CBP/TRS 148/96
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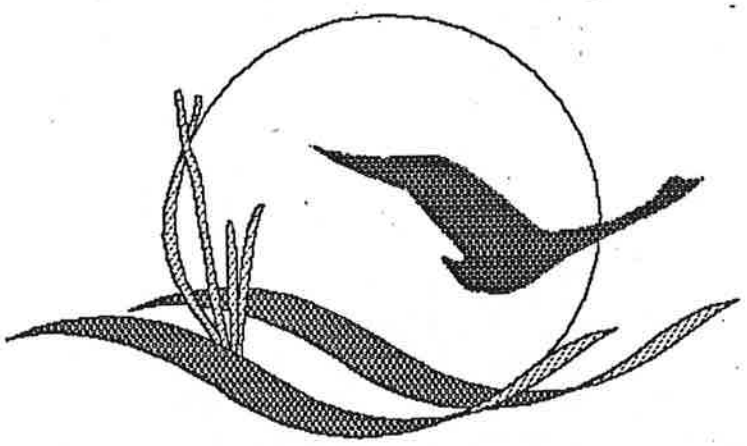
Recommended Guidelines for Sampling and Analyses in the Chesapeake Bay Monitoring Program

August 1996



Chesapeake Bay Program

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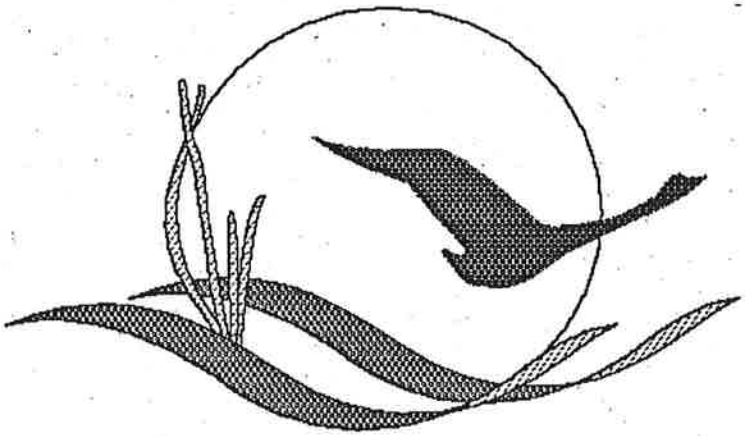


Chesapeake Bay Program

Printed by the U.S. Environmental Protection Agency for the Chesapeake Bay Program

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER I

INTRODUCTION

SECTION A

INTRODUCTION

1. Purpose of this document

The purpose of this document is to provide field and laboratory methods and associated quality control (QC) procedures and criteria that will result in the generation of data of known and documented quality for use in the Chesapeake Bay Monitoring Program. Under this document, the Participant will conduct field measurements and collect and analyze water and sediment samples for specific physical, chemical, and biological parameters that [illegible] accordance with Appendix F and previous data collection efforts. These monitoring data will be used in characterizing the health of the Chesapeake Bay and its tributaries, identifying long term trends, and providing data and guidance to managers and modelers during the restoration phase.

2. Organization of the document

2.1 This document includes the requirements and procedures for field measurements, field sampling, and laboratory analysis in support of the Chesapeake Bay Monitoring Program. The first chapters provide general information regarding technical and contractual requirements, and the remaining chapters have been organized so as to correspond chronologically with the field and laboratory activities performed.

2.2 Specifically, this document has been organized as follows:

2.2.1 Chapter I provides a summary of the technical and management requirements established to ensure attainment of Program objectives.

2.2.2 Chapter II defines the Quality Assurance (QA) protocols and procedures that have been developed for this document including specific requirements for QA procedures. It outlines the chain-of-custody and document control procedures which shall be followed with every sample.

2.2.3 Chapter III specifies all reporting requirements, data management procedures, and software procedures. It provides the deliverables and turnaround times required by this Scope of Work (SOW).

2.2.4 Chapter IV presents specific methods and procedures for water quality monitoring including sampling, field measurements, and analysis and the associated QC requirements.

3. Quality Assurance Considerations

3.1 The Participant must be aware of the importance of maintaining the integrity of the data generated under this contract, as the data may be used to make important decisions regarding the characterization and restoration of the Chesapeake Bay. Data integrity is defined as ensuring that data are complete, consistent, and without

errors, and ensuring the prevention of information corruption and unauthorized data modification.

3.2 Participants will adhere to generally acceptable field and laboratory practices and good automated field and laboratory practices. Good automated practices for this SOW comprise the data management procedures described in Chapter III of this SOW. All procedures shall be carried out by qualified field laboratory personnel to ensure the quality and integrity of the monitoring data being produced. By following the specific analytical and reporting procedures outlined in this document, the Participant will produce monitoring data of known and documented quality. Additional requirements for maintaining generally acceptable practices and good automated practices are provided throughout this SOW.

4. Health and Safety Considerations

4.1 The samples to be collected and analyzed by the Participants' are from the Chesapeake Bay mainstem and tributaries and may contain hazardous materials which could present a risk to human health and a hazard to field and laboratory instrumentation/equipment. The Participant should be aware of the potential hazards associated with the handling and analyses of these samples. It is the Participants' responsibility to take all necessary measures to ensure the health and safety of its employees, and to maintain its analytical instruments in good working condition.

4.2 The Participant will comply with all applicable Occupational Safety and Health Administration (OSHA) requirements.

4.3 The Participant will comply with the applicable requirements as stated in "Health and Safety Protocols for EPA Vessels," which has been included as an appendix to this SOW. This document will become a chapter of the EPA Health and Safety Manual. All contractors are expected to comply with all EPA health and safety requirements. However, the contractor should develop their own Manual to reflect their operating conditions.

4.4 All vessels used to collect samples from the Chesapeake Bay mainstem monitoring stations will be in full compliance with state and federal regulations regarding the use of tributyltin (TBT) anti-fouling paints. Regulations ban the use of paint containing TBT to marine contractors and boatyards.

4.5 All vessels used to collect samples will be in compliance with Section 312 of the Water Quality Act of 1987 which requires the installation of marine sanitation device (MSD) on all vessels with installed toilets operating in the navigable waters of the United States. Type III MSDs, which are designed to prevent the discharge of human waste from boats in any form, will be used.

5. Other Federal and State Requirements

5.1 The Participant will comply with all relevant State and Federal laws and regulations, including the Resource Conservation Recovery Act (RCRA) and the Clean Water Act (CWA).

5.2 Because some substance used in the sample preparation and analysis procedures described in this SOW are hazardous (e.g., formalin and inorganic acids), appropriate state and federal regulations must be followed for their handling and disposal both in the laboratory and in the field.

SECTION B

SUMMARY OF REQUIREMENTS

1. Document Task Areas

1.1 For each sample, the Participant will perform certain tasks. These tasks are: (1) development of a sampling schedule; (2) performance of field measurements; (3) collection, preparation, and transport of field samples; (4) laboratory receipt and preparation of field samples; (5) chemical and biological analyses of field samples; (6) adherence to QA/QC procedures outlined in this document; and (7) data management and reporting.

1.2 These tasks are specifically outlined as follows.

1.2.1 Task 1. Development of a sampling schedule.

1.2.1.1 The Participant will develop a sampling schedule that complies with the frequency and location requirements established in this document. This schedule shall be developed in close coordination with the VADEQ, the CBPO, and the State of Maryland.

1.2.1.2 The Participant will ensure compliance with the sampling schedule through the development and use of contingency plans.

1.2.1.3 The Participant will visit each sampling station as specified in Chapter IV, and verify and record site location according to procedures specified in each Chapter.

1.2.1.4 The Participant will transport the sampling crew and all necessary sampling and field measurement equipment and ensure that they are capable of meeting the specified data quality objectives.

1.2.2 Task 2. Performance of field measurements.

1.2.2.1 The Participant will measure physical and chemical parameters as defined in Chapter IV.

1.2.3 Task 3. Collection, preparation, and transport of field samples.

1.2.3.1 The Participant will develop and implement field chain-of-custody procedures as described in Chapter II.

1.2.3.2 The Participant will collect samples as described in Chapter IV.

1.2.3.3 The Participant will prepare and preserve samples as described in Chapter IV.

1.2.3.4 The Participant will transport samples as described in Chapter IV.

1.2.4 Task 4. Laboratory receipt and preparation of field samples.

1.2.4.1 The Participant will develop and implement laboratory chain-of-custody procedures as described in Chapter II.

1.2.4.2 All CBP monitoring samples shall be received and logged by the sample custodian.

1.2.4.3 The Participant will provide adequate storage for CBP samples awaiting analysis.

1.2.4.4 The Participant will follow the applicable sample preparation procedures outlined in this document.

1.2.5 Task 5. Chemical and biological analyses of field samples.

1.2.5.1 Samples shall be analyzed by the techniques described in the methodologies given in Chapters IV through VII for the target parameters listed.

1.2.5.2 Samples must be analyzed within the maximum specified holding times.

1.2.6 Task 6. Adherence to QA/QC procedures outlined in this SOW.

1.2.6.1 The Participant will adhere to all QA procedures described in Chapter II and all specific QC procedures described in Chapters IV, V, VI, and VII. Records documenting the use of the specified QC protocols shall be maintained in accordance with the document control procedures described in Chapter II.

1.2.6.2 The Participant will establish a Quality Assurance Plan (QAP) with the objective of providing sound monitoring data. This program shall incorporate the QC procedures, any necessary corrective action, and all documentation required during data collection, as well as the quality assessment measures performed by management to ensure acceptable data production.

1.2.6.3 Additional QC may be conducted in the form of the analysis of Performance Evaluation (PE) check samples submitted to the Participant by the CBPO. The results of all such control or PE check samples may be used for performance evaluation. "Compliant performance" is defined as that which yields correct compound identification and concentration values as determined by the CBPO, as well as meeting the method requirements for analysis, quality assurance/quality control, data reporting and other deliverables; including sample custody, sample documentation, and SOP documentation.

1.2.7 Task 7. Data management and reporting.

1.2.7.1 Samples will be analyzed and the data reported to EPA within the turnaround times of 3 months from the last day of sampling. The Participant will prepare electronic and hardcopy data according to the procedures outlined in Chapter II and will report electronic and hardcopy data according to the formats, order, and turnaround times according to this document.

2. Personnel Requirements

2.1 The Participant will provide technical expertise for this contract.

2.2 The Participant will designate and use key personnel to perform the functions described below. The VADEQ and the CBPO reserve the right to review personnel qualifications and experience, and take contract action as appropriate.

2.3 The Participant should have an organization with well-defined responsibilities for each individual in the management system to ensure sufficient resources for this contract and to maintain a successful operation. To establish this capability, the Participant will designate personnel to carry out the following responsibilities for this contract. Functions include, but are not limited to, the following:

2.3.1 Project Manager

Responsible for all aspects of this contract (from sample collection through data delivery) and shall be the primary contact for the VADEQ and CBPO. The project manager shall be responsible for the technical and management aspects of the contract and shall ensure that all contractual requirements are met.

Qualifications:

Education:

Minimum of Masters degree in chemistry, biology, or any scientific/engineering discipline.

Experience:

Minimum of 2 years of field experience, 2 years of laboratory experience, and 1 year of project management experience.

2.3.2 Field Supervisor

Responsible for all field activities performed under this contract.

Qualifications:

Education:

Minimum of Bachelor's degree in chemistry, biology, or any scientific/engineering discipline.

Experience:

Minimum of 4 years of field experience, including at least one year of supervisory experience.

2.3.3 Water Quality Laboratory Supervisor

Responsible for all technical efforts of the water quality laboratory to meet all terms and conditions of this contract.

Qualifications:

Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

Experience:

Minimum of 4 years of water quality laboratory experience, including at least one year of supervisory experience.

2.3.4 Phytoplankton Laboratory Supervisor

Responsible for all technical efforts of the phytoplankton laboratory to meet all terms and conditions of this contract.

Qualifications:

Education:

Minimum of Bachelor's degree in biology or any life science discipline.

Experience:

Minimum of 4 years of phytoplankton laboratory experience, including at least one year of supervisory experience.

2.3.5 Zooplankton Laboratory Supervisor

Responsible for all technical efforts of the zooplankton laboratory to meet all terms and conditions of this contract.

Qualifications:

Education:

Minimum of Bachelor's degree in biology or any life science discipline.

Experience:

Minimum of 4 years of zoological laboratory experience, including at least one year of supervisory experience.

2.3.6 Benthic Laboratory Supervisor

Responsible for all technical efforts of the benthic laboratory to meet all terms and conditions of this contract.

Qualifications:

Education:

Minimum of Bachelor's degree in biology or any life science discipline.

Experience:

Minimum of 4 years of benthic laboratory experience, including at least one year of supervisory experience.

2.3.7 Quality Assurance Officer

Responsible for overseeing the quality assurance aspects of contract data and reporting directly to upper management to meet all terms and conditions of this contract.

Qualifications:

Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

Experience:

Minimum of 3 years of field and laboratory experience, including at least one year of applied experience with QA principles and practices in sampling and analytical procedures.

2.3.8 Sample Custodian

Responsible for receiving the EPA samples (logging, handling, and storage).

Qualifications:

Education:

Minimum High School Diploma with four or more science courses.

Experience:

Minimum of 2 years experience receiving and logging scientific samples.

2.3.9 Data Systems Manager

Responsible for the management and quality control of all computing systems (hardware, software, documentation, and procedures), generating, updating, and quality controlling automated deliverables to meet all terms and conditions of this contract.

Qualifications:

Education:

Minimum of Bachelor's degree with four or more intermediate courses in programming, information management, database management systems, or systems requirements analysis.

Experience:

Minimum of 3 years experience in data or systems management or programming including one year of experience with software utilized for data management and generation of data deliverables.

2.3.10 Field personnel

Responsible for field measurements and collection of monitoring samples in accordance with this SOW.

Qualifications:

Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

Experience:

One year of experience sampling water, benthos, and plankton in estuarine waters. Specifically, experience in using the field instrumentation and sampling devices cited in this SOW.

2.3.11 Water Quality Laboratory personnel

Responsible for the analysis of samples in accordance with this SOW.

Qualifications:

Education:

Minimum of Bachelor's degree in chemistry or any scientific/engineering discipline.

Experience:

One year of experience analyzing nutrients and water quality parameters. Specifically,

experience with the instrumentation and methods cited in this SOW.

2.3.12 Phytoplankton Laboratory expert

Responsible for the analysis of phytoplankton samples in accordance with this SOW.

Qualifications:

Education:

Minimum of Bachelor's degree in biology or any life science discipline.

Experience:

One year of experience analyzing water samples for phytoplankton. Specifically, experience with the instruments and techniques cited in this SOW.

2.3.13 Zooplankton Laboratory expert

Responsible for the analysis of zooplankton samples in accordance with this SOW.

Qualifications:

Education:

Minimum of Bachelor's degree in biology or any life science discipline.

Experience:

One year of experience analyzing water samples for zooplankton. Specifically, experience with the instruments and techniques cited in this SOW.

2.3.14 Benthic Laboratory expert

Responsible for the analysis of benthic samples in accordance with this SOW.

Qualifications:

Education:

Minimum of Bachelor's degree in biology or any life science discipline.

Experience:

One year of experience analyzing benthic samples. Specifically, experience with the instruments and techniques cited in this SOW.

2.3.15 Data Management Analyst

Responsible for the operation and maintenance of software and programs generating, updating and quality controlling analytical databases and automated deliverables to meet all terms and conditions of this contract.

Qualifications:

Education:

Minimum of Bachelor's degree with four or more intermediate courses in information management, information systems, database management systems, or systems requirements analysis.

Experience:

Minimum of two years experience in systems or including one year of experience with the software being utilized for data management and generation of data deliverables.

3. Facilities

3.1 The adequacy of the facilities is of equal importance as the technical staff to accomplish the required work as specified by this contract. Therefore, the Participant will provide the field and laboratory facilities described in this Section.

3.2 Field Facilities

An adequate cruise vessel to safely traverse the waterways and carry the field crew, field instrumentation, sampling equipment, sample preparation equipment and materials, and sample storage facilities.

3.3 Laboratory facilities

3.3.1 Sample Receipt Area

Adequate, contamination-free, well ventilated work space provided with chemical resistant bench top for receipt and safe handling of CBP samples.

3.3.2 Storage Area

Sufficient refrigerator space to maintain unused CBP sample volume for 60 days after data submission. NOTE: Samples or extracts and standards shall each be stored separately. Samples shall be stored in an atmosphere demonstrated to be free from all potential contaminants.

3.3.3 Sample Preparation Area

Adequate, contamination-free, well-ventilated work space provided with:

3.3.3.1 Benches with chemical resistant tops, exhaust hoods.

3.3.3.2 Source of distilled or demineralized organic-free water.

3.3.3.3 Analytical balance(s) located away from drafts and rapid changes in temperature.

3.3.4 Standards and reagents

The Participant will have in-house appropriate standards and reagents to perform the procedures in this SOW.

4. Instrumentation and Equipment

4.1 The Participant will have the field and laboratory instrumentation and equipment described in this Section.

4.2 All equipment and instrumentation specified in this document are recommended and should be in the possession of the Participant and in good condition at all times during the length of the grant. The Participant will ensure that, in the event of instrument or equipment failure, backup instrumentation or equipment in good condition are available to perform field measurements, and sample collection, preparation, and analysis. It is recommended that surge protectors and a temporary backup power supply source are installed in order to protect analytical instruments, PCs, and other equipment in the event of a temporary electrical disruption or power surge.

4.3 In addition, the Participant should have an in-house stock of instrument parts to ensure continuous operation to meet contract-specified holding and turnaround times.

4.4 At a minimum, the Participant should have the following instruments and equipment operative.

4.4.1 Field Instrumentation and equipment

4.4.1.1 Secchi disk.

4.4.1.2 CTD device, equipped with pH probe, DO probe, depth sensor, bottom sensor, light attenuation sensors.

4.4.1.3 Sample collection bottles.

4.4.1.4 System to collect below surface samples.

4.4.1.5 Plankton nets.

4.4.1.6 Stationary Bongo dropnet.

4.4.1.7 Diaphragm pump system.

4.4.1.8 Spade-type coring device.

4.4.2 Water Quality analyses

4.4.2.1 Continuous flow automated analytical system equipped with an autosampler, manifold, proportional pump, colorimeter, phototube, recorder or computer based data system, and heating bath (e.g., Technicon AutoAnalyzer).

4.4.2.2 Nitrogen Analyzer equipped with a combustion tube, reduction tube, water trap, and nitrogen detector.

4.4.2.3 TOC Analyzer which employs high temperature combustion, platinum catalyst, and a nondispersive infrared detector.

4.4.2.4 Air incubator, capable of maintaining 20 $\pm$ 2°C.

4.4.2.5 Dissolved oxygen meter and probe.

4.4.2.6 Centrifuge.

4.4.2.7 Dual beam spectrophotometer with matched cuvettes.

4.4.2.8 Drying oven capable of maintaining 104 $\pm$ 2°C.

4.4.2.9 Muffle furnace capable of maintaining 550 $\pm$ 50°C.

4.4.2.10 pH meter and probe.

4.4.3 Biological analyses

4.4.3.1 Binocular Dissecting microscopes.

4.4.3.2 Fiber optic illuminators.

4.4.3.3 Compound microscopes.

4.4.3.4 Inverted plankton microscope.

4.4.3.5 Epifluorescence microscope.

4.4.3.6 Scintillation counter.

4.4.3.7 Fluorescently lighted magnifiers.

4.4.4 Data Management and Handling

4.4.4.1 Hardware and Software - IBM compatible personal computer running DOS 3.1 or 3.3 with 640K RAM, a 60 megabyte hard disk, an Intel 80286 processor, a 3.5" disk drive, an EPSON FX100 or compatible printer, and a 2400 baud modem with PROCOMM. The Participant will also have word processing software capable of processing and reading ASCII text files.

4.4.4.2 The Participant will submit reports and data packages as specified in Chapter III of this document. Space, tables, and adequate copy machines will be provided to meet the requirements of this document. The Participant will also designate personnel to perform tasks specified in the SOW and to use the hardware and software listed above in the performance of such tasks. The laboratory manager shall authorize by signing any data that have been manually edited.

CHAPTER II
QUALITY ASSURANCE

Section A. Introduction

Section B. General QA/QC Requirements

1. Reporting
2. Chain-of-Custody
3. Participation in Technical Meetings
4. Procedural Change Authorization

Section C. Field QA/QC Procedures

1. Annual Calibration
2. Calibration Check
3. Check Sample

Section D. Laboratory QA/QC Procedures

1. Method Blank
2. Matrix Spike
3. Laboratory Replicate
4. Check Standard
5. Glassware Cleaning

Section E. Data Quality Objectives

1. General DQOs
2. Sampling
3. Field Measurements
4. Water Quality Monitoring
5. Phytoplankton Monitoring
6. Zooplankton Monitoring
7. Benthic Monitoring

Section F. Documentation Recommendations

1. Quality Assurance Plan
2. Quality Assurance Project Plans
3. Standard Operating Procedures
4. Document Control
5. Contingency and Health and Safety Plans

Section G. Performance Assessment

1. Split Sample Program
2. Performance Evaluation Samples
3. Audits of Data Quality
4. On-Site Audits

Section H. References

SECTION A

INTRODUCTION

The Chesapeake Bay Program (CBP) was established by Congressional directive with the objectives of characterizing the state of the Chesapeake Bay, identifying long term trends, and providing data and guidance to managers and modelers during the restoration phase. The Chesapeake Bay Program Office (CBPO) has developed and integrated into all phases of the monitoring and measurement activities under its purview a scheme of quality assurance (QA) practices. These practices, as defined in the CBP QA Program Plan (QAPP), are focused on ensuring that all data generated through the CBP are scientifically valid, defensible, of known quality, and designed to meet data user requirements.

A QA program shall be developed and implemented within the participants' organization that is in accordance with the procedures and recommendations of this document. The purpose of this chapter is to define the recommendations of the participants' QA program. Section B provides an overview of the programmatic QA and quality control (QC) recommendations. Method-specific QC recommendations are provided within each field measurement, sampling, and analytical procedure. Section C provides information on the program's Data Quality Objectives, Section D provides documentation recommendations, Section E provides for initial and continuous performance assessment, and Section F provides a list of relevant references.

SECTION B

GENERAL QA/QC REQUIREMENTS

1. Reporting

1.1 Field data and laboratory analysis information should be entered into an automated data entry and quality assurance program that will be provided by the Chesapeake Bay Program. This Program will provide a first level of statistical range checking, quality control checking and output as recommended by this document.

1.2 Cruise event data collected at the cruise location may be entered on location. Cruise event data points relevant to laboratory analysis should be entered using the guidelines as outlined in the CBP Data Management Plan (DMP).

1.3 Hardcopy records and source documents for both the cruise event data and the laboratory analysis data should be kept for a period of 5 years after the last day of the cruise.

1.4 The CBPCC will provide training for up to 4 employees on the use of the CBP-supplied program, when the software is installed. Henceforth, it will be the responsibility of the Participants to train their staff members.

1.5 The Participants shall keep electronic media backups of the cruise data, for the period of the grant. At the end of the grant, this data must be relinquished to the CBPO.

1.6 The Participants will submit a Cruise Report at the end of each cruise within approximately two days after the end of the cruise.

1.7 The Participants shall submit a complete data package for each cruise. This submission must comprise all field measurement, analytical, and all relevant QC data from all stations sampled during the cruise. This information must adhere to the requirements outlined in the Data Management Plan (DMP).

1.8 The Participants will be provided with a PC based program that can be utilized for entry, verification, and submission of data to the CBPO.

1.8.1 Data may be entered in one of two ways: using manual data entry screens for each type of data; or the program will accept input from another computer or instrument if data are submitted in EPA standard format (ESF).

1.8.2 The program has data entry screens for each type of data. These screens are used to enter the data. While data are being entered, range checks will be run on each item. When an item is out of critical or warning range, the user will be notified.

1.8.3 The program can accept data from another computer via floppy disk that is in ESF format. When these data are input, they will be run through range checks as described in item 1.8.2.

1.8.4 After all data are entered by one of the above methods, the program will print out a number of graphic plots of the data. The Participants will examine the plots, and the laboratory director is required to sign each plot indicating that the data have been examined and appear to be correct.

1.8.5 The program will print out a listing of all values that are above or below warning and critical limits. The laboratory director is required to examine this listing and sign that it is correct.

1.8.6 The program will print out a list of missing values for the cruise. The designated person in charge of the laboratory is required to enter a reason for each of the missing values and print out the list.

1.8.7 The program will write out a disk in accordance to the DMP format that must be submitted to the CBPCC.

1.8.8 The Participant shall provide a cover letter for each submittal indicating, and not limited to:

1.8.8.1 Cruise number.

1.8.8.2 Time period covered by the submitted data.

1.8.8.3 Type of data, i.e., Mainstem Monitoring.

1.8.8.4 A synopsis of major problems, if any.

1.8.8.5 A statement of any changes since the last data submission, if any (a restatement of any issues previously recorded on the "Procedure Change Tracking Form" that affect this submission).

1.8.8.6 A statement indicating Participant willingness to ensure corrections to the data for a period of five years.

1.9 The required submission must include the following:

1.9.1 The data disk (results, QC data, and data summary file);

1.9.2 The plots created under section 1.8.4;

1.9.3 The list of range values created in section 1.8.5;

1.9.4 The list of missing values created in section 1.8.6; and,

1.9.5 A cover letter as described in Section 1.8.8.

1.10 The Participants shall be responsible for correcting any errors found by the CBPCC and resubmitting the data in the required format to the CBPO. The Participants shall be required to correct any errors found for no additional cost for a period of 5 years after sample collection.

2. Chain-of-Custody

2.1 Procedures should be established that ensure that samples are properly collected and preserved from the time the samples are collected until the corresponding data are submitted to the CBPCC.

2.2 A system for assuring positive identification of samples and documentation of all samples must be operational. To ensure sample integrity, chain-of-custody procedures including procedures for sample identification, sample receiving, and sample tracking, should be developed and instituted.

2.2.1 Sample Identification

2.2.1.1 To assure traceability of samples while in possession, there should be a specified method for maintaining identification of samples in the field and throughout the laboratory.

2.2.1.2 Each sample and sample preparation container should be labeled with a unique identifier that is cross-referenced with the corresponding documentation.

2.2.2 Sample Receiving

2.2.2.1 A sample custodian (and an alternate) responsible for receiving all samples should be designated.

2.2.2.2 The condition of the shipping and sample containers should be inspected and documented upon receipt by the sample custodian or his/her representative.

2.2.2.3 The sample custodian or his/her representative should sign and date all forms accompanying the samples at the time of sample receipt.

2.2.3 Sample Tracking

2.2.3.1 Records documenting all phases of sample handling from collection to final analysis should be maintained.

3. Participation in Technical Meetings

3.1 Attendance of Monitoring Subcommittee meetings, Analytical Methods and Quality Assurance Workgroup (AMQAW) meetings, and miscellaneous technical meetings as required, is recommended by the CBPO.

3.2 The CBP Monitoring Subcommittee coordinates multi-jurisdictional efforts to monitor the Chesapeake Bay basin system. It manages and ensures continued accessibility of the resultant environmental data and promotes multi-disciplinary interpretation and reporting of the data on a jurisdiction and program-wide basis. The Monitoring Subcommittee oversees implementation of new and innovative monitoring programs (water quality, living resources, toxics and ecosystem processes) and techniques. It reevaluates existing programs to ensure that environmental data necessary to support implementation of a comprehensive quality assurance program (as part of components of the various monitoring programs) are collected. Emphasis is placed on ensuring collection and management of comparable environmental data of known quality through continued communication and transfer of technologies between the agencies and institutions involved in the Chesapeake Bay Monitoring Program.

3.3 AMQAW comprises technical advisors to the Monitoring Subcommittee concerning field and analytical

methodology and quality assurance issues. These advisors include laboratory directors from the mainstem and tributary laboratories, field managers, and State managers conducting work for the Chesapeake Bay Program. The workgroup's goal is to discuss analytical and field protocols, identify discrepancies (the issues are usually identified by reviewing the data), and take measures to improve the situation. The workgroup provides a forum for exchange of technical information focused on moving towards standardization of methods/use of comparable methods throughout the Chesapeake Bay Monitoring Program. The forum allows the different organizations to share the way they do things and individuals to present new and innovative ideas, potentially for their use.

3.4 AMQAW reviews issues pertaining to the CBP Coordinated Split Sampling Program (CSSP). As directed by the CBPO and AMQAW, the Participants shall conduct follow-up investigations to determine possible causes of inter-organization differences in CSSP results. Funding may be applied for from the Monitoring Subcommittee for special studies to improve the quality of field and laboratory methods.

4. Procedural Change Authorization

4.1 Any substantial or long-term changes to a procedure or method, either in the field or laboratory, should be submitted to the CBP Quality Assurance Officer. These types of changes may include items such as modifications to detection limits, instrument type or sampling stations. All actual and proposed modifications should be documented using the Chesapeake Bay Monitoring Program Procedure Modification Tracking Form (PMTF) (Figure II-1).

4.2 The completed PMTF should be submitted to the CBP QAO within 30 days after the last day of the cruise.

4.3 Minor events occurring in the laboratory should be documented in the data summary file, associated with the data in the diskette.

4.4 At the conclusion of the cruise, a Monitoring Cruise Report should be completed and submitted to the State agency, who will then forward it to the CBPO. The Chesapeake Bay Monitoring Program Cruise Report is shown in Figure II-2.

4.5 Modifications due to emergencies during a sampling cruise are authorized by the Chief Scientist with priorities for safety and completion of the cruise. Modifications should be reported after the cruise. Depending on size or amount of impact on the data the deviation has, the change should be documented in either the PMTF or the Monitoring Cruise Report.

Figure II-1

Chesapeake Bay Monitoring Program
Procedure Modification Tracking Form

CHESAPEAKE BAY MONITORING PROGRAM
PROCEDURE MODIFICATION TRACKING FORM

PMTF # _____
APPROVED __ DENIED __

This form is used to request approval for modifications and to document approved modifications mad methods. It is not a substitute for timely contact with the CBPO Quality Assurance Officer or his/her detailed method description including the proposed modification must be attached to this form prior t

DATE SUBMITTED		DATE APPROVED	
REQUESTOR NAME		ORGANIZATION	
NEWLY PROPOSED [ ] MODIFICATION	FIELD-APPROVED [ ] MODIFICATION	APPROVED BY: DATE:	
TYPE OF PROCEDURE/METHOD	SAMPLING [ ] FIELD [ ] MEASUREMENT	ANALYTICAL [ ] OTHER [ ] SPECIFY:	REPORTING [ ]
DURATION	PERMANENT [ ] TEMPORARY [ ]	EFFECTIVE DATE: START DATE: END DATE:	
PROCEDURE/METHOD DESCRIPTION			
MODIFICATION DESCRIPTION			
JUSTIFICATION FOR MODIFICATION			
ANALYTICAL PARAMETERS THAT MAY BE AFFECTED BY THIS CHANGE			
AFFECTED QA PLAN(S) (INCLUDE TITLE, REVISION, AND DATE)			
AFFECTED CRUISE(S)			
PMTF COMPLETED BY	NAME:		DATE:

STATE APPROVAL: NAME _____ TITLE _____
SIGNATURE _____ DATE _____

CBPO APPROVAL: NAME _____ TITLE _____
SIGNATURE _____ DATE _____

SECTION C

FIELD QUALITY ASSURANCE PROCEDURES

1. Annual Calibration

1.1 An annual calibration is an extensive and thorough calibration using standards or instruments relating back to certified (e.g. National Institute of Standards and Technologies) instruments or standards to ensure the parameter precision.

1.2 These calibrations will be performed on each instrument at least annually.

2. Calibration Check

2.1 A calibration check is a verification performed before and after each cruise to ensure that the instrument response is comparable that which existed at the annual calibration.

2.2 Calibration checks are performed before and after each cruise.

2.3 Calibration by standard operating procedures should include measurements against a reference standard or meter.

2.4 When the calibration check indicates a significant change during a cruise, the instrument should be re-calibrated as described in the annual calibration.

3. Check Sample

3.1 A check sample is a water sample that is collected simultaneously with an in-situ measurement and returned to the laboratory for analysis.

SECTION D

LABORATORY QUALITY ASSURANCE PROCEDURES

1. Method Blank

1.1 A method blank is a volume of ASTM Type II reagent grade water that is carried through the entire analytical procedure. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

1.2 A method blank should be analyzed once for every 10 CBP samples (preferable), however every 20 samples is acceptable for those instances where the concentrations are low and this is the total sample number.

1.3 If the concentration of analyte exceeds the MDL, laboratory or reagent contamination should be suspected. If the analyte concentration is 5 times the MDL or greater, then corrective action is required and reanalysis if possible.

2. Matrix Spike (not required for chlorophyll, PHOSP, TSS, PC and PN)

2.1 A matrix spike is used primarily as a means of evaluating bias that may result from the analysis of a particular matrix when using a specific procedure. The saline, aqueous matrix has been demonstrated to impart bias in some analyses. Sample spike analysis involves the introduction of a know amount of the analyte of interest into one of two aliquots from a well homogenized sample and a calculation of spike recovery.

2.2 The spike concentration must be greater than the original or background concentration of the sample and not less than four times the calculated MDL.

2.3 The sample is spiked prior to all steps in the analytical process, particularly when a digestion is involved.

2.4 Proper assessment requires that the integrity of the sample matrix be maintained. The original sample must not be diluted more than 10% due to the spike process.

2.5 The analytical system response from the sample plus the spike should be in the same range as the sample set undergoing analysis, ideally approximating 50-75% of a full scale response.

2.6 A matrix spike should be analyzed once for every 10 CBP samples.

2.7 Matrix spikes can not be performed on lab or field blanks.

2.8 The percent recovery of analyte from the matrix spike sample is calculated using the following equation:

$$\text{Matrix Spike Recovery} = \frac{SSR - SR}{SA} \times 100 \qquad \text{(Eq. IV.2)}$$

where,

SSR = Spike sample result
SR = Sample result
SA = Spike added

2.9 If the spike recovery is outside the range designated in Table II.3, the spike analysis is repeated after checking for obvious sources of error. At a minimum, this involves an immediate repeat of the instrumental analysis. If the result is still beyond acceptance limits, and the analytical process employed a digestion step, the matrix spike should be reanalyzed including redigestion. If the recovery of the replicated sample spike continues to remain outside the designated range, the recover problem is judged to be matrix related. It is considered a non-system problem, requiring no further corrective action.

2.10 The recovery of a matrix spike should be reported with the concentrations of the background sample and the known, theoretical spike.

3. Laboratory Replicates

3.1 Laboratory replicate analyses provide a measure of laboratory precision. Duplicates are prepared by taking two aliquots for analysis from a well homogenized sample. More replicates may be analyzed and reported.

3.2 A laboratory replicate should be analyzed once for every 10-20 CBP samples preferably, however every 20 samples is acceptable for those instances where the concentrations are low and this is the total sample number.

3.3 The precision is measured by calculating the coefficient of variation (CV) using the following equation:

$$CV = \frac{SD}{MEAN} \times 100, \text{ where } SD = \sqrt{\frac{(X-\bar{X})^2}{(N-1)}} \qquad \text{(Eq. IV.3)}$$

where,

CV = Coefficient of variation
SD = Standard deviation
Mean = Mean of the replicate readings
N = Number of samples

3.4 If the CV does not fall within the range in Table II.3, corrective action should be taken.

4. Check Standard

4.1 An accurately prepared chemical standard is analyzed every 10 CBP samples preferably, however every 20 samples is acceptable for those instances where the concentrations are low and this is the total sample number. The results are compared to the known analyte concentration. If the determined concentration for known analysis is not within 90-110% of the known analyte concentration, a second check standard is prepared and analyzed to confirm or deny the initial "out of control" analysis. If the reanalyzed check standard is within

acceptance limits, sample analysis proceeds; however, if the reanalyzed check standard fails the acceptable limits, the instrument must be recalibrated. All the samples between that check standard and the previous standard must be reanalyzed.

5. Glassware Cleaning

5.1 Standard and Reagent Glassware should be rinsed with 10% HCl once and then rinsed 3 times with reagent grade water.

5.2 Sample Containers should be rinsed with tap water, 10% HCl and then rinsed 4 times with reagent water. Then, before use they should be rinsed 3 times with sample.

5.3 AutoAnalyzer Cups should be rinsed three times with the sample, and then filled.

SECTION E

DATA QUALITY OBJECTIVES (DQO)

1. General DQOs

1.1 Data Quality Objectives are qualitative and quantitative statements that specify the quality of data required to support specific CBPO decisions. DQOs also specify the level of uncertainty that a decision maker is willing to accept in results derived from monitoring data, when the results are used in a regulatory or programmatic decision, such as establishing analytical method requirements, establishing sampling protocols, and revision or development of industry standards.

1.2 The DQOs defined in this Section were developed by the CBPO using existing performance information on the methods and procedures contained in this document. DQOs are established through an iterative process, these values may be adjusted by the CBP QAO as a result of evaluations of performance data generated during this program.

1.3 The main objective of this document is to provide monitoring data of known and consistent quality to the CBPO. This data will be used in characterizing the state of the Chesapeake Bay, identifying long term trends, and providing data and guidance to managers and modelers during the restoration phase.

1.4 The domain of concern for the Chesapeake Bay Monitoring Program comprises the chemical and biological characterization of the waters and sediment of the Chesapeake Bay and its tributaries.

1.5 The levels of quality of sampling activities are expressed in terms of comparability, representativeness, precision, accuracy, and completeness using the following criteria.

1.5.1 Following the sampling procedures and sample locations recommended in this document may ensure sampling comparability and representativeness of data generated to meet the CBP needs.

1.5.2 Overall precision (sampling and analytical) is assessed through field replicate measurements/analyses, and is expressed as coefficient of variation (CV). Sampling precision can be evaluated by comparing overall precision to measurement/analytical precision.

1.5.3 Overall accuracy is assessed through field spike analyses, and is expressed as percent recovery. Sampling accuracy can be evaluated by comparing overall accuracy to measurement/analytical accuracy. However, these are not recommended.

1.5.4 Sampling completeness is calculated based on the ratio of samples collected to samples that were planned, and is expressed as percent completeness.

1.6 The levels of quality of measurement and analytical data are expressed in terms of comparability, representativeness, precision, accuracy, completeness, and method detection limits (MDL) using the following criteria.

1.6.1 Measurement/analytical comparability and representativeness of data generated will be ensured through adherence to the measurement and analytical procedures described methods document.

1.6.2 Precision, expressed as coefficient of variation (CV), for measurement and analytical data is calculated based on replicate measurements/analyses.

1.6.3 Accuracy, expressed as percent of reference value, of measurement data is calculated based on measurements of standard reference materials (where available) and calibrating reference techniques.

1.6.4 Accuracy, expressed as percent recovery, of analytical data is calculated based on the analysis of spiked samples and reference materials.

1.6.5 Completeness of measurement data is calculated based on the ratio of measurements made to measurements planned, and is expressed as percent completeness.

1.6.6 Completeness of analytical data is calculated based on the ratio of samples that are analyzed to the number of samples collected, and is expressed as percent completeness.

1.6.7 Method detection limits should be determined for all parameters using the procedures recommended by the AMQAW as described below.

1.6.7.1 Samples used in the determination of MDLs should be environmental samples collected once each year during winter, or whenever that analyte's concentration is lowest for the year. The sampling location most appropriate and representative for MDL analyses should be determined before collection.

1.6.7.2 MDL values should be determined as 3 times the standard deviation of seven replicate measurements/analyses of the same sample.

1.6.7.3 MDLs should be verified for each parameter on an annual basis or whenever a change is made in the measurement or analytical methodology.

1.6.7.4 A table of MDLs values and all supporting documentation should be maintained by the Participant and made available for review as requested by a CBPO representative. When values change, the revised table of MDL values should be included with each data package.

1.7 Real-time quality control charts for precision and accuracy should be developed and maintained for each parameter and each concentration level, using the most recent 25 points, at least. More points may be used if deemed necessary. The CBPO will provide further information on a PC-based software package to facilitate the calculations and to ensure consistency in the development of the control charts.

1.7.1 Control charts are centered at the arithmetic mean. Unless otherwise specified in the method, the upper and lower control limits are defined at $\pm$ 3 standard deviations from the mean and the upper and lower warning limits are defined at $\pm$ 2 standard deviations from the mean.

1.7.2 Precision and accuracy acceptance windows for implementation during the development phase of the control charts are provided within each method and in Sections 2, 3, 4, 5, and 7.

1.7.3 Once control charts have been established, they should be used to determine if a given analytical or measurement process is in control.

1.7.3.1 A process is out of control if 3 or more data points are outside either control limit.

1.7.3.2 Immediate corrective action is recommended for any process identified as being out of normal control limits. Where possible, this should include reanalysis.

1.7.3.3 A warning of possible systematic error is indicated if 7 successive data points fall away from the mean on the same side of the center line, if 7 or more data points fall outside of either warning limit, or if a discernible trend develops.

2. Sampling

2.1 Sampling precision, accuracy, and completeness objectives are provided in Table II.1.

Table II.1 Sampling Data Quality Objectives

PARAMETERS	REFERENCE	PRECISION	ACCURACY	COMPLETENESS
Water Quality	IV.C.3	< 20%	80 -120%	90%
Phytoplankton	IV.C.4	< 20%	80 -120%	90%
Zooplankton	IV.C.4	< 20%	80 -120%	90%
Benthic	IV.C.4	< 20%	80 -120%	90%

3. Field Measurements

3.1 Precision, accuracy, completeness, and MDL objectives for field measurements are provided in Table II.2.

Table II.2 Objectives for Field Measurements

PARAMETER	REFERENCE	PRECISION	ACCURACY	COMPLETENESS	MDL
pH	IV.C.2.4	< 20%	80 - 120	90%	0.1 pH
D.O.	IV.C.2.4	< 20%	80 - 120	90%	0.2 mg DO/L
Secchi Depth	IV.C.2.3	< 20%	80 - 120	90%	0.1 m
Specific Conductance	IV.C.2.4	< 20%	80 - 120	90%	1 umho/cm
Salinity	IV.C.2.4	< 20%	80 - 120	90%	0.1 ppt
Light Attenuation	IV.C.2.4	< 20%	80 - 120	90%	0.05% @ 100% light
Water Temperature	IV.C.2.4	< 20%	80 - 120	90%	0.1°C
Depth	IV.C.2.4	< 20%	80 - 120	90%	1.0 m

4. Water Quality Monitoring

4.1 Precision. accuracy, completeness, and MDL objectives for water quality analyses are provided in Table II.3.

Table II.3 Objectives for Water Quality Analyses

PARAMETER	REFERENCE	PRECISION	ACCURACY	COMPLETENESS	MDL
Total Dissolved Phosphorus	IV.D.2	< 20% CV	80 - 120% Recovery	90%	0.001mg TDP/L
Dissolved Ortho Phosphate	IV.D.3	< 20% CV	80 - 120% Recovery	90%	0.0006mg PO_4F/L
Particulate Phosphorus	IV.D.4	< 20% CV	N/A	90%	0.0012mg PP/L
Nitrite	IV.D.5	< 20% CV	80 - 120% Recovery	90%	0.0002mg NO_2/L
Nitrite + Nitrate	IV.D.6	< 20% CV	80 - 120% Recovery	90%	0.0002mg NO_{2+3}/L
Ammonia	IV.D.7	< 20% CV	80 - 120% Recovery	90%	0.004mg NH_4/L
Total Dissolved Nitrogen	IV.D.8	< 20% CV	80 - 120% Recovery	90%	0.026mg TDN/L
Particulate Nitrogen	IV.D.9	< 20% CV	N/A	90%	0.019mg PN/L
Particulate Carbon	IV.D.10	< 20% CV	N/A	90%	0.097mg PC/L
Dissolved Organic Carbon	IV.D.11	< 20% CV	80 - 120% Recovery	90%	0.5mg DOC/L
Chlorophyll	IV.D.13	< 20% CV	N/A	90%	0.2μg Chla/L
Total Suspended Solids	IV.D.14	< 20% CV	N/A	90%	2mg TSS/L
Silicates	IV.D.16	< 20% CV	80 - 120% Recovery	90%	0.013mg Si/L

5. Phytoplankton Monitoring

5.1 Precision, accuracy, and completeness objectives for phytoplankton analyses are provided in Table II.4.

Table II.4 Objectives for Phytoplankton Analyses

PARAMETER	REFERENCE	PRECISION	ACCURACY	COMPLETENESS
Phytoplankton Enumeration	V.D.3.3	< 20%	< 20%	95%
Phytoplankton Identification	V.D.3.3	< 10%	< 10%	90%
Phytoplankton Biomass	V.D.3.4			90%
Picoplankton Enumeration	V.D.4.3	< 20%	< 20%	95%
Picoplankton Identification	V.D.4.3	< 10%	< 10%	90%
Picoplankton Biomass	V.D.4.4			90%
Productivity	V.D.5			90%

6. Zooplankton Monitoring

6.1 Precision, accuracy, and completeness objectives for Zooplankton analyses are provided in Table II.5.

Table II.5 Objectives for Zooplankton Analyses

PARAMETER	REFERENCE	PRECISION	ACCURACY	COMPLETENESS
Enumeration	VI.D.3.3	< 5%	< 5%	95%
Identification	VI.D.3.3	< 10%	< 10%	90%
Biomass	VI.D.3.4			90%

7. Benthic Monitoring

7.1 Precision, accuracy, and completeness objectives for benthic analyses are provided in Table II.6.

Table II.6 Objectives for Benthic Analyses

PARAMETER	REFERENCE	PRECISION	ACCURACY	COMPLETENESS
Macrofauna Sorting	VII.D.3.3	< 5%	< 5%	90%
Macrofauna Enumeration	VII.D.3.4	< 5%	< 5%	90%
Macrofauna Identification	VII.D.3.4	< 5%	< 5%	90%
Macrofauna Biomass	VII.D.3.5			90%
Sediment Particle Size	VII.D.4.4			90%
Sediment Organic Content	VII.D.4.5			90%

SECTION F

DOCUMENTATION RECOMMENDATIONS

1. Quality Assurance Plan (QAP)

A QA program with the objective of providing sound monitoring data should be developed and implemented. This program should include the specific procedures for identifying out of control sampling, field measurement, and analytical conditions and implementing and documenting the necessary corrective actions, the mechanisms for the accurate and timely preparation of required documentation, as well as the quality assessment measures performed by management to ensure acceptable data production.

1.1 As evidence of such a program, a written Quality Assurance Plan (QAP) which describes the procedures that are implemented in the field and the laboratory should be prepared to achieve the following:

1.1.1 Maintain data integrity, validity, and usability.

1.1.2 Ensure that sampling and analytical systems are maintained in an acceptable state of stability and reproducibility.

1.1.3 Detect problems through data assessment and establish corrective action procedures to ensure that the sampling, analytical, and measurement processes are reliable.

1.1.4 Document all aspects of the sampling, analytical, and measurement processes in order to provide data that are technically sound and legally defensible.

1.2 The QAP should present, in specific terms, the policies, organization, objectives, and specific QA and QC activities designed to achieve the data quality requirements recommended in this document. Where applicable, Standard Operating Procedures pertaining to each element should be included or referenced as part of the QAP. The QAP should be available during on-site laboratory evaluations. Additional information relevant to the preparation of a QAP can be found in EPA and ASTM publications.

1.3 The following outline identifies the key elements that should be included in the QAP.

I QA Policy and Objectives

II Organization and Personnel

- QA Management
  - Organization
  - Assignment of QA and QC Responsibilities
  - Reporting Relationships
- Personnel
  - Education and Experience Qualifications Pertinent to this document
  - Training Program

III Facilities and Equipment

- Equipment, Instrumentation, and Backup Alternatives
- Maintenance Activities and Schedules
- Materials and Supplies

IV Document Control

- Field and Laboratory Notebook Policy
- Sample and Data Tracking/Custody Procedures and Documentation Requirements
- Logbook Maintenance and Archiving Procedures
- Data Package Organization, Preparation, and Review Procedures
- Procedures for Preparation, Approval, Review, Revision, and Distribution of SOPs

V Field QA/QC

- Field Equipment Maintenance, Calibration, and Operation
- Field Measurements
- Sample Collection
- Sample Handling, Preservation, and Shipping

VI Analytical QA/QC

- Calibration Procedures and Frequency
- Sample Handling and Storage Procedures
- Sample Preparation Procedures

VII Data Generation

- Data Collection Procedures
- Data Reduction Procedures
- Data Review Procedures
- Data Reporting and Authorization Procedures

- Data Management Procedures

VIII Quality Assurance Program Assessment

- Data Audits
- Systems Audits
- Performance Audits
- Corrective Action System
- QA Reporting Procedures

1.4 The Participant's QAP should be submitted to the CBPO within 30 days after grant award. The QAP should be revised based on any comments from the State Agency, EPA Project Officer or EPA QAO.

1.5 The revised QAP must include changes resulting from any of the following evaluations:

1.5.1 The Participant's internal review of their organization, personnel, facility, equipment, policy, and procedures.

1.5.2 The Participant's implementation of the requirements of the grant.

1.5.3 The CBPO's review of the laboratory evaluation sample data, bidder supplied documentation.

1.5.4 Recommendations made during the pre-award laboratory evaluation.

1.6 During the term of grant, the Participant shall amend the QAP when the following circumstances occur:

1.6.1 The grant is modified.

1.6.2 There are deficiencies in the QAP document.

1.6.3 There are deficiencies resulting from the CBPO's review of their QAP document.

1.6.4 Deficiencies resulting from their internal review of their QAP document are identified.

1.6.5 The Participant's organization, personnel, facility, equipment, policy, and/or procedures change, and/or

1.6.6 The Participant identifies deficiencies resulting from the internal review of their organization, personnel, facility, equipment, policy, or procedures.

1.7 The Participant will amend the QAP within 30 days of when the circumstances listed above result in a discrepancy between what was previously described in the QAP and what is presently occurring at the facility.

Note: The date any changes occurred shall be included as part of the amendment with a reference to the old document.

2. Quality Assurance Project Plans

2.1 The Chesapeake Bay Quality Assurance Program requires the development and implementation of a Quality Assurance Project Plan (QAPjP) for each of its monitoring activities. The QAPjPs shall address specific activities to be performed and procedures to be used by the Participant.

2.2 The major goals of the QAPjPs are (1) to ensure that the level of needed data quality will be determined and stated before the data collection efforts begin, and (2) to ensure that all monitoring data generated and processed will reflect the quality and integrity established by the QAPjPs.

2.3 The QA Project Plans shall include all information covered by the sixteen points required by QAMS-005/80 (listed below).

- Title Page -- with provision for approval signatures
- Table of Contents
- Project Description
- Project Organization and Responsibilities
- QA Objectives for Measurement Data
- Sampling Procedures
- Sample Custody
- Calibration Procedures and Frequency
- Analytical Procedures
- Internal Quality Control Checks
- Performance and Systems Audits
- Preventive Maintenance
- Data Reduction, Validation, and Reporting Procedures -- including specific procedures for assessing data precision, accuracy, completeness, representativeness, and comparability.
- Data Review Procedures and Criteria
- Corrective Actions
- Quality Assurance Reports to Management

2.4 Review and Approval of QAPjPs

2.4.1 The CBPO (EPA PO and QAO) and the State agency will review all QAPjPs at least to the "Conditional Approval Recommended" level (all technical issues having been resolved to the satisfaction of the CBPO and VADEQ) prior to data collection. The QAPjPs shall be reviewed and approved in the context of the Program's DQOs.

2.4.2 The CBP QAO shall review and evaluate the implementation of the plans during the operational phase of the monitoring activity. The CBP QAO shall also assess the actual performance of the planned activity and subsequent results according to the criteria described in the QAPjPs.

3. Standard Operating Procedures

3.1 In order to obtain reliable results, adherence to recommended methodology is important. In any operation that is performed on a repetitive basis, reproducibility is best accomplished through the use of Standard Operating Procedures (SOPs). An SOP is a written document which provides directions for the step-by-step execution of an operation, test, or action which is commonly accepted as the method for performing certain routine or

repetitive tasks. These tasks include such operations as sampling, sample tracking, analysis, glassware preparation, instrument calibrations, preventive and corrective maintenance, and data reduction and analysis. SOPs should be expressed in terms of fixed protocols which must be followed. Where options exist, these should be clearly described, and criteria for the selection of alternatives must be included. The SOPs should be written such that the actual practices are recorded. SOPs should be prepared in document control format and should be submitted to the CBP QAO for reference purposes.

3.2 SOPs should be clear, comprehensive, up-to-date, and sufficiently detailed to permit duplication of results by qualified analysts. All SOPs should reflect activities as they are currently performed in the field and laboratory. In addition, all SOPs should be:

3.2.1 Adequate to establish traceability of standards, instrumentation, samples, and monitoring data.

3.2.2 Simple, so that any user with appropriate general education, experience, and training can duplicate the task as historically performed.

3.2.3 Complete enough so the user or auditor follows the directions in a logical step-wise manner through the sampling, analysis, and data handling processes.

3.2.4 Consistent with sound scientific and engineering principles.

3.2.5 Consistent with applicable federal and state regulations and guidelines.

3.2.6 Consistent with the instrument manufacturers' specific instruction manuals.

3.2.7 Consistent with the recommendations of methods consensus workshops approved by the Monitoring Subcommittee.

3.2.8 Consistent with good laboratory practices.

3.3 Benefits of SOPs

3.3.1 Provide a record of the performance of all tasks at any fixed point in time.

3.3.2 Increase the opportunity for thorough review of procedures with appropriate sign-off by management.

3.3.3 Serve as a training document for new employees providing consistent performance of tasks.

3.4 All environmental monitoring should meet established federal and state regulations and guidelines as well as comply with the program consensus decisions once confirmed by the Monitoring Subcommittee. Deviations should be justified, documented, and approved by the CBP QAO and Monitoring Coordinator. The degree of adherence to the approved SOPs should be determined during systems audits. Annually, all SOPS should be reviewed by the user, approved by his/her supervisor, and submitted for review of changes to the CBP QAO and Monitoring Coordinator.

3.5 The format for SOPs may vary depending upon the kind of activity for which they are prepared. However, at a minimum, the following sections must be included:

- Title page
- Scope and application
- Definitions
- Procedures
- QC limits
- Internal review procedures, including procedures for secondary review of information being generated
- Corrective action procedures
- Documentation description and example forms
- Miscellaneous notes and precautions
- References

3.6 A typical SOP should include detailed procedures on the following topics, as they apply:

- Specific sampling site selection
- Sampling methodology
- Analytical methodology; flow charts
- Special precautions and requirements, such as holding times and preservation; interferences
- State and Federal reference, equivalent, and alternate test procedures
- Instrumentation selection and use
- Calibration and standardization
- Preventive and remedial maintenance
- Replicate sampling and analysis
- Blind and spiked samples
- Quality control procedures such as inter- and intra-laboratory or field activities
- Split sample protocols
- Documentation, sample custody, transportation, and handling procedures
- Sample custody and handling procedures
- Sample transportation
- Data management and evaluation procedures; calculations
- Service contracts
- Specific quantitative determinations of precision, accuracy, completeness, representativeness, and comparability
- Document control
- Safety
- References

4. Document Control

4.1 The goal of the document control program is to assure that all documents and electronically stored information from a specified cruise are accountable, secure, and completely retrievable. Document control is recommended for each activity to include electronic as well as hardcopy documentation. Accountable documents should include but not be limited to field and laboratory logbooks, chain-of-custody records, sample work sheets, bench sheets, and other documents relating to the sample or sample analyses. The following document control procedures have been established to assure that all field and laboratory records are assembled and stored for delivery to the CBPO or are available upon request from the CBPO prior to the delivery schedule.

4.2. Preprinted Forms and Logbooks

4.2.1 All documents produced which are directly related to the sampling, preparation, and analysis of CBPO samples should be maintained for inspection by the CBPO. All observations and results recorded by field and laboratory staff but not on preprinted forms should be entered into permanent logbooks. When all data from a cruise are compiled, all original field and laboratory forms and copies of all cruise-related logbook entries should be included in the documentation package.

4.2.2 Pre-printed field and laboratory forms should contain the name of the field crew/laboratory and be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

4.2.3 Logbook entries should be dated (month/day/year) and signed by the person responsible for performing the activity at the time an activity is performed.

4.2.4 Logbook entries should be in chronological order.

4.2.5 Pages in both bound and unbound logbooks should be sequentially numbered.

4.2.6 Data sheets or logs should be maintained to enable a reconstruction of the sample collection or analysis in question.

4.2.7 Corrections to supporting documents and raw data should be made by drawing a single line through the error and entering the correct information. Corrections and additions to supporting documents and raw data should be dated and initialed. No information should be obliterated or rendered unreadable. All notations should be recorded in ink. Unused portions of documents shall be crossed out.

4.3 Consistency of Documentation

4.3.1 A document control officer responsible for the organization and assembly of the data package should be assigned.

4.3.2 All copies of field and laboratory documents should be complete and legible.

4.3.3 Before releasing test results, the document control officer should assemble and cross-check the information on sample tags, custody records, laboratory bench sheets, personnel and instrument logs, and other relevant data to ensure that data pertaining to each particular sample or sample delivery group is consistent throughout the data package.

4.3.4 All documents relevant to each cruise, including logbook pages, bench sheets, screening records, re-preparation records, records of failed or attempted tests, and custody records should be inventoried.

4.4 Storage of Files

4.4.1 Field and laboratory documents will be maintained in a secure location for a period of five years from the date of sample delivery.

5. Contingency and Health and Safety Plans

5.1 The Participant should develop and implement the following additional plans:

5.1.1 A contingency plan covering the availability and/or plan for a backup vessel.

5.1.2 A contingency plan for key field instrumentation failure.

5.1.3 A Health and Safety Plan in accordance with all applicable State and Federal regulations.

SECTION G

PERFORMANCE ASSESSMENT

1. Split Sample Program

1.1 Background and Objectives

The Chesapeake Bay Coordinated Split Sample Program (CSSP) was established in June 1989 by recommendation of AMQAW, to the Monitoring Subcommittee. The major objective of this program is to establish a measure of comparability between sampling and analytical operations for water quality monitoring basin-wide. A secondary objective is to evaluate the in-matrix dilution of standard EPA reference materials. These standard reference materials are analyzed in appropriate matrix, fresh to saline, and concentration level to match the sample. All laboratories participating in basin-wide data collection programs are also required to participate in the CSSP.

1.2 Summary of Criteria

1.2.1 The Participant will participate in the applicable component(s) of the CSSP.

1.2.2 The SOPs that are developed and used should be in accordance with the Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines CBP/TRS 58/91, May 1991 plus any revisions specified by the CBP QAO.

1.2.3 For each of the Virginia and Maryland CSSP stations and on a quarterly basis, the Participant will receive and analyze three sub-samples. Treating each sub-sample as a discrete sample, participating laboratories are generally required to perform only those analyses which they routinely perform in support of basin-wide data collection programs. One of the three sub-samples should be used to generate laboratory duplicates and a laboratory spike. These QC samples should be analyzed concurrently with the associated CSSP sub-samples.

1.2.4 The routine submission of split sample data is the responsibility of each laboratory and its in-house data management organization.

1.2.5 To supplement the analyses of the three sub-samples and the respective QC sample, EPA standard reference material (SRM) for each parameter should be analyzed where available. The analysis of standard reference materials provides a strong measure of comparability between all laboratories and within one laboratory's analytical system over time. Quarterly analysis of SRMs is the most independent evaluation of laboratory performance available at this time. It is a critical element of any diagnostic efforts associated with the CSSP.

2. Performance Evaluation Samples

2.1 Performance evaluation (PE) samples are distributed annually to the laboratories participating in the Mainstem Monitoring Program for Water Quality. Where available, EPA audit samples for nutrient and demand parameters, as well as solids are distributed. An effort is made to adjust PE sample preparation instructions to allow analysis in low concentration ranges more appropriate to the program's ambient monitoring levels.

3. Audits of Data Quality

3.1 Field blank and field duplicate data will be reviewed in order to assess the quality of sampling activities.

3.2 Analytical and measurement data should be reviewed in order to assess the quality of measurement and analytical activities, respectively.

3.3 The CBP-provided software will electronically verify the data quality for every submittal or the data review criteria will be implemented.

3.4 The Participant will prepare and submit a summary with each data set. The summary must include an explanation for each data point that did not meet the QC criteria established for each method, and deviations that occurred during the generation of the data.

3.5 The Participant will be informed if any of the submitted data do not fall within the prescribed QC limits. Any errors found will be corrected by the Participant at no additional cost to the CBPO.

3.6 The CBP Grant Project Officer has the ultimate responsibility to accept or reject each data submittal.

4. On-Site Audits

4.1 The CBP QAO will conduct annual on-site evaluations of field and laboratory activities. The frequency of these on-site audits may be increased depending on the Participant's performance. On-site evaluations are carried out to monitor their ability to collect and analyze samples according to the DQOs established by the CBP Monitoring Program.

4.2 The CBP QAO and a State representative will inspect the Participant's field and laboratory facilities to verify the adequacy and maintenance of instrumentation, the continuity of personnel meeting experience and/or education requirements, and the acceptable performance of analytical and QC procedures. The Participant should expect that items to be monitored will include but not be limited to the following:

- Size and appearance of the facility.
- Quantity, condition, availability, and scheduled maintenance and performance of instrumentation.
- Availability, appropriateness, and use of field and laboratory SOPs.
- Field and laboratory staff qualifications, experience, and personnel training programs.
- Reagents and sample storage facilities.
- Reagent and test solutions preparation logbooks and raw data.
- Field and laboratory bench sheet and logbook maintenance and review.
- Review of the sample analysis/data package inspection procedures.

4.3 Prior to an on-site evaluation, various documentation pertaining to performance of the specific Participant is integrated in a profile package for discussion during the evaluation. Items that may be included are previous on-site reports, laboratory evaluation sample scores, review of data, QA materials, and data trend reports.

4.4 The CBP QAO will discuss his/her findings with the Participant in the presence of a representative from the State agency. During the debriefing, the auditor will present his/her findings and recommendations for corrective actions to field and laboratory personnel.

4.5 Following an on-site evaluation, audit reports which discuss deficiencies found during the on-site evaluation will be forwarded to the Participant. The Participant must respond to the audit report within 30 days of the report and, concurrently, the report must be sent to the CBP QAO and the State representative.

4.5.1 If the Participant fails to take appropriate corrective action to resolve the deficiencies discussed in the on-site reports, any further sampling or analytical activities will not be conducted.

SECTION H

REFERENCES

U.S. Environmental Protection Agency. 1983. Chesapeake Bay: A Framework for Action, Appendix F -- A Monitoring and Research Strategy to Meet Management Objectives. Chesapeake Bay Liaison Office, Annapolis, MD.

U.S. Environmental Protection Agency. 1986. Quality Assurance Program Plan for the Chesapeake Bay Program. Region 3, Chesapeake Bay Liaison Office, Annapolis, MD.

U.S. Environmental Protection Agency. 1991. Chesapeake Bay Coordinated Split Sample Program Implementation Guidelines, Revision 3, CBP/TRS 58/91. Analytical Methods and Quality Assurance Workgroup of the Chesapeake Bay Program Monitoring Subcommittee, Chesapeake Bay Program Office, Annapolis, MD.

CHAPTER III

DATA MANAGEMENT AND DELIVERABLE REQUIREMENTS

Section A. Automation of Data Collection

1. Introduction
2. Development Phases
3. Training

Section B. Hardware Requirements for Automated Entry and Storage

1. Minimum requirements

Section C. Contract Reports and Deliverable Distribution

1. Deliverables
2. Archive of Results
3. Data Dictionary

SECTION A

AUTOMATION OF DATA COLLECTION

1. Introduction

The contractor will be provided with an automated data entry program to input for each water quality data submission and output deliverables in an acceptable format to the Chesapeake Bay Program Office (CBPO). This submission will consist of cruise data, field parameter data, and laboratory analysis data including the quality control data points. This program is currently under development by the EPA and will be available prior to contract award. The purpose of this automated data tool is to:

- o Increase the quality of the CBP monitoring data;
- o Decrease data processing;
- o Standardize data management procedures.

2. Development Phases

The automated system is being developed in three phases. Phase 1 will be available upon contract award, phase 2 and 3 may be implemented at any time during the contract period. The features of each phase are noted below.

Phase 1 will provide:

- o Manual data entry of cruise, field and lab results;
- o Manual data entry of quality control results as required by the Chesapeake Bay Program Data Management Plan (DMP);
- o Create graphical, visual, and hardcopy output of data for both field and laboratory data.
- o Perform automatic checking of field and lab results for valid entry, such that only numbers that are possible for that parameter are accepted;
- o Automatic statistical range check on vertical profile parameters compared to historical CBP monitoring data for that station/depth;
- o An error report to flag missing or out of range data points;
- o File output for submission to the CBP monitoring program in an acceptable format.

Phase 2 will provide:

o Evaluates quality control (QC) data to ensure that values are within the QC limits established by the Scope of Work (SOW);

o Entry of field parameter data electronically;

o Entry of laboratory data electronically via the EPA's ESF format from EPA Order 2180.2, the EPA DATA STANDARDS FOR THE ELECTRONIC TRANSMISSION OF LABORATORY MEASUREMENT RESULTS. The contractor will be responsible to create the data file from the instrument in ESF format.

Phase 3 will provide:

o Integration of quality control charts to the laboratory quality control data;

The contractor will enter cruise, field and laboratory data information into this automated program (see hardware requirements below). For cruise and field data, this program will accept manual keyboard input. For laboratory analysis data, this program will accept manual keyboard input. This program will provide a first level of range checking and quality control as outlined within the constraints of this Monitoring Program, this SOW and the Data Management Plan (DMP). Double key entry will be required.

It is the responsibility of the contractor to keep hardcopy records and source documents for the cruise, field and laboratory analysis data.

3. Training

The EPA will provide training at the beginning of the contract period to four contractor employees on the use of this EPA supplied software program. Updates or enhancements for the software program will be supplied at no cost and training will be provided. A Users' Manual will also be provided on the operation of the software program. Hence forth, throughout the contract period, it will be the responsibility of the contractor to train their staff members.

SECTION B

HARDWARE REQUIREMENTS FOR AUTOMATED ENTRY AND STORAGE

1. Minimum requirements

The minimum hardware requirements for the EPA's automated entry and storage program are an IBM compatible personal computer running DOS 3.3 or greater with 640K RAM, a 60 megabyte hard disk, an Intel 80286 processor , a 1.4 megabyte 3½ inch diskette drive, an EPSON FX100 or compatible printer, and a 2400 baud modem with PROCOMM.

SECTION C

CONTRACT REPORTS AND DELIVERABLE DISTRIBUTION

1. Deliverables

1.1 Each cruise

For each cruise submission, the following deliverables will be required.

On 3½ inch IBM compatible floppy diskette:

1.1.1. An ASCII format copy of the Data Submission Document File (DSDOC) as detailed in the DMP;

1.1.2. The output file(s) from the automated data entry system.

In hardcopy format:

1.1.3. The error report produced by the automated data entry system;

1.1.4. The data verification plots produced by the automated data entry system;

1.1.5. Other field and lab sheets as outlined in Chapter II, Section B.1. Reporting.

1.2 Other reports

For each reporting quarter of the contract period, a Quarterly Report must be submitted. The format and contents for this are outlined in the EPA Scope of Work for the Chesapeake Bay Program.

2. Archive of Results

The contractor will keep two electronic media backups of each cruise submission. This will include the cruise, field and laboratory data for the period of the contract. This data will be retained for five years from the date of collection and the contractor will be responsible to resolve any issues related to the data.

In addition, one hardcopy of the error reports must be retained.

3. Data Dictionary

Prior to contract award, an integrated data dictionary representing all data elements required for this monitoring program as outlined in the automated data entry system's User's Guide will be available.

CHAPTER IV

WATER QUALITY MONITORING

SECTION A

INTRODUCTION

1. Objectives and Scope

1.1 Objectives: Data generated using the procedures in this chapter will be used to meet the water quality monitoring objectives of the Chesapeake Bay Water Quality Program. These objectives are:

- To characterize the present state of the Bay and its tributaries (baseline), including spatial and seasonal variation, using key water quality indicators.
- To determine long-term trends or changes in key water quality indicators in relation to pollution control programs.
- To integrate the information collected in all components of the Monitoring Program to gain a more comprehensive understanding of water quality processes and the relationship between water quality and living resources.

1.2 Scope: The scope of work for the Water Quality Monitoring Program includes the measurement of the chemical and physical parameters for the water column. Parameters such as nutrients, chlorophyll, dissolved oxygen, and water transparency, were selected to provide information to identify nutrient trends, calibrate the water quality models for the Chesapeake Bay, and to correlate living resource data to the water quality data. Other parameters such as salinity and temperature are necessary to provide a more rigorous interpretation of these key water quality indicators. The information from these parameters with their associated detection limits will demonstrate if the water quality goals established for the living resource habitat have been met and will assist managers in instituting programs to regulate controls for point and non-point sources. A complete listing of the water quality parameters and the detection limit requirements is provided in Table IV.1.

2. Rationale

In the 1983 document entitled "Chesapeake Bay: A Framework for Action" the U.S. EPA recommended that a long-term water quality monitoring program was necessary. The purpose of this program is to provide data so that the current state of the Bay can be described and long-term changes can be detected.

SECTION B

WQ PARAMETER LIST AND DETECTION LIMITS

TABLE IV.1

Field Parameter	Detection Limit	Upper Standard
Secchi depth	0.1 meters	
pH	0.01 pH	
Dissolved oxygen	0.02 mg DO/L	
Specific Conductance	10% of scale	
Salinity	0.1 ppt	
Light attenuation	0.05% @ 100% light	
Depth	0.02 meters	
Temperature	0.1 C	
Laboratory Parameter	**Detection Limit**	
Total dissolved phosphorus	0.001 mg TDP-P/L	
Dissolved orthophosphate	0.0006 mg PO_4-P/L	
Particulate phosphorus	0.0012 mg PHOSP-P/L	
Nitrite	0.0002 mg NO_2-N/L	
Nitrate + Nitrite	0.0002 mg NO_2+NO_3-N/L	
Ammonia	0.004 mg NH_4-N/L	
Total dissolved nitrogen	0.026 mg TDN-N/L	
Particulate carbon	0.097 mg PC/L	
Particulate nitrogen	0.019 mg PN/L	

Dissolved organic carbon	0.5 mg DOC/L	
Chlorophyll A	1.0 µg Chla/L	
Phaeophytin	1.0 Pheo µg/L	
Total Suspended Solids	2 mg TSS/L	
Silicates	0.013 mg Si/L	

SECTION C

FIELD MEASUREMENTS AND SAMPLING

1. Introduction

1.1 Sampling Stations: Forty-nine stations in the Chesapeake Bay and fifty stations in the Bay tributaries shall be sampled for water quality in support of the Chesapeake Bay Monitoring Program. Station latitudes and longitudes are provided in Table IV.1.

1.2 Sampling Schedule

1.2.1 Sampling occurs 14 times a year. The Maryland Department of Natural Resources (MDNR) and Virginia Department of Environmental Quality (VDEQ) collaborate to develop an annual sampling schedule that will ensure that samples are collected by both groups within reasonably the same time period.

1.2.2 The station sampling schedule is submitted to the EPA Grant Project Officer.

1.2.3 Weather and sea conditions permitting, all field monitoring and sample collections for each mainstem cruise shall be completed during three days; and all field monitoring and sample collections for each tributary cruise shall be completed as closely as possible to the mainstem dates. Due to the large distance which must be covered in a single day of sampling, it is not practical to sample stations at a selected tidal stage. Instead, cruises shall begin on the designated date in the early morning (staging usually at 5:45 AM) and shall be completed by evening (usually 6 or 7 PM). Sampling should occur during daylight hours. In addition, all "light measurements", i.e., secchi depth and light attenuation, must only be measured during daylight hours. However, if there are unforeseen circumstances that these requirements can not be met, the deviations should be documented at the end of the cruise in the CBP Cruise Report.

1.3 Number of Samples: The number of grab samples taken and the depth at which they are taken varies. At designated stations, four samples will always be collected, surface, bottom and either above and below pycnocline if one is present or 1/3 and 2/3 the total depth or above and below the pycnocline, depending on the absence or presence of a pycnocline. At other stations two samples (surface and bottom) are collected. The presence of a pycnocline and the sampling depths are determined according to the procedures found in Chapter IV Section C 2.4 and 3.3.

TABLE IV.2
SAMPLING STATION LOCATIONS

ation Name	Latitude	Longitude	CBP Segment	River
CB5.4	37 48 00	76 10 30	CB5	CBAY
CB5.4W	37 48 48	76 17 42	CB5	CBAY
CB5.5	37 41 30	76 11 24	CB5	CBAY
EE3.4	37 54 30	75 47 30	EE3	TANG_S
EE3.5	37 47 33	75 50 37	CB7	CBAY
LE3.6	37 35 48	76 17 06	CB6	CBAY
LE3.7	37 31 50	76 18 25	LE3	RAPPA
CB6.1	37 35 18	76 09 45	CB6	CBAY
CB6.2	37 29 12	76 09 24	CB6	CBAY
CB6.3	37 24 41	76 09 36	CB6	CBAY
CB7.1N	37 46 30	75 58 30	CB7	CBAY
CB7.1	37 41 00	75 59 24	CB7	CBAY
CB7.1S	37 34 52	76 03 30	CB7	CBAY
CB7.2	37 24 41	76 04 48	CB7	CBAY
CB7.2E	37 24 41	76 01 30	CB7	CBAY
WE4.1	37 18 42	76 20 48	WE4	MOBJAC
WE4.2	37 14 30	76 23 12	WE4	MOBJAC
WE4.3	37 10 36	76 22 24	WE4	MOBJAC
WE4.4	37 06 36	76 17 36	WE4	MOBJAC
LE5.5	36 59 48	76 18 12	CB8	CBAY

CB8.1	36 59 15	76 10 05	CB8	CBAY
CB8.1E	36 56 42	76 01 30	CB8	CBAY

TABLE IV.2 (Continued)
SAMPLING STATION LOCATIONS

Station Name	Latitude	Longitude	CBP Segment	River
CB7.4N	37 03 29	75 58 23	CB7	CBAY
CB7.3	37 07 00	76 07 32	CB7	CBAY
CB7.3E	37 13 43	76 03 15	CB7	CBAY
CB6.4	37 14 11	76 12 30	CB6	CBAY
ELI2	36 52 56	76 20 21	LE5	ELIZABETH
WBE1	36 50 35	76 21 35	LE5	ELIZABETH
SBE2	36 48 45	76 18 22	LE5	ELIZABETH
SBE5	36 46 11	76 17 47	LE5	ELIZABETH
EBE1	36 50 26	76 17 22	LE5	ELIZABETH

TABLE IV.3
CRUISE SCHEDULE FOR 1996

Month	Cruise Number	Maryland Mainstem	Virginia Mainstem
January	231	Special	16-19
February	232	Special	12-15
[illegible]	233	11-13	11-14
April	235	8-10	8-11
April	236	22-24	No Cruise
May	237	13-15	13-16
May	238	28-30	No Cruise
June	239	10-12	10-13
July	241	8-10	8-11
July	242	22-24	22-25
August	243	5-7	5-8
August	244	26-28	26-29
September	245	9-11	9-12
October	247	7-9	7-10
November	249	18-20	18-21
December	250	9-11	9-12

2. Field Measurements

2.1 At each station, the latitude and longitude (accurate within ± 15 seconds) in degrees, minutes and seconds should be recorded at the beginning of sampling. To obtain accurate location data, Global Positioning Systems (GPS) is recommended for use. The CBP segment location and total depth should also be recorded.

2.2 The weather and sea conditions at the time of sampling should also be recorded. General weather conditions include cloud cover, air temperature, precipitation type, wind speed, and wind direction. Sea conditions that should be recorded include wave height and tidal current stage.

2.3 Secchi depth

2.3.1 Equipment: A 20 cm Secchi disk, a circular plate-like disk painted in alternating black and white quadrants is held by a line that is marked in tenths of meters.

2.3.2 Frequency: The Secchi depth is determined at each station.

2.3.3 Procedure: The Secchi disk is used to give a measurement of transparency of the water column, also called the Secchi depth.

2.3.3.1 Slowly lower the Secchi disk until it is no longer visible and note the depth using the markings on the line.

2.3.3.2 Slowly raise the Secchi disk until it just becomes visible and note the depth using the markings on the line.

2.3.3.3 Perform steps 2.3.3.1 and 2.3.3.2 three times, noting both readings. Record average.

2.3.4 Quality control

2.3.4.1 If the range of measurements for the three sets of readings in section 2.3.3 is greater than 0.5 m, the entire process should be performed again. Raise and lower several times around "disappearing" point.

2.3.4.2 No sunglasses or any other devices should be used to shade the eyes while this procedure is being performed.

2.3.4.3 The Secchi depth should be determined from the shady side of the boat during daylight hours.

2.4 Physiochemical Profile

2.4.1 Equipment

2.4.1.1 A multi-parameter water quality instrument, such as a Sea-bird Sealogger CTD, or any combination of equipment that can provide the same measurements, shall be used.

2.4.1.2 The instrument shall be equipped with the following sensors:

- pressure sensor - used to determine sampling depth,
- a bottom sensor - sounds an alarm on deck when the unit is approaching the bottom,
- Ph meter,
- dissolved oxygen probe, and
- light attenuation sensor - LI-COR LI-192SA underwater sensor, or equivalent
- temperature sensor
- conductivity cell

2.4.1.3 The instrument should be outfitted with a system so that field measurements can be logged from the instrument by computer, with a manual recording backup capability in case of computer failure for as many parameters as possible.

2.4.2 Frequency: The physiochemical profile is determined at every sampling station. The surface reading is taken at 0.5m (MD) and 0.1m (VA) below the surface. Readings are then recorded for 1m, 2m, and 3m below the surface. Finally, readings every 2m to 1m above the bottom. For stations less than 10m readings should be made every meter.

2.4.3 Procedure: The following parameters should be measured at the frequency described in 2.4.2: water temperature, Ph, dissolved oxygen, salinity, light attenuation, depth of measurements, surface radiation, and total depth. The sampling boat should be oriented so that the light sensor is not in the shadow of the boat during data collection. All apparatus should be operated according to manufacturer's instructions.

2.4.4 Quality control

2.4.4.1 Calibration: All probes must be calibrated by manufacturers recommended methods..

2.4.4.1.1 Conductivity sensor: The conductivity sensor must be calibrated against a reference solution, according to manufacturer's specifications. As a minimum conductivity should be verified before and after each cruise.

2.4.4.1.2 Ph meter: As a minimum the pH sensor must be calibrated at the beginning and end of every cruise against two buffer solutions, pH 7 and 10. The pH probe must be rinsed with deionized water and may need to be soaked in pH 7 buffer when not in use. If the probe drifts ± 0.2 pH units, the sensor must be recalibrated using the pH 7 and 10 buffers.

2.4.4.1.3 Dissolved oxygen meter: The dissolved oxygen meter should be verified

using air-saturated water at the beginning of each day. Periodic verification checks should be performed using Winkler titrations. If titrations differ by ± 0.5 mg/l from probes readings the validity of the readings should be verified.

2.4.4.1.4 Thermometer: Calibrate the thermometer once a year against a NIST certified thermometer over a range of temperatures.

2.4.4.1.5 Pressure sensor: Calibrate the depth sensor once a year according to the manufacturer's instructions.

2.4.4.2 The Contractor must maintain logbooks with calibration, replicate, and maintenance information for each instrument and/or probe.

2.4.5 Pycnocline determination: The pycnocline is a region in which the water density changes appreciably with increasing depth and thus forms a layer of much greater stability than is provided by overlying surface waters. The pycnocline calculated threshold value (CTV) is calculated using Equation IV.1. If the CTV is less than 500 microohms/cm, then there is no discernible pycnocline. If the CTV is above 500 microohms/cm, a pycnocline exists with boundaries at the first and last depths where the change in conductivity is greater than the CTV.

$$CTV = \frac{C_b - C_s}{D_b - Ds} \times 2 \qquad \text{(Eq. IV.1)}$$

Where

C_b = bottom conductivity (microohms/cm),
C_s = surface conductivity (microohms/cm),
D_b = depth of bottom conductivity measurement (m),
D_s = depth of surface conductivity measurement (m),
CTV = calculated threshold value (microohms/cm)

3. Sampling

3.1 Equipment

3.1.1 Collection bottles: Two-Four bottles per sampling station.

3.1.2 Hydrocast sampling system: General Oceanics Model 1016 Rosette sampling system, or equivalent.

3.1.3 Laboratory sample bottles

NOTE: Always ensure sample bottles are in a clean state or have been thoroughly cleaned

before reuse. Where ever possible, do not use sample bottles from high concentration samples for low level events.

3.1.4 Filtration apparatus.

3.1.5 Filters:

Specific filter types and diameters are cited, however, alternate diameters can be used. See specific comments throughout the analytical methodology about concerns related to alternate sizes.

3.1.5.1 Whatman GF/F 25 mm diameter, 0.70 µm pores.

3.1.5.2 Whatman GF/F 47 mm diameter, 0.70 µm pores. Pre-wash, dry at 103-105°C, and weigh until a constant weight ±.05 mg is reached. Store in a desiccator while cooling and until weighed.

3.1.5.3 Whatman GF/F 47 mm diameter, 0.70 um pores. Untreated for chlorophyll analysis.

3.1.6 Cooler and freezer.

3.2 Reagents

3.2.1 Magnesium carbonate suspension: Add 1 g of finely powdered $MgCO_3$ to 100 mL water.

3.2.2 Sulfuric acid, H_2SO_4 (6N) // Hydrochloric acid, HCl (6N).

3.2.3 Reagent water, all water referred to in this document, unless otherwise specified, is ASTM Type II water, or equivalent.

3.3 Sample Collection

3.3.1 The cruise vessel should ensure location by LORAN and anchor while taking samples. At those stations where anchoring is not practical, the LORAN shall be used to hold station. The LORAN coordinates must be recorded at the beginning of the sampling time. It must be recorded whether the boat anchored or the station was held using the LORAN.

3.3.2 At stations where pycnocline sampling is designated, if a pycnocline is detected, samples are collected 0.5m (MD) and 1.0 (VA) m below the surface, 1.0 m above the upper boundary of the pycnocline, 1.0 m below the lower boundary of the pycnocline, and 1.0 m above the bottom to nearest 0.5 m. See Chapter IV Section C 2.4.5 for pycnocline calculations and definitions.

3.3.3 If there is no discernable pycnocline at designated stations collections will be made at 0.5 m (MD) and 1.0 (VA) m below the surface, at the closest profile depth above one third of the distance between the surface depth, 1.0 m, and the bottom sample depth, at closest profile depth below two thirds the distance between 1.0 m and the bottom sample depth, and 1.0 m above the bottom to the nearest 0.5 m.

3.3.4 At all other stations, samples are only collected at the 1m below the surface and 1m above the bottom.

3.3.5 Lower the collection system to each sampling depth and fill one bottle per depth. Process the sample

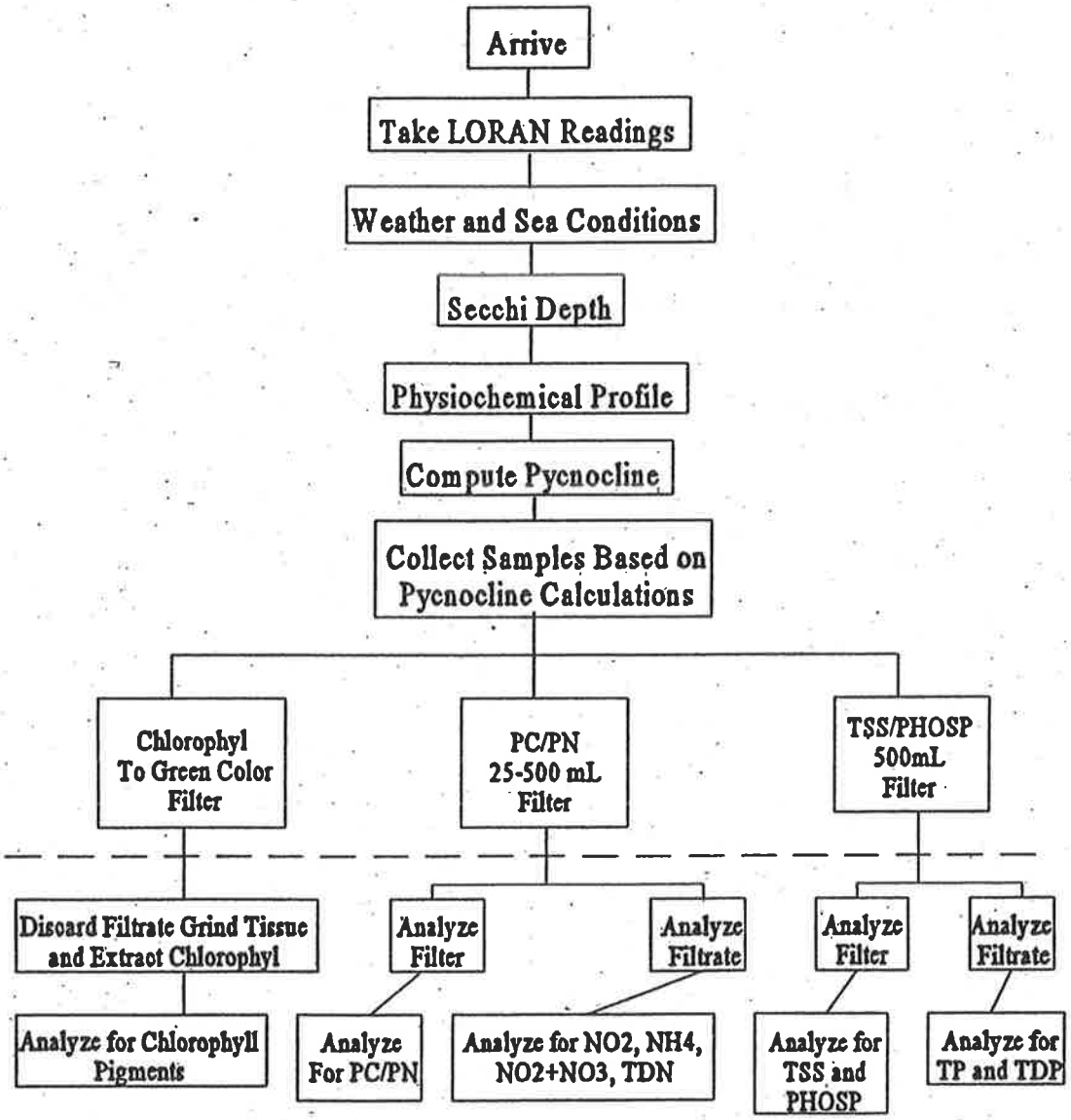
according to 3.4.

3.4 Sample Processing

3.4.1 Sample processing and division for all samples should follow Figure IV.2.

3.4.2 Chlorophyll and phaeophytin: Process sufficient sample (i.e. 100-1500 mL) to produce a green color on the filter pad. For smaller diameter filters (i.e., 13 mm), do not exceed the capacity of the filters with large volumes of sample (i.e., greater than 50ml).

FIGURE IV.2
SAMPLING AND PROCESSING



3.4.2.1 Immediately concentrate the algae by filtering a known volume of sample water (measured with a graduated cylinder) onto a glass fiber filter (Whatman GF/F or equivalent). To avoid cell damage and loss of contents during filtration, do not exceed a vacuum of ½ atm (50 kPa or 15 psi), or a filtration duration greater than 5 minutes. Add 1ml of saturated MgCO3 solution 10mg/l during last few seconds of filtering

3.4.2.2 Samples that cannot be concentrated immediately after collection may be held at 0 to 4°C in the dark for 4 hours before the plankton are concentrated, however any delay is strongly discouraged due to the possible lysis of phytoplankton cells. The residue on the filter may be stored in the dark at -20 ± 2°C for 28 days before extracting the pigments.

3.4.3 Particulate carbon and particulate nitrogen: 25-500 mL of sample is filtered under vacuum through each of two 13 mm GF/F filters. The filters are stored in Petri dishes or foil pouches at -20 ± 2°C. Do not rinse the filters. Do not exceed 15 psi while filtering.

3.4.4 Ammonia, nitrite, nitrite+nitrate, orthophosphate, total dissolved nitrogen, total dissolved nitrogen, dissolved organic carbon, and silicates: The filtrate is stored at -20°±2°C for laboratory analysis, except for silicates, which is stored at 4°±2°C. The DOC samples should have acid preservation (HCl or H_2SO_4) or be frozen.

3.4.5 Total suspended solids and particulate phosphorus: 50-1000 mL of sample is filtered under vacuum through two prepared 47 mm GF/F filters. The filters are stored in Petri dishes or foil pouches at -20 ± 2°C. If separate filters are obtained for each analyses, then the total suspended solids filter can be stored at 4°±2°C. These filters should be rinsed three times with at least 10 ml DI water. If filtrate is saved must save before rinse.

3.4.6 Dissolved orthophosphate and total dissolved phosphorus: The filtrate used to prepare filters for particulate phosphorus and total suspended solids is stored at -20 ± 2°C for laboratory analysis.

3.5 Quality control

3.5.1 Field blanks: A field blank is an equivalent aliquot of reagent water that is processed as a sample. The field blank should be processed at the beginning of every sampling day. If the concentration of any analytes exceeds the MDL, equipment contamination should be suspected.

3.5.2 Field duplicates: A field duplicate is a sample taken at the same sample location and depth as a CBP sample. The duplicate and sample should be taken in quick succession of each other. A field duplicate should be collected once for every 10 CBP samples. The data from field duplicates indicates sampling precision.

CHAPTER IV

WATER QUALITY MONITORING

Section D. Laboratory Analysis

1. General Laboratory QA/QC
2. Total Dissolved Phosphorus
3. Dissolved Orthophosphate
4. Particulate Phosphorus
5. Nitrite
6. Nitrate + Nitrite
7. Ammonia
8. Total Dissolved Nitrogen/Particulate Nitrogen
9. Particulate Carbon
10. Dissolved Organic Carbon
11. Biological Oxygen Demand, 5-day
12. Chlorophyll and Phaeophytin
13. Total Suspended Solids
14. Fixed Suspended Solids
15. Silicates
16. Alkalinity

SECTION D
LABORATORY ANALYSIS

1. General Laboratory QA/QC

1.1 Sample storage and holding times

1.1.1 The following holding times should not be exceeded and the temperatures given should be maintained.

TABLE IV.4
WQ LABORATORY PARAMETER HOLDING TIMES AND TEMPERATURES

Parameter	Holding Time (days)	Temperature (°C)
Total dissolved phosphorus	28	-20
Dissolved orthophosphate	28	-20
Particulate phosphorus	28	-20
Nitrite	28	-20
Nitrate + nitrite	28	-20
Ammonia	28	-20
Total dissolved nitrogen	28	-20
Particulate nitrogen	28	-20
Particulate carbon	28	-20
Dissolved organic carbon	28	-20 or acidify
Chlorophyll and phaeophytin	30	-20
Total suspended solids	7	4
Silicates	28	4

1.1.2 Time allowed for field processing

1.1.3 If samples are analyzed within 24 hrs, then samples may be refrigerated (4° C) rather than frozen.

1.1.4 The samples should be stored in an atmosphere free of all potential contaminants.

1.1.5 Samples and standards should be stored separately.

1.2 Method Blank

1.2.1 A method blank is a volume of ASTM Type II reagent grade water that is carried through the entire analytical procedure. The purpose of a method blank is to determine the levels of contamination associated with the processing and analysis of samples.

1.2.2 A method blank should be analyzed once for every 10-20 CBP samples, including duplicates.

1.2.3 If the concentration of analyte exceeds the MDL, laboratory or reagent contamination should be suspected. If the analyte concentration is 5 times the MDL or greater, then corrective action is required and reanalysis if possible.

1.3 Matrix Spike (not required for chlorophyll, PN, PHOSP, TSS, PC)

1.3.1 In order to evaluate the effects of the sample matrix on the analytical methods, a known quantity of analyte is spiked in an aliquot of sample. The analyte concentration should be high enough to be seen over the original concentration of the sample and should not be less than four times the calculated MDL.

1.3.2 A matrix spike should be analyzed once for every 10-20 CBP samples.

1.3.3 Matrix spikes should not be performed on laboratory or field blanks.

1.3.4 The percent recovery of analyte from the matrix spike sample is calculated using the following equation:

$$Matrix\ Spike\ Recovery = \frac{SSR - SR}{SA} \times 100 \qquad \text{(Eq. IV.2)}$$

where,

SSR = Spike sample result
SR = Sample result
SA = Spike added

1.3.5 If the recovery of the analyte falls outside the range designated in Table II.1, repeat the spike after checking for obvious sources of error. If the recovery of the replicated spike of the same sample again falls outside the designated range, the recovery problem encountered with the spiked sample is judged to be matrix related, not system related and no further corrective action is required.

1.4 Laboratory Replicates

1.4.1 Laboratory replicate analyses provide a measure of laboratory precision. Duplicates are prepared by taking two aliquots for analysis from a well homogenized sample. More replicates may be analyzed and reported.

1.4.2 A laboratory duplicate should be analyzed once for every 10-20 CBP samples.

1.4.3 The precision may be measured by calculating the coefficient of variation (CV) using the following equation:

$$CV = \frac{SD}{MEAN} \times 100, \text{ where } SD = \sqrt{\frac{\sum (X-\overline{X})^2}{(N-1)}} \qquad \text{(Eq. IV.3)}$$

where,

CV = Coefficient of variation
SD = Standard deviation
Mean = Mean of the replicate readings
N = Number of samples

1.4.4 The precision may be measured by calculating Relative Percent Difference (RPD). The following equation is used to calculate RPD:

$$RPD = [|A1 - A2| \div ((A1 + A2) \div 2)] \cdot 100$$

1.5 Check Standard- An a accurately prepared chemical standard that is analyzed after every 10-20 CBP samples. The results are compared to the known analyte concentration. If the determined concentration for known analysis is not within 90-110% of the known analyte concentration, a second check standard is prepared and analyzed to confirm or deny the initial "out of control" analysis. If the reanalyzed check standard is within acceptance limits, sample analysis proceeds; however, if the reanalyzed check standard fails the acceptable limits, the instrument must be recalibrated. All the samples between that check standard and the previous standard must be reanalyzed.

1.6 Reference Materials

1.6.1 Standard reference materials shall be analyzed at the frequency defined within each method.

1.7 See synthetic sea water: Strickland and Parsons

1.7.1 Using analytical reagent grade reagents, dissolve 31g of Sodium Chloride NaCl (CAS No. 7647-14-

5), 10g of magnesium sulfate, Mg SO4 7H20 (CAS No. 10034-99-8) and 0.05g sodium bicarbonate (NaHCO3H2O) (CAS No. 144-55-8) in 1 liter of reagent water.

1.8 Glassware Cleaning

1.8.1 Standard and Reagent Glassware should be rinsed with 10% HCl once and then rinsed 3 times with reagent grade water.

1.8.2 Sample Containers should be rinsed with tap water, 10% HCl and then rinsed 4 times with reagent water. Then, before use they should be rinsed 3 times with sample.

1.8.3 AutoAnalyzer Cups should be rinsed two-three times with the sample, and then filled.

1.9 Reagent grade water: ASTM Type II reagent grade water, or equivalent, should be used in the preparation of reagents and standards. Reverse osmosis systems or distilling units which produce 18 megohm water are two examples of acceptable water sources.

2. Total Dissolved Phosphorus

2.1 Scope and Application

2.1.1 This method provides the procedure for the determination of low level total dissolved phosphorus concentrations normally found in estuarine and /or coastal waters by the automated persulfate oxidation technique in the range of 0.001 to 2.0 mg/L of P.

2.2 Summary of Method

2.2.1 This method involves the digestion of the sample with an oxidizing agent (alkaline persulfate) in an autoclave, which converts all the phosphorus compounds to orthophosphate. This is followed by analysis for orthophosphate by an automated colorimetric method.

2.2.2 The color in the samples is measured in the following manner. Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

2.3 Interferences

2.3.1 Silicon at a level of 100 µg/L causes an interference equivalent to approximately 0.04 µg/L of P/L. This can be avoided by maintaining an acid concentration of 2.45N H_2SO_4 in the reagents and analysis at 37 ± 2°C.

2.4 Apparatus and Materials

2.4.1 Continuous flow automated analytical system equipped with an autosampler, manifold, proportioning pump, colorimeter, phototube, recorder or computer based data system, and heating bath.

2.4.2 Appropriate glassware.

NOTE: Clean all culture tubes by adding 10ml persulfate digestion reagent and heating at 100° C 1 hr, and rinse 3 times with reagent water.

2.4.3 Autoanalyzer cups. see section 1.8.3 Do not reuse cups.

2.4.4 An autoclave that can maintain a temperature of 100 - 110°C.

2.4.5 Culture tubes, 30 mL capacity.

2.5 Reagents

Stock Reagent Solutions

2.5.1 Reagent Grade Water: see section 1.9

2.5.2 Artificial Sea Water: See synthetic seawater 1.7

2.5.3 Borate Buffer Solution: To a two-liter volumetric flask, add approximately 800 mL of reagent water. Add 123.6 g of boric acid (H_3BO_3) and 16.1g low N sodium hydroxide (NaOH) and dilute to 2.0 L with reagent water. Store at room temperature. Stable for two months.

2.5.4 Oxidizing Reagent: To a one-liter volumetric flask, add 400 mL of reagent water. Add 3.0 g of low N NaOH and 20.0 g of low N (0.001%) potassium persulfate ($K_2S_2O_8$), dissolve, and dilute to one liter with reagent water. Store in a glass reagent bottle. This solution is only stable for two hours at room temperature. Make fresh daily.

2.5.5 Sulfuric Acid Solution, 5N: In a 500-mL volumetric flask, add 300 mL of reagent water. Add 70 mL of concentrated sulfuric acid (H_2SO_4). Cool to room temperature and dilute to 500 mL with reagent water.

2.5.6 Potassium Antimony Tartrate Solution: In a 500-mL volumetric flask, add 300 mL of reagent water. Add 0.3 g of $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, dissolve, and dilute to volume with reagent water. Store in a glass-stoppered bottle at room temperature.

2.5.7 Ammonium Molybdate Solution: In a 500-mL volumetric flask, add 400 mL of reagent water. Add 4 g of ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, dissolve, and dilute to volume with reagent water. Store in a plastic bottle at 4 ± 2°C.

2.5.8 Ascorbic Acid: In a 100-mL volumetric flask, add 50 mL of reagent water. Add 1.8 g of ascorbic acid, dissolve, and dilute to 100 mL with reagent water. This solution is stable for about one week at 4 ± 2°C.

2.5.9 Combined Reagent: In a 100-mL volumetric flask, add 50 mL of 5N H_2SO_4, 5 mL of potassium antimony tartrate solution, 15 mL of ammonium molybdate, and 30 mL of ascorbic acid. All reagents should reach room temperature before they are mixed. Add the reagents in the order given and mix the resultant solution after each addition. The combined reagent is stable for 4 hours.

Working Solutions

2.5.10 Stock Glycerophosphate Standard: In a 500-mL volumetric flask, add 400 mL of reagent grade water. Add 0.473 g of B-glycerophosphoric acid-disodium salt-5-hydrate, dissolve, and dilute to volume with reagent water. Add 0.5 mL of chloroform (under a hood) as a preservative. This solution is only stable for ten months at 4 ± 2°C.

2.5.10.1 Working Glycerophosphoric Standard: In a 100-mL volumetric flask, add 50 mL of substitute ocean water . Add 1.0 mL of stock glycerophosphate standard solution, mix, and dilute to volume with substitute ocean water. This solution should be prepared on the day of analysis. (1.0 mL = 0.957 µg P)

2.5.11 Stock Phosphate Standard Solution: In a one-liter volumetric flask, add 500 mL of reagent water. Add 439.3 mg of anhydrous potassium dihydrogen phosphate (KH_2PO_4) that has been dried overnight at 105 ± 2°C (stored in a desiccator), dissolve, and dilute to volume with reagent water.

This solution is stable for six months at 4 ± 2°C. (1.0 mL = 100.0 µg P)

2.5.11.1 Working Standards

2.6 Sample Handling

2.6.1 Samples are filtered through a Whatman GF/F glass fiber filter or equivaleant filter and can be stored at -20 ± 2°C unacidified for a maximum of 28 days. They should not be preserved with sulfuric acid. Do not freeze after digestion; a precipitate will form.

2.7 Procedure

2.7.1 Sample preparation:

2.7.1.1 Pipet 10 mL of filtered sample into a 30 mL screw cap test tubes. Include 5-10% duplicates and 5-10% spikes (spike with 0.30ml working standard).

2.7.1.2 Pipet 10.0 ml of working standards into 30 ml screw cap test tubes. Include two oxidizing reagent blanks which contain only the oxidizing reagent.

2.7.1.3 Pipet 5.0 mL of the oxidizing reagent in each tube. Cap test tubes tightly and very quickly due to volatilization.

NOTE: A precipitate ($Mg(OH)_2$) will form with seawater samples which will not form with saline standards prepared with NaCl. If standards are made with Substitute Ocean Water the precipitate will form.

2.7.1.4 Autoclave tubes at a temperature between 100 - 110°C (follow Autoclave instructions).

2.7.1.5 Remove tubes from the heating apparatus and cool to room temperature. Check volumes for possible fluid loss and indicate any losses on bench sheet. Samples can be refrigerated for several days at this point if necessary to delay analysis.

2.7.2 Add 1.0 mL of borate buffer solution to each tube and cap. Shake very well. The pH of the sample should be around 2. Samples can now be analyzed for orthophosphate.

2.7.3 Allow both the colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding reagent water through the sample line.

2.7.4 Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions and digesting them along with the samples. Digest matrix spike and blanks along with the samples.

2.7.5 Analytical sequence: The samples and associated QC samples and standards should be analayzed according to the following sequence.

2.7.5.1 Five calibration standards with concentration within the linear range of the test.

2.7.5.2 Two method blanks.

2.7.5.3 Ten-twenty CBP samples.

2.7.5.4 One matrix spike sample.

2.7.5.5 One medium concentration calibration standard.

2.7.5.6 One method blank.

2.7.5.7 Steps 2.7.5.1 - 2.7.5.6 are repeated until all samples are analyzed or QC samples indicate that the system is out of control and recalibration is necessary.

2.7.5.8 One high concentration calibration standard.

2.7.5.9 One medium concentration calibration standard.

2.7.5.10 One low concentration calibration standard.

2.7.6 Switch sample line from distilled water to sampler and begin analysis.

2.7.7 Prepare appropriate standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of the samples by comparing sample peak heights with standard curve.

NOTE: Subtract the blank background response from the standards before preparing the standard curve.

2.7.8 Record the stabilized potential of each unknown sample and convert the potential to the TDP concentration using the standard curve.

2.8 Quality Control

2.8.1 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section D.

2.8.2 Calibration

2.8.2.1 Linear calibration range: Calibration standards should bracket the range of CBP samples.

2.8.2.2 Correlation coefficient: The correlation coefficient must be 0.995 or better for the calibration curve to be used.

2.8.3 Method blank: see Chapter II, Section C.

2.8.4 Matrix spike sample: see Chapter II, Section C.

2.8.5 Laboratory duplicate: see Chapter II, Section C.

2.8.6 Reference materials: The laboratory must analyze a standard reference material once a year, as available.

2.9 References

Standard Methods for the Examination of Water and Wastewater, 17th Edition, p 1193.

Annual Book of ASTM Standards, Part 31, "Water", Standard D 515-72, p 389 (1976).

3. Dissolved Orthophosphate

3.1 Scope and Application

3.1.1 This method provides a procedure for the determination of low level orthophosphate concentrations normally found in estuarine and/or coastal waters. It is an automation of the method of Murphy and Riley (1962).

3.1.2 A method detection limit (MDL) of 0.0006 mg P/L has been statistically determined by one laboratory. This MDL is defined as three times the standard deviation of at least seven replicates of a low level estuarine (~15 parts per thousand salinity) sample. The method is linear to 0.050 mg P/L at a standard calibration setting of 9.0 on an AutoAnalyzer II system. Where higher concentrations are encountered, the method is also linear at lower standard calibration settings.

3.1.3 This method should be used by analysts experienced in the use of automated colorimetric analyses and matrix interferences and procedures for their correction. A minimum of six months experience under supervision is recommended.

3.2 Summary of Method

3.2.1 This is an automated colorimetric method for the analysis of low level orthophosphate estuarine samples. Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color produced is proportional to the phosphate concentration present in the sample. A calibration curve is established with standards of known concentrations and the unknown samples are measured against the calibration curve.

3.3 Interferences

3.3.1 It is reported that the interference caused by copper, arsenate and/or silicate is minimal to the orthophosphate determination because of their extremely low concentrations normally found in estuarine or coastal waters. High iron concentrations can cause precipitation of and subsequent loss of phosphorus from the dissolved phase. Hydrogen sulfide effects (samples collected from deep anoxic basins) can be treated by simple dilution of the sample, since high sulfide concentrations are most often associated with high phosphate values (Grasshoff, et al., 1983).

3.3.2 Mercuric chloride, if used as a preservative, interferes (EPA,1977).

3.3.3 Sample turbidity should be removed by filtration prior to analysis.

3.3.4 Refractive Index interferences should be corrected for estuarine/coastal samples.

3.4 Apparatus and Materials

3.4.1 Continuous flow automated analytical system equipped with an autosampler, manifold, proportioning pump, colorimeter, phototube, recorder or computer based data system, and heating

bath.

3.4.2 Phosphate-free glassware: all glassware used in the determination must be low in residual phosphate to avoid sample/reagent contamination. Washing with 10% HCl and thoroughly rinsing with distilled/deionized water have been found to be effective.

3.5 Reagents

3.5.1 Reagent Grade Water: see section 1.9.

3.5.2 Substitute Ocean Water: see section 1.7

3.5.3 Stock Reagent Solutions

3.5.3.1 Ammonium Molybdate Solution (40 g/L): Dissolve 20.0 g of ammonium molybdate tetrahydrate [$(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, CAS RN 12027-67-7] in approximately 400 mL of reagent water and dilute to 500 mL. Store in a plastic bottle out of direct sunlight. This reagent is stable for approximately three months.

3.5.3.2 Antimony Potassium Tartrate Solution (3.0 g/L): Dissolve 0.3 g of antimony potassium tartrate [$(K(SbO)C_4H_4O_6\cdot \frac{1}{2}H_2O$, CAS RN 11071-15-1] in approximately 90 mL of reagent water and dilute to 100 mL. This reagent is stable for approximately three months.

3.5.3.3 Ascorbic Acid Solution (18.0 g/L): Dissolve 18.0 g of ascorbic acid ($C_6H_8O_6$, CAS RN 50-81-7) in approximately 800 mL of reagent water and dilute to one liter. Dispense approximately 75 mL into clean poly bottles and freeze. The stability of the frozen ascorbic acid is approximately three months. Thaw overnight in the refrigerator before use. The stability of the thawed, refrigerated reagent is 10 days.

3.5.3.4 Wetting Agent - use Skalar FFD6.

3.5.3.5 Sulfuric Acid Solution (5.0 N): Add 140 mL concentrated sulfuric acid (H_2SO_4, CAS RN 7664-93-9) to approximately 800 mL reagent water while cooling. After the solution is cooled, dilute to 1000 mL with reagent water.

3.5.3.6 Stock Phosphorus Solution: Dissolve 0.439 g of pre-dried (105± 2°C for 1 hour) potassium phosphate, monobasic (KH_2PO_4, CAS RN 7778-77-0) in reagent water and dilute to 1000 mL (1.0 mL = 0.100 mg P). The stability of this stock standard is approximately three months, if kept refrigerated.

3.5.4 Working Reagents

3.5.4.1 Reagent A: Mix the following reagents in these proportions for 277 mL of Reagent A: 125mL of sulfuric acid, 37.5 mL of PAT, 37.5 mL of Molybdate, 75ml of Ascorbic, and 2mL of FFD6. Prepare daily.

3.5.4.2 Reagent B: Add approximately 2.0 mL of the FFD6 solution to the 1000 mL of DDI. Volumetric accuracy not required. Stability is approximately 10 days if kept refrigerated.

3.5.4.3 Refractive Reagent A: Add 50 mL of 4.9 N H_2SO_4 to 20 mL of reagent water. Add 1 mL of SLS. Prepare every few days.

3.5.4.4 Secondary Phosphorus Solution: Take 1.0 mL of stock phosphorus standard and dilute to 100 mL with reagent water (1.0 mL = 0.0010 mg P). Refrigerate and keep no longer than 10 days.

3.5.4.5 Prepare a series of standards by diluting suitable volumes of standard solutions to 100 mL with reagent water. Prepare these standards daily. When working with samples of known salinity it is recommended that the standard curve concentrations be prepared in substitute ocean water . When analyzing samples of varying salinites, it is recommended that the standard curve be prepared in deionized water and refractive index corrections be made to the sample concentrations.

3.6 Sample Handling

3.6.1 Samples are stored at -20 ± 2°C for a maximum 28 days.

3.7 Procedure

3.7.1 If samples have not been freshly collected and are frozen, thaw the samples to room temperature.

3.7.2 Set up the manifold as instructed by the instrument manufacturer.

3.7.3 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a steady baseline with deionized water pumping through the system, add reagents to the sample stream and after the reagent baseline is steady, reset the "zero" if necessary.

3.7.4 A good sampling rate is approximately 30 samples/hr. with a 60:60:0 sample:wash ratio.

3.7.5 Analytical sequence: The samples and associated QC samples and standards should be run according to the following sequence.

3.7.5.1 Five calibration standards with concentration within the linear range of the test.

3.7.5.2 Two method blanks.

3.7.5.3 Ten - twenty CBP samples.

3.7.5.4 One matrix spike sample.

3.7.5.5 One medium concentration calibration standard.

3.7.5.6 One method blank.

3.7.5.7 Steps 3.7.5.3 - 3.7.5.6 are repeated until all samples are analyzed or QC samples indicate that the system is out of control and recalibration is necessary.

3.7.5.8 One high concentration calibration standard.

3.7.5.9 One medium concentration calibration standard.

3.7.5.10 One low concentration calibration standard.

3.7.6 Calculations

3.7.6.1 Orthophosphate concentrations are calculated from the linear regression obtained from the standard curve in which the concentrations of the standards are employed as the independent variables and their corresponding peak heights are the dependent variables. Need a correction for PO_4 in reagent water. This is done by matching the matrix with the refractive reagent.

3.7.6.2 Refractive Index Correction For Estuarine/Coastal Systems

3.7.6.2.1 Obtain a second set of peak heights for all samples and standards with Refractive Reagent A being pumped through the system in place of Reagent A. Reagent B remains the same and is also pumped through the system. Peak heights for the refractive index correction must be obtained at the same Standard Calibration Setting and on the same colorimeter as the corresponding samples and standards (Froelich and Pilson, 1978). Subtract these peak heights from the corresponding peak heights obtained reagent A.

3.8 Quality Control

3.8.1 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section D.

3.8.2 Calibration

3.8.2.1 Linear calibration range: Calibration standards should bracket the range of CBP samples.

3.8.2.2 Correlation coefficient: The correlation coefficient must be 0.995 or better for the calibration curve to be used.

3.8.3 Method blank: see Chapter II, Section C.

3.8.4 Matrix spike sample: see Chapter II, Section C.

3.8.5 Laboratory duplicate: see Chapter II, Section C.

3.8.6 Reference materials: The laboratory must analyze a standard reference material once a year, as available.

3.9 References

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40 CFR, [part] 136 Appendix B. Definition and Procedure for the Determination of the Method Detection Limit. Revision 1.11.

4. Particulate Phosphorus

4.1 Scope and Application

4.1.1 This method is applicable for the determination of particulate phosphorus in water, wastewater, saline, surface, and ground waters by a semi-automated high temperature combustion, HCL extraction technique in the range of 0.01 to 2.0 mg/L of P (Aspila, et al , 1976).

Note: Final matrix of analysis = 0.2 NHCl

4.2 Summary of Method

4.2.1 Ammonium molybdate and antimony potassium tartrate react in an acid medium with dilute solutions of phosphorus to form an antimony-phospho-molybdate complex. This complex is reduced to an intensely blue-colored complex by ascorbic acid. The color is proportional to the phosphorus concentration.

4.3 Interferences

4.3.1 Silicon at a level of 100 µg/L causes an interference equivalent to approximately 0.04 µg/L of P/L. This can be avoided by maintaining an acid concentration of 2.45N H_2SO_4 in the reagents and analysis at 37 ± 2°C.

4.4 Apparatus and Materials

4.4.1 Continuous flow automated analytical system equipped with an autosampler, manifold, proportioning pump, colorimeter, phototube, recorder or computer based data system, and heating bath. Add a dilution coil to automatically dilute the sample to 10% with reagent water for orthophosphate analysis as per subsection 3.

4.4.2 Appropriate glassware. see section 1.8

NOTE: Clean all glassware two times with 4N HCl and rinse 9 times with reagent water.

4.4.3 Autoanalyzer cups. see section 1.8.3

4.4.4 Muffle furnace capable of maintaining temperatures 550 ± 50°C.

4.4.5 Whatman 47 mm glass fiber filter (0.7 µm pore size).

4.4.6 Centrifuge tubes, 50 mL capacity.

4.4.7 Filter apparatus with a minimum of 100 mL capacity.

4.5 Reagents

4.5.1 Reagent Grade Water: see section 1.9.

4.5.2 Hydrochloric Acid, 1N: In a one-liter volumetric flask, add approximately 800 mL of reagent water. Add 86 mL of concentrated HCl and dilute to one liter with reagent water.

4.5.3 Sulfuric Acid, 5.0N: To a one-liter volumetric flask, add 400 mL of reagent water. Add 140 mL of concentrated H_2SO_4, mix, cool, and dilute to one liter with reagent water.

4.5.4 Potassium Antimony Tartrate Solution: In a one-liter volumetric flask, add 800 mL of reagent water. Add 3.0 g of $K(SbO)C_4H_4O_6 \cdot \frac{1}{2}H_2O$, dissolve, and dilute to volume with reagent water. Store in a glass-stoppered bottle at room temperature.

4.5.5 Ammonium Molybdate Solution: In a one-liter volumetric flask, add 800 mL of reagent water. Add 40.0 g of ammonium molybdate $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, dissolve, and dilute to volume with reagent water. Store in a plastic bottle at 4 ± 2°C away from direct sunlight.

4.5.6 Ascorbic Acid: In a one-liter volumetric flask, add 800 mL of reagent water. Add 18.0 g of ascorbic acid, dissolve, and dilute to one liter with reagent water. Dispense 40 mL into clean polybottle and freeze. Thaw overnight in the refrigerator before use.

4.5.7 Sodium Lauryl Sulfate Solution: In a 100-mL volumetric flask, add 80 mL of reagent water. Add 3.0 g of sodium lauryl sulfate, dissolve, and dilute to 100-mL with reagent water.

4.5.8 Working reagent:

4.5.8.1 Reagent A: In a 100-mL volumetric flask, add 50 mL of 4.9N H_2SO_4, 5 mL of potassium antimony tartrate solution, 15 mL of ammonium molybdate, and 1.0 mL of sodium lauryl sulfate solution. All reagents must reach room temperature before they are mixed. Add the reagents in the order given and mix the resultant solution after each addition. The combined reagent is stable for 4 hours.

4.5.8.2 Reagent B: In a 100-mL volumetric flask, add 30 mL of ascorbic acid, and 0.3 mL of sodium lauryl sulfate solution. All reagents must reach room temperature before they are mixed. Add the reagents in the order given and mix the resultant solution after each addition. The combined reagent is stable for 4 hours.

4.5.9 Stock Phosphate Standard Solution: In a one-liter volumetric flask, add 500 mL of reagent water. Add 1.632 g of anhydrous potassium dihydrogen phosphate (KH_2PO_4) that has been dried overnight at 105 ± 2°C (stored in a desiccator), dissolve, and dilute to volume with reagent water. Add 1.0 mL of chloroform as a preservative. This solution is only stable for six months at 4 ± 2°C. (1.0 mL = 12.0 µg P)

4.6 Sample Handling

4.6.1 Samples are stored at -20 ± 2°C for a maximum 28 days.

4.7 Procedure

4.7.1 Sample preparation:

4.7.1.1 Record the weight of the GF/F filter used for total suspended solids after the total suspended solids have been determined and muffle for PP or refreeze them.

4.7.1.2 Remove the filters from the freezer and store in a clean container and dry overnight in an oven at 50 ± 2°C.

4.7.1.3 Place the dried filters in a clean numbered crucible in a muffle furnace and heat for 2 hours at 550 ± 2°C. Cool overnight.

4.7.2 Place the filters in labelled 50-mL plastic screw cap centrifuge tubes, add 10 mL of 1N HCl, cap and shake gently, several times during a 24-hour period. Dilute to 50 ml with reagent water and measure phosphate concentration.

4.7.3 Transfer the supernatant extract to autoanalyzer cups with a Pasteur pipette, and prepare to measure the phosphate concentration

4.7.4 Allow both the colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding reagent water through the sample line.

4.7.5 Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions with substitute ocean water.

4.7.6 Analytical sequence: The samples and associated QC samples and standards should be run according to the following sequence.

4.7.6.1 Five calibration standards with concentration within the linear range of the test.

4.7.6.2 Two method blanks.

4.7.6.3 Ten-twenty CBP samples.

4.7.6.4 One matrix spike sample.

4.7.6.5 One medium concentration calibration standard.

4.7.6.6 One method blank.

4.7.6.7 Steps 4.7.6.3 - 4.7.6.6 are repeated until are samples are analyzed or QC samples indicate that the system is out of control and recalibration is necessary.

4.7.6.8 One high concentration calibration standard.

4.7.6.9 One medium concentration calibration standard.

4.7.6.10 One low concentration calibration standard.

4.7.7 Switch sample line from distilled water to sampler and begin analysis.

4.7.8 Prepare appropriate standard curve by plotting peak heights of processed standards made up with KH_2PO_4, in a 0.2N Hcl matrix, against known concentrations. Compute concentration of the samples by comparing sample peak heights with standard curve.

NOTE: Subtract the blank background response from the standards before preparing the standard curve.

4.7.9 Record the stabilized potential of each unknown sample and convert the potential reading to the phosphorus concentration using the standard curve.

4.8 Quality Control

4.8.1 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section D.

4.8.2 Calibration

4.8.3 Linear calibration range: Calibration standards should bracket the range of CBP samples.

4.8.3.1 Correlation coefficient: The correlation coefficient must be 0.99 or better for the calibration curve to be used.

4.8.4 Method blank: see Chapter II, Section C.

4.8.5 Matrix spike sample: see Chapter II, Section C.

4.8.6 Laboratory duplicate: see Chapter II, Section C.

4.8.7 Reference materials: The laboratory must analyze a standard reference material once a year, as available.

4.9 References

Aspila, K.I., H Agemian and A.S.Y. Chau. 1976. A semi-automated method for the determination of inorganic, organic, and total phosphate in sediments analysis. 101:187-197.

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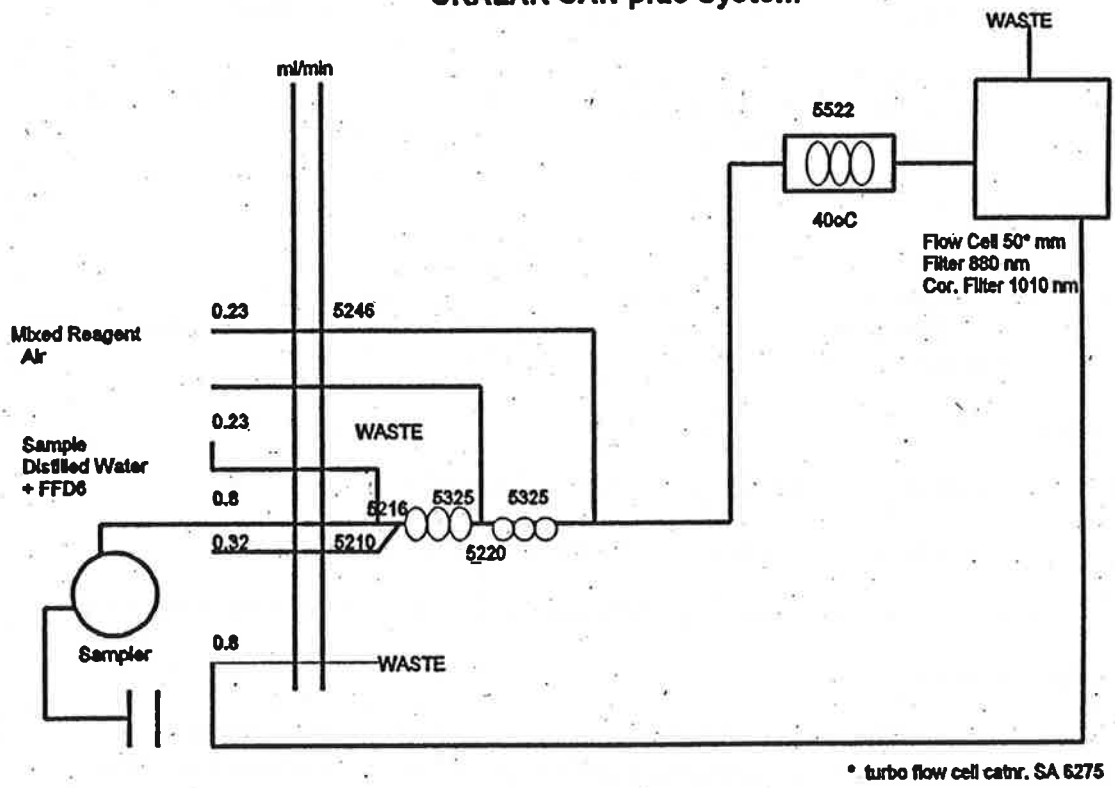
Orthophosphate/Total Dissolved Phosphporus/Particulate Phosphorus

SKALAR SAN plus System



5. Nitrite

5.1 Scope and Application

5.1.1 This method provides a procedure for the determination of low level nitrite concentrations normally found in estuarine and/or coastal waters.

5.1.2 A method detection limit (MDL) of 0.0002 mg N/L has been statistically determined by one laboratory. This MDL is defined as three times the standard deviation of at least seven replicates of a low level estuarine (~15 parts per thousand salinity) sample. The method is linear to 0.070 mg N/L at a standard calibration setting of 9.0 on an AutoAnalyzer II system. Where higher concentrations are encountered, the method is also linear at less sensitive standard calibration settings.

5.1.3 This method should be used by analysts experienced in the use of automated colorimetric analyses, matrix interferences and procedures for their correction. A minimum of six months experience under supervision is recommended.

5.2 Summary of Method

5.2.1 This method is an automated colorimetric method for the analysis of low level nitrite concentrations. Filtered samples are analyzed by deoxidizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form a colored azo dye. The color produced is proportional to the nitrite concentration present in the sample.

5.3 Interferences

5.3.1 Metal ions may produce a positive error if present in sufficient concentrations.

5.3.2 Sample turbidity should be removed by filtration prior to analysis.

5.3.3 Refractive Index interferences should be corrected for when analyzing estuarine/coastal samples.

5.4 Apparatus and Materials

5.4.1 Continuous flow automated analytical system equipped with an autosampler, manifold, proportioning pump, colorimeter, phototube or recorder or computer based data system.

5.4.2 Nitrogen-free glassware: All glassware used in the determination must be low in residual nitrite to avoid sample/reagent contamination. Washing with 10% HCl and thoroughly rinsing with reagent water has been found to be effective.

5.5 Reagents

5.5.1 Stock reagent solutions

5.5.1.1 Ammonium Chloride Reagent: Dissolve 10.0 g of ammonium chloride (NH_4Cl)in one liter of reagent water. Adjust to pH 8.5 by adding three to four NaOH pellets as

necessary. Add 5 drops of 2% copper sulfate solution. No addition of EDTA is necessary. This reagent is stable for one week if kept refrigerated.

5.5.1.2 Color Reagent: Combine 1500 mL reagent water, 200.0 mL concentrated phosphoric acid (H_3PO_4), 20.0 g sulfanilamide, and 1.0 g N-1 napthylethylenediamine dihydrochloride. Dilute to 2000 mL with reagent water. Add 2.0 mL BRIJ-35 (Bran & Luebbe, Elmsford, N.Y.).Store at 4 ± 2°C in the dark. This should be prepared every six weeks.

5.5.1.3 Refractive Reagent: Combine 100 mL of concentrated phosphoric acid (H_3PO_4) with 800 mL reagent water. Dilute to 1000 mL with reagent water. Add 1.0 mL BRIJ-35.

5.5.1.4 Stock Nitrite Solution: Dissolve 0.493 g pre-dried (60 ± 2°C for 1 hour) sodium nitrite ($NaNO_2$) in reagent water and dilute to 1000 mL. 1.0 mL = 0.100 mg N. The stability of this stock standard is approximately 3 months, if kept refrigerated.

5.5.2 Reagent water: see section 1.9

5.5.3 Artificial Sea Water: see section 1.7

5.5.4 Secondary Nitrite Solution: Dilute 1.0 mL of stock nitrite solution to 100 mL with reagent water. 1.0 mL of this solution = 0.001 mg N. Refrigerate and store no longer than 3 days.

5.5.5 Prepare a series of standards by diluting suitable volumes of secondary nitrite solution to 100 mL with reagent water. Prepare these standards daily. When working with samples of known salinity it is recommended that the standard curve concentrations be prepared in substitute ocean water diluted to that salinity and that the sampler wash solution also be substitute ocean water diluted to that salinity. When analyzing samples of varying salinities, it is recommended that the standard curve be prepared in reagent water and Refractive Index corrections be made to the sample concentrations. The following dilutions, brought up to 100 mL with reagent water, are suggested.

mL of standard nitrite solution	Concentration (mg N/L)
0.5	0.005
1.0	0.010
2.0	0.020
4.0	0.040
6.0	0.060

5.5.6 Saline nitrite standards: When analyzing samples of varying salinities, it is also recommended that standards be prepared in a series of salinities in order to quantify the "salt error," the shift in the colorimetric response of nitrite due to the change in the ionic strength of the solution.

5.6 Sample Handling

5.6.1 Samples must be analyzed as quickly as possible. If the samples are to be analyzed within 24 hours of collection, then refrigeration at 4 ± 2°C is acceptable.

5.6.2 If samples will not be analyzed within 24 hours of collection, the sample must be stored at -20 ± 2°C for a maximum of 28 days.

5.7 Procedure

5.7.1 Calibration: Standard curves of varying concentrations should be analyzed through several standard calibration settings (calibrated sensitivity settings). In so doing, where higher concentrations are encountered, the method will also have been checked for linearity using sets of standards of higher concentrations.

5.7.2 Sample analysis

5.7.2.1 If samples have not been freshly collected and are frozen, thaw the samples to room temperature.

5.7.2.2 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a steady baseline with reagent water pumping through the system, add reagents to the sample stream and after the reagent base line is steady, reset the "zero" if necessary.

5.7.2.3 A good sampling rate is approximately 40 samples/hr. with a 9:1 sample:wash ratio.

5.7.2.4 Analytical sequence: The samples and associated QC samples and standards should be run according to the following sequence.

5.7.2.4.1 Five calibration standards with concentration within the linear range of the test.

5.7.2.4.2 Two method blanks.

5.7.2.4.3 Ten CBP samples.

5.7.2.4.4 One matrix spike sample.

5.7.2.4.5 One medium concentration calibration standard.

5.7.2.4.6 One method blank.

5.7.2.4.7 Steps 5.7.2.4.3 - 5.7.2.4.6 are repeated until samples are analyzed or QC samples indicate that the system is out of control and recalibration is necessary.

5.7.2.4.8 One high concentration calibration standard.

5.7.2.4.9 One medium concentration calibration standard.

5.7.2.4.10 One low concentration calibration standard.

5.7.2.5 If a low concentration sample peak follows a high concentration sample peak, a certain amount of carry over can be expected. It is recommended that if there is not a clearly defined low concentration peak, that the sample be reanalyzed at the end of the sample run.

5.7.3 Calculations

5.7.3.1 Nitrite concentrations are calculated from the linear regression obtained from the standard curve in which the concentrations of the standards are entered as the independent variable and their corresponding peak heights are the dependent variable.

5.7.3.2 Refractive Index Correction For Estuarine/Coastal Systems shall be performed in accordance with procedures described in Section 6.7.3.2

5.7.3.3 Correction for Salt Error in Estuarine/Coastal Samples shall be performed in accordance with procedures described in Section 6.7.3.3

5.7.3.4 Results should be reported in mg N/L.

5.8 Quality Control

5.8.1 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section D.

5.8.2 Calibration

5.8.2.1 Linear calibration range: Calibration standards should bracket the range of CBP samples.

5.8.2.2 Correlation coefficient: The correlation coefficient must be 0.995 or better for the calibration curve to be used.

5.8.3 Method blank: see Chapter II, Section C.

5.8.4 Matrix spike sample: see Chapter II, Section C.

5.8.5 Laboratory duplicate: see Chapter II, Section C.

5.8.6 Reference materials: The laboratory must analyze a standard reference material once a year, as available.

5.9 References

Froelich, P.N. and M.E.Q. Pilson. 1978. Systematic absorbance errors with Technicon AutoAnalyzer II calorimeters. Water Research 12: 599- 603.

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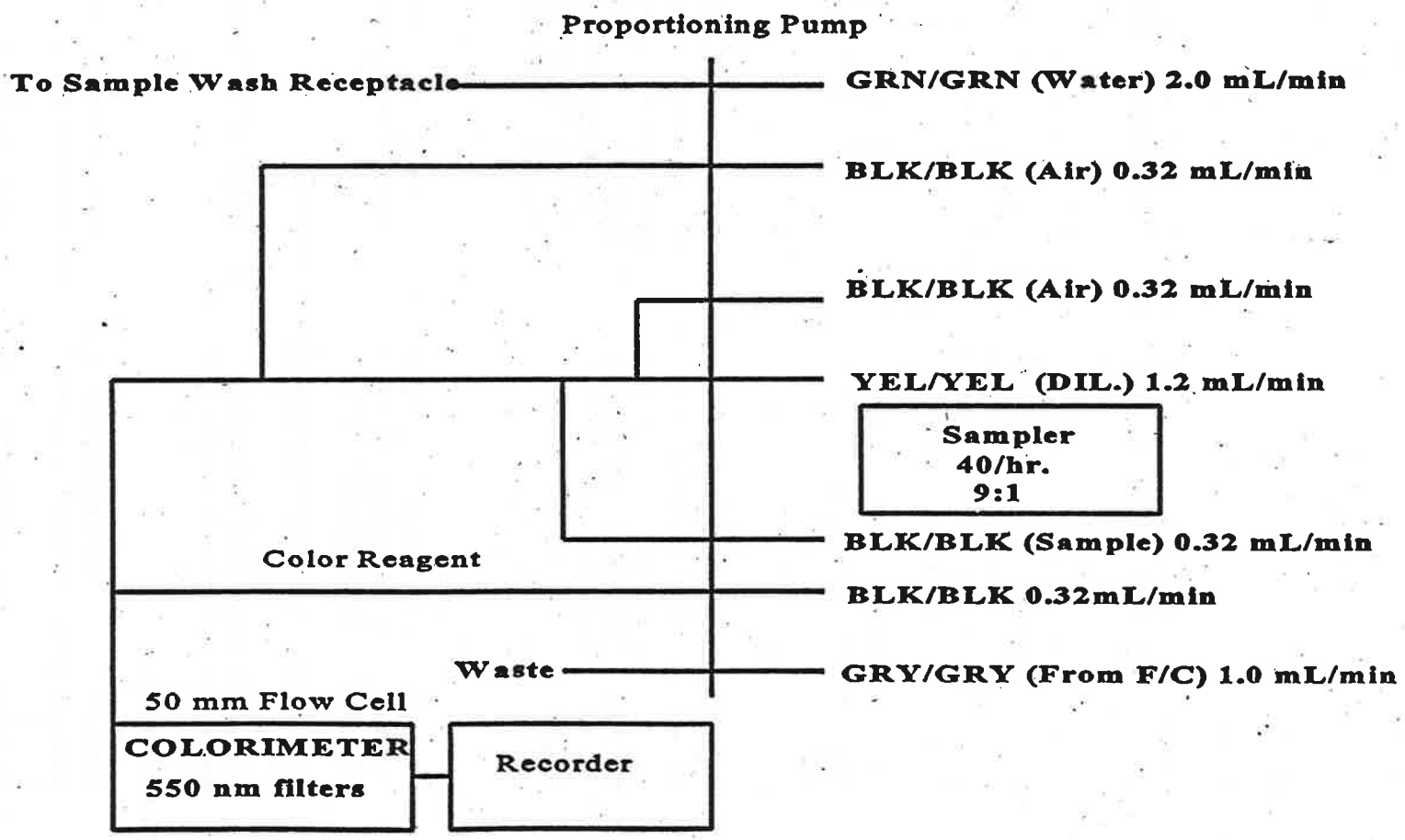
40 CFR, [part] 136 Appendix B. Definition and Procedure for the Determination of the Method Detection Limit. Revision 1.11.

Nitrite - Technicon AAII Series



6. Nitrate + Nitrite

6.1 Scope and Application

6.1.1 This method provides a procedure for the determination of low level nitrite+nitrate concentrations normally found in estuarine and/or coastal waters using the cadmium reduction technique of Wood, et al., 1967.

6.1.2 A determined method detection limit (MDL) of 0.0002 mg N/L has been statistically determined by one laboratory. This MDL is defined as three times the standard deviation of at least seven replicates of a low level estuarine (~15 parts per thousand salinity) sample. The method is linear to 0.070 mg N/L at a standard calibration setting of 9.0 on an AutoAnalyzer II system. Where higher concentrations are encountered, the method is also linear at less sensitive standard calibration settings.

6.1.3 This method should be used by analysts experienced in the use of automated colorimetric analyses and matrix interferences and procedures for their correction. A minimum of six months experience under supervision is recommended.

6.2 Summary of Method

6.2.1 This is an automated colorimetric method for the analysis of low level nitrite+nitrate concentrations. Filtered samples are passed through a granulated copper cadmium column to reduce nitrate to nitrite. The nitrite originally present and the reduced nitrate are then determined by deoxidizing with sulfanilamide and coupling with N-1-naphthylethylenediamine dihydrochloride to form a colored azo dye. The color produced is proportional to the nitrite+nitrate concentration present in the sample. Nitrite values are determined using the same method without the cadmium reduction column. Nitrate values are calculated by subtracting the nitrite concentration from the previously determined nitrate+nitrite value.

6.3 Interferences

6.3.1 Concentrations of iron, copper and other metals above several milligrams per liter alter reduction efficiency. The presence of large concentrations of sulfide and/or sulfate will cause a loss of sensitivity to the copper-cadmium column (EPA, 1977; Grasshoff, et al., 1983).

6.3.2 Sample turbidity should be removed by filtration prior to analysis.

6.3.3 Refractive Index and "Salt Error" interferences should be corrected for when analyzing estuarine/coastal samples by using the procedures included in this method.

6.4 Apparatus and Materials

6.4.1 Continuous flow automated analytical system equipped with an autosampler, manifold, proportioning pump, colorimeter, phototube and recorder or computer based data system.

6.4.2 Nitrogen-free glassware: All glassware used in the determination must be low in residual nitrate to avoid sample/reagent contamination. Washing with 10% HCl and thoroughly rinsing with reagent water have been found to be effective.

6.5 Reagents

6.5.1 Stock Reagent Solutions

6.5.1.1 Ammonium Chloride Reagent: Dissolve 10.0 g of nitrate-free ammonium chloride (NH_4Cl) in one liter of reagent water. Adjust to pH 8.5 by adding three to four NaOH pellets as necessary. Add 5 drops of 2% copper sulfate solution. No addition of EDTA is necessary. This reagent is stable for one week if kept refrigerated.

6.5.1.2 Color Reagent: Combine 1500 mL reagent water, 200.0 mL concentrated phosphoric acid (H_3PO_4), 20.0 g sulfanilamide, and 1.0 g N-1 napthylethylenediamine dihydrochloride. Dilute to 2000 mL with reagent water. Add 2.0 mL BRIJ-35 (Bran & Luebbe, Elmsford, N.Y.). Store at 4 ± 2°C in the dark. This should be prepared fresh every six weeks.

6.5.1.3 Copper Sulfate: Dissolve 2.0 g of copper sulfate ($CuSO_4 \cdot 5H_2O$) in 90.0 mL of reagent water. Bring up to 100 mL with reagent water.

6.5.1.4 Refractive Reagent: Combine 100 mL of concentrated phosphoric acid (H_3PO_4) with 800 mL reagent water. Dilute to 1000 mL with reagent water. Add 1.0 mL BRIJ-35.

6.5.1.5 Stock Nitrate Solution: Dissolve 0.721 g of pre-dried (60 ± 2°C for 1 hour) potassium nitrate (KNO_3) in reagent water and dilute to 1000 mL. 1.0 mL = 0.100 mg N. The stability of this stock standard is approximately 3 months, if kept refrigerated.

6.5.1.6 Stock Nitrite Solution: Dissolve 0.493 g pre-dried (60 ± 2°C for 1 hour) sodium nitrite ($NaNO_2$) in reagent water and dilute to 1000 mL. 1.0 mL = 0.100 mg N. The stability of this stock standard is approximately 3 months, if kept refrigerated.

6.5.2 Reagent Grade Water: see section 1.9.

6.5.3 Substitute Ocean Water: see section 1.7

6.5.4 Cadmium preparation: The following description of cadmium and the column preparation is to be used as a general guideline. Other sizes and shapes of columns which provide equivalent results are acceptable. The ultimate goal is to obtain 100% reduction of nitrate to nitrite.

6.5.4.1 Use good quality cadmium filings. Depending on the reductor column shape and size, cadmium filings should generally be less than 0.5 mm but greater than 0.3 mm for glass columns and in the 25 - 60 mesh size range for columns prepared by using flexible tubing.

6.5.4.2 New cadmium filings should be rinsed with diethyl ether to remove dirt and grease. Approximately 10 g of this cadmium is then treated with 50 mL of 6N HCl in a 150 mL beaker. Swirl VERY CAREFULLY for one minute.

6.5.4.3 Carefully decant the HCl and thoroughly rinse (at least 10 times) with reagent water. Decant the reagent water and add a 50 mL portion of 2% (w/v) copper sulfate solution. While swirling, brown flakes of colloidal copper will appear and the blue color of the

solution will fade. Decant and repeat this sequence several times until the blue color does not fade and a brown colloidal precipitate forms. To avoid contact with air, from this point on the fillings must be kept submerged at all times.

6.5.4.4 Immediately wash the filings thoroughly with reagent water until all blue color is gone and the supernatant is free of particulate matter (usually a minimum of 10 rinses is necessary). The filings are now ready to be packed into the column.

6.5.4.5 Column preparation: Fill the reductor column with ammonium chloride reagent and transfer the prepared cadmium filings to the column using a Pasteur pipette or employ some other method which avoids contact of the Cd particles with air. One end of the reductor column should be plugged with glass wool. Column shape and size varies with users. Some examples include a 22 cm length of 0.110" ID tubing, a 35 cm length of 0.090" ID tubing, or a 3.5" length of glass tubing.

6.5.4.6 When the entire column is fairly well packed with granules, insert another glass wool plug at the top of the column and with reagents pumping through the system, attach the column. Remember to have no air bubbles in the valve and to attach the column to the intake side of the valve first.

6.5.4.7 Check for good flow characteristics (regular bubble pattern) after the addition of air bubbles beyond the column. If the column is packed too tightly, an inconsistent flow pattern will be evident. Prior to sample analysis, condition the column by pumping through the sample line approximately 1 mg N (nitrate)/L for five minutes followed by 1 mg N (nitrite)/L for 10 minutes.

6.5.5 Secondary Nitrate Solution: Dilute 1.0 mL of stock nitrate solution to 100 mL with reagent water. 1.0 mL of this solution = 0.001 mg N. Refrigerate and store no longer than 3 days.

6.5.6 Prepare a series of standards by diluting suitable volumes of secondary nitrate solution to 100 mL with reagent water. Prepare these standards daily. When working with samples of known salinity it is recommended that the standard curve concentrations be prepared in substitute ocean water diluted to that salinity and that the sampler wash solution also be low nutrient seawater diluted to that salinity. When analyzing samples of varying salinities, it is recommended that the standard curve be prepared in reagent water and refractive index corrections be made to the sample concentrations. The following dilutions, brought up to 100 mL with reagent water, are suggested.

mL of standard nitrate solution
0.5
1.0
2.0
4.0
6.0

Concentration (mg N/L)
0.005
0.010

0.020
0.040
0.060

6.5.7 Saline Nitrate Standards: When analyzing samples of varying salinities, it is also recommended that standards be prepared in a series of salinities in order to quantify the "salt error," the shift in the colorimetric response of nitrate due to the change in the ionic strength of the solution.

6.5.8 Secondary Nitrite Solution: Dilute 1.0 mL of stock nitrite solution to 100 mL with reagent water. 1.0 mL of this solution = 0.001 mg N. Refrigerate and store no longer than 3 days.

6.5.9 Working Nitrite Solution: One working standard must be prepared and used as a check on the reduction capability of the cadmium column. Dilute 6.0 mL of secondary nitrite solution to 100 mL to yield a concentration of 0.060 mg N/L.

6.6 Sample Handling

6.6.1 Samples must be analyzed as quickly as possible. If the samples are to be analyzed within 24 hours of collection, then refrigeration at 4 ± 2°C is acceptable.

6.6.2 If samples will not be analyzed within 24 hours of collection, the sample must be stored at -20 ± 2°C for a maximum of 28 days.

6.7 Procedure

6.7.1 Calibration: Prepare calibration curves using calibration standards that bracket the CBP samples.

6.7.2 Sample analysis

6.7.2.1 If samples have not been freshly collected and are frozen, thaw the samples to room temperature.

6.7.2.2 Allow both colorimeter and recorder to warm up for 30 minutes. Obtain a steady baseline with reagent water pumping through the system, add reagents to the sample stream and after the reagent base line is steady, reset the "zero" if necessary.

6.7.2.3 A good sampling rate is approximately 40 samples/hr. with a 9:1 sample:wash ratio.

6.7.2.4 Analytical sequence: The samples and associated QC samples and standards should be analyzed according to the following sequence.

6.7.2.4.1 Calibration standards in reagent water and saline water and working nitrite standards in order of decreasing concentration. Two standards of each composition and concentration should be analyzed.

6.7.2.4.2 Two method blanks.

6.7.2.4.3 Ten-twenty CBP samples.

6.7.2.4.4 One matrix spike sample.

6.7.2.4.5 One medium concentration calibration standard.

6.7.2.4.6 One method blank.

6.7.2.4.7 Steps 6.7.2.4.3 - 6.7.2.4.6 are repeated until all samples are analyzed or QC samples indicate that the system is out of control and recalibration is necessary.

6.7.2.4.8 One standard of each composition and concentration in order of decreasing concentration.

6.7.2.5 The peak height of the 0.060 mg N/L nitrate standard prepared in deionized water must be equal to or greater than 90% of the peak height of the 0.060 mg N/L nitrite standard. If this criteria is not met, a fresh cadmium reduction column must be prepared and checked before any CBP samples may be analyzed.

6.7.2.6 If a low concentration sample peak follows a high concentration sample peak, a certain amount of carry over can be expected. It is recommended that if there is not a clearly defined low concentration peak, that the sample be reanalyzed.

6.7.3 Calculations

6.7.3.1 Concentrations of nitrite+nitrate are calculated from the linear regression obtained from the standard curve in which the concentrations of the standards are entered as the independent variable and their corresponding peak heights are the dependent variable.

6.7.3.2 Refractive Index Correction For Estuarine/Coastal Systems

6.7.3.2.1 The absorbance peak obtained by an automated system for nitrate in a seawater sample (when compared to a reagent [deionized] water baseline) represents the sum of absorbances from at least four sources: (1) the light changes due to the differences in the index of refraction of the seawater and reagent water; (2) reaction products (e.g., precipitates) of BRIJ-35 and the seawater; (3) the absorbance of colored substances dissolved in the sample; and (4) reaction products of the nitrite and the nitrate (reduced to nitrite by the cadmium column) in the sample with the color reagent (Loder and Glibert, 1977). The first three sources of color are corrected for by the refractive index correction described here.

6.7.3.2.2 Obtain a second set of peak heights for all samples and standards with refractive reagent being pumped through the system in place of color reagent. All other reagents remain the same. Peak heights for the refractive index correction must be obtained at the same standard

calibration setting and on the same colorimeter as the corresponding samples and standards (Froelich and Pilson, 1978). Subtract these peak heights form the corresponding peak heights obtained with the color reagent.

6.7.3.3 Correction for Salt Error in Estuarine/Coastal Samples

6.7.3.3.1 When calculating concentrations of samples of varying salinities from standards prepared in reagent water, it is necessary to first correct for Refractive Index errors, then correct for the "Salt Error" alteration in color development due to the ionic strength of the samples.

6.7.3.3.2 Use the CBPO software to generate a line with the salinity of the saline standards as the independent variable (X variable) and the apparent concentration of nitrate (mg N/L) from the peak height corrected for refractive index as the dependent variable (Y variable) for all 0.060 mg N/L standards. The concentrations of the samples of known salinity are corrected for the color enhancement due to Salt Error using the resulting regression.

6.7.3.4 Results should be reported in mg N/L.

6.8 Quality Control

6.8.1 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section D.

6.8.2 Calibration

6.8.2.1 Linear calibration range: Calibration standards should bracket the range of CBP samples.

6.8.2.2 Correlation coefficient: The correlation coefficient must be 0.99 or better for the calibration curve to be used.

6.8.3 Method blank: see Chapter II, Section C.

6.8.4 Matrix spike sample: see Chapter II, Section C.

6.8.5 Laboratory duplicate: see Chapter II, Section C.

6.8.6 Reference materials: The laboratory must analyze a standard reference material once a year, as available.

6.9 References

Froelich, P.N. and M.E.Q. Pilson. 1978. Systematic absorbance errors with Technicon AutoAnalyzer II calorimeters. Water Research 12: 599- 603.

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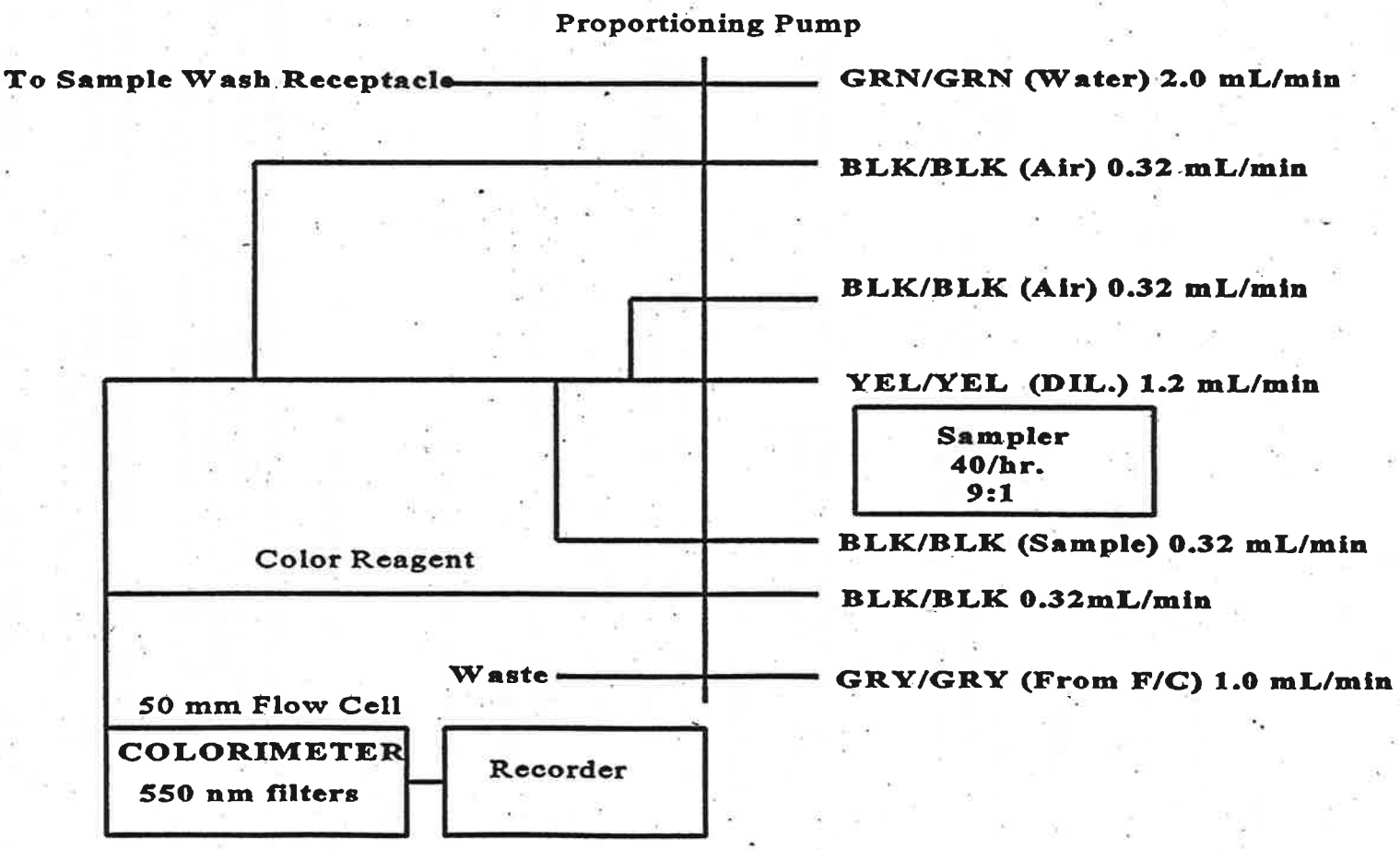
40 CFR, [part] 136 Appendix B. Definition and Procedure for the Determination of the Method Detection Limit. Revision 1.11.

Nitrate + Nitrite - Technicon AAII Series



7. Ammonia

7.1 Scope and Application

7.1.1 This method covers the determination of ammonia in water by the automated phenate method in the range of 0.01 to 2.0 mg/L of NH_4.

7.2 Summary of Method

7.2.1 Alkaline phenol and hypochlorite react with ammonia to form indophenol blue. The color intensity of indophenol blue is proportional to the ammonia concentration. By adding sodium nitroprusside to the mixture, the blue color is intensified for colorimetric measurements.

7.3 Interferences

7.3.1 Precipitation problems can occur if calcium and magnesium ions are present in sufficient amounts. A sodium potassium tartrate solution should be used to prevent this effect.

7.4 Apparatus and Materials

7.4.1 Continuous flow automated analytical system equipped with an autosampler, manifold, proportional pump, colorimeter, phototube, recorder or computer based data system, and heating bath.

7.4.2 Appropriate glassware. see section 1.7

NOTE: Clean all glassware with soap and tap water, then rinse two times with 4N HCl and rinse 9 times with reagent water.

7.4.3 Autoanalyzer cups. see section 1.7.3

7.5 Reagents

7.5.1 Reagent Water: see section 1.9

7.5.2 Complexing Reagent: To a one-liter volumetric flask, add approximately 750 Ml of reagent water. Dissolve 33 g of potassium sodium tartrate ($KNaC_4H_4O_6 \cdot 4H_2O$) and 24 g of sodium citrate [$HOC(COONa)(CH_2COONa)_2 \cdot 2H_2O$]. Adjust the pH of this solution to 5.0 with concentrated sulfuric acid (H_2SO_4). Dilute to one liter with reagent water. Store at 4 ± 2°C.

7.5.3 Sodium Nitroprusside: Add approximately 900 mL of reagent water to a one-liter volumetric flask. Dissolve 0.5 g of sodium nitroprusside ($Na_2Fe(CN)_5NO \cdot 2H_2O$) and dilute to one liter with reagent water. Add Brij-35 only if necessary. Store in a dark bottle at 4 ± 2°C.

7.5.4 Sodium Hypochlorite Solution: To a one-liter volumetric flask, add 400 mL of reagent water. Add 200 mL of a stock sodium hypochlorite solution containing 5.25% of chlorine (NaOCl) and dilute to one liter with reagent water. Add 6 drops of Brij-35. This solution is stable for one week if stored at room temperature.

7.5.5 Alkaline Phenol Solution: In a 500 mL volumetric flask, dissolve 41.5 g of phenol (C_6H_5OH) in approximately 100 mL of reagent water. Make sure phenol is completely dissolved (it will be white and cloudy). Measure out 90 mL of 20% (w/v) of NaOH solution using a graduated cylinder and mix solutions. The solution will turn clear. Dilute to 500 mL with reagent water and mix by inverting. Store in amber glass bottle. This solution should be prepared daily.

Caution: Phenol should be prepared every few days under a hood. It is an extremely dangerous chemical and should be handled accordingly.

7.5.6 Artificial Sea Water: see section 1.7

7.5.7 Wash Water: Dilute substitute ocean water to the average salinity of the samples being analyzed.

7.5.8 Sodium Hydroxide Solution: 20% (w/v), reagent grade.

7.5.9 Ammonia Stock Standard Solution: In a one-liter volumetric flask, add 200 mL of reagent water. Dissolve 0.3310 g of ammonium sulfate $(NH_4)_2SO_4$, mix, and dilute to one liter. Add 1 mL of concentrated H_2SO_4 as a preservative. Store at 4 ± 2°C. This solution is stable for six months.

7.5.9.1 Ammonia Standard Solution A: In a 100 mL volumetric flask, add 50 mL of wash water solution. Add 2 mL of stock standard solution, mix, and dilute to volume with wash water solution. This solution should be prepared on the day of analysis. (1.0 mL = 1.4 mg NH_3-N/L)

7.5.9.2 Ammonia Standard Solution B: In a 100 mL volumetric flask, add 50 mL of wash water solution. Add 10 mL of ammonia standard solution A, mix, and dilute to volume with wash water solution. This solution should be prepared fresh on the day of the analysis. (1.0 mL = 0.14 mg NH_3-N/L).

7.6 Sample Handling

7.6.1 Samples are stored at -20 ± 2°C for a maximum 28 days.

7.7 Procedure

7.7.1 Allow both the colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with deionized water pumping through the system, add reagents to the sample stream, and after the reagent baseline is steady, reset the "zero" if necessary.

7.7.2 Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions of ammonium sulfate.

...alytical sequence: The samples and associated QC samples and standards should be analyzed according to the following sequence.

7.7.3.1 Five calibration standards with concentration within the linear range of the test.

7.7.3.2 Two method blanks.

7.7.3.3 Ten-twenty CBP samples.

7.7.3.4 One matrix spike sample.

7.7.3.5 One medium concentration calibration standard.

7.7.3.6 One method blank.

7.7.3.7 Steps 7.7.3.5 - 7.7.3.8 are repeated until are samples are analyzed or QC samples indicate that the system is out of control and recalibration is necessary.

7.7.3.8 One high concentration calibration standard.

7.7.3.9 One medium concentration calibration standard.

7.7.3.10 One low concentration calibration standard.

7.7.4 Use CBP software to prepare an appropriate standard curve and to calculate the concentration of NH_4. The blank background response should be subtracted from the standards before preparing the standard curve.

7.8 Quality Control

7.8.1 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section D.

7.8.2 Calibration

7.8.2.1 Linear calibration range: Calibration standards should bracket the range of CBP samples.

7.8.2.2 Correlation coefficient: The correlation coefficient must be 0.99 or better for the

calibration curve to be used.

7.8.3 Method blank: see Chapter II, Section C.

7.8.4 Matrix spike sample: see Chapter II, Section C.

7.8.5 Laboratory duplicate: see Chapter II, Section C.

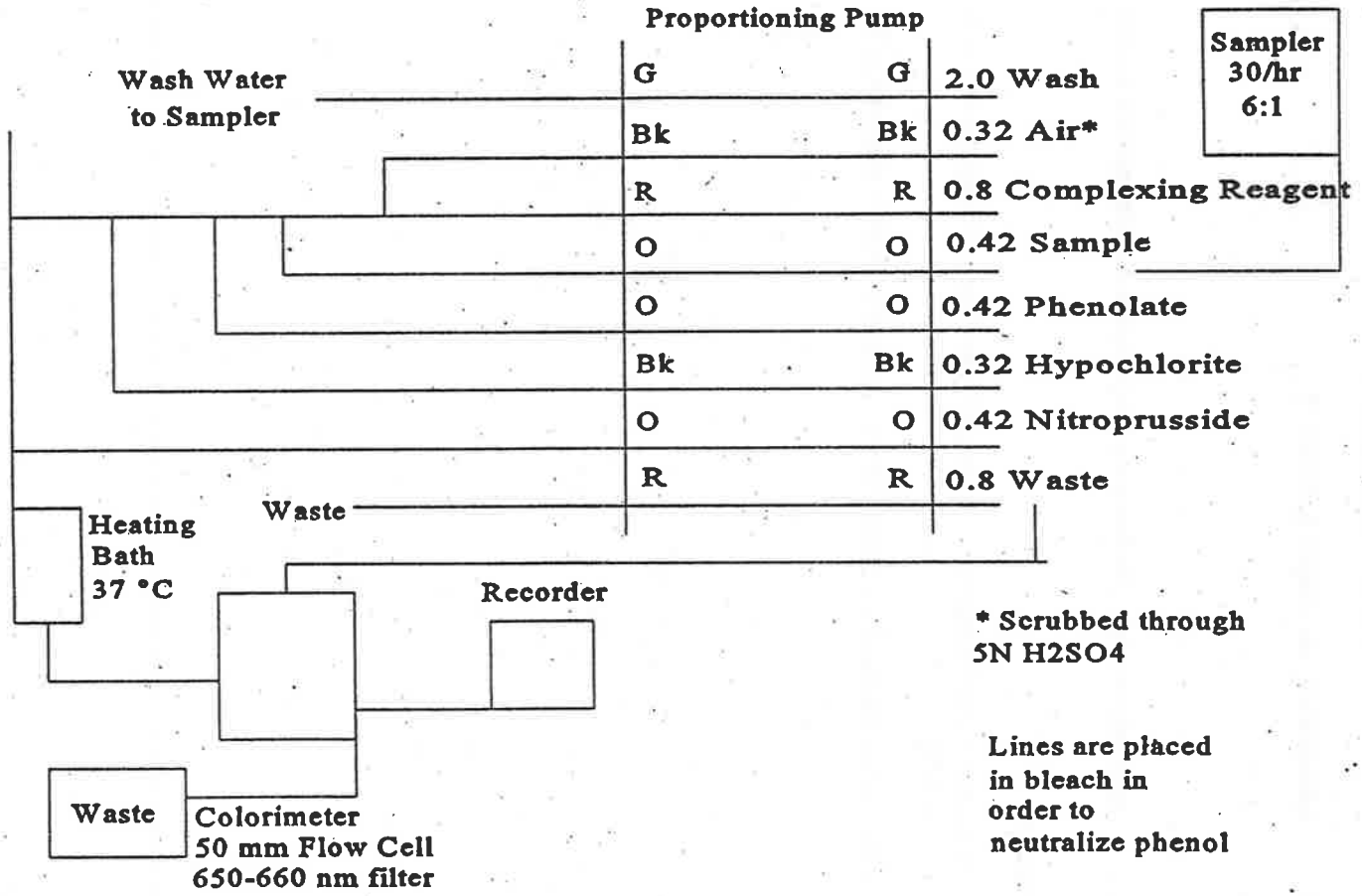
7.8.6 Reference materials: The laboratory must analyze a standard reference material once a year, as available.

7.9 References

Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 410, Method 418A and 418B (1975).

Annual Book of ASTM Standards, Part 31, "Water", Standard D 1426-74, Method A, p 237 (1976).

MANIFOLD CONFIGURATION FOR AMMONIA



8. Total Dissolved Nitrogen

8.1 Scope and Application

8.1.1 This method covers the determination of total dissolved nitrogen in estuarine water by the automated persulfate oxidation technique in the range of 0.01 to 2.0 mg/L of NO_3+NO_2-N.

8.2 Summary of Method

8.2.1 This method is a persulfate oxidation technique for nitrogen where, under alkaline conditions, all forms of nitrogen are oxidized to nitrite. This is followed by analysis for nitrate by an automated colorometric method (subsection 6). The inorganic fractions can then be subtracted from the total dissolved sample to calculate the dissolved organic concentration, if desired.

8.3 Interferences

8.3.1 Metal ions may produce a positive nitrate error if present in sufficient concentrations. The presence of large concentrations of sulfate will cause a large loss of sensitivity to the copper-cadmium column.

8.3.2 Turbidity may interfere with this method if the sample has not been filtered.

8.4 Apparatus and Materials

8.4.1 Continuous flow automated analytical system equipped with an autosampler, manifold, proportional pump, colorimeter, phototube, recorder or computer based data system, and heating bath.

8.4.2 Appropriate glassware. see section 1.7

8.4.3 Autoanalyzer cups. see section 1.7.3

8.5 Reagents

8.5.1 Reagent Grade Water: see section 1.9

8.5.2 Borate Buffer Solution: To a two liter volumetric flask, add approximately 800 mL of reagent water. Add 123.6 g of boric acid (H_3BO_3) and 16.16g of Low N sodium Hydroxide (NaOH) and dilute to two Liters with reagent water. Stable for two months at room temperature.

8.5.3 Oxidizing Reagent: To a one-liter volumetric flask, add 400 mL of reagent water. Add 3.0 g of low nitrogen NaoH and 20.1 g of Baker Instra-analyzed potassium persulfate, dissolve, and dilute to one liter with reagent water. Store in a glass reagent bottle. This solution is only stable for two hours at room temperature.

8.5.4 Ammonium Chloride Preparation Water: Measure out two liters of reagent water with a graduated cylinder into a clean 2-liter Erlenmeyer flask. Add a magnetic Teflon stirring bar. While stirring the water, measure the pH. Adjust the pH to 8.5 by adding one drop of ammonium hydroxide. If the solution becomes too acidic dilute the ammonium with water until the solution reaches a pH of 8.5.

8.5.5 Ammonium Chloride Reagent: In a two-liter volumetric flask, measure out approximately 1.5 L of ammonium chloride preparation water. Add 20 g of ammonium chloride (NH_4Cl) and 0.2 g of disodium EDTA, dissolve, and dilute to two liters with reagent water. Make sure the ammonium chloride and EDTA are completely dissolved. Store in a glass bottle, add 1.0 mL of Brij-35, and 5 drops of 2% copper sulfate ($CuSO_4$) solution.

8.5.6 Color Reagent: In a one-liter volumetric flask, add 500 mL of reagent water. Add 100 mL of concentrated phosphoric acid H_3PO_4 and 10 g of sulfanilamide ($C_6H_8N_2O_2S$), dissolve the mixture using low heat if necessary. Add 0.5 g of N-1-naphthylethylenediamine dihydrochloride ($C_{12}H_{14}N_2 \cdot 2HCl$) and dissolve. Cool to room temperature then, dilute to one liter with reagent water. Pour into a plastic one-liter bottle and add 0.5 mL of Brij-35. Store in the dark at 4 ± 2°C. This solution is stable for one month at 4 ± 2°C.

8.5.7 Copper Sulfate Solution, 2% (w/v): In a one-liter volumetric flask, add 500 mL of reagent water. Add 20.0 g of $CuSO_4$, dissolve, and dilute to volume with reagent water. Store in a plastic bottle at room temperature. This solution is stable for two months.

8.5.8 Phosphoric Acid, 10%: In a 500-mL volumetric flask, add 400 mL of reagent water. Add 50 mL of concentrated phosphoric acid H_3PO_4, dissolve, and dilute to volume with reagent water. Add 0.25 mL of Brij-35. Store in a ground glass-stoppered glass bottle at room temperature.

8.5.9 Artificial Sea Water: see section 1.7

8.5.10 Wash Water: Dilute substitute ocean water to the average salinity of the samples being analyzed. Add 4 mL of Brij-35 per liter. Make this solution daily.

8.5.11 Stock Glutamic Acid Standard: In a 500-mL volumetric flask, add 400 mL of reagent water. Add 0.3705 g of glutamic acid ($HOCOCH_2CH_2CH(NH_2)COOH$), mix, and dilute to volume with reagent water. Add 0.5 mL of chloroform (under a hood) as a preservative. This solution is only stable for ten months at 4 ± 2°C.

8.5.11.1 Working Glutamic Acid Standard: In a 100-mL volumetric flask, add 50 mL of wash water solution. Add 0.5 mL of stock standard solution, mix, and dilute to volume with wash water solution. This solution should be prepared on the day of analysis. (1.0 mL = .3528 mg N/L)

8.5.12 Stock Nitrate Standard: In a one-liter volumetric flask, add 500 mL of reagent water. Add 0.7218 g of potassium nitrate (KNO_3) that has been dried overnight at 103 ± 2°C (stored in a desiccator), mix, and dilute to volume with reagent water. Add 2 mL of chloroform (under a hood) as a preservative. This solution is only stable for six months at 4 ± 2°C.

8.5.13 Stock Nitrite Standard: In a 500-mL volumetric flask, add 400 mL of reagent water. Add 0.6160 g of sodium nitrite ($NaNO_2$) that has been dried overnight at 103 ± 2°C (stored in a desiccator), mix, and dilute to volume with reagent water. Add 2 mL of chloroform (under a hood) as a preservative. This solution is only stable for one month at 4 ± 2°C.

8.5.14 Column preparation:

8.5.14.1 Treatment of cadmium: Approximately 7 g of cadmium are poured into a 125 mL Erlenmeyer flask. Add enough 1N HCl to the flask to cover the cadmium, and swirl for 10 seconds (do not exceed this allotted time). Quickly rinse the cadmium with ASTM type II water until the solution is non-acidic (test with pH paper). Next, add 100 mL portions of 2% $CuSO_4$ solution and swirl for 30 to 40 seconds. The cadmium will start to look very dark, the blue color will fade, and a brown colloidal precipitate forms. Pour off the 2% $CuSO_4$. Wash the cadmium-copper with reagent water (at least ten times) to remove all precipitated copper. The color of the cadmium so treated should be black. Add ammonium chloride reagent to the flask so that it covers the cadmium. The cadmium can be capped tightly and stored this way or used immediately to make a column.

NOTE: When a cadmium column significantly loses its efficiency, or the ammonium chloride the cadmium column is stored in appears cloudy, the column can be recleaned with acid and recoated with copper sulfate according to the above directions, except that it is only exposed to the copper sulfate for 15 seconds.

8.5.14.2 Packing the column: Disconnect the end of the plastic tubing which connects the cadmium column to the second set of mixing coils on the cartridges (farthest from the column). Tape the end high enough so the ammonium chloride reagent will not leak out of the column. Unscrew the column from the cartridge, fill the column with ammonium chloride, pack the column by adding small amounts of the treated cadmium to it and tapping the column so the cadmium is packed without allowing the air into the column.

8.6 Sample Handling

8.6.1 Samples are stored at -20 ± 2°C for a maximum 28 days.

8.7 Procedure

8.7.1 Sample preparation:

8.7.1.1 To each 30 mL screw cap test tube add 10 mL filtered sample. Add 10 mL reagent grade water to 3 test tubes as blanks.

8.7.1.2 Pipet 5.0 mL of the oxidizing reagent in all tubes. Cap test tubes tightly and very quickly due to volatilization. Include two oxidizing reagent blanks which contain only the oxidizing reagent.

NOTE: A precipitate will form with seawater samples which will not form with saline standards prepared with NaCl. If standards are made with substitute ocean water the precipitate will form.

8.7.1.3 Autoclave samples at 100 - 110° (between 3-4 psi) for 30 minutes on the liquid automatic cycle. No volatilization occurs after this point.

8.7.1.4 Remove tubes from autoclave and cool to room temperature (samples can be refrigerated for several days at this point if necessary to delay analysis).

8.7.2 Add 1.0 mL of buffer solution to each tube. The pH of the sample should be around 2.5 after the addition of buffer solution.

8.7.3 Allow both the colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding reagent water through the sample line.

8.7.4 Screw the column onto the cartridge. Untape the other end, and reconnect it to the color reagent line in the 10% phosphoric acid reagent. Once an acceptable baseline has been acquired, place the color reagent line into the color reagent.

8.7.5 Prepare a series of standard solutions covering the concentration range of the samples by diluting either the stock or standard solutions.

8.7.6 Analytical sequence: The samples and associated QC samples and standards should be run according to the following sequence.

8.7.6.1 Two high concentration calibration standards.

8.7.6.2 Two medium concentration calibration standards.

8.7.6.3 Two low concentration calibration standards.

8.7.6.4 Two method blanks.

8.7.6.5 Ten-twenty CBP samples.

8.7.6.6 One matrix spike sample.

8.7.6.7 One medium concentration calibration standard.

8.7.6.8 One method blank.

8.7.6.9 Steps 8.7.7.5 - 8.7.7.8 are repeated until are samples are analyzed or QC samples indicate that the system is out of control and recalibration is necessary.

8.7.6.10 One high concentration calibration standard.

8.7.6.11 One medium concentration calibration standard.

8.7.6.12 One low concentration calibration standard.

8.7.7 Switch sample line from distilled water to sampler and begin analysis.

8.7.8 Prepare appropriate standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of the samples by comparing sample peak heights with standard curve.

NOTE: Subtract the blank background response from the standards before preparing the standard curve.

8.7.9 Test the cadmium column efficiency by analyzing 2 cups of the 0.4 mg NO_3-N/L standard followed by one cup of the 0.4 mg NO_2-N/L standard. The column efficiency must be 90-110%. To ensure that the nitrate standards are correct, also analyze 2 cups of the EPA standard. Complete loading of sampler tray with quality control and unknown samples.

8.7.10 Record the stabilized potential of each unknown sample and convert the potential reading to the TDN concentration using the standard curve.

8.8 Quality Control

8.8.1 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section D.

8.8.2 Calibration

8.8.2.1 Linear calibration range: Calibration standards should bracket the range of CBP samples.

8.8.2.2 Correlation coefficient: The correlation coefficient must be 0.99 or better for the calibration curve to be used.

8.8.3 Method blank: see Chapter II, Section C.

8.8.4 Matrix spike sample: see Chapter II, Section C.

8.8.5 Laboratory duplicate: see Chapter II, Section C.

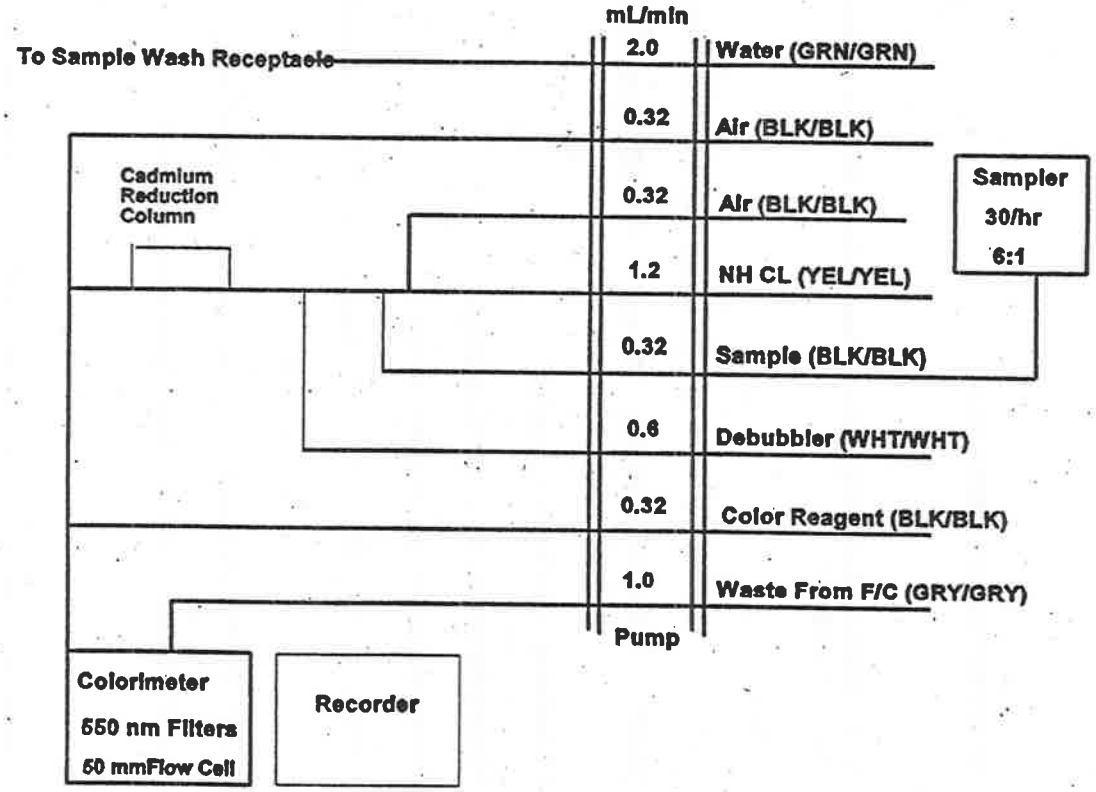
8.8.6 Reference materials: The laboratory must analyze a standard reference material once a year, as available.

8.9 References

Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 427, Method 419D (1975).

Annual Book of ASTM Standards, Part 31, "Water", Standard D 3867, p 453 (1976).

MANIFOLD CONFIGURATION FOR NITRATE/TOTAL DISSOLVED NITROGEN



8.10 Particulate Nitrogen

8.11 Scope and Application

8.12 This method covers the determination of particulate nitrogen in estuarine or sea water.

8.13 Summary of Method

8.13.1 The sample is filtered through a glass fiber filter and the filter is then placed in a combustion chamber for analysis.

8.13.2 The nitrogen determination is made by burning the glass fiber filter in a closed system in the presence of oxygen. The nitrogen in the sample is converted to molecular nitrogen (N_2) and oxides of nitrogen (NO_x) during the combustion. A carrier gas first transports the combustion products to a reduction tube where the NO_x is converted to N_2, and then to a thermal conductivity detector for measurement.

8.14 Apparatus and Materials

8.14.1 Carlo Erba NA 1500 Nitrogen/Carbon Analyzer, or other instrumentation.

8.14.2 Clean metal forceps.

8.14.3 Plastic syringe, 60 mL.

8.14.4 Filter holders with O-rings, 13 mm.

8.14.5 Dichromic acid washed DOC bottle.

8.14.6 Dichromic acid washed 50 mL graduated cylinder.

8.14.7 Glass transfer pipettes.

8.14.8 Desiccator.

8.14.9 Glass fiber filters, mm diameter, with a nominal pore size of 0.7 µm.

8.14.10 Muffle oven.

8.14.11 Analytical balance.

8.15 Reagents

8.15.1 Cleaning Solvents

8.15.1.1 Reagent Grade Water: see section 1.9.

8.16 Sample Handling

8.16.1 Filter preparation

8.16.1.1 Whatman glass fiber filters, or equivalent, are placed in a metal crucible, loosely arranged.

8.16.1.2 Place filters in muffle oven for 1.5 hours at 550°C.

8.16.1.3 Remove from muffle oven, and cover crucible with aluminum foil until cool.

8.16.1.4 Place muffled filters in clean labeled petri dishes until use.

8.16.2 Sample preparation

8.16.2.1 Remove foil pouches containing sample filters from freezer and open them.

8.16.2.2 Put foil pouches in drying oven at 50 ± 1 °C overnight.

8.16.2.3 Next day, remove foil pouches from oven, fold closed and desiccate until ready for analysis.

8.16.2.4 Clean the metal forceps, and ANA metal sealing tray using reagent water and a kimwipe. Never use acid on metal.

8.16.2.5 Using metal forceps, place a clean tin cup in filter loading devise.

8.16.2.6 With metal forceps remove glass fiber filter (sample) from the foil pouch, place in tin cup

8.16.2.7 Place sample in nickel sleeve into auto sampler wheel an desicate until analysis.

8.17 Procedure

8.17.1 Standards and Standard Curve Equipment Preparation

8.17.1.1 Tin cups must always be handled with clean metal forceps. The forceps, metal ANA sealing plate and metal spatula must be rinsed with fresh reagent water and completely dried with Kimwipes. Always work on a clean aluminum foil-covered surface whenever handling standards or samples.

8.17.1.2 Calibrate the electronic microbalance at the 200 mg range each day prior to weighing any standards.

8.17.2 Standardization

8.17.2.1 For PN analysis of glass fiber filters, Chloramine-T (N-chloro-p-toluenesulfonamide

sodium salt) or other suitable standards are used as the standard. Standards should weigh approximately 0.05 to 2.0 mg.

8.17.2.2 Using metal forceps to handle tin cups, weigh a clean tin cup (see cleaning procedure, 1.7.1) on calibrated microbalance, and tare the balance to eliminate the weight of the cup from the weight measurement.

8.17.2.3 Apply balance brake and remove cup. Place cup on clean ANA metal sealing plate and unfold cup somewhat.

8.17.2.4 Using a clean metal spatula, place approximately 0.05 to 2.0 mg Chloramine T into cup and, using forceps (2 pairs), seal tin cup.

8.17.2.5 Place sealed standard on microbalance, weigh, and record weight on data sheet.

8.17.2.6 For the standard curve, 3 blanks (empty clean tin cups), then 7 Chloramine T standards of known weight are analyzed on the Carlo Erba C/N analyzer in conjunction with the Carlo Erba E.A.G.E.R. computer software.

8.17.2.7 Chloramine T standards in the standard curve are analyzed as **STD** sample types and **CHLOR-T** standard types. Blanks are analyzed as **BLANK** sample types.

8.17.2.8 If the correlation coefficient for the standard curve is below the minimum acceptable value, up to 2 standards and/or 1 blank may be omitted from the standard curve (minimum of 2 blanks and 5 standards are required for a standard curve). A standard can be omitted by bypassing the standard in the sample table and recalculating the curve.

8.17.3 Analysis of Glass Fiber Filter Samples

8.17.3.1 Set flow rates as outlined in the Carlo Erba NA 1500 Nitrogen/Carbon Analyzer Instruction Manual. Set control panel parameters as follows:

Filament temperature	190°C
Oxygen injection stop	67 seconds
Peak enable	10 seconds
Cycle stop	410 seconds

(this may need to be increased if carbon peak on Chromatogram is not completed during cycle time).

8.17.3.2 Set autosampler tray with space #1 aligned with window on the front of the autosampler.

8.17.3.3 Place blanks and standards in spaces 1-10 of autosampler tray and, using the Carlo Erba E.A.G.E.R. computer software, generate the standard curve.

8.17.3.4 After an acceptable standard curve has been generated, place one wrapped sample or standard in each space of the autosampler tray and, using the E.A.G.E.R. software, and analyze the samples.

8.17.3.5 In order to demonstrate that the instrument was still in calibration at the end of the analytical run, the last sample analyzed in any series of analyses must be a standard.

8.17.3.6 Samples will have a known volume of sample water filtered onto them. Divide that volume (in mL) by 10, and place this value in the sample weight column of the sample table of the E.A.G.E.R. file.

8.17.3.7 The cycle time used in the E.A.G.E.R. program parameters should be 10 seconds longer than the cycle stop time set on the C/N analyzer instrument panel.

8.18 Quality Control

8.18.1 The correlation coefficient of the calibration curve must ≥ 0.990.

8.18.2 Run a duplicate of each sample, and a Chloramine T standard after every 5 samples (sample and it's duplicate count as one sample). If the samples are not all analyzed in duplicate, a minimum of one duplicate must be analyzed after every 10 samples, and at least 2 duplicates must be analyzed per analytical run.

8.18.3 The calibration check standards are analyzed as unknown sample types. Recovery must be within 90-110% of actual value. If recovery of a standard falls outside these limits, it is considered to be "out-of-control," and all samples analyzed after the last "in-control" standard must be reanalyzed.

8.18.4 Prepare and analyze at least two standards (2 "in-control" standards must occur consecutively before proceeding with analyses).

8.18.5 Re-prepare and reanalyze each sample which was analyzed after the last "in-control" standard.

9. Particulate Carbon

9.1 Scope and Application

9.1.1 This method covers the determination of particulate carbon in estuarine or sea water.

9.2 Summary of Method

9.2.1 The sample is filtered through a glass fiber filter and the filter is then placed in a combustion chamber for analysis.

9.2.2 The carbon determination is made by burning the glass fiber filter in a closed system in the presence of oxygen. The carbon in the sample is converted to carbon dioxide during the combustion. A carrier gas then transports the CO_2 to a thermal conductivity detector for measurement.

9.3 Apparatus and Materials

9.3.1 Carlo Erba NA 1500 Nitrogen/Carbon Analyzer, or other instrumentation.

9.3.2 Clean metal forceps.

9.3.3 Plastic syringe, 60 mL.

9.3.4 Filter holders with O-rings, 13 mm.

9.3.5 Hydrochloric acid washed DOC bottle.

9.3.6 Hydrochloric acid washed 50 mL graduated cylinder.

9.3.7 Glass transfer pipettes.

9.3.8 Desiccator.

9.3.9 Muffle oven.

9.3.10 Analytical balance.

9.4 Reagents

9.4.1 Reagent Grade Water: see section 1.9.

9.5 Sample Handling

9.5.1 Filter preparation

NOTE:

9.5.1.1 Whatman glass fiber filters are placed on aluminum foil in a muffle pan. Filters should not be touching each other.

9.5.1.2 Place filters in muffle oven for 15 minutes at 550°C.

9.5.1.3 Remove from muffle oven, and cover pan with aluminum foil until cool.

9.5.1.4 Wrap muffled filters in aluminum foil and desiccate until use.

9.5.2 Sample preparation

9.5.2.1 Remove foil pouches containing sample filters from freezer. Remove caps from foil pouches and place caps and foil pouches in muffle pan.

9.5.2.2 Put vials in oven at 50 ± 1 °C overnight.

9.5.2.3 Next day, remove foil pouches from oven, recap tightly, place foil pouches in divided cardboard box and desiccate until ready for analysis.

9.5.2.4 Clean the metal forceps, and ANA metal sealing tray using reagent water and a Kimwipe. Never use acid on metal.

9.5.2.5 Using metal forceps, place a clean tin cup in hole #2 of ANA metal sealing tray, and fan the top edges of the cup around edges of hole.

9.5.2.6 With metal forceps remove glass fiber filter (sample) from the glass vial, place in tin cup, seal cup using forceps (2 pair), and form into a ball which should be small enough to drop through the hole in the Carlo Erba C/N analyzer autosampler.

9.5.2.7 Replace foil-wrapped sample into the glass vial, recap, and desiccate until analysis.

9.6 Procedure

9.6.1 Cleaning C/N analyzer tin cups

NOTE: Use the following procedure only if you have unusual contamination.

9.6.1.1 Pour approximately 50 mL of chloroform/methanol cleaning solution into a 100 mL glass beaker. (Level of solution in beaker should allow tin cups standing upright to be completely submerged.)

9.6.1.2 Using clean metal forceps, submerge each cup individually into the chloroform/methanol solution and stand cup upright. Make sure all cups are completely submerged.

9.6.1.3 Cover beaker with aluminum foil and let stand for at least 30 minutes.

9.6.1.4 Decant the cleaning solution from the beaker into a chloroform/methanol waste bottle

without losing any cups. Remove any remaining solution from the beaker using a glass transfer pipette.

9.6.1.5 Using clean metal forceps, transfer cups individually to a 150 mL hydrochloric acid washed glass container of acetone. Hold cup momentarily in acetone then remove and drain acetone from cup. Do this twice for each cup.

9.6.1.6 Transfer cup to 150 mL hydrochloric acid washed glass container of fresh reagent water. Be sure cups are completely submerged and resting on the bottom of the container.

9.6.1.7 Cover container with aluminum foil and let stand at least 15 minutes.

9.6.1.8 Decant water from beaker and remove remaining water with a glass transfer pipette.

9.6.1.9 Place clean cups on a clean sheet of aluminum foil and dry in oven at 100 - 200°C for at least 2 hours. DO NOT exceed 200°C; tin cups will become brittle.

9.6.1.10 Wrap dry cups in aluminum foil or place into a glass, hydrochloric acid cleaned container and desiccate until use.

9.6.2 Standards and Standard Curve Equipment Preparation

9.6.2.1 Tin cups must always be handled with clean metal forceps. The forceps, metal ANA sealing plate and metal spatula must be rinsed with fresh reagent water and completely dried with Kimwipes. Always work on a clean aluminum foil-covered surface whenever handling standards or samples.

9.6.2.2 Calibrate the electronic microbalance at the 200 mg range each day prior to weighing any standards.

9.6.3 Standardization

9.6.3.1 For PC analysis of glass fiber filters, Chloramine-T (N-chloro-p-toluenesulfonamide sodium salt) or other suitable standards are used as the standard. Standards should weigh approximately 0.05 to 2.0 mg.

9.6.3.2 Using metal forceps to handle tin cups, weigh a clean tin cup on calibrated microbalance, and tare the balance to eliminate the weight of the cup from the weight measurement.

9.6.3.3 Apply balance brake and remove cup. Place cup on clean ANA metal sealing plate and unfold cup somewhat.

9.6.3.4 Using a clean metal spatula, place approximately 0.05 to 2.0 mg Chloramine T into cup and, using forceps (2 pairs), seal tin cup.

9.6.3.5 Place sealed standard on microbalance, weigh, and record weight on data sheet.

9.6.3.6 For the standard curve, 3 blanks (empty clean tin cups), then 7 Chloramine T standards of known weight are analyzed on the Carlo Erba C/N analyzer in conjunction with the Carlo Erba E.A.G.E.R. computer software.

9.6.3.7 Chloramine T standards in the standard curve are analyzed as **STD** sample types and **CHLOR-T** standard types. Blanks are analyzed as **BLANK** sample types.

9.6.3.8 If the correlation coefficient for the standard curve is below the minimum acceptable value, for a maximum 2 standards and/or 1 blank may be omitted from the standard curve (minimum of 2 blanks and 5 standards are required for a standard curve). A standard can be omitted by bypassing the standard in the sample table and recalculating the curve.

9.6.4 Analysis of Glass Fiber Filter Samples

9.6.4.1 Set flow rates as outlined in the Carlo Erba NA 1500 Nitrogen/Carbon Analyzer Instruction Manual. Set control panel parameters as follows:

Filament temperature	190°C
Oxygen injection stop	67 seconds
Peak enable	10 seconds
Cycle stop	410 seconds

(this may need to be increased if carbon peak on Chromatogram is not completed during cycle time).

9.6.4.2 Set autosampler tray with space #1 aligned with window on the front of the autosampler.

9.6.4.3 Place blanks and standards in spaces 1-10 of autosampler tray and, using the Carlo Erba E.A.G.E.R. computer software, generate the standard curve.

9.6.4.4 After an acceptable standard curve has been generated, place one wrapped sample or standard in each space of the autosampler tray and, using the E.A.G.E.R. software, and analyze the samples.

9.6.4.5 In order to demonstrate that the instrument was still in calibration at the end of the analytical run, the last sample analyzed in any series of analyses must be a standard.

9.6.4.6 Samples will have a known volume of sample water filtered onto them. Divide that volume (in mL) by 10, and place this value in the sample weight column of the sample table of the E.A.G.E.R. file.

9.6.4.7 The cycle time used in the E.A.G.E.R. program parameters should be 10 seconds longer than the cycle stop time set on the C/N analyzer instrument panel.

9.7 Quality Control

9.7.1 The correlation coefficient of the calibration curve must greater than or equal to 0.990.

9.7.2 Run a duplicate of each sample, and a Chloramine T standard after every 5 samples (sample and it's duplicate count as one sample). If the samples are not all analyzed in duplicate, a minimum of one duplicate must be analyzed after every 10 samples, and at least 2 duplicates must be analyzed per analytical run.

9.7.3 The calibration check standards are analyzed as unknown sample types. Recovery must be within 90-110% of actual value. If recovery of a standard falls outside these limits, it is considered to be "out-of-control," and all samples analyzed after the last "in-control" standard must be reanalyzed.

9.7.4 Prepare and analyze at least two standards (2 "in-control" standards must occur consecutively before proceeding with analyses).

9.7.5 Re-prepare and reanalyze each sample which was analyzed after the last "in-control" standard.

10. Dissolved Organic Carbon

10.1 Scope and Application

10.1.1 This method includes the measurement of dissolved organic carbon in surface and saline waters. The method is most applicable to measurement of dissolved organic carbon above 1 mg/L.

10.2 Summary of Method

10.2.1 The sample is filtered, acidified to a pH of 3, and purged with high purity air immediately prior to analysis in order to remove inorganic carbon. The dissolved organic carbon is converted to carbon dioxide (CO_2) by catalytic combustion using a platinum catalyst at 680 ± 2°C. Carbon atoms are oxidized into carbon dioxide which is measured by the nondispersive infrared detector. The amount of CO_2 is directly proportional to the concentration of dissolved carbonaceous material in the sample.

10.3 Interferences

10.3.1 Carbonate and bicarbonate carbon represent an interference under the terms of this test and must be removed or accounted for in the final calculation. (Frequently removed by sparging sample with high purity air immediately prior to sample analysis.)

10.3.2 This procedure is applicable only to homogeneous samples which can be injected into the apparatus reproducibly by means of a microliter type syringe or pipette. The openings of the syringe or pipette limit the maximum size of particles which may be included in the sample.

10.4 Apparatus and Materials

10.4.1 TOC analyzer equipped with a platinum catalyst and a nondispersive infrared detector.

10.4.1.1 A number of companies manufacture systems for measuring carbonaceous material in liquid samples. Considerations should be made as to the types of samples to be analyzed, the expected concentration range, and forms of carbon to be measured.

10.4.1.2 No specific analyzer is recommended as superior, however, the analyzer being used must have the capacity to maintain a combustion temperature of 680 ± 2°C.

10.4.2 Glassware: Because carbon contamination is difficult to avoid, all glassware must be stringently cleaned. One method is to wash with 10% HCl, rinse with DI water, rinse with acetone, rinse with DI water, and dry in a 100°C oven. A second method is to wash with 10% HCl, rinse with DI water, and place in muffle furnace at 450 ± 2°C for two hours.

10.5 Reagents

10.5.1 Reagent Grade Water: see section 1.9.

10.5.2 Potassium Hydrogen Phthalate, stock solution, 1000 mg carbon/L: Dissolve 0.2128 g of potassium hydrogen phthalate (Primary Standard Grade) in distilled water and dilute to 100.0 mL.

NOTE: Sodium oxalate and acetic acid are not recommended for stock solutions.

10.5.3 Potassium Hydrogen Phthalate, standard solutions: Prepare at least four standard solutions from the stock solution by dilution with distilled water and add 4 mL of 6 N HCl/liter to each.

10.5.4 Carbonate-bicarbonate, standard solution: Prepare a series of standards similar to step 10.5.3. A minimum of three standards and a blank must be used for calibration.

NOTE: This standard is not required by some instruments.

10.5.5 Blank Solution: Use the same distilled water (or similar quality water) used for the preparation of the standard solutions.

10.5.6 Hydrochloric Acid (HCl), 6N.

10.6 Sample Handling

10.6.1 Samples must be acidified to a pH of less then or equal to 3 with H_2SO_4 or HCland stored at 4 ± 2°C if the sample will be analyzed within 28 days. If the sample will not be analyzed within 28 days, freeze the sample prior to acidification and store it at -20 ± 2°C.

10.6.2 Sampling and storage of samples in glass bottles is preferable. Sampling and storage in plastic bottles such as conventional polyethylene and cubitainers is permissible if it is established that the containers do not contribute contaminating organics to the samples or alter the carbon concentration. Some plastics actually absorb carbon out of samples.

NOTE: A brief study performed in an EPA Laboratory indicated that distilled water stored in new, one quart cubitainers did not show any increase in organic carbon after two weeks exposure.

10.6.3 Because of the possibility of oxidation or bacterial decomposition of some components of aqueous samples, the lapse of time between collection of samples and start of analysis should be kept to a minimum. Also, samples should be kept cool (4 ± 2°C) and protected from sunlight and atmospheric oxygen.

10.7 Procedure

10.7.1 The pH of the filtered samples is adjusted to less than 3 using 6N HCl.

NOTE: Under normal conditions, the sample should arrive at the laboratory as a filtrate. The Contractor shall ensure that all DOC samples have been filtered as required for the analysis.

10.7.2 The compressed air is turned on and the TOC Analyzer is allowed to come to steady state at 680 ± 2°C and in accordance with manufacturer's specifications.

10.7.3 Set conditions for automated analysis per manufacturer's specifications.

10.7.4 Check syringe position with injection port, make sure compressed air is on, and make sure SPARGE switch is on if sparging is required.

10.7.5 For calibration of the instrument, it is recommended that a series of at least four to five standards encompassing the expected concentration range of the samples be used.

10.7.6 Follow manufacturer's instructions for calibration.

10.7.7 Analytical sequence: The following sequence is reccommended for sample analysis.

10.7.7.1 Four to five calibration standards with concentrations within the linear range of the test.

10.7.7.2 Two method blanks.

10.7.7.3 Ten CBP samples.

10.7.7.4 One matrix spike sample and one sample duplicate.

10.7.7.5 One medium concentration calibration standard.

10.7.7.6 One method blank.

10.7.7.7 Steps 10.7.7.3 - 10.7.7.6 are repeated until are samples are analyzed or QC samples indicate that the system is out of control and recalibration is necessary.

10.7.7.8 One high concentration calibration standard.

10.7.7.9 One medium concentration calibration standard.

10.7.7.10 One low concentration calibration standard.

10.8 Quality Control

10.8.1 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section E.

10.8.2 Calibration

10.8.2.1 Linear calibration range: Calibration standards should bracket the range of CBP samples.

10.8.2.2 Correlation coefficient: The correlation coefficient must be 0.99 or better for the calibration curve to be used.

10.8.3 Method blank: see Chapter II, section D.

10.8.4 Matrix spike sample: see Chapter II, section D.

10.8.5 Reference materials: The laboratory must analyze a standard reference material once a year, as available.

10.8.6 All CBP samples must be analyzed a minimum of two times.

10.9 References

Annual Book of ASTM Standards, Part 31, "Water", Standard D 2574-79, p 469 (1976).

Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 532, Method 505, (1975).

11. Biochemical Oxygen Demand, 5 Day

11.1 Scope and Application

11.1.1 The 5-day Biochemical Oxygen Demand (BOD_5) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of surface waters, wastewaters, effluents, and polluted waters. This test measures the amount of oxygen used over a 5-day incubation period for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to oxidize inorganic material such as sulfides and ferrous iron. It also may measure the oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor.

11.2 Summary of Method

11.2.1 Upon arrival in the laboratory, each BOD_5 sample is brought to approximately 20°C. Sample dilutions are made so as to approximate a final DO of at least 1 mg/L and a DO uptake of at least 2 mg/L. Diluted samples are neutralized and treated with a nitrification inhibitor, if required, and an initial dissolved oxygen (DO) reading is taken and recorded for each sample. The BOD bottles are sealed with DI water, capped, and incubated at 20 ± 1°C for a period of 5 days. After the 5-day incubation period, a final DO reading is made and the BOD_5 is calculated from the difference between the initial and final DO.

11.3 Interferences

11.3.1 Nitrogenous oxygen demand as a result of the oxidation of reduced forms of nitrogen by microorganisms is the most common interference in determining BOD_5 values.

11.3.1.1 The extent of nitrogenous demand during the 5-day incubation period depends on the presence of microorganisms capable of carrying out the oxidation.

11.3.1.2 Nitrogenous oxygen demand can be prevented by the use of an inhibitory chemical. If an inhibitory chemical is not used, the oxygen demand measured is the sum of carbonaceous ($CBOD_5$) and nitrogenous ($NBOD_5$) demands.

11.3.2 Because the BOD_5 test is a bioassay, its results can be influenced greatly by the presence of toxicants such as residual chlorine and heavy metals. Care should be taken in the cleaning of glassware and sample containers, and in the preparation of reagents.

11.3.3 Photosynthetic production of DO may also influence BOD_5 results. Care should be taken to store and incubate BOD_5 samples in the dark.

11.4 Apparatus and Materials

11.4.1 Incubation bottles, 250- or 300-mL glass-stoppered BOD bottles with plastic caps. Clean bottles, stoppers, and caps with a laboratory detergent, rinse thoroughly, and drain before use.

11.4.2 Air incubator, thermostatically controlled at 20 ± 1 °C.

11.4.3 DO meter and probe, calibrated.

11.5 Reagents

NOTE: Discard reagents that show any sign of biological growth.

11.5.1 Phosphate Buffer Solution: pH 7.

11.5.2 Nitrification Inhibitor: 2-chloro-6-(trichloro methyl) pyridine.

11.5.3 Glucose-Glutamic Acid Solution: Dry reagent grade glucose and reagent grade glutamic acid at 103 ± 2 °C for 1 hour. Add 150 mg glucose and 150 mg glutamic acid to distilled water and dilute to 1 L. Prepare fresh before each use.

11.5.4 Magnesium Sulfate Solution: Dissolve 22.5 g $MgSO_4 \cdot 7H_2O$ in distilled water and dilute to 1 L.

11.5.5 Calcium Chloride Solution: Dissolve 27.5 g $CaCl_2$ in distilled water and dilute to 1 L.

11.5.6 Ferric chloride solution: Dissolve 0.25 g $FeCl_3 \cdot 6H_2O$ in distilled water and dilute to 1 L.

11.5.7 Acid and alkali solutions, 1N, for neutralizing caustic or acidic samples:

11.5.7.1 Acid: Slowly and while stirring, add 28 mL concentrated sulfuric acid (H_2SO_4) to distilled water. Dilute to 1 L.

11.5.7.2 Alkali: Dissolve 40 g sodium hydroxide (NaOH) in distilled water. Dilute to 1 L.

11.5.8 Dilution water: Place the desired amount of ASTM type II water (see section 1.9) in a suitable container. For every liter of water add 1 mL each of phosphate buffer, $MgSO_4$, $CaCl_2$, and $FeCl_3$ solutions. Before use bring to 20 ± 2 °C and saturate with DO by shaking in a partially filled bottle or by aerating with organic-free filtered air.

11.6 Sample Handling

11.6.1 Sample holding time: The recommended holding time is 6 hours or less. The maximum allowable holding time is 48 hours from sample collection.

11.6.2 Sample preservation and storage: Samples for BOD_5 analysis may degrade significantly during storage and analysis, resulting in low BOD_5 values.

11.6.2.1 If analysis is not started within 2 hours of collection, keep samples in the dark and at 4 ± 2°C.

11.6.2.2 If analysis is started within 2 hours of collection, cold storage is unnecessary.

11.7 Procedure

11.7.1 Sample preparation

11.7.1.1 Allow the samples to stabilize to 20 ± 2°C.

11.7.1.2 Neutralize samples to pH 6.5 to 7.5 with either the 1N H_2SO_4 solution or the 1N NaOH solution.

11.7.1.3 Using the dilution water from 12.5.8, make several dilutions of each sample to obtain a final DO of at least 1 mg/L and a DO uptake of at least 2 mg/L. Dilutions may be made directly in the BOD bottles by adding the desired volume of sample and filling the BOD bottle to about 2/3 with dilution water. Experience with the samples from specific monitoring stations may permit use of a smaller number of dilutions. In general, dilutions of 25 to 100 percent may be needed.

11.7.1.4 For each sample dilution, pour approximately 200 mL of the diluted sample into a cleaned BOD bottle and add 3 mg 2-chloro-6-(trichloro methyl) pyridine.

11.7.1.5 Fill the BOD bottle to the top with either dilution water or diluted sample, depending on whether the dilution was made in the BOD bottle or in a graduated cylinder.

11.7.2 Initial DO measurement

11.7.2.1 Using a calibrated DO meter and probe, measure and record the DO for each field and QC sample.

11.7.2.2 Reduce the DO in samples containing more than 9 mg DO/L at 20 ± 2°C by vigorous shaking or by aeration with clean, filtered compressed air. Measure and record the DO for the sample.

11.7.2.3 Rinse the DO electrode between determinations to prevent cross-contamination of samples.

11.7.3 Incubation

11.7.3.1 Replace any displaced contents and gently insert the glass stopper so that it displaces all air, leaving no bubbles.

11.7.3.2 Cap and water-seal the stoppered bottle and incubate for 5 days at 20 ± 1°C.

11.7.4 Final DO measurement

11.7.4.1 Using a calibrated DO meter and probe, measure and record the DO for each field and QC sample.

11.8 Quality Control

11.8.1 Glucose-glutamic acid check

11.8.1.1 Check dilution water quality and analytical technique at a frequency of no less than once every six months.

11.8.1.2 Determine BOD_5 at 20 ± 1°C for a 2 percent dilution of the glucose-glutamic acid standard check solution using the same techniques used to determine BOD_5 for the CBP samples.

11.8.2 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section D.

11.8.3 Calibration

11.8.3.1 Linear calibration range: Calibration standards should bracket the range of CBP samples.

11.8.3.2 Correlation coefficient: The correlation coefficient must be 0.99 or better for the calibration curve to be used.

11.8.4 Method blank: The laboratory must analyze method blanks of both substitute ocean water and reagent water at a minimum of every 10 CBP samples. Method blank data are used to assess contamination from the laboratory environment. If the concentration of analyte in the reagents blank exceeds the MDL, then laboratory or reagent contamination should be suspected. If the analyte concentration is 5 times the MDL or greater, then corrective action is required and reanalysis if possible.

11.8.5 Matrix spike sample: The laboratory should add a known amount of analyte to a minimum of 10% of the routine samples or one sample per sample set, whichever is greater. The analyte concentration should be high enough to be seen above the original concentration of the sample and should not be less than four times the calculated minimum detectable concentration.

11.8.5.1 Calculate the percent recovery of analyte from the matrix spike sample using the following equation:

$$Matrix\ Spike\ Recovery = \frac{SSR - SR}{SA} \times 100 \qquad \text{(Eq. IV.21)}$$

where,

SSR = Spike sample result
SR = Sample result
SA = Spike added

11.8.5.2 If the recovery of the analyte falls outside the designated range, repeat the spike after checking for obvious sources of error. If the recovery of the replicated spike of the same sample again falls outside the designated range, the recovery problem encountered with the spiked sample is judged to be matrix related, not system related and no further corrective action is required.

11.8.6 Laboratory duplicate: A laboratory duplicate must be analyzed once for every 10 CBP samples.

11.8.6.1 The precision is measured by calculating the coefficient of variation (CV) using the following equation:

$$CV = \frac{SD}{MEAN} \times 100, \text{ where } SD = \sqrt{\frac{(X-\overline{X})^2}{(N-1)}} \qquad \text{(Eq. IV.22)}$$

where,

CV = Coefficient of variation
SD = Standard deviation
Mean = Mean of the replicate readings
N = Number of samples

11.8.6.2 If the CV does not fall within the control limits listed in Table II.1, corrective action should be taken.

11.8.7 Reference materials: The laboratory must analyze a standard reference material once a year, as available.

11.9 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater, 17th Edition.

12. Chlorophyll and Phaeophytin

12.1 Scope and Application

12.1.1 This spectrophotometric method is used in the determination of chlorophyll *a*, *b*, and *c*, phaeophytin-*a*, and carotenoids. This method can be used to estimate phytoplankton biomass.

12.2 Summary of Method

12.2.1 The reference for this method is ASTM Method D3731-79. In brief, algal cells are ground in aqueous acetone to extract the pigments. The extract is analyzed using a spectrophotometer to measure the absorbances at the correct wavelengths.

12.3 Apparatus and Materials

12.3.1 Laboratory coat: worn at all times and with an apron when handling acids.

12.3.2 Protective eyewear: worn at all times.

12.3.3 PVC gloves: worn at all times.

12.3.4 Glass fiber filter: Whatman GF/F or equivalent.

12.3.5 Centrifuge.

12.3.6 Dual beam spectrophotometer: or scanning spectrophotometer with matched cuvettes.

12.3.7 Tissue Grinder.

12.3.8 Filtration Apparatus

12.4 Reagents

12.4.1 Solvents:

12.4.1.1 Hydrochloric acid (1N), Hcl.

12.4.1.2 Sodium bicarbonate solution (1N), ($NaH(CO_3)_2$), dissolve 8.4 g sodium bicarbonate in 100 mL water.

12.4.1.3 Magnesium carbonate suspension, ($MgCO_3$), add 1 g finely powdered magnesium carbonate to 100 Ml water.

12.4.1.4 Aqueous acetone (90%), add 1 part water to 9 parts of reagent grade acetone, add 5 drops of $NaH(CO_3)_2$ solution to every volume, made within 24-48 hours of time of use.

12.4.2 Reagent Grade Water: See section 1.9.

12.4.2.1 Reference standards: use EPA SRM reference standards if provided.

12.5 Sample Handling

12.5.1 After the addition of magnesium carbonate, samples can be held for 24 hours at 0-4°C. The extract can be store at -20 ± 2°C for a maximum 30 days.

12.6 [illegible]uon Procedure

12.6.1 Using a 47 mm GF/F, Pour a measured amount of well mixed sample (typically 500ml) through filter. Apply vacuum to complete filtration process.

12.6.2 Add approximately 1 ml of Magnesium Carbonate Suspension and apply vacuum to dryness.

12.6.3 Release vacuum and remove filter. Store as required. Record sample volume filtered.

12.7 Grinding Procedure

12.7.1 Place filter in grinding vessel and add 2-3 ml of 90% acetone.

12.7.2 Insert pestle into grinding vessel and turn on grinder.

12.7.3 Grind filter for approximately 2 minutes being sure there are no discernible pieces remaining.

12.7.4 Pull pestle from vessel and rinse with 90% acetone.

12.7.5 Transfer sample to centrifuge tube using a glass funnel and 90% acetone for rinsing.

12.7.6 Record filtration volume.

12.8 Procedure

12.8.1 Adjust the temperature of the centrifuge so that unit cools to 4 ± 2°C. Centrifuge samples for 30 minutes at 4500 rpm. Keep centrifuged samples level, cool, and in a dark box.

12.8.2 Zero the dual beam spectrophotometer at 750 nm using the 90% acetone reagent. After zeroing the spectrophotometer, leave the cuvette in the reference cell.

12.8.3 Using a matched pair of cuvettes, one cuvette is used to zero the spectrophotometer at each wavelength; and the other cuvette contains the sample, so that the chlorophyll sample is not transferred back to the chlorophyll tube after the initial turbidity absorbance is obtained at the 750 nm wavelength. To account for any differences between the two cuvettes, the cuvette which will contain the samples is first filled with 90% acetone and the absorbance is read on the spectrophotometer. If this absorbance is not zero, the value obtained is used to adjust all of the chlorophyll readings. The acetone in the reference and zeroing cuvettes must be rehomogenized periodically throughout the analysis.

12.8.4 Record sample volume filtered and extract volume in screw-cap test tube onto the data sheet. Note that the volume of the filter residue in the bottom of the centrifuge tube must be subtracted from the total volume to obtain extract volume. Then carefully dispense the sample into the sample cuvette using a disposable glass pipette, and measure absorbances at the following wavelengths: 750 nm, 664 nm, 647 nm, 630 nm, 480 nm, and 510 nm.

12.8.5 Re-zero spectrophotometer with 90% acetone before reading at each wavelength. After the 510 nm reading is taken, add 2 drops of 1N HCL. After 1 minute, but not longer than 2 minutes after acidification, measure sample absorbances at 750 nm and 665 nm. Zero with the blank at each absorbance before reading.

12.9 Quality Control

12.9.1 The initial absorbance reading at 750 nm must be less than or equal to .007, or sample(s) must be re-centrifuged. If after re-centrifugation the absorbance reading at 750nm is greater than .007, continue to measure the absorbances at the rest of the wavelengths and write in the comment section that the sample had been recentrifuged.

12.9.2 It is especially important to maintain the spectrophotometers in peak operating condition. This should be confirmed by the following guidelines:

12.9.2.1 Analyzing an EPA SRM reference standard for chlorophyll analysis if provided.

12.9.2.2 Periodic evaluation of the slopes of calibration curves from spectrophotometer analyses for other parameters for which there are reliable standards (e.g. orthophosphate, nitrite, etc.). If significant slope deviation or consistent unidirectional slope change over time is noted, an alternate spectrophotometer should be used until the problem is corrected by an authorized repair person.

12.9.2.3 The holmium oxide absorption spectrum should be analyzed at least annually or when problems are suspected. Details are not provided here since this and subsequent evaluation should be performed only by or under direct supervision of experienced personnel.

12.9.3 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section D.

12.9.4 Method blank: see Chapter II, Section C.

12.9.5 Laboratory duplicate: see Chapter II, Section C.

12.9.6 Reference materials: The laboratory must analyze a standard reference material once a year, as available.

12.10 References

American Public Health Association. Standard Methods for the Examination of Water and Wastewater, 17th Edition.

Parsons, T., Y. Maita and C . Lalli. 1984. A Manual of Chemical and Biological Methods for Seawater Analysis. Pergamon Press, pp. 101-112.

13. Total Suspended Solids

13.1 Scope and Application

13.1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes. The practical range of the determination is 2 to 20,000 mg/L.

13.2 Summary of Method

13.2.1 A well-mixed sample is filtered through a glass-fiber filter, and the residue retained on the filter is dried to constant weight at 103 - 105°C.

13.3 Interferences

13.3.1 Filtration apparatus, filter material, pre-washing, post-washing, and drying temperature are specified because these variables have been shown to affect the results.

13.3.2 Samples high in filterable residue (dissolved solids), such as saline waters, brines and some wastes, may be subject to a positive interference. Care must be taken in selecting the filtering apparatus so that washing of the filter and any dissolved solids in the filter minimizes this potential interference.

13.4 Apparatus and Materials

13.4.1 Glass fiber filter discs: Whatman 47 mm diameter,.70 µm pore size, or equivalent.

13.4.2 Filter support: Filtering apparatus with reservoir and a coarse (40-60 microns) fritted disc as a filter support.

NOTE: Many funnel designs are available in glass or porcelain. Some of the most common are Hirsch or Büchner funnels, membrane filter holders and Gooch crucibles. All are available with coarse fitted disc.

13.4.3 Suction flask.

13.4.4 Drying oven: Capable of maintaining a temperature of 103-105°C.

13.4.5 Desiccator.

13.4.6 Analytical balance: Capable of weighing to 0.1 mg.

13.5 Sample Handling

13.5.1 Non-representative particulates such as leaves, sticks, fish, and lumps of fecal matter should be excluded from the sample if it is determined that their inclusion is not desired in the final result.

13.5.2 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration 4 ± 2°C, or freezing -20 ± 2°C to minimize microbiological decomposition of solids, is recommended.

13.6 Procedure

13.6.1 Preparation of filters:

13.6.1.1 Number glass fiber filters with a fine-point indelible ink pen. Allow ink to dry for 24 hours.

13.6.1.2 Place the numbered glass fiber filter on the membrane filter apparatus.

13.6.1.3 While vacuum is applied, wash the filter with three successive 30 ml volumes of deionized, distilled water. Allow the vacuum pump to run until the filters are "dry".

13.6.1.4 Remove the filter from membrane filter apparatus and dry in an oven at 103 - 105°C for four hours.

13.6.1.5 Cool in a desiccator, weigh each filter, record the filter number and weight in a notebook set aside for this purpose, and return the filter to the drying tray.

13.6.1.6 Return the tray to the oven, 103 - 105°C , for one hour. Repeat the drying cycle until a constant weight is obtained (weight verification 0.5 mg or less is obtained).

13.6.1.7 Record the second filter weight in the notebook and store the filters in aluminum cups in an oven at 60 ± 5°C, or in a desiccator until needed.

13.6.2 Sample analysis:

13.6.2.1 List filter numbers and sample indefications on Suspended Solids sheet.

13.6.2.2 Assemble the filtering apparatus, place a pre-weighed numbered filter on it, and begin suction.

13.6.2.3 Shake the sample vigorously and with a small portion of sample. Quantitatively measure 500 mL of sample into the graduated cylinder. Record the volume of sample used beside the corresponding filter and sample on the Suspended Solids sheet.

NOTE: A smaller volume may be used if sample contains a large amount of suspended matter.

13.6.2.4 Pour the measured sample volume onto the filter. Remove all traces of water by continuing to apply vacuum after sample has passed through.

13.6.2.5 With suction on, wash the filter, non-filterable residue and filter funnel wall with three portions of deionized, distilled water allowing complete drainage between washing. Remove all traces of water by continuing to apply vacuum after water has passed through.

13.6.2.6 Carefully remove the filter from the filter support. Alternatively, remove crucible and filter from crucible adapter. Dry at least one hour at 103-105°C. Cool in a desiccator and

weigh. Repeat the drying cycle until a constant weight is obtained (weight loss of 0.5 mg or less is obtained). Record both weights on the data sheet and determine the concentration of the Suspended Solids in mg/L.

13.7 Quality Control

13.7.1 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section E.

13.7.2 Method blank: see Chapter II, Section D.

13.7.3 Laboratory duplicate: see Chapter II, Section D.

13.7.4 Reference materials: The laboratory must analyze a standard reference material once a year, as available.

13.8 References

U.S. EPA, 1979, "Methods for Chemical Analysis of Water and Wastes", Method 160.2.

14. Fixed Suspended Solids

14.1 Scope and Application

14.1.1 This method is used to obtain the amount of fixed suspended solids present in the solid fraction of sewage, activated sludge, industrial wastes, or bottom sediments.

14.2 Summary of Method

14.2.1 The residue obtained from the determination of total suspended solids is ignited at 550 ± 2°C in a muffle furnace. The remaining solids after ignition is reported as mg fixed suspended solids/L.

14.3 Interferences

14.3.1 The principal source of error in the determination is failure to obtain a representative sample.

14.3.2 The test is subject to many errors due to loss of water of crystallization, loss of volatile organic matter prior to combustion, incomplete oxidation of certain complex organics, and decomposition of mineral salts during combustion.

14.4 Apparatus and Materials

14.4.1 Filtration flask.

14.4.2 Drying oven: Capable of maintaining a temperature of 103-105 ± 2°C.

14.4.3 Muffle furnace.

14.4.4 Desiccator.

14.4.5 Analytical balance: Capable of weighing to 0.1 mg.

14.5 Sample Handling

14.5.1 Preservation of the sample is not practical; analysis should begin as soon as possible. Refrigeration 4 ± 2°C, or freezing -20 ± 2°C to minimize microbiological decomposition of solids is recommended.

14.6 Procedure

14.6.1 Ignite the residue from the suspended solids procedure at 550 ± 50°C for approximately 15 to 20 minutes in a muffle furnace to a constant weight.

14.6.2 Let the dish or filter disk partially cool in air until most of the heat has dissipated. Transfer to a desiccator and cool to room temperature. Repeat the drying cycle until a constant weight is obtained (weight verification of 0.5 mg or less is obtained). Record the weight on the data sheet and determine the

concentration of the fixed suspended solids by using the following equation in mg/L by subtracting the weight of the residue plus the dish after ignition from the weight of the dish times 1000 over the volume of sample used.

$$Concentration \quad (mg/L) = \frac{(W_{RD} - W_D) \times 1000}{V} \qquad \text{(Eq. IV.25)}$$

where,

W_{RD} = Weight of residue and dish
W_D = Weight of dish
V = Volume of sample filtered

14.7 Quality Control

14.7.1 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section E.

14.7.2 Method blank: see Chapter II, Section C.

14.7.3 Laboratory duplicate: see Chapter II, Section C.

14.7.4 Reference materials: The laboratory must analyze a standard reference material once a year, as available.

14.8 References

U.S. EPA, 1979, Methods for Chemical Analysis of Water and Wastes, Method 160.2.

Annual Book of ASTM Standards, "Fixed and Volatile Solids Ignited at 550°C", Standard D 2540, Method E, p 2-77 (1980).

15. Silicates

15.1 Scope and Application

15.1.1 This method is applicable to drinking, surface, and saline waters, domestic and industrial wastes.

15.1.2 The working range of the method is approximately 0.01 to 1.4 mg/L of SiO_2.

15.2 Summary of Method

15.2.1 A well-mixed sample is filtered through a 0.45 µ Whatman GF/F. The filtrate, a silicamolybdate in acidic solution, is reduced to "molybdenum blue" by ascorbic acid. Oxalic acid is introduced to the sample stream before the addition of ascorbic acid to eliminate interference from phosphates.

15.3 Interferences

15.3.1 Excessive color and/or turbidity interfere. Correct by running blanks prepared without addition of the ammonium molybdate solution.

15.3.2 Large amounts of iron and sulfide interfere.

15.3.3 Contact with glass should be minimized, silica free reagents should be used as much as possible. A blank should be run.

15.4 Apparatus and Materials

15.4.1 Continuous flow automated analytical system equipped with an autosampler, manifold, proportional pump, colorimeter, phototube and recorder or computer based data system.

15.4.2 Appropriate glassware: Whenever possible, all reagents and standards should be made and stored in plastic containers. Contact with glass should be minimized.

15.5 Reagents

15.5.1 Reagent Grade Water: See section 1.9.

15.5.2 Ammonium Molybdate: To a one-liter volumetric flask, add approximately 500 mL of 0.1 N sulfuric acid (H_2SO_4). Dissolve 10 g of ammonium molybdate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$). Dilute to one liter with 0.1 N H_2SO_4. Store in an amber plastic container. This solution is stable for approximately one month at 4°C.

15.5.3 Oxalic Acid: Add approximately 900 mL of reagent water to a one liter volumetric flask. Dissolve 50 g of oxalic acid ($H_2C_2O_4$) (or 70 g of $(COOH)_2\cdot 2H_2O$) and dilute to one liter with reagent water stable indefinitely at 4°C.

15.5.4 Ascorbic Acid: To a one liter volumetric flask, add 500 mL of reagent water. Dissolve 17.6 g of ascorbic

acid ($C_6H_8O_6$), add 50 mL of acetone (CH_3COCH_3), mix, and dilute to one liter with reagent water stable at one month at 4°C.

15.5.5 Silica Stock Solution: In a one liter volumetric flask, add 500 mL of reagent water. Dissolve 1.88 g of sodium fluorosilicate (Na_2SiF_6) and dilute to volume with reagent water. Store in tightly stoppered plastic bottle at room temperature.

15.5.6 Silica Standard Solutions: Prepare at least four standard solutions from stock solution by dilution with reagent water. Prepare standard solutions on the day of analysis.

15.6 Sample Handling

15.6.1 Samples are filtered through a Whatman GF/F glass fiber filter or equivalent filter and stored at unacidified for 28 days 4°C .

15.7 Procedure

15.7.1 Allow both the colorimeter and recorder to warm up for 30 minutes. Obtain a stable baseline with all reagents, feeding reagent water through the sample line.

15.7.2 Analytical sequence: The following sequence is recommended for sample analysis..

15.7.2.1 Five calibration standards with concentrations within the linear range of the test.

15.7.2.2 Two method blanks.

15.7.2.3 Ten CBP samples.

15.7.2.4 One matrix spike sample and one sample duplicate.

15.7.2.5 One medium concentration calibration standard.

15.7.2.6 One method blank.

15.7.2.7 Steps 15.7.3.5 - 15.7.3.8 are repeated until are samples are analyzed or QC samples indicate that the system is out of control and recalibration is necessary.

15.7.2.8 One high concentration calibration standard.

15.7.2.9 One medium concentration calibration standard.

15.7.2.10 One low concentration calibration standard.

15.7.3 Switch sample line from distilled water to sampler and begin analysis.

15.7.4 Prepare appropriate standard curve by plotting peak heights of processed standards against known concentrations. Compute concentration of the samples by comparing sample peak heights with standard

curve.

NOTE: Subtract the blank background response from the standards before preparing the standard curve.

15.7.5 Record the stabilized potential of each unknown sample and convert the potential reading to the silica concentration using the standard curve.

15.8 Quality Control

15.8.1 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section E.

15.8.2 Calibration

15.8.2.1 Linear calibration range: Calibration standards should bracket the range of CBP samples.

15.8.2.2 Correlation coefficient: The correlation coefficient must be 0.99 or better for the calibration curve to be used.

15.8.3 Method blank: see Chapter II, Section D.

15.8.4 Matrix spike sample: see Chapter II, Section D.

15.8.5 Laboratory duplicate: see Chapter II, Section D.

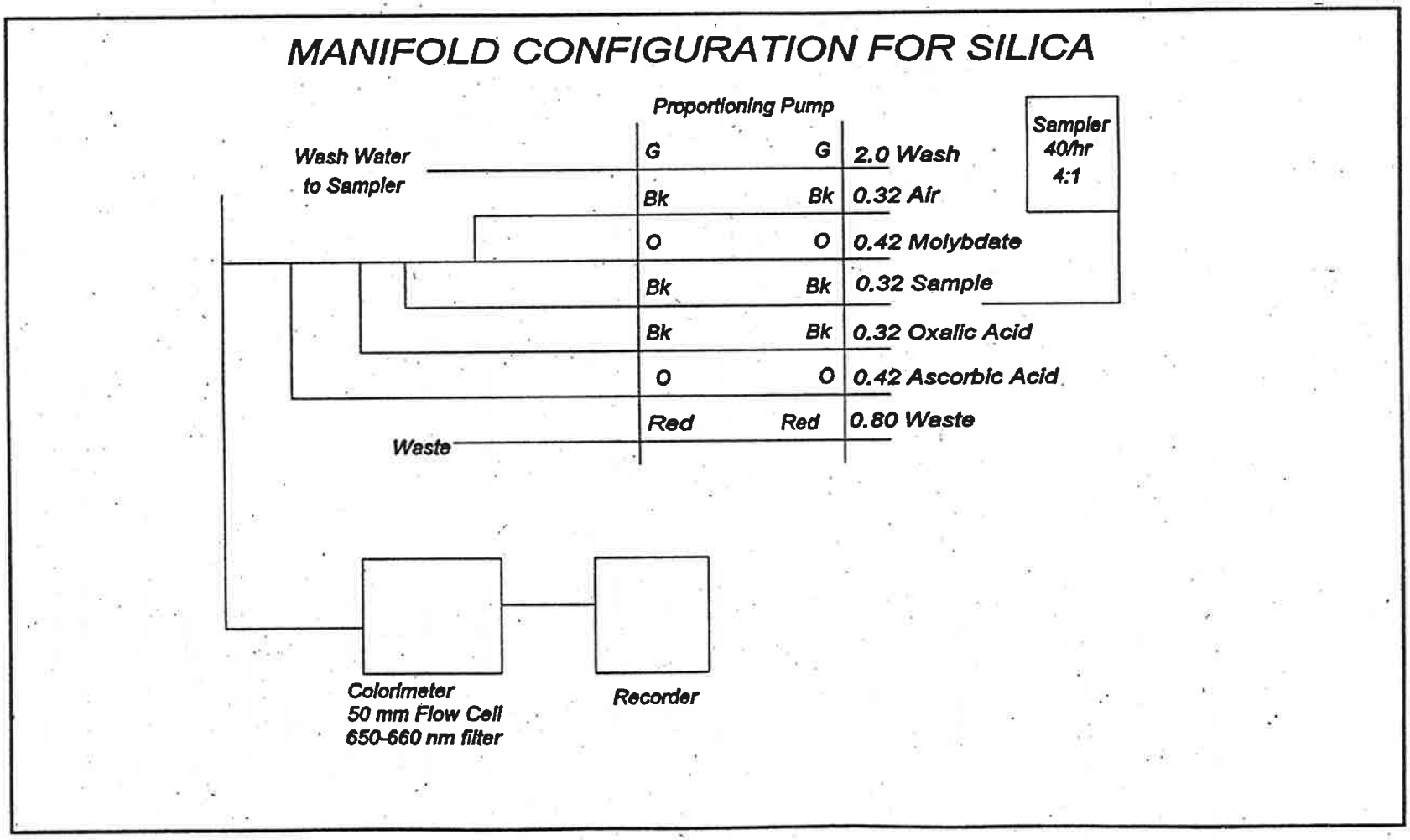
15.8.6 Reference materials: The laboratory must analyze a standard reference material once a year, as available.

15.9 References

Standard Methods for the Examination of Water and Wastewater, 14th Edition, p 487, Method 426 F (1975).

Annual Book of ASTM Standards, Part 31, "Water", Standard D 859-68, p 401 (1976).

Standard Methods for Chemical Analyses of Water and Wastes, EPA-600/4-79-020, Edition 1978, p 370.1-1, Method 370.1 (1978).


MANIFOLD CONFIGURATION FOR SILICA
Proportioning Pump
Sampler
40/hr
4:1
Wash Water
to Sampler
G
G
2.0 Wash
Bk
Bk
0.32 Air
O
O
0.42 Molybdate
Bk
Bk
0.32 Sample
Bk
Bk
0.32 Oxalic Acid
O
O
0.42 Ascorbic Acid
Red
Red
0.80 Waste
Waste
Colorimeter
50 mm Flow Cell
650-660 nm filter
Recorder

16. Alkalinity

16.1 Scope and Application

16.1.1 The alkalinity of a water is its acid-neutralizing capacity, and it comprises the sum of all titrable bases. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known. While alkalinity values may include contributions from borates, phosphates, silicates, and other bases, the alkalinity of most surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content.

16.2 Summary of Method

16.2.1 Alkalinity is dependent upon the pH of the solution and is a measure of its quantitative capacity to neutralize a strong acid to a designated pH (hydroxyl ions are neutralized). In this instance, the initial pH is taken and the solution is carefully titrated with a standardized H_2SO_4 solution to a pH of 8.3 (if necessary) and then to a pH of 4.5. Carbonate and total alkalinity values are calculated directly from the titration data, and any existing bicarbonate alkalinity is calculated as the difference between total and carbonate alkalinities.

16.3 Interferences

16.3.1 Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium and clean electrode more frequently. Do not filter, dilute, concentrate, or alter the sample.

16.3.2 Dissolved gases contributing to alkalinity, such as CO_2, hydrogen sulfide, or ammonia, may be lost or gained during sampling, storage, or titration.

16.4 Apparatus and Materials

16.4.1 pH meter and electrode, calibrated according to manufacturer's specifications at pH 4, 7, and 10.

16.4.2 Buret, bororsilicate glass, of appropriate volume to contain enough titrant for at least one complete titration.

16.4.3 Titration vessels, the size and form will depend on the electrode and the sample size.

16.4.4 Parafilm.

16.4.5 Magnetic stirrer.

16.4.6 Pipets, volumetric.

16.4.7 Flasks, volumetric, 1-L.

16.4.8 Analytical balance, capable of weighing to 0.001 g and calibrated according to manufacturer's specifications using Class S weights.

16.5 Reagents

16.5.1 Certified pH buffer solutions for pH 4, 7, and 10.

16.5.2 Sodium Carbonate Solution, approximately 0.05N: Dry 3 to 5 g primary standard Na_2CO_3 at 250 ± 2°C for 4 hours and cool in desiccator. Weigh 2.5 ± 0.2 g (to the nearest mg), transfer to a 1-L volumetric flask, fill with approximately 500 mL of distilled water, swirl until the Na_2CO_3 is dissolved, and then fill the flask to the 1-L mark with distilled water. Do not keep for longer than 1 week.

16.5.3 Standard Sulfuric Acid Solution, 0.02N: Prepare acid solution of approximate normality. Standardize daily by potentiometric titration of Na_2CO_3 standard solution.

16.6 Sample Handling

16.6.1 Sample holding time: The recommended maximum holding time is 24 hours from sample collection.

16.6.2 Sample preservation and storage:

16.6.2.1 If analysis is not started within 2 hours of collection, keep samples at or below 4 ± 2°C.

16.6.2.2 If analysis is started within 2 hours of collection, cold storage is unnecessary.

16.6.3 To minimize loss or absorption of gases, avoid sample agitation and prolonged exposure to air.

16.7 Procedure

16.7.1 Calibrate the pH meter and electrode using certified buffer solutions at pH 4, 7, and 10. A fresh aliquot of each buffer should be used daily.

16.7.2 Rinse electrode with distilled water.

16.7.3 Rinse and fill burette with H_2SO_4 solution.

16.7.4 Standardize the H_2SO_4 solution by titrating 10.00 mL of the 0.05N Na_2CO_3 standard solution. Please note that the actual normality of the Na_2CO_3 solution must be calculated based on the exact weight of dried standard used.

16.7.5 Adjust sample to room temperature (if necessary), pour sample aliquot (100ml) into a clean titration vessel, introduce a Teflon coated stirring bar into the sample and place on a magnetic stirrer.

16.7.6 Position burette so that the acid goes directly into the titration vessel. The buret tip must be above sample level at all times.

16.7.7 Cover the titration vessel with parafilm, making small apertures for the pH electrode and the tip of the buret.

16.7.8 Measure and record the initial pH.

16.7.9 Record initial buret reading.

16.7.10 If the initial pH is less than 8.3, then proceed to Section 17.7.12, otherwise continue as described in Section 17.7.11.

16.7.11 Slowly add standard sulfuric acid solution until a pH of 8.3 is reached. Record pH and the titration volume.

16.7.12 Add standard sulfuric acid solution until a pH of approximately 6 is reached. Slowly add more acid, until a pH of 4.5 is reached, record pH and the final titration volume.

16.7.13 Calculate and report carbonate and total alkalinities. If the initial pH was 8.3 or greater, also calculate and report bicarbonate alkalinity.

16.8 Quality Control

16.8.1 Method detection limits (MDL): Method detection limits should be established using the guidelines in Chapter II, Section D.

16.8.2 Laboratory duplicate: see Chapter II, Section C.

16.8.3 Reference materials. must analyze a standard reference material once a year, as available.

16.9 References

American Public Health Association. 1989. Standard Methods for the Examination of Water and Wastewater, 17th Edition.

McGraw-Hill, Chemistry and Environmental Engineering, pp. 364-376.

Strickland and Parsons, A Practical Handbook of Seawater Analysis, pp. 27-28.