Memo

To: DEQ Wastewater Permitting Program

From: Scott Hoatson, Agency Quality Assurance Officer

Date: 11/15/2017

Subject: Recommendations on Measuring Chlorine and Ammonia in NPDES 900-J General Permits for Seafood Processing

State of Oregon
Department of
Environmental
Quality

Laboratory and Environmental Assessment Program
7202 NE Evergreen Pkwy.
Suite 150
Hillsboro, OR 97124
Phone: 503-693-5700

Fax: 503-693-4999
Contact: Scott Hoatson

www.oregon.gov/DEQ

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Background

The wastewater generated from seafood processing operations is complex and presents challenges for the testing of residual chlorine and ammonia. The testing requires the proper equipment and a trained person to perform the tests. In 2006, a consultant requested that the DEQ laboratory help test the performance of a specific brand of chlorine and ammonia ion specific electrodes (ISE) and the associated meter for potential use by seafood processing operations for characterization or compliance testing of their wastewater. The test evaluated the performance of the chlorine ISE compared to other approved methods in 40 CFR Part 136.3. Chlorine testing by the ISE method did not perform well in the seafood processing wastewater matrix. The ammonia ISE was not tested.

Following this study, the following language was added to the 900-J General Permit issued 7/18/06: "*Samples for chlorine and ammonia must be taken only if cleaning operations using chlorine and/or ammonia products are being conducted. Sampling will not be required until the first season after the DEQ Laboratory has developed and promulgated sampling and analysis protocols for chlorine and ammonia.*"

Current Status

The DEQ wastewater permitting section requested the DEQ Laboratory program to re-evaluate the issue of ammonia and chlorine in seafood wastewater and provide guidance to the program as to the availability of other approved test methods for performing both ammonia and residual chlorine testing.

The 2006 study performed by the DEQ lab only pertained to chlorine, so it is unclear why ammonia was included in the exception since the ammonia procedure includes a distillation that removes many of the interferences. The 2006 chlorine study indicated many of the concerns that have been raised but did not discount the DPD method entirely and did not state that chlorine could not be analyzed in seafood matrices. The report indicated that the back titration amperometric method (SM 4500-Cl C) is the preferred method but was more technically challenging. Based on the limited data contained in the 2006 report, the Hach® Ultra Low Level DPD method (easiest to perform) showed to be very comparable to the back titrated amperometric method when the sample was diluted 10 or 40 times.

The report was geared towards method limitations but without corresponding quality objectives (permit limits), it lacks context about what might work for chlorine testing and what options would exist.

Memo

This memo is an attempt at providing the information and recommendations to the wastewater permitting section in response to the statement in the 900-J General Permit "*Sampling will not be required until the first season after the DEQ Laboratory has developed and promulgated sampling and analysis protocols for measuring chlorine and ammonia*" in seafood processing wastewater and guidance on sampling methods that may be conducted by seafood processors in order to meet the requirements of 40 CFR Part 136.3. It is our opinion that this testing should be very possible.

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APPROVED TEST METHODS FOR NPDES MONITORING FOR CHLORINE AND AMMONIA With DEQ Supplemental Guidance for Seafood Processing Wastewaters

NPDES Monitoring- Approved Test Methods

The relevant method regulations for NPDES compliance testing are found in 40 CFR 136.3 (including footnotes) and 40 CFR part 136.7. These regulations document appropriate methods for each analyte and include detailed information on containers, sampling, sample handling, hold time and analysis.

- For sample containers, preservation and holding times see 40 CFR 136.3 (e) Table II
- For Ammonia (as N) analysis methods see 40 CFR 136.3 (a) Table IB Inorganic Tests (#4)
- For Total Residual Chlorine analysis methods see 40 CFR 136.3 (a) Table IB Inorganic Tests (#17)
- For basic Quality Control requirements and methods see 40 CFR part 136.7
- For other guidance see DEQ *Quality Assurance Guidance for Self-Monitoring Laboratories (NPDES and WPCF)* found at: **www.oregon.gov/deq/FilterDocs/**QAguidance**SML.pdf**

Ammonia Testing

40 CFR Part 136.3(a) Table 1B requires that samples for ammonia be **distilled** prior to using one of several methods unless it can be demonstrated that distillation is not needed for the specific waste stream. In the case of seafood processing, the waste stream is expected to have significant interferences so the laboratory performing the analysis **must distill** the samples before testing. The distillation process should remove all or almost all of any potential matrix interferences but it also means the ammonia analysis needs to be performed in a laboratory with the appropriate equipment. With distillation, the tests approved for ammonia in 40 CFR 136.3 should perform satisfactorily. Fortunately, ammonia samples have 28 days holding time when properly acid preserved. DEQ suggests that samples for ammonia be sent to an accredited commercial laboratory as the costs of the equipment, supplies and training of a technician likely do not justify attempting to run ammonia analyses at the facility. Any associated shipping costs should be negligible since the permittees are already sending samples to commercial labs for other tests (e.g. BOD, Oil and Grease, etc).

Guidance for sample preservation for ammonia, 2 steps at collection prior to shipping:

1) See the preservation and sample containers identified in Table II of 40 CFR 136.3 and use an approved container. DEQ suggests using 500 mL polyethylene bottles to make step 2 easier. The permittee should contact their laboratory for additional guidance.

2) If residual chlorine is present, the permittee must treat the sample with a de-chlorinating agent prior to acidifying. Since the permittee will be testing for chlorine anyway and it has to be done at the time of sampling, they can use the test results to determine the presence /absence of chlorine:

   a. Test the sample to identify how many mg/L or ppm of chlorine are present. If no chlorine present, proceed to step 3)

   b. For every mg/L chlorine, add 1 ml of sodium thiosulfate solution (de-chlorinating agent) per 500 mL of sample volume. This must be done prior to acidification. Your selected laboratory can provide the thiosulfate solution. .

3) Add a small amount of sulfuric acid (H_2SO_4) to lower the pH to <2; this is usually 0.5 – 1 mL but it is dependent on the initial pH of the sample. Discuss with the laboratory about the amount of acid to add. Record the amount used.

4) Pack the sample in a small cooler with ice and deliver (ship) to your laboratory. Contact the laboratory for their preferred shipping method and instructions. Remember to include your filled out chain of custody form. **Make a note on the chain of custody form that the sample is for an NPDES permit requirement and you are requesting the lab to distill the sample prior to analysis.**

5) This guidance does not represent the entire method and requirements. Refer to the full text of the regulations and methods.

Chlorine Testing

The Total Residual Chlorine test is an analysis that must be done as soon as possible, per 40 CFR 136.3, within 15 minutes of sampling. This means analysis must be performed on-site. The 2006 DEQ study provided discussion regarding chlorine testing and the inherent difficulties due to the high organic nature of the waste stream from seafood processing operations. The study emphasized that the technician needs to use care regardless of what method is used. The ISE method, which was the focus of the study, did not show consistent results on this waste stream and required careful analysis by the technician.

The method the study indicated was the most accurate on the seafood processing wastewater was a titrimetric back titration method (SM[1] 4500-CL C - Iodometric Method II). This method, however, requires the most skill and training of the laboratory technician (However, it should be noted that there are autotitrators available that may be used). Low level or ultra low level DPD colorimetric test kits (such as kits made by Hach® Company[2] or others) are available and more user-friendly and generally meet the requirements in the SM[1] 4500-CL G *DPD Colorimetric Method* which is an approved method (Do NOT use methods with a color comparator, use only those that use a colorimeter or spectrophotometer).

The DPD method should be able to reliably report down to 0.01 or 0.02 mg/L on a clean sample (the ultra low method is quoted down to 0.002 mg/L[3]), however due to the high organic nature of the waste stream interferences by color, turbidity or overall waste strength may be encountered which will likely require filtration and/or a dilution of the sample by somewhere between 10 and 100 times and will affect the overall reporting limit. (In the study, dilutions of 10:1 and 40:1 were successfully used). To compensate for color and turbidity in the sample, the analyst will need to analyze a blank sample (without color reagent) and then the sample again with color reagent. The difference in the results obtained is the value to report. If the results are not detected, then the reporting limit is multiplied by the dilution factor and reported as < RL (e.g. if the method used has a reporting limit of 0.01mg/L and the sample was not detected at a 10x dilution, you would report < 0.1 mg/L.

If overall waste stream strength causes analytical difficulty (e.g. excessive turbidity that can't be compensated), the analyst may need to dilute the sample 10x (or 20x, 40x, 50x etc) if the sample is really bad. I would recommend that the permittee start with a 10x – 20x dilution. To achieve ten times dilution mix 1 ml of the sample with 9 ml of de-ionized (or distilled) water and proceed with the test. The result is then multiplied by 10 to obtain the value to be reported. Similarly for a 40 times dilution mix 1 ml of sample with 39 ml of de-ionized (or

[1] Standard Methods for the Examination of Water and Wastewater; (2012 or 2017) American Public Health Association (APHA)

[2] This is not an endorsement of Hach®, but is just an example since they are well known to the regulated community. Hach® DPD method was used in the method comparison study. There are other companies that provide equivalent technology.

[3] Though the cost is higher, the Hach® ultra low method would allow for a larger dilution and still the ability to achieve the permit limit objectives.

distilled) water and proceed with the test. The result is then multiplied by 40 to obtain the value to be reported. The reporting limit will also need to be raised by any dilution factor. The permittee should document the reason for dilutions.

There are other approved methods in 40 CFR Part 136.3 that may provide acceptable results as well, depending on the specific waste stream from the permittee's facility. **Unless the permittee has experience in total chlorine analysis, I recommend they contact a laboratory consultant for the initial start-up of any method.**

Disclaimers:

DEQ does not "approve" specific instrumentation manufacturers and equipment and it is not our intent to imply that a permittee must use Hach® equipment and methods, there are other options available that are based on Standard Methods 4500-Cl G.

This guidance does not represent the entire method and requirements. Refer to the full text of the regulations and methods.

General Quality Control

Basic quality control is required by 40 CFR part 136.7 (blanks, duplicates, matrix spikes, control samples, calibration verification, demonstration of capability, documentation, training, etc.). The 900-J permit requires adherence to the methods including the quality control procedures. Analytical equipment and reagents will be needed and should include various analytical glassware, measuring pipettes, laboratory manual and forms, standards for validating calibration, known spike materials for validating analytical technique. Therefore, DEQ suggests that permittees consult with their laboratory or a consultant concerning their monitoring program to develop their written procedure document for quality control. See also the references at the end of this document.

It should be noted that where chlorine in samples is not detected and accompanied by poor or no matrix spike recovery, this may indicate that the presence of residual chlorine may not be possible due to the high organic content of the samples creating a chemically reducing environment (provided other quality control samples are acceptable).