Formation of Disinfection By-Products from Hydraulic Fracturing Fluid Constituents

Quality Assurance Project Plan

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_____/s/_____ __10/5/11_____
Principal Investigator Date

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Sam Hayes, WSWRD Associate Division Director Date

_____/s/_____ __10/12/11_____
Christopher A. Impellitteri, Technical Research Lead for Produced Water Treatment/Disposal Date

_____/s/_____ __10/5/11_____
John Olszewski – WSWRD QA Manager Date

EPA does not consider this internal planning document an official Agency dissemination of information under the Agency's Information Quality Guidelines, because it is not being used to formulate or support a regulation or guidance; or to represent a final Agency decision or position. This planning document describes the quality assurance/quality control activities and technical requirements that will be used during the research study. EPA plans to publish the research study results in a draft report, which will be reviewed by the EPA Science Advisory Board. The final research report would be considered the official Agency dissemination. Mention of trade names or commercial products in this planning document does not constitute endorsement or recommendation for use.

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1.0 DISTRIBUTION LIST

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2.0 ACRONYMS/DEFINITIONS

ADD-Associate Division Director
AWBERC-Andrew W. Breidenbach Environmental Research Center
DBP-Disinfection By-Product
DI-Deionized Water
GC-Gas Chromatography
HAA-Haloacetic acid
HF-Hydrofracking
IC-Ion Chromatography
ICP-OES-Inductively Coupled Argon Plasma-Optical Emission Spectrometer
ICV-Internal calibration Verification
IDL-Instrument Detection Limit
MDL-Method Detection Limit
MS-Mass Spectrometer
NOM-Natural Organic Material
NRMRL-National Risk Management Research Laboratory
ORD-Office of Research and Development
OST-Office of Science and Technology
OW-Office of Water
PFG
PI-Principal Investigator
POTW
QAM-Quality Assurance Manager
QMP-Quality Management Plan
RSD-Relative Standard Deviation
SOP-Standard Operating Procedure
TDS-Total Dissolved Solids
THM-Trihalomethane
WQMB-Water Quality Management Branch
WSWRD-Water Supply and Water Resources Division

3.0 PROJECT MANAGEMENT

3.1 Project/Task Organization

The PI, Toby Sanan, will be responsible for planning and coordination of all lab work, data analyses, manuscript preparation. The QA Manager, John Olszewski, is responsible for ensuring the Quality Assurance Plan and assurance objectives follows EPA-ORD guidelines. This may include review of data validation and procedures. Chris Impellitteri will serve as Technical Research Lead and interact with interested parties including EPA-Office of Water and utilities in EPA Region 3, and serve as liason with EPA Region 3. Darren Lytle, Thomas Speth and Sam Hayes will review any products generated within this Project Plan. Heath Mash will serve as technical advisor and reviewer for the data generated. The technical reviewers will examine representative samples of data (approximately 10 to 20 %) and identify any problems. If problems are identified, a more extensive review will occur.

Name	Organization/Title
Christopher A. Impellitteri	EPA/Principal Investigator (PI)
John Olszewski	EPA/Quality Assurance Manager
Darren Lytle	EPA/Co-PI
Tom Speth	EPA/Co-PI
Heath Mash	EPA/Co-PI
Toby Sanan	Post Doc /Co-PI

3.2 Problem Definition/Background

Hydraulic fracturing (hydrofracking, HF) is a technique now in widespread use which assists in the extraction of natural gas reserves; however, its use results in the generation of large amounts of produced or flowback waters which must be treated prior to disposal. This flowback water typically contains high levels of dissolved solids (including chloride and bromide salts), heavy metals, and hydrocarbons, as well as chemical additives from various stages of the fracturing process. In general, treatment of HF water occurs through either admixture to normal wastewater inputs or post-treated wastewater. However, to date the impacts of such inputs, and in particular the effects of high total dissolved solids (TDS) levels, on subsequent water disinfection have not

been ascertained. The elevated TDS levels are particularly worrisome because wastewater treatment is not effective at their removal.

Literature studies on the effects of bromide ions under chlorination disinfection conditions have demonstrated increased propensity for formation of brominated disinfection by-products (DBPs) upon reaction with natural organic material (NOM), and although the highest levels were observed upon ozonation, chlorination/chloramination also produce brominated DBPs.[1,2] Brominated DBPs are considerably more toxic than corresponding chlorinated DBPs, in addition to being of higher molecular weight (which would mean reduced concentrations would be needed to exceed MCLs), and it is accordingly of interest to EPA to assess and quantify the effects of flowback water on DBP generation.[3]

In addition to high TDS levels, hydraulic fracturing techniques frequently employ anti-fouling/biocidal agents, brominated organic molecules which themselves may be brominated DBP precursors. These molecules are typically employed in very low percentages of total fracturing fluid composition, but given the volumes involved may be produced in sufficient quantities to warrant further study.

Accordingly, there are two primary research objectives for this project: Evaluation of the effects of high TDS upon chlorination, chloramination, or ozonation of hydrofracking-impacted waters. Critical analytes include elevated concentration levels of the halide anions chloride, bromide and iodide. As such, the formation of disinfection by-products including Trihalomethanes (THMs), Haloacetic Acids (HAAs) and nitrosamines are of critical interest. Secondary objectives include a) the analysis and characterization of these hydrofracking-impacted waters and b) differences in blended waters downstream of the discharge point whether added at the headstream of a wastewater treatment plant or post-treatment where a mixed wastewater/hydrofracking discharge blend will occur. As such, analysis of total organic carbon (TOC), chemical composition and oxidation potential will also be monitored.

The second primary objective will investigate specific organic chemicals used during hydrofracking activities, in particular biocides. The primary analytes will be the oxidative by-products observed after reaction. The secondary objective is to investigate various solution matrices to determine their effect on the distribution of by-products and effect of the reaction kinetics. Such matrix composition parameters to be investigated include TDS content, organic material type and concentration and pH.

3.3 Project/Task Description

The project is sub-divided into 3 distinctive tasks. Table 3.1 summarizes the various tasks that will be performed as part of this research project.

Table 3.1. List of experimental tasks

Task 1	Analysis of EPA Region 3 Water Samples for TDS and NOM Content and Character

Task 2	Effects of Elevated TDS on DBP Formation
Task 3	Kinetics of Formation and Identification of Degradates of Resource Extraction Biocides

3.3.1 *Task 1*

Task 1 will include assessing DBP formation potentials and reaction kinetics taking place in waters to be obtained from several sources in EPA Region 3, all of which can be influenced by the character of the water source. Samples will be initially analyzed for the presence of disinfection by-products including THMs (Method 551.1), HAAs (Method 552.1) and *N*-nitrosamines (Method 521). The samples will also be analyzed for elemental composition, anion concentration, TDS and TOC (See Section 4.4).

Additionally, the water samples will be subjected to formation potential experiments in the presence of typical drinking water oxidants. Formation potential measures will be obtained separately for THMs, HAAs and Nitrosamines.

3.3.2 *Task 2*

Bench-scale experiments will be performed to assess the effects of elevated bromide and chloride levels on DBP formation in several water matrices. Disinfection techniques including ozonation, chlorination, and chloramination will be utilized. Experiments in this study will focus on water samples including: de-ionized water (DI), DI fortified with several organic material isolates from different water sources, and flowback waste-water sources as mentioned in Task 1 (prior to and after treatment). DBP assessment will focus on THMs, HAAs, and *N*-nitrosamines, as discussed in Task 1, and NOM sources will include both locally obtained natural waters as well as freeze-dried NOM concentrate.

3.3.3 *Task 3*

Task 3 will assess the degradation of biocides used in hydrofracking operations using bench-top experiments. Proposed experimental variables include pH, NOM source/concentration and halide concentration. Analysis will be performed by a combination of HPLC/MS (for identification of organic reaction products) and the known EPA methods for analysis of THM/HAA formation (described in Task 1). The kinetics for degradation will be evaluated, degradation products will be identified/characterized and lifetimes of observed intermediates/products will be determined. Results from this study will be used to identify molecules which may be important for further study from a toxicological standpoint. The list of proposed biocides to be investigated are shown in Table 3.2.

Table 3.2. List of proposed biocides

Target Biocide	CAS Number

2-(Thiocyanomethylthio) benzothiazole	21564-17-0
2,2-dibromo-3-nitropropionamide	10222-01-2
2,2-Dibromomalonamide	73003-80-2
2-bromo-2-nitrol-1,3-propanediol	52-51-7
2-Methyl-4-Isothiazolin-3-one	2682-20-4
3,3-methylenebis(5-methyloxazolidine)	66204-44-2
5-chloro-2-methyl-4-isothiazolin-3-one	26172-55-4
Benzisothiazolinone	2634-33-5
Sodium dichloroisocyanurate	2893-78-9

3.4 Timeline

The proposed timeline between project initiation and conclusion is summarized in Table 3.3.

Table 3.3. Project Timeline

	2011				2012			
	1	2	3	4	1	2	3	4
Project Planning		X	X					
Experimental Tasks			X	X	X	X		
Sample Analysis and Data Verification					X	X		
Audits				X		X		
Report Writing						X	X	
Report Submission of ORD Clearance							X	

3.5 Documents and Records

All research related documents and records will conform to guidelines in accordance with ORD's Policy and Procedures Manual, Chapter 13, Section 13.2: *Paper Laboratory Records* (U.S. Environmental Protection Agency, 2008) and the HF Quality Management Plan (QMP). Raw data will be kept as hard copies and computer files. Manuscripts/reports for submission to peer reviewed journals will be submitted for internal QA review before submission to the journal. All corrections/changes will be made prior to submission to the journal.

Equipment maintenance logs will be recorded on hardcopy in the lab, including results from ongoing instrument calibration and maintenance. Raw data from chemical instrumentation will be retained throughout the duration of the project, and will be backed up onto a separate external hard drive. Experimental procedures and results of experimental analysis will also be recorded in laboratory notebooks maintained by all laboratory personnel contributing to the project.

Archival copies will be stored in back up hard drives depending on the frequency of analysis. All physical records will be maintained for the duration of the study.
Computer files can also be stored on the shared ORD drive, O:\, in accordance with the HF QMP, Section 5.1 at O:\Priv\NRP_SSWR_HF\. In naming computer files, researchers will also follow naming convention guidelines in accordance with the HF QMP, Section 5.2

3.6 Project Quality Objectives and Criteria

This is a NRMRL Category I research project. All quality control criteria required for a Category I project as described by the NRMRL QMP will be adhered to. Quality control criteria and verification for methods used during this project will be integrated within Section 4.4, Analytical Methods.

3.7 Special Training/Certification

Work at the EPA's T&E facility must be performed by staff that has completed the OSHA 40-hour HAZMAT Course and RCRA 8-hour training. Staff located in AWBERC must have all safety/health requirements up-to-date. Documentation to this effect is on record with SHEM. The Health and Safety Plan (HASP) on file also includes information regarding the safety training and requirements for the project.
Prior to performing sample analysis with a technique/method/instrument for which proficiency has not been previously demonstrated and documented, the analyst must demonstrate proficiency by: 1) performing valid initial calibrations, 2) performing method detection limit determination, if appropriate, 3) demonstrating that their results meet all minimum QA/QC acceptance criteria as presented in the method document, e.g., the SOP, and if available, 4) satisfactorily analyzing a performance evaluation sample or a second source standard. Documentation of these activities shall be maintained by the Supervisor or designee. Training requirements for the experimental and analytical techniques employed in this project will be documented. Employee experience and training will also be recorded as necessary. Each lab will need to demonstrate a level of competency by demonstrating proficiency as measured by the associated QA objectives outlined in the specific analysis performed.

4.0 DATA GENERATION AND ACQUISITION

4.1 Task 1 – Analysis of EPA Region 3 Water Samples for TDS and NOM Content/Character

4.1.1 *Objective*

Hydraulic fracturing techniques produce a large quantity of waste waters which may be sent to publicly owned treatment works (POTWs), commercial wastewater treatment facilities, or

treated on site for reuse. In any treatment scenario, there is a final waste product that must be treated and disposed of. In some areas, HF wastewaters are treated by POTWs either by mixing at the headwaters or blended with the POTW effluent. The impact of effluent discharge into surface water sources on drinking water treatment has not yet been evaluated, nor is it clear at this point the extent of dilution upon arrival at drinking water input streams. We propose to evaluate water samples obtained at varying distances from known resource extraction sites (i.e. downstream of effluent introduction into the surface water system) to characterize the nature and extent of flowback water impacts on the character of the water samples. Care will be taken with regard to the collection of water samples, as a number of factors, including flow rate, collection techniques, and source conditions are important considerations in data analysis. The results of this study will be used for refinement of the conditions employed in the TDS research component.

It is known that the amount and type of TDS and halide content in water can influence aqueous chemistry, particularly upon water treatment/disinfection. This is particularly true with water which has been impacted by wastewater input from a variety of industrial/resource extraction processes. In this component of study we will analyze water samples obtained from EPA Region 3 for TDS and characterize the NOM present as a precursor for further studies in Task 2. In addition, the incoming water samples will be analyzed for the presence of disinfection by-products to ensure that background effects are properly taken into consideration for Task 2 and Task 3.

4.1.2 *Key Ideas*

Formation of disinfection by-products has been shown to be dependent on a variety of factors in source water, including the character of natural organic material (NOM), the presence and concentration of halogen salts, temperature, water treatment methods and pH. The components of this study include assessing DBP formation potentials and reaction kinetics taking place in water to be obtained from several sources in EPA Region 3, all of which can be influenced by the character of the water source. Accordingly, it is of great importance to first characterize the water samples according to the NOM and halide content, to improve our ability to interpret Task 2 and Task 3 results.

Additional work will focus on analyzing for the presence of disinfection by-products, in particular THMs, HAAs, and *N*-nitrosamines, in the water samples in advance of exposure to disinfection techniques.

Finally, one area of interest is the ability of wastewater treatment (or on-site treatment at the resource extracting facility) to remove potential contaminants from the HF wastewater; this work will attempt to quantify the composition and concentration of chemicals both pre- and post-wastewater (or on site) treatment.

4.1.3 *Sampling Methods*

Water samples will be collected by EPA Region 3 researchers according to established SOPs. Documentation regarding sample collection procedures will be obtained from EPA Region 3 and included in any reports/publications related to this project. Information regarding samples, including the date, location and quantity obtained will all be recorded. Otherwise, no special sampling method requirements are anticipated.

4.1.4 *Sample Handling and Custody*

Field samples will be shipped on ice via Fed-Ex and/or UPS according to established SOPs. Sample descriptions and information will be recorded on chain of custody forms and the date samples were received will be recorded in a laboratory notebook. Upon receipt, samples will be refrigerated at 4 °C prior to analysis.

4.1.5 *General Experimental Information*

Characterization of samples obtained form EPA Region 3 will include routine analysis as described in Sections 4.4 (e.g. TDS analysis, elemental composition, DBP quantification) and will be performed by qualified personnel. Other analytics, including NOM characterization and nitrosamine analysis will be integrated into the current experimental framework as necessary; their methodology will be added as supplemental appendices. Any additional methods utilized will be appended to the end of the QAPP as supplemental sections.

4.2 Task 2 – Effects of Elevated TDS on DBP Formation

4.2.1 *Objective*

To determine the effects of high levels of dissolved chloride and bromide on DBP formation potentials in several representative water samples under chlorination, chloramination, and ozonation disinfection conditions.

4.2.2 *Key Ideas*

The enhanced formation of disinfection by-products as a result of high halide levels in water has been previously documented in the literature.[1,2] Elevated levels of dissolved bromide, in particular, have been implicated in the formation of brominated DBPs, which demonstrate significantly higher toxicity than chlorinated equivalents. In general, the range of concentrations explored in previous literature studies has extended only to a maximum of 1-2 mg/L; while the natural range of bromide concentration in the US ranges from 5-429 ug/L (and thus, well below the experimentally explored limits), the increased prevalence of resource extraction techniques may result in a substantial increase in the concentration of halides in produced flowback waters.[4] Reports from state agencies in the Marcellus region have suggested concentrations in excess of 500 mg/L of bromide are being detected in flowback waters prior to treatment. As such, it is of interest to assess the implications of chloride and bromide levels, in excess of the previous

studies, on DBP formation. In addition, the use of several water sources from areas impacted by resource extraction techniques will assist in determining whether variances in NOM character have an impact on DBP formation in conjunction with elevated halide concentration.

4.2.3 *General Experiment Information*

Chlorination, chloramination, and ozonation of water samples (see SOPs, located in appendices B-D) will be performed to explore the effects of halogen ion content on overall formation of disinfection by-products. This will be accomplished through analysis for DBP formation using EPA methods 551, 552, and 521 for quantification of trihalomethanes (THMs), haloacetic acids (HAAs), and *N*-nitrosamine formation, respectively, following disinfection of water samples. Anticipated variables to be explored include:

- Concentration of disinfectant
- Halogen ion concentration (bromide and chloride, independent or in tandem)
- Water source (de-ionized blank, 'authentic' water samples obtained from water treatment input streams, de-ionized with admixed HF wastewater)
- Duration of disinfection (or contact time)
- NOM concentration
- Solution pH

4.2.4 *Proposed Experiments*

Disinfection by-product formation will be assessed in drinking water matrices including those analyzed in Task 1, with the addition of varying bromide and chloride ion concentrations. Chlorination, chloramination, and ozonation disinfections will be run, and additional variables will include pH, halogen ion concentrations, and duration/concentration of disinfectants. Analysis, including characterization and quantification of DBP formation, will be performed using the EPA methods 551, 552, and 521, including the various QA requirements. Residual disinfectants will be quantified using well-described colorimetric/spectrophotometric methods (e.g. DPD). Initial analysis will focus on determination of total DBP formation potentials after set reaction times; however, additional experiments may explore the kinetics of degradation of disinfectants and/or formation of select DBPs. To account for matrix effects, QA samples (e.g. laboratory fortified matrix blanks) will be included in analysis as described in the individual EPA methods.

4.3 Task 3 – Kinetics of Formation and Identification of Degradates of Resource Extraction Biocides

4.3.1 *Objective*

To determine the DBP formation potential of several biocides employed in resource extraction technologies. Initial work will assess formation in deionized water to obtain baseline information. Additional studies will expand to include the elevated bromide/chloride levels explored in Task 1 to assess any possible impacts thereof on degradation reactions/kinetics.

4.3.2 *Key Ideas*

The biocides employed in resource extraction include a number of brominated organic and quarternary ammonium molecules which may be susceptible to degradation both in raw water as well as under disinfection conditions. One of the brominated biocides (2,2-dibromo-3-niltrilopropionamide) is a known precursor to both dibromoacetamide (DBAM) and cyanoacetamide (CAN) via two distinct pathways, with the presence of NOM influencing the reaction progression.[5]

We propose to explore the degradation of these biocides using bench-top experiments focusing on both kinetic reduction of the biocide parent compound and the identification of by-products. An experimental matrix will include varying pH, NOM source type and halide concentration. HPLC/MS (for identification of larger organic reaction products) and published EPA methods (methods 551.1, 552.1) for the analysis of THM/HAA will be used during analysis. The kinetics for degradation will be evaluated, degradation products will be identified/characterized, and we will attempt to ascertain the lifetime of intermediates formed. Results from this study will be used to identify molecules which may be important for further study from a toxicological standpoint.

4.3.3 *General Experimental Information*

Biocides employed as anti-fouling agents will be assessed for aqueous stability, and breakdown products will be identified and characterized where possible using chromatography and mass spectrometric methods. Specific equipment to be employed will include a UPLC-LTQ-Orbitrap system, as well as an HPLC-TOF system. Both instruments allow for high mass resolution (exact mass), and accordingly allow for assignment of unique molecular formulae for products. The use of tandem MS-MS methods will be employed where necessary to aid in product identification (by analysis for characteristic fragmentation patterns, product ions).

Conditions to be studied include:

- Water matrix: De-ionized background, surface water samples
- Elevated halide ion concentrations
- Exposure to water disinfection conditions, including chlorination, chloramination, ozonation

4.3.4 *Proposed Experiments*

Brominated and chlorinated biocides used in resource extraction (Table 3.2) will be added to the water samples and chlorine (in the form of sodium hypochlorite), chloramine, or ozone will be introduced, following procedures described in the SOPs in appendices B-D. Chloramines will be produced prior to addition by mixing sodium hypochlorite with an ammonium chloride solution, with excess ammonium used to preclude the presence of free chlorine. The solution pH will be controlled using phosphate buffers, with the exact pH of the buffer set through titration and addition of nitric acid or sodium hydroxide as necessary. To evaluate the effects of elevated TDS, including chloride and bromide, laboratory standards will be spiked with varying levels of the two ions. Baseline aqueous stability of biocides will also be assessed through the use of buffered solutions without disinfectant. After a defined period of time the disinfection reactions will be quenched by the addition of ascorbic acid or sodium thiosulfite and the samples will be analyzed for HAAs, THMs and nitrosamines following their respective EPA analytical methods. Residual biocide concentrations will be established through LC/MS quantification. Note that due to the dearth of data regarding degradation of some biocides, initial assessment of aqueous stability, both in buffer and under disinfection conditions, will be performed to determine appropriate reaction times, and the QAP will be updated on the basis of these results. The disinfectant concentrations examined will initially be 2, 5, and 10 ppm, and if it becomes necessary to include a different range, the QAP will be updated accordingly.

Analytical Methods

4.3.5 *pH Measurements*

All solution pH measurements will be using a combination pH probe with temperature correction attached to a Hach SensIon 156 meter. Calibration of the pH meter will be done with three standard buffers; pH 4, 7, and 10. Quality control is summarized in Table 4.1. The calibration slope value calculated by the pH meter will be 59.14 1/mV ± 10%. Recalibration will be performed in the case of failure. Additional failure will result in maintenance as recommended by the manufacturer. The calibration will be checked daily with a known standard solution, measurement is required to be ± 0.05 pH units of the known value. In the event the value fails its tolerance, the unit will be re-calibrated and the standards run again. Additional failure will result in maintenance as recommended by the manufacturer. All pH data will be kept in a daily log.

Table 4.1. Quality Control Procedure for pH Measurement

QC Sample Type	Frequency	Acceptance Criteria	Corrective Action
Calibration	pH meters will be calibrated twice daily, morning and afternoon.	pH within +/- 0.05 of the known value.	Recalibration of instrument, and re-analysis of all samples since point of failure.
Buffer verification	A pH buffer similar to target pH will be tested every 10 samples.	pH reading must be +/- 0.1 of buffer pH.	Recalibration of instrument, and re-analysis of all samples since point of failure.

4.3.6 *Analysis for Trace Metals and Anions*

4.3.6.1 *Citations, Existing QAPPs and/or HASPs*

Information on the methods are provided in EPA Method 200.7 rev. 4.4, 1994 (metals) and EPA Method 300.1 rev. 1.0, Part A, 1997 (anions). Perchlorate analysis is published in EPA Method 332.0 rev. 1.0, 3/2005, EPA Document # EPA/600/R-05/049. The proposed list of analytes are shown in Table 4.2; this list describes elements/compounds which may be characterized and quantified using the method. Initial quantification and characterization of waters impacted by resource extraction will allow for more specifics regarding the trace analysis, and the QAP will be amended accordingly following initial study. Full texts of the EPA Methods are included in Appendix 8.0.

Table 4.2. List of Elements/Compounds Appropriate for Study Using USEPA/ NRMRL Trace Elements Method

Compound	CAS Number
Aluminum	7429-90-5
Antimony	7440-36-0
Arsenic	7440-38-2
Barium	7440-39-3
Beryllium	7440-41-7
Bromide	7726-95-6
Boron	7440-42-8
Cadmium	7440-43-9
Calcium	7440-70-2
Cerium	7440-45-1
Chloride	16887-00-6
Chromium	7440-47-3
Cobalt	7440-48-4
Copper	7440-50-8
Fluoride	7782-41-4
Iron	7460-89-6
Lead	7430-92-1
Lithium	7439-93-2
Magnesium	7439-95-4
Manganese	7439-96-5
Mercury	7439-97-6
Molybdenum	7439-98-7
Nickel	7440-02-0
Nitrate	84145-82-4
Perchlorate	87081-35-4
Phosphate	98059-61-1
Phosphorus	7723-14-0
Potassium	7440-09-7
Selenium	7782-49-2
Silica	7631-86-9
Silver	7440-22-4
Sodium	7440-23-5
Strontium	7440-24-6
Sulfate	7664-93-9
Thallium	7440-28-0
Tin	7440-31-5
Titanium	7440-32-6
Vanadium	7440-62-2
Zinc	7440-66-6

4.3.6.2 *Special Training/ Certification*

Sample preparation/analysis will be conducted by experienced staff chemists following the SOP described in Appendix E. Staff chemists will train and supervise any persons that may be needed to assist with sample preparation/analysis. Training requirements will be accordance with those mentioned in Section 3.7.

4.3.6.3 *Documents and Records*

Documentation and record management are discussed for this project in Section 3.5 .

4.3.6.4 *Quality Control*

Details of the Quality Control measurements used for these methods can be found in Section 9 of the method (pp. 200.7-23, 300.1-13 and 332.0-16). A summary of the quality control measurements can be found in Table 4.3.

Table 4.3. Quality Control Samples for USEPA/NRMRL Methods for Trace Elements Analyses (EPA Method 200)

QC Sample Type	Frequency	Acceptance Criteria	Corrective Action
Laboratory Reagent Blank	One every 20 field samples analyzed	< MDL	Reanalyze samples after corrective action
Laboratory Fortified Blank	One every 20 field samples analyzed	metals: 85- 115 %/ anions: 75-125%	Reanalyze samples after corrective action
Instrument Performance Check	1 every 10 field samples	metals: ± 10 % of calibration / anions: PFG =0.8-1.15	Reanalyze samples after corrective action
Laboratory Fortified Matrix	10% of samples	metals: 70- 130 % /anions: 75-125%	Flag in comments

4.3.6.5 *Corrective Actions*

Corrective Actions are discussed in Section 4 (pp. 200.7-7 and 300.1-5) and Section 11.6 (p 332.0-29) of the methods.

4.3.6.6 *Instrument/ Equipment Testing, Inspection, and Maintenance.*

Testing, inspection and maintenance of equipment required for completion of analytical measurements will be conducted as needed to ensure proper operation. All records are to be kept by the individual responsible for the equipment. Maintenance will be performed by manufacturer's representative as needed.

4.3.6.7 *Instrument/ Equipment Calibration and Frequency.*

Instrument calibration is discussed in Section 10 (pp. 200.7-28, 300.1-19 and 332.0-24) of the methods, section 7.9 (pp. 200.7-18-19), and Table 3 (pp.200.7-44).

4.3.6.8 *Inspection/ Acceptance of Supplies and Consumables.*

Supplies are discussed in Section 6 (pp. 200.7-11, 300.1-8 and 332.0-24) of the methods. Supplies and consumables will be inspected upon receipt by the person that will be using the supplies and consumables. Acceptance of these will be based upon visually determining that received material is consistent with project requirements, packaging is intact or there is no obvious damage to the received materials. Items identified as damaged or contaminated will be declined.

4.3.6.9 *Data Management*

Data analysis and calculations are discussed in Section 12 (pp. 200.7-35, 300.1-22 and 332.0-30) of the methods. Final data reports will be entered into a database.

4.3.7 ***TDS Analysis***

TDS analysis will be performed via EPA Method 160.1

4.3.7.1 *Citations, Existing QAPPs and/or HASPs*

Information on the method is provided in EPA Method 160.1 rev. 11/16/1999. Full texts of the EPA methods are included in Appendix A.

4.3.7.2 *Special Training/ Certification*

Sample preparation/analysis will be conducted by experienced staff chemists. Staff chemists will train and supervise any persons that may be needed to assist with sample preparation/analysis. Training requirements will be accordance with those mentioned in Section 3.7.

4.3.7.3 *Documents and Records*

Documentation and record management are discussed in Section 3.5.

4.3.7.4 *Quality Control*

Details of the Quality Control measurements used for these methods can be found in section Table 4.4.

Table 4.4. Quality Control Samples Method for Total Dissolved Solids (TDS) Analyses

QC Element	Frequency	Acceptance Criterion	Corrective Action
Analytical Balance Check: Weights of 100 g, 1 g, 100 mg	Daily	Difference < 0.5 mg	Identify and document problem in maintenance log.
Method Blank (MB)	One per batch, 1 per 20 samples minimum.	< CRDL (20 mg/L)	1. If lowest sample concentration is more than 10X the blank conc., no action. 2. If samples are non-detected, no action. 3. If detected sample concentrations are less than 10X blank conc., all associated samples must be prepared again with another method blank and reanalyzed.
Duplicate Sample (DUP)	One per batch, 1 per 20 samples minimum.	RPD < 20% for samples, >5X CRDL, +/- CRDL for samples <5X CRDL.	Flag associated data with *, and annotate.
Mineral Reference Samples	One per batch, 1 per 20 samples minimum.	+/- 15% from expected concentration.	Terminate analysis, identify, document, correct problem, re-analyze samples since last successful MRS.

4.3.7.5 *Corrective Actions*

Corrective Actions are discussed in Table 4.4

4.3.7.6 *Instrument/ Equipment Testing, Inspection, and Maintenance.*

Testing, inspection and maintenance of equipment required for completion of analytical measurements will be conducted as needed to ensure proper operation. All records are to be kept by the individual responsible for the equipment. Maintenance will be performed by manufacturer's representative as needed.

4.3.7.7 *Instrument/ Equipment Calibration and Frequency.*

Instrument calibration is discussed in Table 4.4, and will be performed daily.

4.3.7.8 *Inspection/ Acceptance of Supplies and Consumables.*

Supplies and consumables are listed in section 6.0 of the attached method, and will be inspected upon receipt by the person that will be using the supplies and consumables. Acceptance of these will be based upon visually determining that received material is consistent with project requirements, packaging is intact or there is no obvious damage to the received materials. Items identified as damaged or contaminated will be declined.

4.3.7.9 *Data Management*

Data analysis and calculations are discussed in Section 8.0 (p. 160.1.2) of the methods. Final data reports will be entered into a database.

4.3.8 ***TOC Analysis***

4.3.8.1 *Citations, Existing QAPPs and/or HASPs*

Information on the methods are provided in EPA Method 415.3 rev. 1.1, 2/2005, EPA Document # EPA/600/R-05/055. Full texts of the EPA Methods are included in Appendix A.

4.3.8.2 *Special Training/ Certification*

Sample preparation/analysis will be conducted by experienced staff chemists. Staff chemists will train and supervise any persons that may be needed to assist with sample preparation/analysis. Training requirements will be accordance with those mentioned in Section 3.7.

4.3.8.3 *Documents and Records*

Documentation and record management are discussed in Section 3.5.

4.3.8.4 *Quality Control*

Details of the Quality Control measurements used for these methods can be found in section 9 of the method (p. 415.3-22). A summary of the quality control measurements can be found in Table 4.5, and a more extensive discussion is located in Appendix A.2.

4.3.8.5 *Corrective Actions*

Corrective Actions are discussed in Section 4 (p. 415.3-8) of the methods.

4.3.8.6 *Instrument/ Equipment Testing, Inspection, and Maintenance.*

Testing, inspection and maintenance of equipment required for completion of analytical measurements will be conducted as needed to ensure proper operation. All records are to be kept by the individual responsible for the equipment. Maintenance will be performed by manufacturer's representative as needed.

Table 4.5. Quality Control Samples Method for Total Organic Carbon (TOC) Analyses

QC Sample Type	Frequency	Acceptance Criteria	Corrective Action
Laboratory Reagent Blank	One every 20 field samples analyzed	≤ 0.35 mg/L organic carbon	Reanalyze samples after corrective action
Continuing Calibration Verification (CCV)	1 every 10 field samples and after last sample	Low CCC: ± 50 % of true value Mid CCC: ± 20 % of true value High CCC: ± 15 % of true value	Reanalyze samples after corrective action
Laboratory Fortified Matrix	One every 20 field samples analyzed	70- 130 %	Flag in comments
Laboratory Field Blank	One field blank for each TOC sample set	<0.35 mg/L organic carbon	Reanalyze samples after corrective action
Initial Demonstration of Capability	Performed whenever a new instrument/analyst is trained	Satisfactory completion of IDC regime	
Field Duplicate	One FD per analysis batch	FD > 2 mg/L OC < 20% RPD. UVA < 10% RPD	Results flagged and cause identified.
Quality Control Sample	Analyzed during IDC, after each new calibration curve, with each new calibration batch, and at least quarterly	Analyzed values (1-5 mg/L) must be within +/- 20% of the real value	Re-make calibration solution, if other problems are not identified and corrected.
Spectrophotometer Performance Check	Day-to-day performance monitored using COMM-SCS or KHP-SCS prior to any sample analysis	UVA must be within +/- 10% of expected values	If instrument is outside range, re-prepare or purchase calibration mixture, and repeat. Record all values in instrument logbook.
Spectrophotometer Blank	A second source LRW is analyzed every time the instrument is zeroed	Second source LRW must be UVA < 0.01 cm^{-1}	
Calibration Curve	A new calibration curve is generated each time new standards are obtained, or CCC is outside QC limit.	R^2 values must be > 0.993.	Record values in instrument logbook. If calibration QC cannot be met, consult instrument/lab SOP for corrective actions.

4.3.8.7 *Instrument/ Equipment Calibration and Frequency.*

Instrument calibration is discussed in section 10 (pp. 415.3-10) of the methods and shown in Table 4.5.

4.3.8.8 *Inspection/ Acceptance of Supplies and Consumables.*

Supplies are discussed in Section 6.0 (p. 415.3-10) of the methods. Supplies and consumables will be inspected upon receipt by the person that will be using the supplies and consumables. Acceptance of these will be based upon visually determining that received material is consistent with project requirements, packaging is intact or there is no obvious damage to the received materials. Items identified as damaged or contaminated will be declined.

4.3.8.9 *Data Management*

Data analysis and calculations are discussed in Section 12.0 (p. 415.3-37) of the methods. Final data reports will be entered into a database.

4.3.9 ***Disinfection By-Product Analysis***

4.3.9.1 *Citations, Existing QAPPs and/or HASPs*

Information on the methods are provided in EPA Method 551, 1990. The proposed list of analytes is shown in Table 4.6. Full texts of the EPA Methods are included in Appendix A.

4.3.9.2 *Special Training/ Certification*

Sample preparation/analysis will be conducted by experienced staff chemists. Staff chemists will train and supervise any persons that may be needed to assist with sample preparation/analysis. Training requirements will be accordance with those mentioned in Section 3.7.

4.3.9.3 *Documents and Records*

Documentation and record management are discussed in Section 3.5.

4.3.9.4 *Quality Control*

Details of the Quality Control measurements used for these methods can be found in Section 10 of the method (p. 551-14). A summary of the quality control measurements can be found in Table 3.1.

Table 4.6. List of Analytes in US EPA Method 551

Analyte	CAS Registry Number
Bromochloroacetonitrile	83463-62-1
Bromodichloromethane	75-27-4
Bromoform	75-25-2
Carbon Tetrachloride	56-23-5
Chloral Hydrate	75-87-6
Chloroform	67-66-3
Chloropicrin	76-06-2
Dibromoacetonitrile	3252-43-5
Dibromochloromethane	124-48-1
1,2-Dibromo-3-chloropropane [DBCP]	96-12-8
1,2-Dibromoethane [EDB]	106-93-4
Dichloroacetonitrile	3018-12-0
Trichloroacetonitrile	545-06-2
Tetrachloroethylene	127-18-4
1,1,1-Trichloroethane	71-55-6
Trichloroethylene	79-01-6
1,1,1-Trichloro-2-propanone	918-00-3
1,1-Dichloro-2-propanone	513-88-2

Table 4.7. Quality Control Samples Method for Trihalomethane (THM) Analyses

QC Sample Type	Frequency	Acceptance Criteria	Corrective Action
Laboratory Reagent Blank (LRB)	Prior to analyzing any samples, and with each sample set. Also required with changes in reagents.	The LRB should not produce peaks within the retention time window of any analytes.	If this occurs, the source of contamination must be identified and removed before processing samples.
Initial Demonstration of Capability (IDC)	Prior to analyzing any samples	LFB, IDA, IDP, and MDL must be performed.	
Initial Demonstration of Accuracy (IDA)	Prior to analysis of IDC samples	At least 7 IDC samples must be analyzed. Mean recoveries must be within +/- 20% of the actual value.	Analyze for sources of error, repeat with 8 samples until performance is acceptable.
Initial Demonstration of Precision (IDP)	Prior to analysis of IDC samples	At least 7 IDC samples must be analyzed. Mean standard deviations must be less than 15%.	Analyze for sources of error, repeat with 8 samples until performance is acceptable.
Detection Limit (DL)	Prior to analysis of non-IDC samples.	Ascertain detection limit by analysis as described in method.	N/A
Laboratory Fortified Blank (LFB)	LFBs are included in IDC and CCC.		
Laboratory Fortified Sample Matrix (LFSM)	One sample/set, or 10% of samples, must be LFSM, for NH_4Cl and Na_2SO_3 dechlorinated matrices.	Analyte recovery must be of +/- 25% of expected values, and 90% of analytes must not exceed 20% deviation.	Matrix induced bias is assumed, and data reported as suspect. If the unfortified matrix has background levels higher than the fortified matrix, a duplicate must be prepared at a higher concentration. If not possible, the data for the sample from which the LFSM was prepared should not be reported.
Continuing	CCCs are	Analyte recoveries must be	Re-analyze CCC to

Calibration Check (CCC)	performed for all sample runs, must contain all compounds of interest. Calibration checks are required every 10 samples and at the beginning and end of each analytical batch.	within +/- 25% of the expected values. 90% of analytes must fall within +/- 20% of the expected values.	determine if responses are repeateable. If accuracy standards cannot be met, instrument must be re-calibrated, and previous samples re-analyzed. Alternatively, analyte results outside of the acceptable limit must be reported as suspect.
Field Duplicates (FD1, FD2)	Field duplicates must be analyzed at 10% of total sample count, or one per sample set, whichever is greater.	Duplicate results must not show relative percent differences (RPD) greater than 25%. RPD is $RPD = \frac{(FD1 - FD2)}{1/2(FD1+FD2)} \times 10$ Where FD1 and FD2 are the concentrations calculated of an individual analyte for the initial and duplicate samples.	If the RPD criterion is not met, the analysis must be repeated. Upon repeated failure, sampling must be repeated, or the analyte results not meeting the standard must be reported as suspect.
Calibration	pH meters will be calibrated twice daily, morning and afternoon.		
Buffer verification	A pH buffer similar to target pH will be tested every 10 samples.	pH reading must be +/- 0.05 of buffer pH.	Recalibration of instrument, and re-analysis of all samples since point of failure.

4.3.9.5 *Corrective Actions*

Corrective actions are discussed in Section 11.3 (p. 551.19) of the method.

4.3.9.6 *Instrument/ Equipment Testing, Inspection, and Maintenance.*

Testing, inspection and maintenance of equipment required for completion of analytical measurements will be conducted as needed to ensure proper operation. All records are to be kept by the individual responsible for the equipment. Maintenance will be performed by manufacturer's representative as needed.

4.3.9.7 *Instrument/ Equipment Calibration and Frequency.*

Instrument calibration is discussed in Section 9 (pp. 551-12) of the methods and summarized in Table 4.7.

4.3.9.8 *Inspection/ Acceptance of Supplies and Consumables.*

Supplies are discussed in Section 7 (p. 551-7) of the methods. Supplies and consumables will be inspected upon receipt by the person that will be using the supplies and consumables. Acceptance of these will be based upon visually determining that received material is consistent with project requirements, packaging is intact or there is no obvious damage to the received materials. Items identified as damaged or contaminated will be declined.

4.3.9.9 *Data Management*

Documentation and record management are discussed in Section 3.5.

4.3.10 ***HAA Formation***

4.3.10.1 *Citations, Existing QAPPs and/or HASPs*

Information on the methods are provided in EPA Method 552.3 rev. 1.0, 7/2003, EPA Document # EPA/815/B-03/002. Full texts of the EPA Methods are included in Appendix A.

4.3.10.2 *Special Training/ Certification*

Sample preparation/analysis will be conducted by experienced staff chemists. Staff chemists will train and supervise any persons that may be needed to assist with sample preparation/analysis. Training requirements will be accordance with those mentioned in Section 3.7.

4.3.10.3 *Documents and Records*

Documentation and record management are discussed in Section 3.5.

4.3.10.4 *Quality Control*

Details of the Quality Control measurements used for these methods can be found in section 9 of the method (p. 552.3-17 - 552.3-26). A summary of the quality control measurements can be found in Tables 4.8 and 4.9.

Table 4.8. Quality Control Samples Method for Haloacetic acid (HAA) Analyses

QC Sample Type	Frequency	Acceptance Criteria	Corrective Action
Initial Demonstration of Low Background	Prior to analysis of any samples.	No significant background contamination.	Identify sources of contamination and remove them.
Initial Demonstration of Accuracy (IDA)	Prior to analysis of IDC samples	Analyte recovery of a mid-range QCS within +/- 30% of expected value. After this, analysis of a LFB series with mid-range concentrations must show recoveries within +/- 20%.	If accuracy is outside the minimum range, analyze for the source of error, correct, and repeat.
Initial Demonstration of Precision (IDP)	Prior to analysis of IDC samples	Relative standard deviations (RSD) of IDA samples must be less than 20%.	Analyze for the source of imprecision, repeat after corrections are made.
Initial Detection Limit (DL)	Prior to analysis of non-IDC samples.	Ascertain detection limit through analysis of a series of 7 or more samples near expected limit.	N/A
Minimum Reporting Level (MRL)	Prior to analysis of non-IDC samples	MRL should be at least 3 times the DL. The lowest calibration standard should be at or below the MRL.	
Laboratory Reagent Blank (LRB)	Prior to analyzing any samples, and along with any sample set	LRB must be reasonably free from contamination, less than 1/3 of the MRL.	Identify source of contaminants, and repeat.

4.3.10.5 *Corrective Actions*

Corrective actions are discussed in Tables 4.8 and 4.9, and in the QC section of the method.

4.3.10.6 *Instrument/ Equipment Testing, Inspection, and Maintenance.*

Testing, inspection and maintenance of equipment required for completion of analytical measurements will be conducted as needed to ensure proper operation. All records are to be kept by the individual responsible for the equipment. Maintenance will be performed by manufacturer's representative as needed.

Table 4.9. Quality Control Samples Method for Haloacetic acid (HAA) Analyses (Cont.)

QC Sample Type	Frequency	Acceptance Criteria	Corrective Action
Continuing Calibration Check (CCC)	Every 10th sample during analysis.	Analyte recovery must be +/- 30% of the expected values, save the lowest amount, which must be +/- 50%.	If CCC fails, all data for the target analyte must be considered suspect from that run. Re-analyze any samples since the last successful calibration run once re-calibration is successful.
Laboratory Fortified Blank (LFB)	N/A, addressed in CCC	N/A	N/A
Internal Standards (IS)	Internal standards are included in all samples.	IS response cannot deviate more than +/- 50% from initial calibration.	Poor injection is the likely source of error – reinject a second aliquot. If not corrected, repeat CCC, and respond as needed, either re-calibrating instrument, or repeating sample extraction if CCC is valid. If holding time is exceeded, report data as suspect.
Surrogate Recovery (SR)	Surrogate standards are added to calibration standards, samples, and appropriate blanks.	Surrogate recovery must be +/- 30% of expected values.	If failure is a blank, sample, or CCC: Check for sources of error: 1. Calculation error; 2. Standard solutions for degradation; 3. Contamination; 4. Instrument failure. Correct and re-analyze. If re-extract passes, report only those results.
Laboratory Fortified Sample Matrix (LFSM)	Required in each extraction batch, 1 per 20 samples.	Percent recovery must be +/- 30%, except near MRL where it must be +/- 50%.	If recovery is outside the limits, and CCC is accurate, recovery is matrix-dependent. Label data suspect/matrix for that analyte.
Field Duplicate/(Laboratory Fortified Sample Matrix Duplicate (FD/LFSMD)	Required with each extraction batch.	RPDs (as calculated below) must be within +/- 30%. Within a factor of 2xMRL, values within +/- 50%.	RPDs outside the limit, when CCC is acceptable for that analyte, are indicative of matrix effects biasing results. Label unfortified results for that analyte suspect/matrix.

4.3.10.7 *Instrument/ Equipment Calibration and Frequency.*

Instrument calibration is discussed in Section 10 (pp. 552-24) of the methods and summarized in Table 4.7.

4.3.10.8 *Inspection/ Acceptance of Supplies and Consumables.*

Supplies are discussed in Section 6 (p. 552-8) of the methods. Supplies and consumables will be inspected upon receipt by the person that will be using the supplies and consumables. Acceptance of these will be based upon visually determining that received material is consistent with project requirements, packaging is intact or there is no obvious damage to the received materials. Items identified as damaged or contaminated will be declined.

4.3.10.9 *Data Management*

Documentation and record management are discussed in Section 3.5.
HAA formation analysis will be performed according to the published EPA Method 552.1.

4.3.11 ***Nitrosamine Formation***

4.3.11.1 *Citations, Existing QAPPs and/or HASPs*

Information on the methods are provided in EPA Method 521.1 rev. 1, 9/2004, EPA Document # EPA/600/R-05/054. Full texts of the EPA Methods are included in Appendix A.

4.3.11.2 *Special Training/ Certification*

Sample preparation/analysis will be conducted by experienced staff chemists. Staff chemists will train and supervise any persons that may be needed to assist with sample preparation/analysis. Training requirements will be accordance with those mentioned in Section 3.7.

4.3.11.3 *Documents and Records*

Documentation and record management are discussed in Section 3.5.

4.3.11.4 *Quality Control*

Details of the Quality Control measurements used for these methods can be found in section 9 of the method (p. 521.1-16 – 521.1-23). A summary of the quality control measurements can be found in Tables 4.10 and 4.11.

Table 4.10. Quality Control Samples Method for Nitrosamine Analyses

QC Procedure	Frequency	Acceptance Criteria	Corrective Actions
Initial Demonstration of Capability	Before study of samples	LRB Background < 1/3 of MRL	MRL must be above LRB concentration + 3σ.
Initial Demonstration of Precision	Before study of samples	RSD of replicates must be ≤ 20% for all method analytes/surrogates.	Repeat IDP, analyze for method problems.
Initial Demonstration of Accuracy	Before study of samples	Average recover must be 70-130% of the true value.	Repeat IDA, analyze for method problems.
MRL Confirmation	Before study of samples	Upper PIR ≤ 150% recovery. Lower PIR ≥ 50% recovery.	Increase MRL, repeat MRL confirmation.
DL Determination	Before study of samples		Do not report values below DL.
Continuing Calibration	The beginning of every day when samples are analyzed, and every 10 samples	Absolute peak areas for the IS must not have changed 30% from previous calibration, or 50% from initial calibration levels. Calibration Analytes in the high and medium concentration range must be within 70-130% of the true value. Low concentration analytes must be within 50-150% of the true value.	Re-calibrate, analyze for instrument problems. Re-analyze field samples obtained since previous passed calibration. If maintenance is required, repeat initial calibration.
Internal Standards (IS)	IS must be included in every sample	IS response must not deviate by more than 30% from the most recent CCC, and 50% from initial calibration.	If IS response is outside limits, inject a second aliquot. If this fails, re-run CCC. If CCC passes, re-extract the sample, if it is within the holding time. Otherwise, note results may be flawed in report, or collect a new sample.

Table 4.11. Quality Control Samples Method for Nitrosamine Analyses

QC Procedure	Frequency	Acceptance Criteria	Corrective Actions
Surrogate Recovery (SUR)	Surrogate is added to every calibration standard, sample, LFB, LFSM, LFSMD, FD, and LRB.	Surrogate recovery must be 70-130% of the fortified amount.	Check calculations, standard solutions, for contamination, and instrument performance. Reanalyze if no faults are located.
Laboratory Fortified Blanks (LFB)	LFB must be included in each extraction batch. High, medium, and low concentration LFBs must be rotated.	Low LFB must be within 50-150% of the true value. Medium/High LFBs must be within 70-130% of the true value.	
Laboratory Fortified Sample Matrix (LFSM)	1 sample must be spiked/20 samples.	Recoveries must be within 70-130%.	If lab accuracy is verified, consider the matrix suspect and label data accordingly.
Laboratory Fortified Reagent Blank (LRB)	LRB must be included in each extraction batch, or whenever a new supply of reagent is employed.	Background must be ≤ 1/3 of the MRL.	
Laboratory Fortified Sample Matrix Duplicates	Required with each extraction batch.	RPDs (as calculated below) must be within +/- 30%. Within a factor of 2xMRL, values within +/- 50%.	RPDs outside the limit, when CCC is acceptable for that analyte, are indicative of matrix effects biasing results. Label unfortified results for that analyte suspect/matrix.
Field Duplicates (FD)	One every 20 samples analyzed	≤50 % RPD	Flag in comments

4.3.11.5 *Corrective Actions*

Corrective actions are discussed in Section 9 (p. 521.1.16 – 521.1-23) of the method.

4.3.11.6 *Instrument/ Equipment Testing, Inspection, and Maintenance.*

Testing, inspection and maintenance of equipment required for completion of analytical measurements will be conducted as needed to ensure proper operation. All records are to be kept by the individual responsible for the equipment. Maintenance will be performed by manufacturer's representative as needed.

4.3.12 ***Instrument/ Equipment Calibration and Frequency.***

Instrument calibration is discussed in Section 10 (pp. 521.1-23) of the methods and summarized in Table 4.9.

4.3.12.1 *Inspection/ Acceptance of Supplies and Consumables.*

Supplies are discussed in Section 6 (p. 521.1-8) of the methods. Supplies and consumables will be inspected upon receipt by the person that will be using the supplies and consumables. Acceptance of these will be based upon visually determining that received material is consistent with project requirements, packaging is intact or there is no obvious damage to the received materials. Items identified as damaged or contaminated will be declined.

4.3.12.2 *Data Management*

Documentation and record management are discussed in Section 3.5.

5.0 ASSESSMENT AND OVERSIGHT

5.1 Assessments and Response Actions

Christopher A. Impellitteri and/or Heath Mash will serve as technical reviewers for the data generated. The technical reviewers will examine representative samples of data (approximately 10 to 20 %) and identify any problems. If problems are identified, a more extensive review will occur. In addition to technical review of the data, a technical systems audit (TSA) and audit of data quality (ADQ) will be required in accordance with the NRMRL QMP. These audits may be performed by the WSWRD QAM and/or an external auditor as designated by the QAM. An outside contractor, Neptune, has been contracted by QA management for this purpose. A preliminary report detailing the results of these audits will be reported to the PI within 10 days of the completion of the audits. Following any changes or clarifications as requested by the PI to the preliminary report, a final copy of the audit reports will be sent to the PI, WQMB Branch Chief, WSWRD ADD and Project QAM and logged into the NRMRL QA tracking database, QLog. Should there be any findings during the audits, the PI will respond in writing to the WSWRD QAM describing the corrective actions taken to address these findings. The frequency of QA audits will be dictated by the progress of the project, but anticipated to be performed in intervals of 8 months (one-third and two-thirds) into the project and highlighted in the Project Timeline Table 3.3. Additional audits may be performed at the request of the PI, WSWRD ADD or Project QAM. Scheduling of all audit activities will be agreed upon by the PI and WSWRD QAM. A Performance Evaluation (PEs) of the critical analytes are also required and will be performed by the WSWRD QAM or designated representative coordinated with the PI.

5.2 Reports to Management

During the course of the research, monthly meetings will take place between the primary investigators. These meetings will summarize the major accomplishments during the period, and should include any QC problems and preliminary data. Quarterly reports will be generated as required of the WSWRD project tracking requirements. At the end of the project, written products (journal manuscripts) will be prepared for the project and reviewed and cleared via EPA-ORD protocols. The reports and manuscripts may be stored either as a hard copy, or as a Microsoft Word file. The data will be summarized in a Microsoft Excel workbook.

6.0 DATA VALIDATION AND USABILITY

6.1 Data Review, Verification and Validation

Principle analytic personnel and Principle Investigators use their expertise to verify and validate the data, which determines which data is worthy of inclusion in the final data set for the project. The guiding principles for the data acceptance/ selection will be:

Sampling

- Sample descriptions obtained from EPA Region 3
- Correctness of dates and times
- Correctness of sample location and identification

Analysis

- Legibility of data records
- Correctness of sample identification
- Concurrence of electronic and hard-copy data
- Reasonableness of results (i.e., results not appearing grossly wrong)
- Acceptability of associated QC results
- Presence of other factors supporting acceptance (or rejection).

The PI will review, validate, and verify results by examination of fortified sample and second-source check standard recoveries and matrix blank analyses. Precision will be analyzed by examining the %RSD values for replicate samples and standards.

6.2 Precision

Precision is broadly defined as the scatter within any set of repeated measurements. For samples that are measured in duplicate, precision will be calculated as relative percent difference (RPD).

$$\mathbf{RPD = (C_1 - C_2) / ((C_1 + C_2) / 2) * 100} \qquad \mathbf{(4\text{-}1)}$$

where C_1 and C_2 are the two measurements. For samples that are measured in triplicate or higher, the precision will be measured as the relative standard deviation (RSD).

$$\mathbf{RSD = (S / SM) * 100} \qquad \mathbf{(4\text{-}2)}$$

where S is the standard deviation, and SM is the sample mean. Precision of the measurements that cannot be calculated with 3-1 and 3-2 will be determined by absolute range (AR).

$$\mathbf{AR = |M_1 - M_2|} \qquad \mathbf{(4\text{-}3)}$$

where M_1 and M_2 are the two measurements.

6.3 Accuracy

Accuracy is broadly defined as how close the analyses will come to the true concentration in the sample. The accuracy of measurements incorporating a standard reference material or a second source standard will be calculated as percent recovery.

$$\mathbf{\%\ Recovery = 100\% * (C_s/C_{mst})} \qquad \mathbf{(4\text{-}4)}$$

where C_s is the measured concentration of the standard and C_{mst} is the actual concentration of the standard. The accuracy of the analyses that use matrix spikes will be calculated by

$$\mathbf{\%\ Recovery = 100\% * (C_{sp} - C_{msa}) / C_{ac}} \qquad \mathbf{(4\text{-}5)}$$

where C_{sp} is the measured concentration of the spiked aliquot, C_{msa} is the measured concentration of the sample, and C_{ac} is the actual concentration of the spiked aliquot.
The accuracy of the samples that cannot be determined with Equations 3-4 and 3-5 will be calculated by the measurement bias.

6.4 Bias

$$\mathbf{Bias = M_b - M_k} \qquad \mathbf{(4\text{-}6)}$$

where M_b is the measurement with bias, and M_k is the known value.

6.5 Representativeness

The sampling and analytical procedures developed in this QAPP have been designed to establish that the collected data are representative. Multiple samples will be collected at the various sampling locations. Duplicate studies will be performed at random intervals to assure that the samples and processes represent the true outcome of the experiment

6.6 Comparability

Data comparability will be maintained through the use of defined and consistent sampling and analytical procedures.

6.7 Completeness

Completeness is broadly defined as what percent of samples are deemed to be valid (%C)

$$\%C = (V / TOT) * 100 \qquad (4\text{-}7)$$

where V is the number of samples determined to be valid, and TOT is the total number of measurements.

6.8 Sensitivity

Sensitivity is the capability of a method or instrument to discriminate between measurement responses representing different levels of the variable of interest. The minimum concentration will be determined by method, thus the method detection limit (MDL) is implemented.

6.9 Verification and Validation Methods

Initial data verification is always the responsibility of those entering data. Those filling out laboratory notebooks should review them to see that they are complete and legible. The PI will have the next role in verifying data, and the final role is played by the USEPA QA Manager.

The person receiving samples must make sure that the sampe description and procedure for collection are obtained and maintained. The PI must verify, post analysis, that the data is apparently reasonable, and that no transcription errors occurred during any of the data manipulation. The PI are also responsible for verifying data quality; that is, to make sure that all associated QC results were satisfactory. The data will be verified by external review as listed in 5.1, above.

6.10 Reconciliation with Data Quality Objectives

Analytical results obtained from the experiments will be reconciled with the DQO by data validation and usability. The data will be evaluated to check if they conform to the QA objectives of the project. A statistical assessment for accuracy, precision, and completeness will be performed.

All analyses will be required to meet data quality objectives before formulation of the final report and/or manuscript. The individual EPA method or SOPs fdocumenting an analysis (e.g. Method 521 for *N*-nitrosamine analysis) will include adiscussion of data verification including ascertaining matrix effects and instrumental biases. Where failures are observed in the individual methods, data will be marked as suspect.

7.0 REFERENCES

8.0 APPENDIX A.

EPA Methods and SOPs

1. **Analysis of Metallic and Nonmetallic Trace Elements**

USEPA Methods
300_1 rev1_0.pdf

USEPA Methods
200_7 rev4_4.pdf

USEPA Methods
332_0 rev 1.pdf

2. **Analysis of Total Organic Carbon**

USEPA Methods
415_3 rev1_1.pdf

3. **Analysis of Chlorinated Disinfection By-Products and Chlorinated Solvents**

USEPA Methods
551.pdf

4. **Analysis of Nitrosamines**

EPA Method 551.pdf

5. **Analysis of Haloacetic Acids**

EPA Method
552.3.pdf

9.0 APPENDIX B.

SOP for chlorination of samples

I. Scope and Application

This standard operating procedure describes the steps for simulation of chlorination disinfection conditions on the bench-top scale. Applications of this SOP aim to minimize artifacts and ensure reproducibility in method.

II. Method Summary

Chlorination reactions are performed under conditions where background chlorine demand is minimized and other interferences are removed.

III. Interferences and Potential Problems

Exposure to light could result in photochemical reactions. This is minimized by performing the reactions in amber glass or covered vials.

Chlorine can be consumed by non-pre-treated glass or other material present in the vials. Pre-treatment of the reaction vessels with 10 mg/mL free chlorine can quench residual chlorine demand, and thorough cleaning prior to this will remove other contaminants.

IV. Health, Safety, and Environmental Compliance

Appropriate PPE will be employed to minimize contact with potentially harmful chemicals and disinfection by-products.

V. Sample Preservation, Containers, Handling, and Storage

Samples will be quenched using sodium thiosulfite to remove residual chlorine at indicated times. Samples intended for use in THM assays will be stored in headspace-free containers to minimize loss of analytes to volatilization prior to analysis.

VI. Equipment

Sterile glass pipettes
Sample bottles
Laboratory timers

VII. Reagent Preparation

Chlorine demand-free 0.05 M phosphate buffer – prepares 5L

Potassium phosphate monobasic (KH_2PO4): 34 g, 136.09 g/mol, 0.25 mol
Sodium hypochlorite solution (1:20 dilution): 7 mL
10N NaOH, HNO_3 – used to adjust pH to desired level
Deionized Water – 5 L

1. Combine 2 L of deionized water and 34 g of KH_2PO_4 in a 6L container with a magnetic stir bar, and mix.
2. Add 7 mL of dilute hypochlorite solution, which at the final concentration will provide ~3.5 mg/L Cl_2.
3. Add deionized water to 5L.
4. Adjust pH by addition of NaOH or HNO_3 dropwise, allowing for mixing between additions.
5. Heat solution to boil, or as near to boil as possible for 5 minutes. After heating, allow to cool to RT.
6. Transfer the buffer solution to 4L beakers, and expose to UV light for 2 days to quench residual chlorine.
7. Transfer the buffer to 2 L beakers and autoclave for 30 minutes at 120^o C, label. Remove from heat, label as necessary, along with the pH and date.
8. Prior to use, assess residual and free chlorine levels in the buffer.

Chlorine solutions - 10 mg/L, prepares 5 L

Chlorine oxidant stock mixtures will be prepared from stock solutions provided by outside vendors. These usually are between 5-6% NaOCl. If using Cl_2, the concentration is typically 1 g/L. Due to instability of the reagent, the concentration should be assessed more exactly through titration, via the following protocol, which is to be performed in a chemical fume hood.

1. Using a 1 mL pipette, add either 0.1-0.5 mL of NaOCl (bleach) solution, or 1-3 mL of Cl_2 solution to a 150 mL beaker.
2. Add 20 mL of distilled water to the beaker, and stir with a magnetic stir bar.
3. Add 1-2 mL of glacial acetic acid, followed by ~1 g KI. The solution will turn to a dark yellow.
4. Using 0.100N thiosulfate solution, titrate the sample to a pale yellow color.
5. Add a squirt of 1% aq. starch indicator solution (e.g. Aldrich 319554). The solution will turn to a shade of blue.
6. Titrate to the colorless endpoint, again using the 0.100N thiosulfate solution.
7. Calculate the concentration of Cl using the equation:

VIII. Procedure for Chlorination Disinfection of Samples

1. Chlorination studies will be performed in chlorine-demand free, 300 mL bottles. Prior to reaction, the vials will be rinsed with 10 mg/mL chlorine solutions (from NaOCl) to remove any residual chlorine demand.

2. Model water will be buffered using phosphate buffer, adjusted to the desired pH using either HNO_3 or NaOH. Halides will be added as NaCl or NaBr to obtain desired concentrations of Cl^- or Br^- ions.
3. Chlorine will be added from the HOCl stock solution to obtain the desired concentration of Cl_2 in mg/L.
4. Following addition of all reagents, sample vials will be capped tightly, vigorously shaken, and stored headspace-free for the desired reaction time.
5. Where temperature control is necessary, reactions will be performed in a water bath maintained at the desired temperature.
6. Aliquots will be removed by pipette for analysis as needed.

IX. Procedure for Quenching Reactions

1. Prior to quenching of the reaction, residual chlorine in the reaction mixture will be assessed using the DPD-FAS method on a 20 mL aliquot removed from the reaction mixture, and the total and free chlorine will be calculated.[6]
2. An equimolar amount of sodium thiosulfite will be added to the reaction mixture to quench the free chlorine.
3. Following reaction quenching, withdraw aliquots of the reaction mixture for all desired analytical methods, accounting for necessary redundancies and controls.

10.0 APPENDIX C.

SOP for chloramination of samples

I. Scope and Application

This standard operating procedure describes the steps for simulation of chlorination disinfection conditions on the bench-top scale. Applications of this SOP aim to minimize artifacts and ensure reproducibility in method.

II. Method Summary

Chlorination reactions are performed under conditions where background chlorine demand is minimized and other interferences are removed.

III. Interferences and Potential Problems

Exposure to light could result in photochemical reactions. This is minimized by performing the reactions in amber glass or covered vials.

Chlorine can be consumed by non-pre-treated glass or other material present in the vials. Pre-treatment of the reaction vessels with 10 mg/mL free chlorine can quench residual chlorine demand, and thorough cleaning prior to this will remove other contaminants.

IV. Health, Safety, and Environmental Compliance

Appropriate PPE will be employed to minimize contact with potentially harmful chemicals and disinfection by-products.

V. Sample Preservation, Containers, Handling, and Storage

Samples will be quenched using sodium thiosulfite to remove residual chlorine at indicated times. Samples intended for use in THM assays will be stored in headspace-free containers to minimize loss of analytes to volatilization prior to analysis.

VI. Equipment

Sterile glass pipettes

Sample bottles

Laboratory timers

VII. Reagent Preparation

1. Chloramine stock solution
    a. Prepare an ammonia stock solution at 100 mg N/L, and adjust the pH to 8.3 using H_2SO_4 (conc.).
    b. Prepare a NaOCl stock solution, determining the concentration of Cl as Cl_2, and adjust to pH 8.3 using NaOH (10 M).
    c. Determine the desired concentration of NH_2Cl, as well as the desired ratio of Cl:N. In general this will be 1:1.2, to minimize the formation of di- or trichloramine.

d. Add the calculated amount of 100 mg N/L NH_3 stock solution to a 500 mL volumetric flask, and dilute to 500 mL using DI water.
e. Measure out 100 mL of the stock solution in a volumetric flask, and pour into a 250 mL bearker.
f. Cool the 250 mL beaker in an ice bath while stirring on a stir plate. Add dropwise the NaOCl solution. Monitor pH and adjust using NaOH or H_2SO_4 as necessary to maintain it at 8.3.
g. Remove monochloramine from the ice bath, and utilize within 30 minutes.

I. Procedure for Chloramination Disinfection of Samples

1. Chlorination studies will be performed in chlorine-demand free, 300 mL bottles. Prior to reaction, the vials will be rinsed with 10 mg/mL chlorine solutions (from NaOCl) to remove any residual chlorine demand.
2. Model water will be buffered using phosphate buffer, adjusted to the desired pH using either HNO_3 or NaOH. Halides will be added as NaCl or NaBr to obtain desired concentrations of Cl^- or Br^- ions.
3. Chlorine will be added from the HOCl stock solution to obtain the desired concentration of Cl_2 in mg/L.
4. Following addition of all reagents, sample vials will be capped tightly, vigorously shaken, and stored headspace-free for the desired reaction time.
5. Where temperature control is necessary, reactions will be performed in a water bath maintained at the desired temperature.
6. Aliquots will be removed by pipette for analysis as needed.

II. Procedure for Quenching Reactions

1. Prior to quenching of the reaction, residual chlorine in the reaction mixture will be assessed using the DPD-FAS method on a 20 mL aliquot removed from the reaction mixture, and the total and free chlorine will be calculated.[6]
2. An equimolar amount of sodium thiosulfite will be added to the reaction mixture to quench the free chlorine.
3. Following reaction quenching, withdraw aliquots of the reaction mixture for all desired analytical methods, accounting for necessary redundancies and controls.

11.0 APPENDIX D.

SOP for ozonation of samples

I. Scope and Application. This standard operating procedure describes the steps involved in ozonation of a water sample. The typical application of this SOP would be to simulate wastewater treatment via ozonation.

II. Method Summary. A sample is exposed to ozone in a sealed, covered vessels to prevent exposure to light, as some disinfection by-products (e.g. nitrosamines) are light sensitive. This SOP is described to ensure uniformity in reaction conditions, regent preparation, and quenching.

III. Interferences and Potential Problems: Degradation of by-products by exposure to light. This will be minimized by performing the reaction in sealed vessels protected from light exposure either through amber tinting or a light-impermeable enclosure.

IV. Health, Safety, and Environmental Compliance
Ozone is hazardous to human health. Some molecules being studied are also likely toxic. Appropriate PPE will be used, and ozone generation will be done in a chemical fume hood.

V. Sample Preservation, Containers, Handling, and Storage

VI. Equipment
- Corona discharge generator
- Sample Bottles
- Glass Pipettes

VII. Reagent Preparation

VIII. Procedure for Ozone Disinfection of Samples

IX. Procedure for Quenching Reactions

Typical Sample Preparation Standard Operating Procedure

Materials: Reactor (500 mL glass beaker, Teflon stir bar, stir plate), volumetrics for stock solutions, pipetters, corona discharge-based ozone generator.

Reagents: deionized water, humic acid, nitric acid, sodium hydroxide, halogenated biocidal compounds, hydrofracturing flowback fluid, bromide, chloride.

1. Prepare ozone stock solution by bubbling output of the corona discharge generator into a 1 L receiving vessel filled with deionized water.
2. Model water will be buffered using phosphate buffer, adjusted to the desired pH using either HNO_3 or NaOH. Halides will be added as NaCl or NaBr to obtain desired concentrations of Cl^- or Br^- ions.
3. Ozone will be added from the HOCl stock solution to obtain the desired concentration of Cl_2 in mg/L.

4. Following addition of all reagents, sample vials will be capped tightly, vigorously shaken, and stored headspace-free for the desired reaction time.
5. Where temperature control is necessary, reactions will be performed in a water bath maintained at the desired temperature.
6. Aliquots will be removed by pipette for analysis as needed.

12.0 APPENDIX E.

Typical Sample Preparation Standard Operating Procedure

Materials: Reactor (500 mL glass beaker, teflon stir bar, stir plate), volumetrics for stock solutions, pipetters.

Reagents: water, humic acid, sodium hypochlorite, chloramine (ammonium chloride and sodium hypochlorite), nitric acid, sodium hydroxide, halogenated biocidal compounds.

1. Add 500 mL of water sample to clean glass beaker on a stir plate (non-heated).
2. Adjust to target pH using 0.01 or 0.1 M HNO_3 or NaOH.
3. If necessary, add humic acid stock solution using a pipetter for a final humic acid concentration of 1 mg/L.
4. Using a pipetter, add halogenated biocidal compound from stock solution for a final concentration of 20 mg/L dibromoacetonitrile, 100 mg/L 2,2-dibromo-3-nitrilopropionamide, or 100 mg/L glutaraldehyde.
5. Using a pipetter, add appropriate amount of disinfectant (either sodium hypochlorite or chloramine), from stock solution for a final concentration of 2 mg disinfectant/L water.
6. Stir for defined period of time using teflon stir bar.
7. Quench reaction with ascorbic acid (or sodium thiosulfite for chloramine).
8. Analyze sample for DBPs by GC/MS (EPA Method 521, 551.1, 552.3; see attached references).

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