directly into the sample bottle containing the preservative. This will reduce the risk of losing the preservative or having it wash out of the sample bottles during the collection process.
- If preservative is added to the sample container after the sample is collected, tightly recap the sample and invert twice to mix the preservative into the sample.

### 8.3 *Groundwater Sampling*

The type of equipment used for well purging and sample withdrawal can affect the quality of the sample and how the data is interpreted. Samples of groundwater from monitoring wells are generally withdrawn using a submersible pump, a peristaltic or valveless metering pump, or a point sampler such as a bailer, thief sampler or syringe. The sampling device must be conditioned with well water before being used to collect samples. Pumping is the preferred method for withdrawal of groundwater samples.
If using a pump sampler, the field rinsing is accomplished with well purging assuming

that the well will be purged with the same equipment that will be used for sample withdrawal.

If a point sampler will be used for collection of the sample, lower it smoothly into the well so as to disturb the water as little as possible. Fill the sampler partially with the water to be sampled; shake or swirl to cover all interior parts of the sampler. Drain the rinse water through the nozzle or bottom-emptying device into a container or into an area that is distanced from the well head. Repeat this procedure three times. Finally, lower the sampler and allow it to fill for collection of sample water.

An effective bottle filling method is to insert the discharge end of clean sample tubing to the bottom of the bottle so that the sample fills the container from the bottom up to overflowing. Cap the bottle quickly. This method is not practical for every sample type.
Once the sample has been collected, it needs to be processed. This involves sample filtration, storage in appropriate containers and sample preservation.

### 8.3.1 *Purging of the Well*

The well must be purged of standing water prior to sampling to reduce artifacts from well installation or sampler deployment. This ensures that the sample water will be withdrawn directly from the aquifer. The well must be pumped at a rate that does not overly stress the aquifer, creating draw down and mobilizing particulates. Pumping rate during purging must remain constant and be maintained as the pumping rate for sample withdrawal and collection. Fluctuations in pumping rate can affect sample quality. After purging, the water level in the well must recover to approximately 90% of its starting level before sampling commences. Purged water is to be collected in a container or disposed in an area distanced from the well head.

Low-yielding wells, especially those that exhibit slow recovery or are pumped dry, are not recommended for water-quality sampling.

The standard United States Geological Survey (USGS) purge procedure requires removal of three or more well volumes of standing water while monitoring the water level and the stabilization of routine field measurements. Any modifications to the standard well-purging procedure must be documented.

## *9.0 Shipping Samples*

The shipping schedule must take into account the hold time on the specific parameters to be tested. There must be enough time allowed for samples to be taken, prepared for shipping, shipped by the shipping agency and received by the laboratory for analysis before the hold time has expired.

Samples must be packed upright in a cooler surrounded by ice or ice packs. The samples that are more likely to deteriorate must be the ones closest to the ice pack. Glass sample bottles need to be wrapped in bubble wrap or some other packaging material to prevent

breakage during shipping.

All sample bottles must be double checked to ensure that they are labeled. The laboratory requisition forms must be filled out, put in a plastic bag and placed inside the cooler with the samples. Make sure that all samples are clearly identified with a unique sampling site and sampling locations.

Minimum information:

- Name of Client (who is requesting to have the analysis)
- Site Name
- Sample Identification
- Date and time of collection
- Name of the collector
- Field Measurement
- Sample analysis to be carried out
- Any other comments deemed to be relevant

Documentation must be completed for the laboratory as thoroughly and detailed as possible. The sample cooler must be sealed with heavy-duty packing tape to reduce the chance that it will accidentally open during transit and to prevent tampering with the samples. Ensure all coolers are properly labeled with the shipping address.

## *10.0 References*

Environment Canada, The Inspector's Guide: A Sampling Manual and Reference Guide for Environment Canada Inspectors, 1995, ISBN 0-662-23513-4.

British Columbia Field Sampling Manual – for Continuous Monitoring Plus the Collection of Air, Air-Emission, Water, Wastewater, Soil, Sediment and Biological Samples (1996 Edition).

Environment Canada, Guidance Document for the Sampling and Analysis of Metal Mining Effluents, April 2001, Report EPS 2/MM/5, ISBN 0-660-18239-4.

U.S. Geological Survey, Techniques of Water Resources Investigations. National Field Manual for the Collection of Water Quality Data, Revised 2006.

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