Region 4
U.S. Environmental Protection Agency
Science and Ecosystem Support Division
Athens, Georgia

OPERATING PROCEDURE

Title: **Reaeration Measurement using Krypton Gas**

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Revision History

The top row of this table shows the most recent changes to this controlled document. For previous revision history information, archived versions of this document are maintained by the SESD Document Control Coordinator on the SESD local area network (LAN).

History	Effective Date
SESDPROC-506-R3, *Reaeration Measurement using Krypton Gas*, replaces SESDPROC-506-R2. **General:** Corrected any typographical, grammatical and/or editorial errors. **Title Page:** Changed Ecological Assessment Branch Chief From Bill Cosgrove to John Deatrick. Changed Field Quality Manager from Laura Ackerman to Bobby Lewis. **Revision History:** Changes were made to reflect the current practice of only including the most recent changes in the revision history. **Section 1.2**: Added the following sentence: "Mention of trade names or commercial products in this operating procedure does not constitute endorsement or recommendation for use." **Section 3.2**: Removed equipment list **Section 4**: Removed first sentence of second paragraph. **Section 4.2**: Added clarification regarding purpose of first bulleted item. Added "When feasible" to fourth bullet item. Added "Other diffuser materials/designs may also be suitable" to last paragraph of section. **Section 4.3**: In second paragraph, removed reference to equipment list in Section 3.2.	May 30, 2013
SESDPROC-506-R2, *Reaeration Measurement using Krypton Gas*, replaces SESDPROC-506-R1.	November 3, 2009
SESDPROC-506-R1, *Reaeration Measurement using Krypton Gas*, replaces SESDPROC-506-R0.	November 1, 2007
SESDPROC-506-R0, Reaeration Measurement using Krypton Gas, Original Issue	February 05, 2007

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1 General Information

1.1 Purpose

The purpose of this operating procedure is to document both general and specific methods and considerations to be used when measuring stream reaeration using krypton gas.

1.2 Scope/Application

This document describes both general and specific methods to be used by field investigators when obtaining data for the purposes of determining stream reaeration. In the event that Science and Ecosystem Support Division (SESD) field investigators determine that any of the procedures described in this section are either inappropriate, inadequate or impractical for a given site or station or that another procedure must be used to obtain a representative measurement, the variant procedure will be documented in the field log book, along with a description of the circumstances requiring its use. Mention of trade names or commercial products in this operating procedure does not constitute endorsement or recommendation for use.

Reaeration is the rate at which atmospheric oxygen diffuses across the air-water interface of the surface of a stream.

1.3 Documentation/Verification

This procedure was prepared by persons deemed technically competent by SESD management, based on their knowledge, skills and abilities and has been tested in practice and reviewed in print by a subject matter expert. The official copy of this procedure resides on the SESD local area network (LAN). The Document Control Coordinator (DCC) is responsible for ensuring the most recent version of the procedure is placed on the LAN and for maintaining records of review conducted prior to its issuance.

1.4 References

Nation Council on Air and Stream Improvement (NCASI). 1989. Development of a Gas Chromatographic Protocol for the Measurement of Krypton Gas in Water and Demonstration of Its Use in Stream Reaeration Rate Measurement. Prepared by Technical Resources Inc. for NCASI , EPA Contract 68-03-3305,

SESD Operating Procedure for Hydrological Studies, SESDPROC-501, Most Recent Version.

SESD Operating Procedure for Logbooks, SESDPROC-010, Most Recent Version.

United States Geologic Survey (USGS). 1989. Determination of Stream Reaeration Coefficients by Use of Tracers, Applications of Hydraulics, Book 3, Chapter A18

US EPA. Safety, Health and Environmental Management Program Procedures and Policy Manual. Region 4 SESD, Athens, GA, Most Recent Version

1.5 General Precautions

1.5.1 Safety

Proper safety precautions must be observed when conducting reaeration studies. Refer to the SESD Safety, Health and Environmental Management Program Procedures and Policy Manual and any pertinent site-specific Health and Safety Plans (HASP) for guidelines on safety precautions. These guidelines, however, should only be used to complement the judgment of an experienced professional. For example, these methods may be employed during periods of high stream flow.

1.5.2 Procedural Precautions

The following precautions should be considered when conducting reaeration measurements studies:

- All instrumentation should be in good condition and operating within the manufacturer's recommended tolerances.
- All instrumentation should be calibrated and deployed in accordance with the manufacturer's requirements.

2 Special Sampling Considerations

2.1 Quality Control

The reaeration rate coefficient is expressed as a rate in 1/day corrected to 20° Celsius (C). Three to four replicate samples are collected with each sampling event. Generally, multiple sampling events will occur at each sampling station. Details of the sampling effort should be documented in the Quality Assurance Project Plan.

Krypton sample holding time is 14 days.

2.2 Records

Information generated or obtained by SESD field investigators will be organized and accounted for in accordance with SESD records management procedures. Field notes, recorded in a bound logbook will be generated, in accordance with SESD Operating Procedure for Logbooks (SESDPROC-010), as well as chain-of-custody documentation. All measurements shall be thoroughly documented in field records. All measurements shall be traceable to the personnel making the measurements and the equipment utilized.

3 General Considerations

3.1 General

The techniques and equipment described in Section 4 of this procedure document are designed to provide representative measurements of stream reaeration rates. Care should be applied in the selection of measurement sites and/or reaches to ensure personnel and equipment safety. For example, unattended monitoring equipment or samplers should be located above anticipated water levels during stream bank deployments. Safety precautions should be taken when working with compressed gas. For example, tanks should be secured in the transport vehicle to prevent rolling. On site, vertically deployed tanks should be secured to a stationary object such as a bridge piling. If necessary, conduit or rebar may be driven into the ground to allow secure vertical deployment of the gas tank.

3.2 Equipment Selection Considerations

The type and size of the water body under investigation will often dictate the equipment required for reaeration measurement. For example, in larger or higher velocity waters, diffuser plates may be mounted on weighted boards. The anticipated river flow and resulting anticipated gas flow, in concert with professional judgment, will dictate the number of diffuser plates required.

Generally, dye monitoring will be conducted by personnel on site to allow sampling on the dye plateau. However, based on predicted travel times, unattended equipment may be deployed in advance of the dye arrival at a station. Such equipment may include a logging fluorometer or automatic sampler.

4 Stream Reaeration Measurement

The determination of the stream reaeration rate coefficient is a measure of the rate at which atmospheric oxygen can move across the air-water interface. This is a measure of the rate of potential oxygen transfer. The actual quantity of oxygen transferred to the water column is a function of the water column dissolved oxygen deficit and the reaeration rate coefficient.

The degasification of tracer gas is related to oxygen absorption into the stream. For example, the US Geological Survey developed a measurement technique using propane gas (USGS, 1989). In the late 1980’s/early 1990’s the Environmental Protection Agency’s (EPA) Region 4 SESD developed a similar technique for measuring stream reaeration rate coefficients using non-radioactive krypton as a tracer gas.

In general, the method involves the simultaneous and continuous injection of rhodamine WT dye and noble krypton gas. The purpose is to create a sustained, steady plateau of gas and dye in the stream. Therefore, a relatively steady stream flow is required for the implementation of this method. The plateau is then sampled at successive downstream locations for the purpose of measuring degasification of krypton in the waterbody. This provides the information necessary to compute associated reaeration rate coefficients.

4.1 Injection Site Selection

A reaeration injection requires the introduction of a tracer gas and liquid dye into the water column. The EPA methodology uses a steady-state injection of both the noble gas krypton and rhodamine WT dye. The degasification gas (krypton) is dispersed into the water through the use of micro bubble diffuser plates. Simultaneous dye-tracer injection at a center point relative to the gas plates is controlled via a constant rate injection pump. When selecting a krypton suitable injection site, the following should be considered:

- The stream at this site should be reasonably deep (>2 feet) at the injection site with an even velocity in cross-section;

- It is preferable for the stream to have some degree of sinuosity below the injection site allowing for the greatest mixing potential.

4.2 Gas and Dye Injection

Prior to conducting a reaeration study, estimates of the required gas and dye injection rates should be made with the following considerations:

- To avoid excess use of dye, rhodamine WT should be injected at a constant rate to maintain a plateau concentration in the subject stream less than 100 parts per billion (ppb); however, higher concentrations do not invalidate the measurement;

- At no time should the dye concentration exceed 50 ppb at the point of withdrawal for any water supply within the study reach;

- The noble gas krypton should be injected at a constant rate to achieve a plateau of sufficient concentration and duration to allow for the measurable loss of gas along the entire study reach;

- When feasible, the dye and associated gas should have at least three hours of plateau at the farthest downstream station;

- Sampling locations should be sited to allow for a target 60 percent reduction in gas due to loss to the atmosphere from upstream to downstream.

A reconnaissance survey of the study stream reach can provide useful information for predicting required dye and gas concentrations. Reconnaissance information should include stream width, depth and mean-reach velocity. The reconnaissance survey also provides an opportunity to locate a suitable injection site and accessible sampling locations.

Deployment at the injection site begins with securing the krypton gas cylinders and connecting the regulator and gas flowmeters via gas hoses. Next, gas hoses are connected to the diffuser plates. Sufficient hose length is required between the flowmeter and the plates to allow for deployment of the plates in the stream. Placement of the plates should be across the main flow of the channel to maximize initial mixing. The number of plates required is dictated by the required gas flow rate and the manufacturer's designated maximum flow rate through the plate. Other diffuser materials/designs may also be suitable. A small gas flow should be running through the plates as they are deployed to prevent flooding of the diffuser. Gas flow is controlled by flowmeter using existing calibration curves. The dye pump should be calibrated on site using a graduated cylinder. Dye and gas injection rates should be constant throughout the injection period.

4.3 Dye Monitoring and Gas Sampling

Based on predicted travel times, automatic sequential samplers or unattended fluorometers may be deployed at sampling stations prior to initiation of dye injection to ensure that the dye cloud is monitored prior to the arrival of the sampling crew. Following initiation of dye injection, sampling teams will arrive at each sampling station well in advance of the predicted dye plateau onset to begin dye monitoring.

Once dye is observed at the first sampling location below the injection point (usually identified as the pickup station), complete mix is confirmed by fluorometric readings across the stream channel and at multiple depths. Generally, this is accomplished using a submersible pump connected to a flow-thru fluorometer; however, other equipment is acceptable. If the dye is not mixed throughout the width and depth of the water column, a new station must be located farther downstream and complete mix reevaluated at the new station. If the mixing is complete in the cross-section, fluorometric monitoring continues until a sustained plateau dye concentration is observed. Krypton sampling is conducted with specially designed weighted buckets that allow for the collection of four replicate water samples without inducing aeration. Specially designed bottles are placed in the sampler and the sampler lid installed. The lid has a tube for venting of the sample chamber during collection. The sampler should be submerged in the water column until the vent tube no longer releases bubbles indicating the sample bottles are full. In addition, the sampler itself will be full of water. The bottle caps should be inserted while the bottles are still submerged in the sampler. This sampling procedure is usually repeated through four equally spaced intervals in time (normally 30 minutes).

After the gas sampling is completed, an automatic sequential sampler or unattended fluorometer is then installed at the site to continue dye monitoring at the station throughout passage of the entire dye cloud. This provides the data necessary for computing time of travel.

Krypton samples are held in cool conditions (e.g, light ice) until released to the laboratory. Cool conditions are recommended to prevent bottle breakage associated with temperature related volume changes. Krypton/argon ratio analysis is presently conducted at the University of Georgia’s Center for Applied Isotope Studies (UGA-CAIS) Laboratory in Athens, Georgia using a dedicated gas chromatographic mass spectrometer (GC/MS) system equipped with a unique gas extraction cleanup line.

4.4 Reaeration Rate Coefficient Calculation

Once the field data have been processed, degasification rate coefficients are calculated for each reach. Degasification calculations require stream travel time, flow rate and krypton/argon ratios at consecutive downstream stations. Travel times are calculated based on centroids of successive downstream dye clouds. Flows are computed using a mass balance dye dilution calculation on dye plateau concentration results and/or by gaging measurements, as described in the SESD Operating Procedure for Hydrological Studies (SESDPROC-501). Computed degasification rate coefficients are converted to oxygen absorption rates (reaeration rate coefficients) using the relative transfer rates. Contractors working for EPA, Whittemore and Krause, established the relative transfer rate of krypton degasification to oxygen absorption at 0.83 +/- 0.04 (NCASI 1989). Lastly, reaeration rate coefficients are temperature corrected to a base temperature of 20°C

The following equations are used to compute the reaeration rate coefficient for each reach.

(1) $K_{krypton} = (1/tt)\ln[Q_{up}(Kr/Ar)_{up}/Q_{down}(Kr/Ar)_{down}]$

(2) $K_a@tEC = K_{krypton}/0.83$

(3) $K_a@20EC = K_a@tEC\ (1.0241^{\{20.0-[(Tup+Tdown)/2]\}})$

$K_{krypton}$ = Krypton degasification rate coefficient (1/day)

K_a = Reaeration rate coefficient (1/day)

$K_a@tEC$ = Reaeration rate coefficient at ambient temperature

tt = travel time (days)

Q_{up} = flow at upstream station (cubic feet per second [cfs])

Q_{down} = flow at downstream station (cfs)

$(Kr/Ar)_{up}$ = Krypton:Argon ratio upstream (unitless)

$(Kr/Ar)_{down}$ = Krypton:Argon ratio downstream (unitless)

T_{up} = upstream temperature (EC)

T_{down} = downstream temperature (EC)