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Canada

## **TECHNICAL OPERATING PROCEDURE**

### **PROCEDURE TITLE:**

Procedures for Measurement of Ammonia in Stream Water

### **APPLICABILITY:**

Procedure is used to measure ammonia in stream water when conditions of concern exist. Ammonia concentrations are seldom found at a level considered a safety concern for a lampricide treatment. However, this procedure may be performed when a lampricide block is going to pass through areas containing feedlots, sanitation disposal areas, areas of heavy agricultural use, and slow moving stretches of stream particularly when preliminary water chemistry data indicates low dissolved oxygen concentrations, neutral to high pH, and high temperature.

### **PRINCIPLE:**

Aqueous un-ionized ammonia is detrimental to the health of most fish species. Additionally, TFM and ammonia have an additive toxic effect on aquatic organisms (Marking and Bills 1985). This procedure uses a multiparameter instrument to produce a direct readout of un-ionized ammonia concentration from measurements of ammonium, pH, and temperature. Resulting values are compared with threshold criteria to determine potential for impact on the efficacy or safety of a treatment. Generally, a concentration of un-ionized ammonia greater than 0.1 mg/L is considered a level of concern.

### **SAMPLE COLLECTION AND PRESERVATION:**

The most reliable results are obtained from fresh stream water samples and analyses should be conducted in stream or stream side whenever possible. Samples for stream side measurements are collected in a clean glass or Nalgene containers. Samples for measurement in the field laboratory are collected in clean, capped glass or Nalgene bottles. Samples are not stored longer than two hours.

**EQUIPMENT REQUIRED:**

YSI ProPlus multiparameter meter equipped with ammonium, pH, and temperature sensors

**POTENTIAL INTERFERENCES:**

Saline water and high total alkalinity (>500 mg/L) water interfere with measurements. See IOP:019A.x for potential interferences.

**SAFETY:**

Standard laboratory safety procedures are followed when handling calibration solutions. No specialized safety procedures are required.

**DISPOSAL:**

There are no special requirements for the disposal of calibration solutions or water samples.

**REAGENTS:**

pH calibration solutions (pH 4, 7 and 10)  
Ammonium calibration solutions (1 and 100 mg/L)

**PROCEDURES:**

I. Introduction

Ammonia exists in water as un-ionized ammonia (NH<sub>3</sub>) and ammonium ions (NH<sub>4</sub><sup>+</sup>). The toxicity of aqueous ammonia is almost entirely attributable to the un-ionized form. Laboratory experiments have demonstrated that the toxic concentration of NH<sub>3</sub> for a variety of fish species ranges from 0.2 to 2.0 mg/L. The lowest lethal concentration reported for salmonids is 0.2 mg/L NH<sub>3</sub>. At fish hatcheries, NH<sub>3</sub> concentrations greater than 0.0125 mg/L is considered detrimental to fish growth and induces damage to fish gills, kidneys, and liver. The LC<sub>50</sub> for shortnose sturgeon (*Acipensar brevirostrum*) fingerlings is 0.58 mg/L NH<sub>3</sub> and the no observed mortality level is 0.34mg/L (Fontenot, 1998). The U.S. Environmental Protection Agency set an acute aquatic life water quality criterion for total ammonia (pH 7, 20 °C) that translates to 0.067 mg/L NH<sub>3</sub>. For the purposes of the Sea Lamprey Control Program, an NH<sub>3</sub> concentration greater than 0.1 mg/L indicates a potential for atypical treatment effects and is considered a level of concern.

The percent of total ammonia present as NH<sub>3</sub> is primarily dependent on and positively correlated with both pH and temperature (Emerson, 1975). In this analytical method ammonium concentration, pH and temperature are measured and the un-ionized ammonia concentration is calculated by the multiparameter instrument.

II. Instrument setup and calibration

- A. Prepare the multiparameter meter according to IOP:019A.x.
- B. Calibrate the pH sensor according to IOP:019A.x.
- C. Calibrate the ammonium sensor according to IOP:019A.x.

III. Sample collection

- A. Samples of water are collected in clean glass or Nalgene containers. If ammonia measurements will not be conducted in stream or stream side, the water temperature and pH are measured streamside (TOP:006.x) and the sample containers are capped.

- B. Preferably, measurements are made in stream or stream side. If necessary, samples are transported to analysis trailer and samples are analyzed within 2 hours of collection.
- IV. Measurement of Ammonia
- A. Un-ionized ammonia concentration  $[NH_3]$  is measured according to IOP:019A.x.
- V. Documentation
- A. Standardization of the meter is documented in the instrument log book each day.
    - 1. An entry is made each morning that the meter is used. The entry includes date, time, stream, pH or concentration and temperature of the standards used.
    - 2. The function of the meter is again checked at the end of the day. The value of each standard is measured and recorded in the instrument log book.
  - B. The pH, temperature and  $[NH_3]$  values of each water sample are recorded on the Water Chemistry Data Form (Appendix M).

**REFERENCES:**

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- Thurston, RV. and Russo, RC. Acute Toxicity of Ammonia to Rainbow Trout. *American Fisheries Society*. 1983;112:696-704.
- U.S. Environmental Protection Agency. *Aquatic Life Ambient Water Quality Criteria for Ammonia - Freshwater*. Washington, D.C.; 2013.
- YSI ProPlus User Manual

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This procedure has been reviewed and approved by the undersigned representatives of the U.S. Fish and Wildlife Service and Fisheries and Oceans Canada.

REVIEWED/APPROVED \_\_\_\_\_ DATE \_\_\_\_\_  
Field Supervisor (U.S.)

REVIEWED/APPROVED Julie Spivak DATE 05 MAR 2020  
Program Manager (Canada)