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and

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Sea Lamprey Control Centre
1219 Queen Street East
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TECHNICAL OPERATING PROCEDURE

PROCEDURE TITLE:

Receipt, Identification, Storage, Preparation, and Handling of Lampricide Analytical, Field, and Working Standards

APPLICABILITY:

United States Fish and Wildlife Service; Marquette Biological Station (MBS), Marquette, MI; Ludington Biological Station (LBS), Ludington, MI; Department of Fisheries and Oceans, Sea Lamprey Control Centre (SLCC), Sault Ste. Marie, Ontario, Canada; U.S. Geological Survey; Hammond Bay Biological Station (HBBS), Millersburg, MI; and the Upper Midwest Environmental Sciences Center (UMESC), LaCrosse, WI; Lake Champlain Fish and Wildlife Management Cooperative (LCFWMC); and New York State Department of Environmental Conservation.

PURPOSE:

To document the necessary procedures to properly receive, identify, prepare, store, archive, and handle samples of lampricide analytical, field, and working standards. Adherence to these procedures assures that all units involved in the control of sea lampreys are provided accurate standards which allow precise measurement of lampricide concentrations during field applications and on-site toxicity tests.

DEFINITION OF TERMS:

ANALYTICAL STANDARD: A commercially prepared sample of 3-trifluoromethyl-4-nitrophenol (TFM) or 2',5-dichloro-4'-nitrosalicylanilide (niclosamide) of high purity, usually 95% or greater. The analytical standard must be accompanied by a Certificate of Analysis from the manufacturer stating the purity.

FIELD STANDARD: A laboratory formulated TFM or niclosamide standard prepared in an appropriate solvent. TFM field standards are formulated at 0.0, 4.0, 8.0, and 12.0 mg/L in sodium tetraborate buffered deionized water, and are used for on-site analyses of TFM concentration during stream treatments and toxicity tests. Niclosamide field standards are formulated at 100 mg/L in dimethylformamide.

WORKING STANDARD: A dilution of the niclosamide field standard to a suitable concentration for on-site analyses of niclosamide concentrations during stream treatments and toxicity tests.

PROCEDURES:

I. Analytical Standards

A. Receipt, identification, and verification of analytical standard

1. Upon receipt of an analytical standard from a vendor, the UMESC Administrative Officer, HBBS Administrative Support Assistant Officer, or designee informs the analytical chemist that the material has arrived at the laboratory, and provides a certified copy of the shipping receipt to the analytical chemist.

2. The analytical chemist inspects the packing and contents to determine that the vessel containing the analytical standard is undamaged. If damage to the vessel has occurred, the analytical chemist notifies the vendor immediately and arranges to have the analytical standard returned and replaced with a new analytical standard.

3. After receiving the analytical standard in satisfactory condition, the analytical chemist prepares an Analytical Standard Data Form (Attachment 1), and verifies that the following information has been received from the manufacturer of the analytical standard:
   a. Documentation concerning the authenticity, identity, quantity, and purity of the analytical standard; the manufacturer, lot number, date of receipt from the manufacturer, and the physical characteristics of the analytical standard and the Chemical Abstracts Service number. This information is recorded on the first page of the analytical standard use log.
   b. The analytical chemist will provide the original Material Safety Data Sheet/Safety Data Sheet (MSDS/SDS) from the manufacturer to the Laboratory Safety Officer for retention in the MSDS/SDS Master File. The analytical chemist will also ensure that a copy of the MSDS/SDS is on file in the laboratory where the analytical standard will be used, and that individuals who will be working with the analytical standard have read the MSDS/SDS before handling the material.
   c. All persons handling the analytical standard are required to wear proper protective clothing. Generally, this consists of appropriate outer protective garments such as a lab coat or smock, latex or rubber gloves and either plastic goggles or safety glasses. Requirements for additional protective wear will be made by the analytical chemist in accordance with information found on the MSDS/SDS.

4. The Analytical Standard Use Log (Attachment 2) is bound and contains the following in the order listed:
   a. Cover page
   b. A copy of this standard operating procedure
   c. A copy of the MSDS/SDS
   d. A copy of the Analytical Standard Data Form (Attachment 1)
   e. Lined, blank pages for recording usage entries
   f. Sufficient pages are bound into the log book to record all amounts of the analytical standard removed for the lifetime of the analytical standard received in this shipment.

5. The original weight of the analytical standard and container are determined by weighing on an appropriate balance. This weight is recorded on the page following the MSDS/SDS.

B. Storage of Analytical standard

1. The analytical standard is stored in a secured area under conditions deemed by the analytical chemist to be non-hazardous and of low potential for degradation. Normally, this is in a locked freezer or a locked vault that is cool, dry, ventilated and darkened. A subsample of each analytical standard is archived according to UMESC SOP AEH 011 (Archiving of Test Chemicals; Appendix Q) and HBBS SOP LAB 334 (Archiving of Chemicals; Appendix Q).

C. Handling of the Analytical standard

1. If the analytical standard is stored in a freezer, allow it to come to ambient room temperature before weighing and withdrawing samples.

2. The weight of the analytical standard and container are determined by weighing it on an appropriate balance. The initial weight is recorded in the Analytical Standard Use Log. Note: Containers are weighed with the cover on the container. If this is not done, indicate in the log book that the container without the cover was weighed.

3. The sample of analytical standard is weighed in a tared container. The weight of the analytical standard sample is recorded in the Analytical Standard Use Log.

4. After the sample of analytical standard is withdrawn from the storage container, again weigh the container of the analytical standard (and cover); record all information in the Analytical Standard Use Log.

5. Repeat Steps 2, 3, and 4 each time the analytical standard is removed. Discrepancies in weight are brought to the attention of the analytical chemist. Explanatory remarks are made in the Analytical Standard Use Log.

6. Return the remaining analytical standard to the storage area and secure.

7. When the Analytical Standard Use Log is full or the entire analytical standard has been used, the log is archived according to UMESC SOP AEH 007 (Archives Management for Regulated Studies; Appendix Q).

D. Verification of the purity of the analytical standard

1. The purity of the standard reported by the manufacturer is verified by High Performance Liquid Chromatography (HPLC) before the standard is used.

II. Field Standards

A. Preparation of field standards and confirmation of TFM or niclosamide concentration

1. Field Standards are prepared at HBBS.
   a. Field standards of TFM (0.0, 4.0, 8.0, and 12.0 mg/L) and niclosamide (100 mg/L) are prepared according to HBBS SOP LAB 335 (Preparation and packaging of TFM field standards for Sea Lamprey Control Agents) and 423 (Preparing TFM and Niclosamide Solutions, Appendix Q).
   b. Analysis of concentrations of TFM in field standards is conducted according to HBBS SOP LAB 322 (TFM determination using the HPLC method; Appendix Q).
   c. Analysis of concentrations of niclosamide in field standards is conducted according to HBBS SOP LAB 303 (Niclosamide determination using the HPLC method; Appendix Q).
   d. A subsample of each lot and/or batch of field standard is archived at the HBBS according to HBBS SOP 334 (Archiving of Chemicals; Appendix Q). Archived samples are retained for a period of two years after the field standard is used.
   e. After standards are bottled, sealed, and labeled with the appropriate hazard identification at HBBS, a set of standards is sent to UMESC for additional analysis to confirm that the final products are of stated concentrations.

2. The concentration of TFM or niclosamide in field standards is confirmed at UMESC.
   a. Subsamples of each batch of TFM and niclosamide field standards are transferred to UMESC. Each subsample includes a certificate of formulation that identifies the lot and/or batch number of the field standard, date of preparation, date of transfer, lot or batch number of the lampricide formulation from which the standard was prepared, identification (lot or batch) of the analytical standard used to determine the concentration of the field standard, and manufacturer.
   b. Confirmation of the concentrations of TFM and niclosamide in field standards is conducted according to UMESC SOP AEH 409 (Determination of percent purity of technical grade, manufacturing-use and end-use products of Bayluscide and 3- trifluoromethyl-4-nitrophenol (TFM) lampricide formulations; Appendix Q).
   c. TFM standards are accepted if analyses at UMESC confirm that concentrations are within ± 0.2 mg/L of stated value. Niclosamide standards are accepted if concentrations are within ± 2 µg/L.
   d. UMESC provides a summary report to HBBS, MBS, LBS, and SLCC confirming the results of the purity analysis of the TFM and niclosamide field standards.

B. Distribution of Field Standards

1. The field standards are packaged and distributed to MBS, LBS, SLCC, and LCFWMC along with documentation of transfer, documentation of identity and quantity of the field standard following SOP LAB 333 (Receipt, Identification, Preparation, Storage, and Handling of Lampricide Analytical and Field Standards; Appendix Q).

C. Receipt of field standards

1. Documentation of Receipt
   a. HBBS prepares a statement of formulation that is provided to MBS, LBS, SLCC and LCFWMC with each lot/batch of TFM and niclosamide field standard. This statement of formulation includes the concentration of the lampricide, a description of the parent material used to prepare the field standard, the procedure followed to prepare the field standard, a description of the analytical standard, and the procedure used to measure the lampricide in the field standard.
   b. HBBS prepares a statement of transfer when the field standards are transferred to MBS, LBS, SLCC, and LCFWMC. This statement of transfer includes the date of transfer, volume of standard, and code numbers for the samples of the field standard. The statement of transfer is signed by the formulator, the individual transferring the standard, the individual receiving the standard, and the individual placing the standard in storage. Copies of the transfer documents are retained by HBBS, MBS, LBS, SLCC, and LCFWMC.
   c. Upon receipt of the field standards of TFM and niclosamide the individual in charge inspects the containers for damage. If damage has occurred the individual in charge notifies HBBS and arranges for a replacement field standard.
   d. After receiving the field standard the individual in charge prepares a Field Standard Use Log (Attachment 3). Each container of field standard is coded with the year the formulation was prepared, nomenclature for identification which represents the station (MBS, LBS, or SLCC), field standard number, and a decimal extension that designates the concentration (e.g., 99MBS001.04). A Field Standard Use Log is maintained at MBS, LBS, and SLCC storage facilities.
   e. As field standards are depleted, new samples are removed from the storage area.

D. Confirmation of lampricide concentration in the field standard

1. Samples of field standards used to determine concentrations of lampricides in stream water and in on-site toxicity tests are analyzed to confirm the lampricide concentration. After any lampricide treatment where unusual observations were noted, subsamples of field standards are returned to the HBBS to confirm the concentrations of lampricide within the standards. A single unopened standard is sent with each set of samples as a check sample. In addition, unopened standards are sent to HBBS at the end of the field season to confirm the viability (shelf-life) of the standards. Analyses of standards are completed within 10 working days, and anomalous results are reported immediately to the Chemist-Sea Lamprey Control. Confirmation of the lampricide concentrations is conducted according to HBBS SOP LAB 322 (TFM determination using the HPLC method; Appendix Q) and/or HBBS SOP LAB 303 (Niclosamide determination using the HPLC method; Appendix Q) A summary report of the analyses of the field standards is provided to MBS, LBS, SLCC by HBBS.

E. Storage of field standards

1. Station storage
   a. The TFM standards, after receipt from HBBS, are placed in storage in a cool, dark area. Standards are not retained year to year.
   b. The niclosamide standards, after receipt from HBBS, are placed in refrigerated storage. Standards are not retained year to year.
2. Transport and field storage
   a. Standards are not exposed to direct sunlight during transport.
   b. TFM field standards are stored in a cool, dry, dark area until used.
   c. Niclosamide field standards are refrigerated until used.

F. Procedures for use:

1. Documentation of TFM field standards
   a. The absorbance of each field standard is recorded in the Spectrophotometer Log along with the code number of each standard. A standard with an absorbance that does not correlate with other field standards in the group is discarded and replaced. Field standards are analyzed periodically during routine TFM analyses to assure that the instrument response remains constant.

2. Procedures for use of the TFM field standards
   a. See TOP:018.x
   b. Unused or excess field standards are disposed of in accordance with pesticide label instructions (Appendix E) and/or information provided on the MSDS/SDS (Appendix F).

III. Preparation of niclosamide working standards

A. Documentation of niclosamide field standard use

1. The code number of the field standard used to formulate working standards is recorded onto the container which holds the working standard. The code number recorded on the working standards is copied into the HPLC Log Book. These code numbers are used to track all niclosamide analyses in which a working standard was used.

B. Procedure for preparation of niclosamide working standards

1. Determine the number of niclosamide standards required and the proper concentration of each standard. The range of concentrations in the working standards must include and bracket the concentrations of niclosamide expected in the unknown water samples.

2. For preparation of the niclosamide working standards, filter sufficient volumes of stream water (approximately 1000 mL for each niclosamide working standard) through Whatman 2V filter paper or equivalent to remove solids that may cause interference during analysis.

3. Dispense 0.250 mL of the niclosamide field standard into a 500 mL volumetric flask and dilute to 500 mL with the filtered stream water. Use an HPLC 250 uL syringe to measure the standard into the flask. Place a stopper in the flask and mix. This provides a 0.050 mg/L working standard. Niclosamide field standard must be warmed to ambient air temperature before use.

4. If additional standards are required, repeat the procedure while substituting

volumes of standard proportional to the desired concentrations.

5. The volumetric flask is labeled with date prepared, site from which the stream water was collected, concentration of niclosamide, and field standard code number.

6. The niclosamide working standards are stored in the dark in a locked mobile storage facility.

7. Unused or excess working standards are disposed of in accordance with the pesticide label instructions (Appendix E) and/or information provided on the MSDS/SDS (Appendix F). Standards are not retained between treatments.

C. Procedures for use:

1. Documentation of niclosamide working standards
   a. The absorbance of the working standard (peak area units) and response factor are recorded in the HPLC log book with the number of the field standard. A standard with an absorbance that does not correlate with the other working standards is discarded and replaced. If the response factor for the new working standard is still significantly different from that of the previous working standards, the function of the HPLC is checked. The absorbencies of the working standards are periodically checked during analyses to ensure that the instrument response is unchanged.

2. Procedures for use of niclosamide working standards
   a. Method 1: The response of the HPLC detector is linear for niclosamide concentrations less than 0.050 mg/L, therefore the use of a single working standard is acceptable for calibration of the HPLC data module. Multiple injections of the working standard (minimum of 3) are required to demonstrate reproducibility. A working standard with a niclosamide concentration of less than 0.050 mg/L is acceptable for analyses of samples containing niclosamide concentration less than that of the standard (TOP:021.x).
   b. Method 2: A series of working standards with varying concentrations of niclosamide may also be used for analysis by HPLC. The data module provides input options which allow calibration by multiple standards (TOP:021.x).

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 Jessica M. Barber Digitally signed by JESSICA BARBER Date: 2020.03.10 11:34:02 -04'00' DATE _____
Field Supervisor (U.S.)

REVIEWED/APPROVED Luke Shivers DATE 05 MAR 2020
Program Manager (Canada)