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Environmental Technology Verification Protocol

Drinking Water Systems Center

PROTOCOL FOR EQUIPMENT VERIFICATION TESTING FOR ARSENIC REMOVAL

Prepared by

NSF International

Under a Cooperative Agreement with
U.S. Environmental Protection Agency

EPA/NSF ETV
PROTOCOL FOR EQUIPMENT VERIFICATION TESTING FOR ARSENIC REMOVAL

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Drinking Water Systems
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U.S. ENVIRONMENTAL PROTECTION AGENCY

Throughout its history, the U.S. Environmental Protection Agency (EPA) has evaluated technologies to determine their effectiveness in preventing, controlling, and cleaning up pollution. EPA is now expanding these efforts by instituting a new program, the Environmental Technology Verification Program---or ETV---to verify the performance of a larger universe of innovative technical solutions to problems that threaten human health or the environment. ETV was created to accelerate the entrance of new environmental technologies into the domestic and international marketplace. It supplies technology buyers and developers, consulting engineers, states, and U.S. EPA regions with high quality data on the performance of new technologies. This encourages more rapid availability of approaches to better protect the environment.

ETV Drinking Water Systems Center

Concern about drinking water safety has accelerated in recent years due to much publicized outbreaks of waterborne disease and information linking ingestion of arsenic to cancer incidence. The EPA is authorized through the Safe Drinking Water Act (SDWA) to set numerical contaminant standards and treatment and monitoring requirements that will ensure the safety of public water supplies. However, small communities are often poorly equipped to comply with all of the requirements; less costly package treatment technologies may offer a solution. These package plants can be designed to deal with specific problems of a particular community; additionally, they may be installed on site more efficiently---requiring less start-up capital and time than traditionally constructed water treatment plants. The opportunity for the sales of such systems in other countries is also substantial.

The EPA has partnered with NSF International (NSF) to verify performance of small drinking water systems that serve small communities. It is expected that both the domestic and international markets for such systems are substantial. The EPA and NSF have formed an oversight stakeholders group composed of buyers, sellers, and states (issuers of permits), to assist in formulating consensus testing protocols. A goal of verification testing is to enhance and facilitate the acceptance of small drinking water treatment equipment by state drinking water regulatory officials and consulting engineers while reducing the need for testing of equipment at each location where the equipment use is contemplated. NSF will meet this goal by working with equipment manufacturers and other agencies in planning and conducting equipment verification testing, evaluating data generated by such testing, and managing and disseminating information. The manufacturer is expected to secure the appropriate resources to support its part of the equipment verification process, including provision of equipment and technical support.

The verification process established by the EPA and NSF is intended to serve as a template for conducting water treatment verification tests that will generate high quality data for verification of equipment performance. The verification process can help in moving small drinking water equipment into routine use more quickly. The verification of an equipment's performance involves five sequential steps:

1. Development of a Product Specific Test Plan (PSTP);
2. Execution of verification testing;
3. Data reduction, analysis, and reporting;

4. Performance and cost factor (labor, chemicals, energy) verification; and
5. Report preparation and information transfer.

This verification testing program is being conducted by NSF with participation of manufacturers, under the sponsorship of the EPA Office of Research and Development (ORD), National Risk Management Research Laboratory (NRMRL), Water Supply and Water Resources Division (WSWRD) - Cincinnati, Ohio. NSF's role is to provide technical and administrative leadership and support in conducting the testing. It is important to note that verification of the equipment does not mean that the equipment is "certified" by NSF or EPA. Rather, it recognizes that the performance of the equipment has been determined and verified by these organizations.

Partnerships
The EPA and NSF cooperatively organized and develop the ETV Drinking Water Systems (DWS) Center to meet community and commercial needs. NSF and the Association of State Drinking Water Administrators (ASDWA) have an understanding to assist each other in promoting and communicating the benefits and results of the project.

NSF INTERNATIONAL

Mission Statement:
NSF, an independent, non-governmental organization, is dedicated to being the leading global provider of public health and safety-based risk management solutions while representing the interest of all stakeholders.

NSF Purpose and Organization
NSF is an independent not-for-profit organization. For more than 52 years, NSF has been in the business of developing consensus standards that promote and protect public health and the environment and providing testing and certification services to ensure manufacturers and users alike that products meet those standards. Today, millions of products bear the NSF Name, Logo and/or Mark, symbols upon which the public can rely for assurance that equipment and products meet strict public health and performance criteria and standards.

Limitations of use of NSF Documents
This protocol is subject to revision; contact NSF to confirm this revision is current. The testing against this protocol does not constitute an NSF Certification of the product tested.

ORGANIZATION AND INTENDED USE OF PROTOCOL AND TEST PLANS

NSF encourages the user of this protocol to also read and understand the policies related to the verification and testing of drinking water treatment systems and equipment.

The first chapter of this document describes the protocol required in all studies verifying the performance of equipment or systems removing arsenic. The remaining chapters, or Technology Specific Test Plans (TSTPs), describe the additional requirements for equipment and systems using specific technologies to attain the goals and objectives of the protocol: the removal of arsenic.

Prior to the verification testing of drinking water treatment systems, plants and/or equipment, the equipment manufacturer and/or supplier must select an NSF-qualified, Field Testing Organization (FTO). This designated FTO must write a PSTP to define the testing plan specific to the product. The equipment manufacturer and/or supplier will need this protocol and the TSTP(s) contained herein and possibly other ETV protocols and TSTPs to develop the PSTP, depending on the treatment technologies used in the unit processes or treatment train of the equipment or system. More than one protocol and/or TSTP may be necessary to address the equipment's capabilities in the treatment of drinking water.

Testing shall be conducted by an NSF-qualified FTO that is selected by the manufacturer. Water quality analytical work to be completed as a part of a TSTP shall be contracted with a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA. For information on a listing of NSF-qualified FTOs and state, third-party, or the U.S. EPA- accredited laboratories, contact NSF.

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TABLE OF CONTENTS

Page

Chapter 1: EPA/NSF ETV Protocol for Equipment Verification Testing for Arsenic Removal: Requirements for All Studies 1-1

Chapter 2: EPA/NSF ETV Equipment Verification Testing Plan - Removal of Arsenic by Ion Exchange 2-1

Chapter 3: EPA/NSF ETV Equipment Verification Testing Plan - Coagulation and/or Co-Precipitation and Filtration for Removal of Arsenic 3-1

Chapter 4: EPA/NSF ETV Equipment Verification Testing Plan - Electrodialysis Processes for the Removal of Arsenic: See Test Plan for Removal of Inorganic Constituents by Electrodialysis and Electrodialysis Reversal 4-1

Chapter 5: EPA/NSF ETV Equipment Verification Testing Plan - Reverse Osmosis Processes for the Removal of Arsenic: See Test Plan for Removal of Inorganic Constituents by Reverse Osmosis 5-1

Chapter 6: EPA/NSF ETV Equipment Verification Testing Plan - Adsorptive Media Processes for the Removal of Arsenic 6-1

CHAPTER 1

EPA/NSF ETV
PROTOCOL FOR EQUIPMENT VERIFICATION TESTING FOR ARSENIC REMOVAL

REQUIREMENTS FOR ALL STUDIES

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TABLE OF CONTENTS

Page

1.0 INTRODUCTION 1-4
1.1 Objectives 1-6
1.2 Scope 1-6

2.0 EQUIPMENT VERIFICATION TESTING RESPONSIBILITIES 1-7
2.1 Verification Testing Organization and Participants 1-7
2.2 Organization 1-8
2.3 Verification Testing Site Name and Location 1-8
2.4 Site Characteristics 1-8
2.5 Responsibilities 1-8

3.0 EQUIPMENT CAPABILITIES AND DESCRIPTION 1-9
3.1 Equipment Capabilities 1-9
3.2 Equipment Description 1-10

4.0 EXPERIMENTAL DESIGN 1-11
4.1 Objectives 1-11
4.2 Equipment Characteristics 1-12
4.2.1 Qualitative Factors 1-12
4.2.2 Quantitative Factors 1-12
4.3 Water Quality Considerations 1-13
4.3.1 Feed Water Quality 1-13
4.3.2 Treated Water Quality 1-14
4.4 Recording Data 1-14
4.5 Recording Statistical Uncertainty 1-15
4.6 Verification Testing Schedule 1-16

5.0 FIELD OPERATIONS PROCEDURES 1-17
5.1 Equipment Operations and Design 1-17
5.2 Communications, Documentation, Logistics, and Equipment 1-17
5.3 Initial Operations 1-18
5.4 Equipment Operation and Water Quality Sampling for Verification Testing 1-18

6.0 QUALITY ASSURANCE PROJECT PLAN 1-19
6.1 Purpose and Scope 1-19
6.2 Quality Assurance Responsibilities 1-19
6.3 Data Quality Indicators 1-19
6.3.1 Representativeness 1-19
6.3.2 Completeness 1-20
6.3.3 Accuracy 1-21
6.3.4 Precision 1-22
6.3.5 Statistical Uncertainty 1-23

TABLE OF CONTENTS (continued)

Page

6.4 Quality Control Checks 1-23
6.4.1 Quality Control for Equipment Operation 1-23
6.4.2 Water Quality Data 1-23
6.4.2.1 Duplicate Samples 1-24
6.4.2.2 Method Blanks 1-24
6.4.2.3 Spiked Samples 1-24
6.4.2.4 Travel Blanks 1-24
6.4.2.5 Performance Evaluation Samples for Water Quality Testing 1-24
6.5 Data Reduction, Validation, and Reporting 1-25
6.5.1 Data Reduction 1-25
6.5.2 Data Validation 1-25
6.5.3 Data Reporting 1-26
6.6 System Inspections 1-26
6.7 Reports 1-26
6.7.1 Status Reports 1-26
6.7.2 Inspection Reports 1-26
6.8 Corrective Action 1-27

7.0 DATA MANAGEMENT AND ANALYSIS, AND REPORTING 1-28
7.1 Data Management and Analysis 1-28
7.2 Report of Equipment Testing 1-28

8.0 SAFETY AND ENVIRONMENTAL MEASURES 1-29

APPENDICES

Appendix A Arsenic Speciation Method Developed by Battelle for EPA

1.0 INTRODUCTION

This document is the protocol to be used for verification testing of equipment designed to achieve arsenic removal. The Field Testing Organization (FTO) is requested to adhere to the requirements of this protocol in developing a Product Specific Test Plan (PSTP).

The testing of new technologies and materials that are unfamiliar to NSF International (NSF) and/or the EPA will not be discouraged. It is recommended that resins or membranes or any other material or chemical in the equipment conform to NSF/American National Standards Institute (ANSI) Standard 60 and 61.

The final submission of the PSTP shall:

- Include the information requested in this protocol;
- Conform to the format identified herein; and
- Conform to the specific Environmental Technology Verification (ETV) Technology Specific Test Plan(s) [TSTP(s)] related to the manufacturer's statement(s) of performance capabilities that are to be verified.

The PSTP may incorporate the requirements of more than one TSTP. For example, testing might be undertaken to verify performance of a system employing coagulation and filtration for arsenic removal and for removal of microbiological and particulate contaminants or for removal of disinfection byproduct precursors.

This protocol document is presented in two fonts. The non-italicized font provides the rationale for the requirements and background information that the FTO may find useful in preparation of the PSTP. *The italicized text indicates specific protocol deliverables that are required of the FTO and of the manufacturer and that must be incorporated in the PSTP.*

The following glossary terms are presented here for subsequent reference in this protocol:

- Distribution System - A system of conduits by which a primary water supply is conveyed to consumers typically by a network of pipes.

- EPA - The United States Environmental Protection Agency, its staff or authorized representatives.

- Field Testing Organization (FTO) - An organization qualified to conduct studies and testing of drinking water treatment equipment in accordance with protocols and TSTPs. The role of the FTO is to complete the application on behalf of the company; to enter into contracts with NSF, as discussed herein, arrange for or conduct the skilled operation of equipment during the intense period of testing during the study and the tasks required by the protocol.

- Manufacturer - A business that assembles and/or sells package plant equipment and/or modular systems. The role of the manufacturer is to provide the package plant and/or

modular system and technical support for the verification testing and study. The manufacturer is also responsible for providing assistance to the FTO during operation and monitoring of the package plant or modular system during the verification testing and study.

- Modular System - A packaged functional assembly of components for use in a drinking water treatment system or package plant that provides a limited form of treatment of the feed water(s) and which is discharged to another module of the package plant or the final step of treatment to the distribution system.

- NSF - NSF International, its staff, or other authorized representatives.

- Package Plant - A complete water treatment system including all components from connection to the raw water(s) through discharge to the distribution system.

- Plant Operator - The person working for a small water system who is responsible for operating water treatment equipment to produce treated drinking water. This person also may collect samples, record data, and attend to the daily operations of equipment throughout the testing periods.

- Product Specific Test Plan (PSTP) - A written document of procedures for on-site/in-line testing, sample collection, preservation, and shipment and other on-site activities described in the EPA/NSF ETV protocol(s) and TSTP(s) that apply to a specific make and model of a package plant/modular system.

- Protocol - A written document that clearly states the objectives, goals, and scope of the study as well as the TSTP(s) for the conduct of the study. The protocol shall be used for reference during manufacturer participation in the verification testing program.

- Report - A written document that includes data, tests results, findings, and any pertinent information collected in accordance with a protocol, analytical methods, procedures, etc., in the assessment of a product whether such information is preliminary, draft, or final form.

- Surface Water - All water which is open to the atmosphere and subject to surface runoff. For purposes of this document, surface water includes water from surface sources such as lakes, reservoirs, canals, rivers, or streams; and it also includes ground water under the direct influence of surface water.

- Technology Specific Testing Plan (TSTP) - A written document that describes the procedures for conducting a test or study for the application of water treatment technology. At a minimum, the TSTP will include detailed instructions for sample and data collection, sample handling and sample preservation, precision, accuracy, reproducibility goals, and quality assurance and quality control (QA/QC) requirements.

- Testing Laboratory - An organization certified by a third-party independent organization, federal agency, or a pertinent state regulatory authority to perform the testing of drinking water samples. The role of the testing laboratory in the verification testing of drinking water treatment equipment is to analyze the water samples in accordance with the methods and meet the pertinent QA/QC requirements described in the protocol, TSTP, and PSTP.

- Verification - To establish the evidence on the range of performance of equipment and/or device such as a package plant or modular system under specific conditions following a predetermined protocol(s) and TSTP(s).

- Verification Statement - A written document that summarizes a final report reviewed and approved by NSF on behalf of the EPA or directly by the EPA.

- Water System - The water system that operates water treatment equipment to provide treated water to its customers.

1.1 Objectives

The specific objectives of verification testing may be different for each drinking water treatment system, depending upon the statement of performance capabilities of the specific equipment to be tested. Verification testing conducted at a single site may not represent every environmental situation which may be acceptable for the equipment tested, but it will provide data of sufficient quality to make a judgment about the application of the equipment under conditions similar to those encountered in the verification testing. The objectives developed by each manufacturer shall be defined and described in detail in the PSTP developed for each piece of equipment. The objectives of the equipment verification testing may include:

- Generation of field data appropriate for verifying the performance of the equipment and
- Evaluation of new advances in equipment and equipment design.

An important aspect in the development of the verification testing is to describe the procedures that will be used to verify the statement of performance capabilities made for water treatment equipment. A PSTP incorporates the QA/QC elements needed to provide data of appropriate quality sufficient to reach a defensible position regarding the equipment performance.

1.2 Scope

This protocol outlines the verification process for equipment designed to achieve arsenic removal. The scope of this protocol includes TSTPs for drinking water treatment systems employing ion exchange, coagulation and/or co-precipitation and filtration, electrodialysis, electrodialysis reversal, reverse osmosis (RO), and adsorptive media, for the removal of arsenic.

An overview of the verification process and the elements of the PSTP to be developed by the FTO are described in this protocol. Specifically, the PSTP shall define the following elements of the verification testing:

- Roles and responsibilities of verification testing participants;
- Procedures governing verification testing activities such as equipment operation and process monitoring; sample collection, preservation, and analysis; and data collection and interpretation (see Section 5.0 - Field Operations Procedures);
- Experimental Design (see Section 4.0);
- QA/QC procedures for conducting the verification testing and for assessing the quality of the data generated from the verification testing;
- Health and safety measures relating to electrical, mechanical and other safety codes; and
- Environmental concerns relating to the disposal of biological and/or chemical wastes.

Content of PSTP:

The structure of the PSTP must conform to the outline below: The required components of the Document shall be described in greater detail in the sections below.

- *TITLE PAGE*
- *FOREWORD*
- *TABLE OF CONTENTS -The Table of Contents for the PSTP shall include the headings provided in this document although they may be modified as appropriate for a particular type of equipment to be tested.*
- *EXECUTIVE SUMMARY -The Executive Summary describes the contents of the PSTP (not to exceed two pages). A general description of the equipment and the statement of performance capabilities which shall be verified during testing shall be included, as well as the testing locations, a schedule, and a list of participants.*
- *ABBREVIATIONS AND ACRONYMS - A list of the abbreviations and acronyms used in the PSTP shall be provided.*
- *EQUIPMENT VERIFICATION TESTING RESPONSIBILITIES (described in the sections below)*
- *EQUIPMENT CAPABILITIES AND DESCRIPTION (described in the sections below)*
- *EXPERIMENTAL DESIGN (described in the sections below)*
- *FIELD OPERATIONS PROCEDURES (described in the section below)*
- *QUALITY ASSURANCE PROJECT PLAN (described in the section below)*
- *DATA MANAGEMENT AND ANALYSIS (described in the section below)*
- *SAFETY PLAN (described in the section below)*

2.0 EQUIPMENT VERIFICATION TESTING RESPONSIBILITIES

2.1 Verification Testing Organization and Participants

The required content of the PSTP and the responsibilities of participants are listed at the end of each section. In the development of a PSTP, a manufacturer and its designated FTO shall provide a table which includes the name, affiliation, and mailing address of each participant, a point of contact, their role, and telephone, fax and E-mail address.

The equipment provided by the manufacturer shall explicitly meet all the requirements of Occupational Safety and Health Association (OSHA), National Electrical Manufacturers Association (NEMA), Underwriters Laboratory (UL), NSF and other appropriate agencies to ensure operator safety during verification testing.

2.2 Organization

The organizational structure for the verification testing showing lines of communication shall be provided by the FTO in its application on behalf of the manufacturer.

2.3 Verification Testing Site Name and Location

This section discusses background information on the verification testing site(s), with emphasis on the quality of the feed water, which in some cases may be the source water at the site and may include surface as well as ground waters. The PSTP must provide the site names and locations. In most cases, the equipment may be demonstrated at more than one site. In all cases, the equipment should be tested under different feed water quality (or source water quality) and where applicable, under seasonal weather conditions (e.g., surface waters).

2.4 Site Characteristics

The PSTP must include a description of the test site. This should include a description of where the equipment will be located. If the feed water is the source water for an existing water treatment plant, the following information should be provided:

- Characteristics of the feed water where it enters the treatment system;
- Analytical data results from the analysis of the raw water (without the addition of any water treatment chemicals) for use as the feed water to the equipment being tested;
- Pattern of operation of the raw water pumping system (is it continuous or intermittent?); and
- Characteristics of the facilities which will be used for handling treated water and waste (i.e., residuals) from the testing program.

The PSTP shall include the following waste product(s) considerations, when applicable to water treatment plant testing:

- The finished and wastewater flows produced by the equipment being tested should be analyzed and discharged appropriately.
- Obtain a water pollution discharge permits, if needed.

2.5 Responsibilities

This section identifies the organizations involved in the testing and describes the primary responsibilities of each organization. The responsibilities of the manufacturer will vary depending on the type of verification testing. Multiple manufacturer testing at one time is also an option.

In brief, the FTO shall be responsible for:

- Preparation of the PSTP;
- Providing needed logistical support, establishing a communication network, and scheduling and coordinating the activities of all verification testing participants;
- Ensuring that locations selected as test sites have feed water quality consistent with the objectives of the verification testing (manufacturer may recommend a verification testing site(s));
- Managing, evaluating, interpreting, and reporting on data generated by the verification testing; and
- Evaluating and reporting on the performance of the technologies.

The manufacturer shall be responsible for providing the equipment to be evaluated.

Content of PSTP Regarding Verification Testing Responsibilities:

The FTO shall be responsible for including the following elements in the PSTP:

- *A table which includes the name, affiliation, and mailing address of each participant, a point of contact, their role, and telephone, fax and email address;*
- *Definition of the roles and responsibilities of appropriate verification testing participants;*
- *Organization of operational and analytical support;*
- *List of the site name(s) and location(s); and*
- *Description of the test site(s), the site characteristics and identification of where the equipment will be located.*

The manufacturer shall be responsible for:

- *Provision of complete, field-ready equipment for verification testing;*
- *Provision of logistical, and technical support, as required;*
- *Provision of assistance to the qualified FTO during operation and monitoring of the equipment during the verification testing;*
- *Reviewing the PSTP; and*
- *Reviewing the verification report.*

3.0 EQUIPMENT CAPABILITIES AND DESCRIPTION

3.1 Equipment Capabilities

The manufacturer and its designated FTO must provide the water quality objectives to be achieved in the statement of performance capabilities of the equipment to be evaluated in the verification testing. The manufacturer's performance capabilities are used to establish data quality objectives (DQOs) to develop the experimental design of the verification test. The broader the performance objectives, the more comprehensive the PSTP must be to achieve the

DQOs. Statements should also be made regarding the applications of the equipment, what advantages it provides over existing equipment and the known limitations of the equipment. The statement of performance capabilities must be specific and be verifiable by a statistical analysis of the data. An example of a satisfactory statement of performance capabilities would be:

> "This reverse osmosis system is capable of achieving a minimum of 95 percent arsenic removal when the arsenic in the feed water is between 10 and 200 μg/L."

A statement of performance capabilities such as:

> "This system will be capable of meeting the anticipated arsenic maximum contaminant level (MCL) on a consistent and dependable basis,"

would not be acceptable.

The statement of performance capabilities shall indicate the range of water quality with which the equipment can be challenged while successfully treating the feed water. Statements of performance capabilities that are too easily met may not be of interest to the potential user, while performance capabilities that are overstated may not be achievable. The statement of performance capabilities forms the basis of the entire verification testing and must be chosen appropriately. Therefore, the design of the PSTP should include a sufficient range of feed water quality to permit verification of the statement of performance capabilities.

3.2 Equipment Description

Description of the equipment to be used in verification testing shall be included in the PSTP. Data plates shall be permanent and securely attached to each production unit. The data plate shall be easy to read in English or the language of the intended user, located on the equipment where it is readily accessible, and contain at least the following information:

- Equipment Name;
- Model #;
- Manufacturer's name and address;
- Electrical requirements - volts, amps, and Hertz;
- Serial Number;
- Warning and Caution statements in legible and easily discernible print size; and
- Capacity or output rate (if applicable).

Content of PSTP Regarding Equipment Capabilities and Description:

The PSTP shall include the following elements:

- *Description of the treatment train and each unit process included in the equipment, including photographs from relevant angles or perspectives;*
- *Brief introduction and discussion of the engineering and scientific concepts on which the water treatment equipment is based;*

- *Description of the treatment train and each unit process included in the equipment including all relevant schematics;*
- *Brief description of the physical construction/components of the equipment, including the general environmental requirements and limitations, weight, transportability, ruggedness, power and other consumables needed, etc.*;
- *Statement of typical rates of consumption of chemicals and rates of production of wastes (concentrates, residues, etc.);*
- *Definition of the performance range of the equipment;*
- *Identification of any special licensing requirements associated with the operation of the equipment;*
- *Description of the applications of the equipment and what advantages it provides over existing equipment by providing comparisons in such areas as: treatment capabilities, requirements for chemicals and materials, power, labor requirements, suitability for process monitoring and operation from remote locations, ability to be managed by part-time operators; and*
- *Discussion of the known limitations of the equipment including such items as the range of feed water quality suitable for treatment with the equipment, the upper limits for concentrations of regulated contaminants that can be removed to concentrations below the manufacturer's performance capabilities, level of operator skill required to successfully use the equipment.*

4.0 EXPERIMENTAL DESIGN

This section discusses the objectives of the verification testing, factors that must be considered to verify the performance capabilities, and the statistical and other means that the FTO will use to evaluate the results of the verification testing.

4.1 Objectives

The objectives of this verification testing are to evaluate equipment in the following areas:

- Performance relative to manufacturer's stated range of equipment capabilities;
- Impacts of feed water quality variations on its performance;
- Logistical, human, and economic resources necessary to operate the equipment; and
- Reliability, ruggedness, cost factors, range of usefulness, and ease of operation.

The PSTP shall include those treatment tests listed in TSTPs that are most appropriate to challenge the drinking water treatment system. For example, if equipment is only intended for use with ground water, the use of untreated river water as the feed water would not be appropriate.

4.2 Equipment Characteristics

This section discusses factors that will be considered in the design and implementation of the verification testing. These factors include:

- Ease of operation;
- Degree of operator attention required;
- Response of equipment and treatment process to changes in feed water quality;
- Electrical requirements;
- Feed water flow requirements;
- Discharge requirements (residuals and treated water flows);
- Equipment footprint;
- Unit processes included in treatment train; and
- Chemicals needed.

Verification testing procedures will simulate routine conditions as much as possible and in most cases testing may be done in the field; hence, in that circumstance, field condition simulation would not be necessary.

4.2.1 Qualitative Factors

Some factors, while important, are difficult or impossible to quantify. These are considered qualitative factors. Important factors that cannot easily be quantified are the portability of equipment and logistical requirements necessary for using it.

Typical qualitative factors to be discussed are listed below, and others may be added. The PSTP should discuss those factors that are appropriate to the test equipment, including:

- Reliability or susceptibility to adverse environmental conditions and
- Effect of operator experience on the treatment results.

4.2.2 Quantitative Factors

Many factors in this verification testing can be quantified by various means. Typical quantitative factors to be discussed are listed below, and others may be added. The PSTP shall discuss those factors that are appropriate to the test equipment, including:

- Power and consumable supply (such as chemical) requirements;
- Cost factors of operation and waste disposal (such as labor hours and quantity of wastes generated);
- Budget for preventative maintenance;
- Length of operating cycle; and
- Chemical composition assessment of any solid waste produced for disposal purposes by Toxicity Characteristic Leaching Procedure (TCLP) and the

California Waste Extraction Test (WET). TCLP shall be performed in the laboratory using SW-846 and EPA Method 1311, including Method SW-846 6010B for As, Ba, Cd, Cr, Cu, Ni, Pb, Se, Ag, and Zn; and Method SW-846 7470A for Hg. The California WET shall be performed in the laboratory, including Method SW-846 6010B for As, Ba, Cd, Cr, Cu, Ni, Pb, Se, Ag, and Zn; and Method SW-846 7470A for Hg.

These quantitative factors will be used as an initial benchmark to assess equipment performance.

4.3 Water Quality Considerations

Water treatment equipment is used to treat water and change the quality of feed water (or raw water) so it does not contain harmful contaminants and is aesthetically pleasing and palatable. The experimental design shall be developed so the relevant questions about water treatment equipment capabilities can be answered.

Equipment manufacturers should recognize that it is highly unlikely that any single item of water treatment process equipment can successfully treat any conceivable feed water containing all of the regulated contaminants and produce a treated water that meets the quality requirements for every regulated contaminant. Although multiple processes could be placed in a treatment train to accomplish such a goal, for most public water systems such comprehensive treatment capability is not needed and would not be cost effective. Therefore, drinking water treatment has focused on improving the water quality aspects of concern for particular locations.

The range of contaminants or water quality problems that can be addressed by water treatment equipment varies, and some treatment equipment can address a broader range of problems than other types. Manufacturers should carefully consider the capabilities and limitations of their equipment and have PSTPs prepared that challenge their product sufficiently to provide data for a broad market. FTOs shall use TSTPs as the basis for preparation of the specific PSTPs.

4.3.1 Feed Water Quality

One of the key aspects related to performance verification is the range of feed water quality that can be treated successfully, resulting in treated water quality that meets water quality objectives or regulatory requirements. As the range of feed water quality that can be treated by the equipment becomes broader, the potential applications for treatment equipment with verified performance capabilities should also increase. One of the questions often asked by regulatory engineers in approving water treatment equipment is, “Has it been shown to work on the water where you propose to put it?” By covering a large range of water qualities, the verification testing is more likely to provide an affirmative answer to that question. Characteristics of feed water quality that can be important for treatment equipment intended for arsenic removal include:

- Turbidity, suspended particles;
- Arsenic concentration;

- Arsenic species;
- Other ions in solution, particularly sulfate, fluoride, and silica;
- Temperature, with temperatures near freezing having potential for the most difficult treatment conditions;
- Dissolved organic carbon (DOC), total organic carbon (TOC);
- pH, alkalinity, and hardness;
- Iron and manganese; and
- Total dissolved solids (TDS).

4.3.2 Treated Water Quality

Treated water quality is very important. If a manufacturer's statement of performance capabilities states that water treatment equipment can be used to achieve a targeted arsenic removal under a range of influent arsenic levels, the verification testing must be performed to confirm this statement. In addition, the manufacturer may wish to make a statement about performance capabilities of the equipment for removal of other contaminants.

In some cases, when the treated water arsenic concentration is crucial to determine the breakthrough of arsenic during the verification test, field test kits may be used to monitor arsenic, which can provide immediate information on the arsenic concentrations in the treated water. These kits are not acceptable for final verification data, but can be used to indicate when arsenic is increasing in the treated water.

Furthermore, some water treatment equipment can be used to meet aesthetic objectives. Water quality considerations that may be important for some small systems include:

- Color, taste and odor;
- TDS; and
- Iron and manganese.

Finally, other water quality parameters are useful for assessing equipment performance. These may include:

- Particle count or concentration and
- TOC.

The manufacturer and FTO are encouraged to address these factors in the design of the verification testing program.

4.4 Recording Data

For all arsenic removal experiments, data shall be maintained on the pH, temperature, and other water quality parameters listed in Sections 4.3.1 and 4.3.2 above. The following items of information shall also be maintained for each experiment:

- Type of chemical addition, dose and chemical combination, where applicable (e.g. alum, ferric chloride, ferric sulfate, cationic polymer, anionic polymer, ozone, monochloramine, scale inhibitor, etc.);
- Water type (raw water, pretreated or spiked feed water, product water, waste water); and
- Experimental run (e.g. 1st run, 2nd run, 3rd run, etc.).

4.5 Recording Statistical Uncertainty

For the analytical data obtained during verification testing, 95% confidence intervals shall be calculated by the FTO for water quality parameters in which eight or more samples were collected. The PSTP shall specify which water quality parameters shall be subjected to the requirements of confidence interval calculation. DQOs and the vendor's statement of performance capabilities shall be used to assess which water quality parameters are critical and thus require confidence interval statistics. As the name implies, a confidence interval describes a population range in which any individual population measurement may exist with a specified percent confidence. The following formula shall be employed for confidence interval calculation:

$$\text{Confidence Interval} = \bar{x} \pm t_{n-1,1-\frac{\alpha}{2}}\left(\frac{S}{\sqrt{n}}\right)$$

where: $\bar{x}$ is the sample mean;
S is the sample standard deviation;
n is the number of independent measurements included in the data set;
t is the Student's distribution value with n-1 degrees of freedom; and
α is the significance level, defined for 95% confidence as: 1 - 0.95 = 0.05.

According to the 95% confidence interval approach, the α term is defined to have the value of 0.05, thus simplifying the equation for the 95% confidence interval in the following manner:

$$\text{95\% Confidence Interval} = \bar{x} \pm t_{n-1,\,0.975}\left(\frac{S}{\sqrt{n}}\right)$$

With input of the analytical results for pertinent water quality parameters into the 95% confidence interval equation, the output will appear as the sample mean value plus or minus the second term. The results of this statistical calculation may also be presented as a range of values falling within the 95% confidence interval. For example, the results of the confidence interval calculation may provide the following information: 520 +/- 38.4 mg/L, with a 95% confidence interval range described as (482, 558).

Calculation of the confidence intervals shall not be required for equipment performance results (e.g., filter run length, cleaning efficiency, in-line turbidity, or in-line pH monitoring, etc.) obtained during the verification testing program. However, as specified by the FTO, calculation of confidence intervals may be required for such analytical parameters as grab samples of arsenic, TOC, fluoride, sulfate, or silica. To provide sufficient analytical data for statistical

analysis, the FTO shall collect a minimum of eight discrete water samples at one set of operational conditions for each of the specified water quality parameters during a designated testing period. The procedures and sampling requirements shall be provided in detail in the PSTP.

4.6 Verification Testing Schedule

Verification testing activities include equipment set-up, initial operation, verification operation, and sampling and analysis. Initial operations are intended to be conducted so equipment can be tested to be sure it is functioning as intended. If feed water (or source water) quality influences operation and performance of the equipment being tested, the initial operations period serves as the shake-down period for determining appropriate operating parameters. The schedule of testing may also be influenced by coordination requirements with a utility.

For water treatment equipment involving coagulation and filtration for arsenic removal, a period of bench-scale testing (jar testing) followed by initial equipment operation may be needed to determine the appropriate coagulant chemical doses and pH values of coagulated water. Procedures for jar testing are provided in the American Water Works Association's (AWWA) Manual M37, "Operational Control of Coagulation and Filtration Processes."

The extent of verification testing depends upon the nature of the source water the equipment is intended to treat. For example, the following conditions may be encountered:

- Cold temperatures (1° to 5^oC) can have an adverse affect on some water treatment processes due to the increase in water viscosity at cold temperatures;
- The presence of some inorganics may interfere with arsenic removal by ion exchange and by coagulation;
- The presence of natural organic matter may interfere with arsenic removal by coagulation; and
- The water flow rate required by some types of water treatment equipment can be so great (80 to 100 liters/minute, or greater) that use of mechanical refrigeration to attain temperatures of 1° to 5^oC would be prohibitively expensive.

Verification testing that is intended to be used to verify the performance of a product would be done after an initial operations phase is completed.

Content of PSTP Regarding Experimental Design:

The PSTP shall include the following elements:

- *Identification of the qualitative and quantitative factors of equipment operation to be addressed in the verification testing program;*
- *Identification and discussion of the water treatment problem or problems that the equipment is designed to address, how the equipment will solve the problem, and who would be the potential users of the equipment;*

- *Identification of the range of key water quality parameters, given in applicable TSTPs, which the equipment is intended to address and for which the equipment is applicable;*
- *Identification of the key parameters of treated water quality that will be used for evaluation of equipment performance for arsenic removal. Parameters of significance for treated water quality were listed above in Section 4.3.2 and in applicable TSTPs; and*
- *Detailed outline of the verification testing schedule, with regard to seasonal testing periods and testing periods at different temperature conditions.*

5.0 FIELD OPERATIONS PROCEDURES

5.1 Equipment Operations and Design

The TSTP specifies procedures that shall be used to ensure the accurate documentation of both water quality and equipment performance. Careful adherence to these procedures will result in definition of verifiable performance of equipment. (Note that this protocol may be associated with a number of different TSTPs for different types of arsenic removal process equipment.)

Design aspects of water treatment process equipment often provide a basis for approval by state regulatory engineers and can be used to ascertain if process equipment intended for larger or smaller flows than that evaluated in the verification testing program actually involves the same operating parameters that were relevant to the verification testing. Specific design aspects to be included in the PSTP are provided in detail.

5.2 Communications, Documentation, Logistics, and Equipment

The successful implementation of the verification testing will require detailed coordination and constant communication between all verification testing participants. All field activities shall be thoroughly documented. Field documentation will include field logbooks, photographs, field data sheets, and chain-of-custody forms. The FTO shall be responsible for maintaining all field documentation. The following guidelines shall be followed:

- Field notes shall be kept in a bound logbook;
- Field logbooks shall be used to record all water treatment equipment operating data;
- Each page shall be sequentially numbered;
- Each page shall be labeled with the project name and number;
- Completed pages shall be signed and dated by the individual responsible for the entries; and
- Errors shall have one line drawn through them and this line shall be initialed and dated.

All photographs shall be logged in the field logbook. These entries shall include the time, date, subject of the photograph, and the identity of the photographer. Any deviations from the approved final PSTP shall be thoroughly documented in the field logbook, made available at the time of inspection, and included in the verification report.

Original field sheets and chain-of-custody forms shall accompany all samples shipped to the analytical laboratory. Copies of field sheets and chain-of-custody forms for all samples shall be provided at the time of QA/QC inspection and included in the verification report.

5.3 Initial Operations

Initial operations will allow equipment manufacturers to refine their operating procedures and to make operation adjustments as needed to successfully treat the feed water. Information generated through this period of operation may be used to revise the PSTP, if necessary. A failure at this point in the verification testing could indicate a lack of capability of the process equipment and the verification testing might be canceled.

5.4 Equipment Operation and Water Quality Sampling for Verification Testing

All field activities shall conform to requirements provided in the PSTP that was developed and approved for the verification testing being conducted. If unanticipated or unusual situations are encountered that may alter the plans for equipment operation, water quality sampling, or data quality, the situation shall be discussed with the verification entity. Any deviations from the approved final PSTP shall be thoroughly documented.

During routine operation of water treatment equipment, the following items should be documented and described by the qualified FTO, the water system, or the plant operator:

- Total number of hours during which the equipment was operated each day;
- Number of hours each day during which the operator was working at the treatment plant and performing tasks related to water treatment and the operation of the treatment equipment; and
- Tasks performed during equipment operation.

Content of PSTP Regarding Field Operations Procedures:

The PSTP shall include the following elements:

- *A table summary of the proposed time schedule for operating and testing;*
- *Field operating procedures for the equipment and performance testing, based upon the TSTP, including:*
  - *listing of operating parameters,*
  - *ranges for feed water quality, and*
  - *sampling and analysis strategy;*
- *Provision of all equipment needed for field work associated with this verification testing;*
- *Provision of a complete list of all equipment to be used in the verification testing. A table format is suggested;*
- *Provision of field operating procedures; and*
- *At a minimum, a table(s) showing all parameters to be analyzed, the analytical methods, the laboratory reporting limits or quantification limits, sample volume, bottle type, preservation method, and holding times.*

6.0 QUALITY ASSURANCE PROJECT PLAN

Every PSTP for verification testing must include a Quality Assurance Project Plan (QAPP) that specifies procedures that shall be used to ensure data quality and integrity. Careful adherence to these procedures will ensure that data generated from the verification testing will provide sound analytical results that can serve as the basis for performance verification.

6.1 Purpose and Scope

The purpose of this section is to outline steps that shall be taken by operators of the equipment and by the analytical laboratory to ensure that data resulting from this verification testing are of known quality and that a sufficient number of critical measurements are taken.

6.2 Quality Assurance Responsibilities

A number of individuals may be responsible for monitoring equipment, operating parameters, and for sampling and analysis QA/QC throughout the verification testing. Primary responsibility for ensuring that both equipment operation and sampling and analysis activities comply with the QA/QC requirements of the PSTP (Section 6) shall rest with the FTO.

QA/QC activities for the analytical laboratory that analyzes samples sent off-site shall be the responsibility of that analytical laboratory's supervisor. If problems arise or any data appear unusual, they shall be thoroughly documented and corrective actions shall be implemented as specified in this section. The QA/QC measurements made by the off-site analytical laboratory are dependent on the analytical methods being used.

6.3 Data Quality Indicators

The data obtained during the verification testing must be of sound quality for conclusions to be drawn on the equipment. For all measurement and monitoring activities conducted for equipment verification, NSF and EPA require that data quality parameters be established based on the proposed end uses of the data. Data quality parameters include five indicators of data quality: representativeness, completeness, accuracy, precision, and statistical uncertainty.

Treatment results generated by the equipment must be verifiable for the purposes of this program to be fulfilled. High quality, well-documented analytical laboratory results are essential for meeting the purpose and objectives of this verification testing. Therefore, the following indicators of data quality shall be closely evaluated to determine the performance of the equipment when measured against data generated by the analytical laboratory.

6.3.1 Representativeness

Representativeness refers to the degree to which the data accurately and precisely represent the conditions or characteristics of the parameter represented by the data. In this verification testing, representativeness will be ensured by executing consistent sample collection procedures, including sample locations, timing of sample collection,

sampling procedures, sample preservation, sample packaging, and sample shipping. Representativeness also will be ensured by using each method at its optimum capability to provide results that represent the most accurate and precise measurement it is capable of achieving.

For equipment operating data, representativeness entails collecting a sufficient quantity of data during operation to be able to detect a change in operations. For most water treatment processes involving arsenic removal, detecting a +/- 10 percent change in an operating parameter (i.e. headloss, pressure) is sufficient. Mixing energies and flows should also be recorded on a daily basis to track changes in operational conditions that exceed this 10 percent range.

6.3.2 Completeness

Completeness refers to the amount of data collected from a measurement process compared to the amount that was expected to be obtained. Completeness refers to the proportion of valid, acceptable data generated using each method. This portion of the required data for the selected test plan will be reported at the conclusion of each testing period.

The completeness objective for data generated during verification testing is based on the number of samples collected and analyzed for each parameter and/or method. The test plans will likely require a large number of samples to be collected for key and most important parameters and/or methods. The following chart illustrates the completeness objectives for performance parameter and/or method based on the sample frequency:

Number of Samples Per Parameter and/or Method	Percent Completeness
0-10	80%
11-50	90%
>50	95%

Completeness is defined as follows for all measurements:

$$\%C = (V/T) \times 100$$

where: %C = percent completeness;
V = number of measurements judged valid; and
T = total number of measurements.

Additional testing and collection of additional sample will be required if the percent completeness objectives are not met. If the completeness objectives are still not met through the collection of additional samples, then a retest will be required.

The following are examples of instances that might cause a sample analysis to be incomplete:

- Instrument failure;
- Calibration requirement not being met; and
- Elevated analyte levels in the method blank.

6.3.3 Accuracy

The definition of accuracy depends on the context, and is defined as the following:

- Water quality analyses - difference between a sample result and the reference or true value for the sample. Loss of accuracy can be caused by:
  - errors in standards preparation,
  - equipment calibrations,
  - loss of target analyte in the extraction process,
  - chemical interferences, and
  - systematic or carryover of contamination from one sample to the next.

- Equipment operating parameters - difference between the reported operating condition and the actual operating condition.

- Water flow - difference between the reported flow indicated by a flow meter and the flow as actually measured on the basis of known volumes of water and carefully defined times (bucket and stopwatch technique) as practiced in hydraulics laboratories or water meter calibration shops.

- Mixing equipment - difference between an electronic readout for equipment RPMs and the actual measurement based on counted revolutions and measured time.

- Head loss measurement - determined by using measuring tapes to check the calibration of piezometers for gravity filters or by checking the calibration of pressure gauges for pressure filters.

Meters and gauges must be checked periodically for accuracy, and when proven to be dependable over time, the time interval between accuracy checks can be increased. In the PSTP, the FTO shall discuss the applicable ways of determining the accuracy of the operational conditions and procedures.

From an analytical perspective, accuracy represents the deviation of the analytical value from the known value. Since true values are never known in the field, accuracy measurements are made on analysis of QC samples analyzed with field samples. QC samples for analysis shall be prepared with laboratory control samples, matrix spikes and spike duplicates. It is recommended for verification testing that the PSTP include

laboratory performance of one matrix spike for determination of sample recoveries. Recoveries for spiked samples are calculated in the following manner:

% Recovery = 100 x (SSR-SR)/SA

where: SSR = spikes sample result;
SR = sample result; and
SA = spike amount added.

Recoveries for laboratory control samples are calculated as follows:

% Recovery = 100 x (found concentration)/(true concentration)

For acceptable analytical accuracy under the verification testing program, the recoveries reported during analysis of the verification testing samples must be within control limits, where control limits are defined as the mean recovery plus or minus three times the standard deviation.

6.3.4 Precision

Precision refers to the degree of mutual agreement among individual measurements and provides an estimate of random error. Analytical precision is a measure of how far an individual measurement may be from the mean of replicate measurements. The standard deviation and the relative standard deviation recorded from sample analyses may be reported as a means to quantify sample precision. The percent relative standard deviation may be calculated in the following manner:

%Relative Standard Deviation = $S(100) / X_{average}$

where: S = standard deviation and
$X_{average}$ = the arithmetic mean of the recovery values.

Standard Deviation is calculated as follows:

$$\text{Standard Deviation} = \sqrt{\frac{\sum_{i=1}^{n}(X_i - X)^2}{n-1}}$$

where: X_i = the individual recovery values;
X = the arithmetic mean of then recovery values; and
n = the number of determinations.

For acceptable analytical precision under the verification testing program, the percent relative standard deviation for drinking water samples must be less than 30%. If the data generated during the ETV test does not meet the data quality objectives defined in this QA/QC section, additional testing and sampling will be required. If the data quality

objectives are still not met through additional testing and the collection of additional samples, then a retest will be required.

6.3.5 Statistical Uncertainty

Statistical uncertainty of the water quality parameters analyzed shall be evaluated through calculation of the 95% confidence interval around the sample mean. Description of the confidence interval calculation is provided in Section 4.5 - Recording Statistical Uncertainty.

6.4 Quality Control Checks

This section describes the QC requirements that apply to the treatment equipment, the on-site water quality analyses, and the off-site water quality analyses. It also contains a discussion of the corrective action to be taken if the QC parameters fall outside of the evaluation criteria.

The quality control checks provide a means of measuring the quality of data produced. The FTO may not need to use all the quality control checks identified in this section. The selection of the appropriate quality control checks depends on the equipment, the experimental design and the performance capabilities. The selection of quality control checks will be based on discussions among the manufacturer, the FTO and NSF.

6.4.1 Quality Control for Equipment Operation

This section will explain the methods to be used to check the accuracy of equipment operating parameters and the frequency with which these quality control checks will be made. If the quality of the equipment operating data cannot be verified, then the water quality analytical results may be of no value. Because water cannot be treated if equipment is not operating, obtaining valid equipment operating data is a prime concern for verification testing.

An example of the need for QC for equipment operations is an incident of state rejection of test data because the treatment equipment had no flow meter to use for determining engineering and operating parameters related to flow.

6.4.2 Water Quality Data

After treatment equipment is being operated and water is being treated, the results of the treatment are interpreted in terms of water quality. Therefore, the quality of water sample analytical results is just as important as the quality of the equipment operating data. Therefore, the QAPP must emphasize the methods to be employed for sampling and analytical QA. Analytical methods for on-site and off-site monitoring are presented within each TSTP. If new methods are published and approved or current methods updated, the most current methods shall be used. The important aspects of sampling and analytical QA are given below:

6.4.2.1 Duplicate Samples. Duplicate samples must be analyzed to determine the precision of analysis. The procedure for determining samples to be analyzed in duplicate shall be provided with the frequency of analysis and the approximate number. Duplicate samples must include field duplicates and laboratory duplicates. Field duplicates measure the precision of the overall sampling and analysis procedures. Laboratory duplicates measure the precision associated only with the lab procedures.

6.4.2.2 Method Blanks. Method blanks are used to evaluate analytical method-induced contamination, which may cause false positive results.

6.4.2.3 Spiked Samples. The use of spiked samples will depend on the testing program and the contaminants to be removed. The FTO must specify in the PSTP the procedure and frequency of spiking, as well as acceptance criteria, and actions if criteria are not met.

6.4.2.4 Travel Blanks. Travel blanks should be provided to the analytical laboratory to evaluate travel-related contamination.

6.4.2.5 Performance Evaluation Samples for Water Quality Testing. Performance evaluation samples are samples of unknown concentration prepared by an independent performance evaluation (PE) lab and provided as unknowns to an analyst to evaluate his or her analytical performance. Analysis of PE samples shall be conducted onsite by the FTO and by the offsite laboratory before verification testing is initiated. If recent PE reports from the laboratory are not available, PE samples shall be submitted by the FTO to the analytical laboratory. The control limits for the PE samples will be used to evaluate the FTO's and analytical laboratory's method performance. One kind of PE sample that would be used for on-site QA in most studies performed under this protocol would be a pH PE sample.

A PE sample comes with statistics that have been derived from the analysis of the sample by a number of laboratories using EPA-approved methods. These statistics include a true value of the PE sample, a mean of the laboratory results obtained from the analysis of the PE sample, and an acceptance range for sample values. The analytical laboratory is expected to provide results from the analysis of the PE samples that meet the performance capabilities of the verification testing.

Arsenic speciation using the Battelle method (Appendix A) may be an important part of the verification test. Please note when using this method that ultra-pure (optimum) grade sulfuric acid must be used (not reagent grade) to avoid the trace amounts of arsenic that can be present in reagent grade sulfuric acid. In addition to all normal QA requirements for handling field samples and for arsenic determination, a special check of the resin used for the speciation procedure is required. The resin must be prepared properly in accordance with the procedures given in the method, and the capability of the resin to properly separate arsenic III from V must be demonstrated. It cannot be assumed that a batch of resin has been properly prepared without validating the separation process using water spiked with known concentrations of arsenic III and V. This QC check should

include having the laboratory make a solution with a mixture of arsenic III and V, having the field staff perform the separation using their standard procedures, and then having the laboratory analyze the samples for arsenic III and V. The results of the QC check sample must demonstrate the separation procedure is working properly. This check must be done for each new batch of resin used during the verification test.

6.5 Data Reduction, Validation, and Reporting

To maintain good data quality, specific procedures shall be followed during data reduction, validation, and reporting. These procedures are detailed below.

6.5.1 Data Reduction

Data reduction refers to the process of converting the raw results from the equipment into concentration or other data in a form to be used in the comparison. The procedures to be used will be equipment dependent. The purpose of this step is to provide data that will be used to verify the statement of performance capabilities. These data shall be obtained from logbooks, instrument outputs, and computer outputs as appropriate.

6.5.2 Data Validation

There are two types of data validation which need to be addressed, field data and laboratory data. For the field data (including data collected from field laboratories):

- The operator shall check the correctness of data acquisition and reduction;
- The field team supervisor or another technical person shall review calculations and inspect laboratory logbooks and data sheets to check accuracy of data recording and sampling;
- Calibration and QC data will be examined by the individual operators and the laboratory supervisor; and
- Laboratory and project managers shall check that all instrument systems are in control and that QA objectives for accuracy, precision, and method detection limits have been met.

For the laboratory data:

- Calibration and QC data will be examined by the individual analysts and the laboratory supervisor; and
- Laboratory managers shall check that all instrument systems are in control and that QA objectives for accuracy, completeness, and method detection limits have been met.

Analytical outlier data are defined as those QC data lying outside a specific QC objective window for precision and accuracy for a given analytical method. Should QC data be outside of control limits:

- The analytical laboratory or field team supervisor will investigate the cause of the problem;
- If the problem involves an analytical problem, the sample will be reanalyzed;
- If the problem can be attributed to the sample matrix, the result will be flagged with a data qualifier; and
- The data qualifier will be included and explained in the final analytical report.

6.5.3 Data Reporting

This section contains a list of the water quality and equipment operation data to be reported. At a minimum, the data tabulation shall list the results for feed water and treated water quality analyses and equipment operating data. All QC information such as calibrations, blanks and reference samples are to be included in an appendix. All raw analytical data should also be reported in an appendix. All data should be reported in hardcopy and electronically in a spreadsheet or database format.

6.6 System Inspections

On-site system inspections for sampling activities, field operations, and laboratories may be conducted as specified by the TSTP. These inspections will be performed by the verification entity to determine if the TSTP is being implemented as intended. Separate inspection reports will be completed after the inspection and provided to the participating parties.

6.7 Reports

6.7.1 Status Reports

The FTO shall prepare periodic reports to pertinent parties such as the manufacturer, the EPA, and the community where testing is done. These reports should discuss project progress, problems and associated corrective actions, and future scheduled activities associated with the verification testing. When problems occur, the manufacturer and FTO project managers shall discuss them and estimate the type and degree of impact, and describe the corrective actions taken to mitigate the impact and to prevent a recurrence of the problems. The frequency, format, and content of these reports shall be outlined in the PSTP.

6.7.2 Inspection Reports

Any QA inspections that take place in the field or at the analytical laboratory while the verification testing is being conducted shall be formally reported by the FTO to the verification entity and manufacturer.

6.8 Corrective Action

Each PSTP must incorporate a corrective action plan. This plan must include the predetermined acceptance limits, the corrective action to be initiated whenever such acceptance criteria are not met, and the names of the individuals responsible for implementation.

Routine corrective action may result from common monitoring activities, such as:

- Routine site performance evaluation audits and
- Routine technical systems audits.

Content of PSTP Regarding the QAPP:

The PSTP shall include the following elements:

- *Description of methodology for measurement of accuracy;*
- *Description of methodology for measurement of precision;*
- *Description of methodology for reporting of statistical uncertainty;*
- *Description of the methodology adopted for use of blanks, the materials used in the blanks, the frequency for using blanks, the criteria for accepting blanks and the actions which will be taken if these criteria are not met;*
- *Description of any specific procedures appropriate to the analysis of the PE samples;*
- *Outline of the procedure for determining samples to be analyzed in duplicate, the frequency for performing duplicate analyses and approximate number of samples which will be included in this program;*
- *Description of the procedures used to assure that the data are correct;*
- *Listing of equations used for any necessary data quality indicator calculations. These include: representativeness, completeness, accuracy, precision, and statistical uncertainty (e.g., confidence interval calculation);*
- *Outline of the frequency, format, and content of reports to be submitted to each party involved in the tests; and*
- *Description of the action which will be used to correct problems as they occur during the tests.*

The FTO shall be responsible for the following:

- Provision of all QC information such as calibrations, blanks and reference samples in an appendix. All raw analytical data should also be reported in an appendix; and
- Provision of all data in hardcopy and electronic form in a common spreadsheet or database format.

7.0 DATA MANAGEMENT AND ANALYSIS, AND REPORTING

7.1 Data Management and Analysis

A variety of data will be generated during verification testing. Each piece of data or information identified for collection in the TSTP will need to be provided in the report. The data management section of the PSTP should describe what types of data and information needs to be collected and managed. It should also describe how the data will be reported.

Laboratory Analyses: The raw data and the validated data must be reported. These data should be provided in hard copy and in electronic format. As with the data generated by the innovative equipment, the electronic copy of the laboratory data should be provided in a spreadsheet in the report. In addition, all QA/QC summary forms must be provided.

Other items that must be provided include:

- Field notebooks;
- Photographs, slides and videotapes (copies); and
- Results from the use of other field analytical methods.

7.2 Report of Equipment Testing

The FTO shall prepare a draft report describing the verification testing that was carried out and the results of that testing. This report shall include the following topics:

- Foreword;
- Introduction;
- Executive Summary;
- Description and Identification of Product Tested;
- Procedures and Methods Used in Testing;
- Results and Discussion (discussion of results should be kept at a minimum to a avoid conclusions and recommendations);
- References;
- QA/QC Results; and
- Items described in Section 7.1 of this document.

Content of PSTP Regarding Data Management and Analysis, and Reporting:

The PSTP shall include the following:

- *Description of what types of data and information needs to be collected and managed and*
- *Description of how the data will be reported.*

8.0 SAFETY AND ENVIRONMENTAL MEASURES

The FTO shall prepare a document identifying the safety procedures that shall be used during the fieldwork. The safety considerations addressed in this document will include the following, as applicable:

- Storage, handling, and disposal of hazardous chemicals including acids, caustic and oxidizing agents;
- Conformance with electrical and plumbing codes applicable at the test site(s);
- Arsenic handling procedures (if spiking tests are to be performed) and disposal of wastes containing arsenic; and
- Ventilation of equipment or of trailers or buildings housing equipment, if there are gases generated by the equipment that could present a safety hazard (one example is the use of ozone).

Content of PSTP Regarding Safety:

The PSTP shall address safety and environmental considerations that are appropriate for the equipment being tested.

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CHAPTER 2

EPA/NSF ETV EQUIPMENT VERIFICATION TESTING PLAN FOR REMOVAL OF ARSENIC BY ION EXCHANGE

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TABLE OF CONTENTS

1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN 2-5

2.0 INTRODUCTION 2-5

2.1 Arsenic Speciation and Occurrence 2-5
2.2 The Arsenic Ion-Exchange Process 2-6
2.2.1 Effect of Sulfate on Arsenic Removal 2-7
2.2.2 Effect of Multiple Contaminants 2-7
2.2.3 Low Effluent pH in the Early Stages of Exhaustion 2-8
2.2.4 Spent Brine Reuse and Treatment 2-8

3.0 GENERAL APPROACH 2-9

4.0 OVERVIEW OF TASKS 2-9

4.1 Task 1: Selection and Characterization of Feed Water 2-9
4.2 Task 2: Preparation, Coordination and Startup 2-9
4.3 Task 3: Initial Plant Characterization 2-9
4.4 Task 4: Verification Testing Runs 2-10
4.5 Task 5: Data Management 2-10
4.6 Task 6: Quality Assurance and Quality Control, QA/QC 2-10

5.0 TESTING PERIODS 2-10

6.0 DEFINITIONS 2-11

7.0 TASK 1: SELECTION AND CHARACTERIZATION OF FEED WATER 2-17

7.1 Introduction 2-17
7.2 Objectives 2-17
7.3 Work Plan 2-18
7.4 Schedule 2-19
7.5 Evaluation Criteria 2-20

8.0 TASK 2: PREPARATION, COORDINATION, AND STARTUP 2-20

8.1 Introduction 2-20
8.2 Objective 2-20
8.3 Work Plan 2-21
8.4 Schedule 2-21

TABLE OF CONTENTS (continued)

9.0 TASK 3: INITIAL PLANT CHARACTERIZATION 2-21

9.1 Introduction 2-21
9.2 Objective 2-22
9.3 Work Plan 2-22
9.3.1 Arsenic Spiking 2-22
9.3.2 Attainment of Steady State Operation 2-23
9.3.3 Collection of Preliminary Data 2-24
9.3.4 Determination of Variable Effluent Quality and Arsenic Peaking Potential 2-24
9.3.5 Preliminary Assessment of Plant Performance: 2-25
9.4 Schedule 2-25

10.0 TASK 4: VERIFICATION TESTING RUNS 2-25

10.1 Introduction 2-25
10.2 Objectives 2-25
10.3 Work Plan 2-26
10.3.1 Plant Operating Conditions and Equipment Performance 2-26
10.3.2 Feed Water and Product Water Quality 2-26
10.3.3 Arsenic Removal Performance 2-29
10.4 Schedule 2-30
10.5 Evaluation Criteria 2-30
10.5.1 Treatment Equipment Performance. 2-30
10.5.2 Product Water Quality 2-30
10.5.3 Arsenic Removal Performance 2-31

11.0 TASK 5: DATA MANAGEMENT 2-31

11.1 Introduction 2-31
11.2 Objectives 2-31
11.3 Work Plan 2-31
11.3.1 Data Handling 2-31
11.3.2 Statistical Analysis 2-33

12.0 TASK 6: QUALIITY ASSURANCE/QUALITY CONTROL 2-33

12.1 Introduction 2-33
12.2 Objectives 2-33
12.3 Work Plan 2-34
12.3.1 Daily QA/QC Verifications 2-34
12.3.2 Bi-weekly QA/QC Verifications 2-34
12.3.3 QA/QC Verifications for Each Test Period 2-34

12.4 On-Site Analytical Methods 2-34
12.4.1 pH..... 2-35

TABLE OF CONTENTS (continued)

12.4.2 Sulfate, Nitrate, Chloride and Alkalinity by Test Kits..... 2-35
12.4.3 Conductivity..... 2-35
12.4.4 Temperature (Optional for Ion Exchange)..... 2-35
12.4.5 Color 2-36
12.5 Chemical and Biological Samples Shipped Off-Site for Analyses..... 2-36

13.0 OPERATIONS & MAINTENANCE (O&M) 2-36

13.1 Maintenance..... 2-37
13.2 Operation..... 2-37
13.2.1 Operation Manuals:..... 2-37
13.2.2 Troubleshooting Guide: 2-38
13.2.3 History of Ion Exchange Equipment Operability: 2-39

14.0 REFERENCES..... 2-40

TABLES

Table 1 Generic Schedule for Verification Testing Plan Completion 2-11
Table 2 Historical Water Quality Data 2-18
Table 3 Operation and Performance Data from Verification Test Runs..... 2-27
Table 4 Water Quality Sampling and Measurement Schedule 2-28
Table 5 Analytical Methods..... 2-29

1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN

This document is the ETV Testing Plan for evaluation of water treatment equipment for arsenic removal utilizing the ion exchange process. This Testing Plan is to be used as a guide in the development of Product-Specific Test Plan (PSTP) procedures for testing ion exchange equipment, within the structure provided by the ETV Protocol Document entitled "Protocol for Equipment Verification Testing for Arsenic Removal." This Equipment Verification Testing Plan is applicable only to ion-exchange processes that use strong-base anion resin beads in fixed or moving packed beds.

In order to participate in the equipment verification process for ion exchange, the equipment Manufacturer shall employ the procedures and methods described in this test plan and in the referenced ETV Protocol Document as guidelines for the development of the Product-Specific Test Plan. The procedures shall generally follow those Tasks related to Verification Testing that are outlined in this test plan, with changes and modification made for adaptations to specific equipment. Each Product-Specific Test Plan shall include Tasks 1 through 6 as defined below. And, at a minimum, the format of the procedures written for each Task should consist of the following sections:

(1) Introduction,
(2) Objectives,
(3) Work Plan,
(4) Analytical Schedule,
(5) Evaluation Criteria.

2.0 INTRODUCTION

2.1 Arsenic Speciation and Occurrence

Arsenic has been found in many of the nations drinking water supplies, and, at these trace levels, chronic exposure can cause liver, lung, kidney, and bladder cancer in addition to the previously determined risk of skin cancer (Smith, 1992). Of the chemical constituents that present the greatest health threat in public ground water supplies in the USA, arsenic was accorded the highest priority. Arsenic toxicity depends on its chemical form, with inorganic forms of arsenic more toxic than the organic forms. Inorganic arsenic can be present as the anionic and neutral forms arsenate, As(V), and arsenite As(III). Although As (III) is acutely more toxic, human metabolic processes can convert As (V) to As (III). Thus, current and proposed Environmental Protection Agency (EPA) regulations on arsenic in drinking water deal only with total arsenic, which includes As(III), As(V) and organic arsenic. Because of its lower toxicity and the fact that (a) it is rarely found in ground water, and (b) its concentration in surface water rarely exceeds 5 µg/L, organic arsenic is not dealt with in this Verification Testing Plan. With regard to inorganic arsenic, either As(V) or As(III) or a mixture of the two may be found in arsenic-contaminated ground water. Surface waters contaminated with inorganic arsenic are expected to contain predominantly As(V) because they are in contact with the atmosphere. The ion exchange process is designed to remove only As(V), thus, if As(III) is to be removed, it must be oxidized, e.g., by chlorine, to As(V) prior to treatment (Frank and Clifford, 1986).

2.2 The Arsenic Ion-Exchange Process

Typically, oxidized and filtered raw water is passed through a bed of chloride-form strong-base anion (SBA) resin (RCl), and the chloride-arsenate ion-exchange reaction, Eq. (1), takes place to yield resin in the arsenate form ($\overline{R_2HAsO_4}$). When the column capacity for arsenic is exhausted, the arsenic "breaks through" into the effluent, and its concentration rises rapidly and generally exceeds the influent arsenic concentration if run beyond breakthrough. The reaction is easily reversed, and regeneration, according to Eq. (2), returns the resin to the chloride form, ready for another exhaustion cycle:

$$2\,\overline{RCl} + HAsO_4^{2-} = \overline{R_2HAsO_4} + 2\,Cl^- \qquad \text{... (1)}$$

$$\overline{R_2HAsO_4} + 2NaCl = 2\,\overline{RCl} + Na_2HAsO_4 \qquad \text{...(2)}$$

Although chloride-arsenate ion exchange appears simple, several issues must be addressed when implementing the process for drinking water treatment. Among the important factors that would be expected to influence Verification Testing are the following: (1) effect of competing ions such as sulfate, (2) multiple contaminants such as arsenic and nitrate, (3) low pH of the column effluent early in the run, and (4) spent brine reuse and treatment. If the source water has < 500 mg/L TDS and < 220 mg/L sulfate, ion exchange may be the arsenic-removal process of choice. As mentioned, preoxidation to convert As(III) to As(V) is necessary (Frank and Clifford, 1986), but pH adjustment is not because the chloride-arsenate exchange reaction takes place readily in the pH range of natural waters.

The main advantages of the ion-exchange process for removing arsenic from water are as follows:

(1) The process is simple, robust, compact, easy to automate, and can be operated on-demand.

(2) It is routinely possible to lower arsenic to less than 1 µg/L.

(3) Water recovery rates ≥95% are possible.

(4) No feed water pH adjustment is necessary; the process works very well in the usual pH range of natural waters (6.5-9.2).

(5) The potential problems with variable effluent water quality including low pH and potential nitrate and arsenic peaking can be solved by operating several columns in parallel and at different stages of exhaustion.

(6) Exhausted resin can be easily regenerated using salt (NaCl) solution, and the spent regenerant can be reused directly without treatment to remove arsenic.

Potential problems with the ion exchange process for arsenic removal are of the are as follows:

(1) As(III) when present must be converted to As(V) for efficient removal.

(2) High sulfate and TDS can reduce run length significantly.

(3) Because sulfate is more preferred than As(V) and nitrate, arsenic and nitrate peaking

can occur if their breakthroughs are exceeded.

(4) Effluent pH can be reduced to as low as 5.0 in the first 100 BV due to bicarbonate conversion to carbonate and CO_2 by the resin.

(5) Prefiltration, upstream of the ion-exchange column, may be required to prevent resin fouling.

(6) Spent brines require disposal.

2.2.1 Effect of Sulfate on Arsenic Removal

Because arsenic is a trace species, its concentration does not greatly influence the run length to arsenic breakthrough. However, because sulfate, a common ion, is preferred over arsenate, nitrate, chloride, bicarbonate, and most other common anions, its concentration largely determines the run length to arsenic breakthrough. For example in a low-sulfate (5 mg/L) water in McFarland, California, arsenic run length exceeded 3500 bed volumes (one bed volume is a quantity of treated water equal to the volume of the resin bed). On the other hand, a McFarland, California water spiked to contain 220 mg/L sulfate, the arsenic run length was only 250 BV. Thus, in testing an ion exchange process for arsenic removal, considerable attention must be paid to the background sulfate concentration.

Not only does increasing sulfate concentration lead to shorter arsenic-removal runs, it leads to chromatographic peaking of arsenic or "dumping" after arsenic breakthrough. For example, arsenic effluent concentration peaks in the range of 1.3 to 6 times the raw water arsenic concentration would not be unusual following arsenic breakthrough. Of course, these peaks would normally be avoided by stopping a run at or before arsenic breakthrough. Another way of coping with the potential peaking of arsenic or any other contaminant less preferred than sulfate is to exhaust several columns in parallel and in different stages of exhaustion. Thus, if one column does run beyond breakthrough, its effluent arsenic peak is diluted by the arsenic-free effluents from the other columns. The columns operated in parallel may be fixed or in motion as is the case with the carousel moving bed designs.

2.2.2 Effect of Multiple Contaminants

Often, sub-MCL levels (< 10 mg NO_3-N/L) of nitrate will be present along with arsenic as a drinking water contaminant, and, for a time, the ion exchange system will remove both nitrate and arsenic. However, nitrate will generally break through before arsenic and sulfate, and a nitrate peak will appear in the effluent if the column if it is allowed to run to arsenic breakthrough. To avoid the nitrate peak in the event it would exceed the nitrate MCL, the column may be stopped at nitrate rather than arsenic breakthrough. This will lead to shorter run lengths, but will avoid exceeding the nitrate MCL even for a short time. Another approach to avoiding the nitrate peak is to exhaust multiple, fixed or moving, beds in parallel. Even if one of the beds is subject to a nitrate peak, effluents from the other beds will dilute and smooth out the peak.

The implication of multiple contaminants on the Verification Testing Plan is that the Product-Specific Test Plan must address the potential problem of multiple contaminants and explain how the testing plan will deal with the issue if it is present.

2.2.3 Low Effluent pH in the Early Stages of Exhaustion

When a chloride-form strong-base anion exchange resin is used to treat natural water as in the arsenic ion exchange process, the effluent pH during the first 50-300 bed volumes can be significantly reduced compared with the influent pH. For example, effluent pHs as low as 5.0 can be observed (Clifford, 1990; Benjamin, 1998). The reason for the pH reduction is the conversion of bicarbonate to carbonate within the resin (Horng and Clifford, 1997). This conversion occurs with the resulting expulsion of a proton (H^+ ion), which increases the H^+ ion concentration and lowers the pH. The bicarbonate-to-carbonate reaction occurs because all standard SBA resins prefer divalent, e.g., carbonate, to monovalent, e.g., bicarbonate, ions at the typical TDS levels found in drinking water supplies. (An exception to this preference for divalent ions occurs with the so-called nitrate-selective, or nitrate over sulfate selective (NSS) resins, which are designed to prefer monovalent nitrate to divalent sulfate. The NSS resins do not exhibit the pH lowering effect.)

The extent of the pH lowering depends primarily on the characteristics of the resin and the bicarbonate concentration in the raw water. Because seriously acidic pHs must be avoided when delivering treated water into a distribution system, the pH of the ion-exchange system under Verification Testing for arsenic removal must be measured and recorded.

As is the case with potential arsenic and nitrate peaking, it is possible to avoid the low pHs observed during the early stages of a single column anion exchanger run by exhausting multiple columns in parallel. In this way the low-pH column effluent from one of the columns will be blended with the other column effluents to produce a neutral-pH water. Again, the parallel columns may be fixed or moving beds.

2.2.4 Spent Brine Reuse and Treatment

It has been found that direct reuse of the spent arsenic-contaminated ion-exchange brine is possible for regeneration of the spent resin (Clifford and Ghurye, 1998). Brine reuse can substantially cut down on (a) the volume of brine discharged and (b) the salt (NaCl) consumption by the process.

With or without brine reuse, the Product-Specific Test Plan must address the issue of volume and mass of brine discharge from the plant under test. If the once-used or recycled brine is decontaminated by iron or alum precipitation to remove arsenic before discharge, the volume and solids concentration of the sludge must also be determined along with the arsenic concentration of the dried sludge and the TCLP test result for the sludge.

3.0 GENERAL APPROACH

Testing of equipment covered by this Verification Testing Plan will be conducted by an NSF-qualified Field Testing Organization (FTO) that is selected by the Manufacturer. Water quality analytical work to be carried out as a part of this Verification Testing Plan will be contracted with a state-certified or third-party or EPA-accredited analytical laboratory.

4.0 OVERVIEW OF TASKS

The following section provides a brief overview of the recommended tasks that may be included in Initial Plant Characterization Tests and of the tasks required to be included in the arsenic ion exchange Verification Testing program.

4.1 Task 1: Selection and Characterization of Feed Water

Generally, the ion exchange plant to be tested will be installed and started up at the selected location just prior to implementing the Verification Testing Plan. The test location should be chosen so as to be representative of a class of arsenic contaminated drinking waters to which the particular ion exchange process would be applied. For example, if the primary intended use of the plant is arsenic contaminated ground water, then it should be tested on ground water rather than surface water or arsenic-spiked surface water. Similarly, if the intended use is primarily surface water, it should be tested on surface water because ground waters will be lower in particulates and total organic carbon (TOC).

The objective of Task 1 is to obtain a chemical and physical characterization of the feed water. Generally a ground water with representative arsenic, sulfate, nitrate and TDS concentrations will be selected for Verification Testing. The depth of the well and historical data on water quality parameters should be recorded. However, if a surface water is chosen, a brief description of the watershed that provides the feed water shall be provided, to aid in interpretation of feed water characterization.

4.2 Task 2: Preparation, Coordination and Startup

Orientation meetings will be held, preferably at the plant site. The manufacturer will meet with the testing organization personnel to explain the process, the detailed plant design, the testing program and the schedule. Discussion of the program, its objectives, and responsibilities of each participant will be clarified. If the plant is not already operating, it is recommended that the manufacturer start it up with representatives of the testing organization present for training purposes.

4.3 Task 3: Initial Plant Characterization

The manufacturer will develop objectives of the plant's performance based knowledge of the ion exchange process and the water quality characterization. The manufacturer's performance objectives are used to establish data quality objectives (DQOs) in order to develop the

experimental design of the verification test. The broader the performance objectives, the more comprehensive the PSTP must become to achieve the DQOs. Preliminary tests will be conducted to measure the plant's basic performance including, for example, the arsenic leakage and run length to arsenic breakthrough. These tests will produce baseline information, which can be used to evaluate changes that occur as the plant ages. If the plant does not meet water quality objectives, the manufacturer will be notified and adjustments made. Alternatively, further testing may be canceled at this point.

4.4 Task 4: Verification Testing Runs

This task, which comprises the actual Verification Testing Runs, is the core of the Verification Testing Plan. During this task, the arsenic-removal ion exchange plant shall be operated for at least 240 hours over a period of at least 14 days during one testing period to collect data on equipment performance and water quality for purposes of performance verification. If a manufacturer chooses to demonstrate the effectiveness of their plant under a significantly different set of background water conditions, the option exists for a second test period to be carried out at a different site with the same transportable ion-exchange plant.

The objectives of the Verification Testing Runs are to (a) observe and record the plant operating conditions and equipment performance, (b) determine the overall feed water and finished water quality, and (c) establish the arsenic-removal performance of the plant.

4.5 Task 5: Data Management

The objective of this task is to establish an effective field protocol for data management at the field operations site and for data transmission between the Field Testing Organization and NSF for data obtained during Verification Testing, plus the requirement for statistical analysis of the data.

4.6 Task 6: Quality Assurance and Quality Control

An important aspect of Verification Testing is the protocol developed for quality assurance and quality control. The objective of this task is to assure accurate measurement of operational and water quality parameters during Verification Testing of the arsenic ion exchange plant.

5.0 TESTING PERIODS

The required tasks in the Verification Testing Plan (Task 4) are designed to be carried out over one 240-hour period, not including the time required for mobilization, start- up, and Initial Operations. See Table 1 for additional details of the schedule, which includes time for planning, coordination, startup, and initial plant characterization.

Table 1. Generic Schedule for Verification Testing Plan Completion			
Test period	Planning, Coordination and Startup, Estimated Time[&]	Initial Plant Characterization, Estimated Time[†]	Verification Testing Runs, Estimated Time**
1	1-2 weeks	4-6 weeks	240 hrs over 14 days

* Only one test period will be required if the water quality at the site is constant as is the case with many ground waters. If a manufacturer chooses to demonstrate the effectiveness of their plant under a significantly different set of background water conditions, the option exists for a second test period to be carried out at a different site with the same transportable ion-exchange plant.

[&] Time for planning, coordination, and startup will depend on whether the plant is already in operation and level of familiarity of Field Test Organization with details of plant operation and Product-Specific Test Plan.

[†] Initial Plant Characterization time may be shortened considerably if the plant is already in operation. If a second test is conducted at a different site, the Initial Plant Characterization tests may take as long as at the first site.

**Verification Testing Runs may take as little as 240 hours total elapsed time during a period of 14 days of non-continuous operation. Plant operation, especially with regard to starting and stopping, should be similar to what is expected during normal operation at an actual installation.

6.0 DEFINITIONS

Adsorption - The step in the ion-exchange process that removes arsenate from water by chemical or physical attraction to a medium such as an ion exchange resin. It is also referred to as the service step or the exhaustion step. **Note:** In this document, the term adsorption is used in its general sense as a process for removing contaminants from a liquid by adsorbing them on a solid adsorbent by processes including ion-exchange, adsorption, and ligand exchange.

Anion - A negatively charged ion. The major anions of concern are divalent arsenate ($HAsO_4^{2-}$), monovalent arsenate ($H_2AsO_4^-$), nitrate (NO_3^-), sulfate (SO_4^{2-}), chloride (Cl^-), and bicarbonate (HCO_3^-).

Anion Exchange Resin - A polymeric matrix, usually polystyrene crosslinked with divinylbenzene, containing fixed positively charged functional groups that hold exchangeable anions by electrostatic attraction. During an anion-exchange reaction, a harmless ion such as chloride is exchanged for a target contaminant ion such as arsenate ($HAsO_4^{2-}$).

Attrition - Breakage and wear of ion exchange resin beads.

Back Washing - The upward flow of water through an ion exchange bed to clean it of foreign material and reduce the compaction of the resin bed. Usually the bed is fluidized by the upward flow of water.

Bed - The ion exchange material contained in a column or vessel of an operating unit.

Bed Depth - The height of the resin material in the column after the exchanger has settled into a packed-bed condition.

Bed Expansion - The effect produced during backwashing: when the bed is fluidized, the resin particles become separated and rise in the column.

Bed Volumes (BV) or Bed Volumes Treated - A dimensionless ratio that refers to the volume of water that can be treated by a bed of resin. BV = Volume of water treated/volume of resin including voids.

Breakthrough - The portion of the effluent history curve that exhibits a rapid increase in effluent concentration of a substance, which signals that adsorption of the substance is near completion, and further operation of the column will not be productive. During plant operation, the adsorption cycle is terminated prior to breakthrough of the ion of interest. (The breakthrough point can be defined in several different ways such as the point on the breakthrough curve where the concentration of the target contaminant reaches the MCL or a predetermined fraction of the MCL, or where the inflection point in the breakthrough curve occurs. Breakthrough can be gradual or sharp depending on several factors including the isotherm shape, the resin particle size, mass transfer considerations, channeling in the bed, and etc.

Brine Recycle - The reuse of spent brine with or without treatment to remove the target contaminant, arsenic. Direct brine reuse, or brine recycling without treatment to remove arsenic, is possible during arsenic ion exchange because arsenate is removed as a divalent ion, $HAsO_4^{2-}$, undergoes electroselectivity reversal and is not attracted to the resin when it is in contact with high concentration brine.

Capacity - Generally, the advertised ion exchange capacity expressed in milliequivalents per milliliter or equivalents per liter. The number of equivalents of exchangeable ion contained in one liter of an ion exchange material. The volume is measured when the material is wet and is fully saturated with adsorbed water.

Channeling - Random paths of relatively lower flow resistance in the resin bed resulting from improper operating procedures including failure to remove particulates, improper backwashing, insufficient flow velocity, etc. Channeling, which can occur during exhaustion or regeneration, results in diminished mass transfer between the water and the resin.

Chromatography - The separation of ions, molecular species, or complexes into highly purified fractions by means of ion exchange materials or adsorbents.

Chromatographic Peaking - The phenomenon that causes the effluent concentration of an ion to be higher than the influent concentration for a short time during the effluent history. Chromatographic peaking is also referred to as "dumping" and it occurs immediately following the breakthrough of each ion. All ions in the feed water are subject to peaking except the most-preferred ion, which is usually sulfate. During chromatographic peaking, significant amounts of the adsorbed ion are "dumped" from the resin bed into the effluent water.

Clumping - The formation of resin agglomerations in an ion exchange bed due to fouling, chemical depositions, scaling, or admixture with highly cohesive substances, such as certain clays and silts.

Column Influent -The water entering an ion exchange column or columns. Column influent water may have been subjected to pretreatment such as filtration or oxidant addition and, thus, may differ from feed water, which is the raw (source) water before pretreatment.

Column Operation - The most common method of employing ion exchange materials, in which the liquid to be treated passes through a fixed bed of ion exchange resin held within a cylindrical vessel or column.

Counter Flow Operation - An ion exchange operation in which the direction of flow of water through a bed and the subsequent regenerant flow are in opposite directions.

Cross-Linking - Connecting together at numerous points the linear polymer chains in the matrix of an ion exchange polymer using a bridging agent in order to produce a three-dimensional insoluble product. Lightly crosslinked resins are relatively more flexible, take up more water, and can absorb larger molecules more easily.

Cycle - A complete series of operational steps. For instance, a complete cycle of arsenate ion exchange would involve; the complete adsorption step, followed by backwashing, regeneration, slow rinsing, fast rinsing, and return to adsorption service.

Degradation - The physical or chemical reduction of ion exchange properties due to particulate fouling, organic fouling, chemical (including chlorine) oxidation, excessive heating and other aggressive operating conditions. Some effects are bead cracking, capacity loss, particle size reduction, excessive swelling, or any combination of the above.

Divalent Ion - An ion with two negative charges such as sulfate, SO_4^{2-}, or arsenate, $H_2AsO_4^{2-}$

Down Flow - Conventional direction in which water and brines flow through an ion exchange bed during processing: inlet at the top, outlet at the bottom of the bed or column.

Dumping - The phenomenon that causes the effluent concentration of an ion to be higher than the influent concentration for a short time during the effluent history. Dumping is also referred to as "chromatographic peaking" and it occurs immediately following the breakthrough of an ion. All ions in the feed water are subject to peaking except the most-preferred ion, which is

usually sulfate. During chromatographic peaking, significant amounts of the adsorbed ion are "dumped" from the resin bed into the effluent water.

Effluent - column effluent is the treated water leaving an ion-exchange column. Process effluent is synonymous with product or treated water, which can be the result of blending several column effluents together to smooth out water quality variations resulting from a single column. Process Effluent can also contain bypass water that has not been treated by ion exchange. The regenerant emerging from the column after regeneration is referred to as the eluent, eluate or spent regenerant.

Effluent History Curve- An x-y plot showing the relationship between time or bed volumes (BV) of water passed through a bed of ion-exchange resin (on the x-axis) and the effluent concentration (on the y-axis). Effluent concentration may be expressed as milliequivalents/L, mg/L, or the ratio $C_{Effluent}/C_{Influent}$. Contaminant breakthrough occurs when effluent history curve begins to rise sharply. The run is terminated at the breakthrough point when the effluent concentration reaches the MCL or some predetermined fraction of the MCL. Prior to contaminant breakthrough, the measurable amount of contaminant in the effluent history curve is referred to as leakage. As long as the leakage is below the predetermined MCL it is tolerable.

Elution - The stripping of adsorbed ions from the ion exchanger by the regenerant solution, which is usually highly concentrated, e.g., 1-2 molar NaCl (6-12% NaCl).

Electroselectivity Reversal - The reversal of selectivity, which occurs when the ionic strength of the aqueous solution is changed between natural water (low ionic strength, e.g., 0.005 M) and brine solution (high ionic strength, e.g., 1.0 M). Divalent ions such as sulfate and arsenate undergo selectivity reversal during regeneration and are easily stripped from the resin during regeneration, even though they are strongly attracted to the resin during exhaustion, which occurs in low ionic strength water.

Empty Bed Contact Time - The time it would take for water to pass through the volume of the column occupied by the resin bed. It is calculated as though the resin is not present, hence "Empty Bed" Contact Time. It is calculated as the volumetric flow rate divided by the resin bed volume. For example if the flow rate is 350 gal/min and one Bed Volume is 700 gallons, the EBCT is 2 minutes (i.e., 2 min/BV or 0.5 BV/min, or 30 BV/hr).

Equivalent - Short for gram equivalent weight, the molecular weight of an ion divided by its ionic charge. One equivalent of ions contains Avagadro's number (6.023×10^{23}) of ionic charges. For example one equivalent (i.e., one gram equivalent weight = 139.9/2 = 69.95 grams) of divalent arsenate ($HAsO_4^{2-}$) anions contains 6.023×10^{23} negative charges. Equivalents rather than grams of ions are used in ion exchange calculations because one equivalent of chloride (35.5/2 = 17.75 grams) is replaced by exactly one equivalent of arsenate (69.95 grams).

Exhaustion - That portion of the operating cycle during which the resin adsorbs (actually, removes by ion exchange) the contaminant from the raw water. The resin is spent or exhausted at the end of the exhaustion step.

Feed Water - Raw water from the source before pretreatment of any kind.

Fouling - Any deposit or concentration of foreign material on or in an ion exchange material which interferes with the chemical and physical processes. Typical foulants are: lubricating oil from pump lubricants, clays, silts, bacteria, algae, etc. Fouling can cause reduced efficiency, channeling, loss of resin during backwashing and many other plant malfunctions.

Freeboard - The space provided above the resin bed in a vessel or column to accommodate the expansion of the resin bed during the backwash cycle.

Headloss - The loss of liquid pressure head resulting from the passage of water through a bed of ion exchange material.

Hydraulic Loading Rate - Also referred to as the approach velocity (v_0) or the volume of water passing through a given area of resin within a given time. Hydraulic loading rate is usually expressed in terms of gallons per minute per square foot of bed cross sectional area. Hydraulic loading rate is not the same as the service flow rate (SFR), which is expressed as volumetric flow rate divided by resin bed volume, e.g., gal/min ft^3. For arsenic ion-exchange processes, these values are typically as follows: v_0 = 10-15 gal/min ft^2; SFR = 3-5 gal/min ft^3.

Influent - column influent is the raw, arsenic-contaminated water entering an ion exchange column. Column influent is not necessarily the same as the process influent, which is the feed water or raw water entering the process before any pretreatment. Column influent differs from feed water in that it may be filtered or oxidized and filtered, or otherwise subject to pretreatment before ion exchange.

Interstitial Volume - The space between the particles of an ion exchange material in a column or an operating unit (see Void Volume).

Leakage - The presence of the target contaminant (arsenate in this case) in the treated water exiting from an ion exchange column before its breakthrough has occurred giving the impression that the contaminant has "leaked" through the resin bed. Leakage is different from breakthrough- the rapid increase in contaminant concentration, which occurs in the effluent history curve just before the run is terminated at the breakthrough point.

Milliequivalent (meq) - Short for one milligram equivalent weight, - one thousandth of an equivalent, i.e., 6.023×10^{20} ionic charges.

Monovalent Ion - An ion with a single negative or positive charge. Nitrate, NO_3^-, and chloride, Cl^-, are monovalent anions. Sodium, Na^+, and hydrogen, H^+, are monovalent cations.

Nitrate Selective Resin - Same as nitrate-to-sulfate selective (NSS) resin. An ion-exchange resin that prefers nitrate to sulfate even in low ionic strength waters ($\leq$0.01 M). All resins are selective for nitrate over chloride, but may not be nitrate selective. Only special resins (NSS resins) are selective for nitrate over sulfate in the range of drinking water concentrations. Also, all resins are selective for nitrate over sulfate at brine concentrations ($\geq$0.25 M). Because

arsenate is adsorbed as a divalent ion ($HAsO_4^{2-}$) like sulfate, nitrate selective resins are generally not good for arsenic removal from drinking water.

Operating Cycle - A single completion of all steps in the exhaustion-regeneration process consisting of adsorption, backwash, regeneration, fast rinse, slow rinse, and, stand by.

Physical Stability - The ability of an ion exchange material to resist breakage caused by mechanical manipulation.

Presaturant - The harmless or innocuous ion adsorbed on the resin by saturating the resin with the ion prior to a column operation. In arsenate treatment, the presaturant is chloride ion.

Preferred Ion - The one of at least two different ions having equal concentrations that will be adsorbed on the resin to the greatest extent.

Recontamination - A potential problem in ion-exchange systems consisting of removing a contaminant from one point in a water supply and then adding the same and/or other contaminant into the supply at a different point. For example, by incomplete rinsing of resin beds, arsenate, nitrate, chloride, bicarbonate, sulfate and sodium can be added to the supply. Also, by running beds beyond their bed life, arsenate ion can be "dumped" from the bed into the treated water.

Regenerant - The solution (6-12% NaCl for arsenate removal) used to convert an ion exchange material from its exhausted state to the desired regenerated form for reuse.

Regeneration - Conversion of the spent resin back to the presaturant condition by elution of the contaminants after completion of the exhaustion and backwashing steps. In arsenate treatment, the regeneration is performed by passing a sodium chloride brine slowly through the bed in either a co- or countercurrent direction.

Regeneration Level - The amount of regenerant chemical used per unit volume of ion exchanger bed, commonly expressed as lb/ft^3 or equivalents Cl^-/equivalent resin. Also see salt loading. The lower the regeneration level, the more efficient is the process.

Resin - Synthetic organic ion-exchange materials, usually in bead form, with a large number ($\geq 6 \times 10^{23}$ sites/L resin) of charged ion-exchange sites within the hydrated solid. The typical strong-base anion (SBA) resins used in arsenate anion removal from water are divinylbenzene crosslinked polystyrene polymers with positively charged quaternary amine functional groups.

Resin Bed Volume - The volume of ion exchange resin material in a bed including voids between particles. The volume of the resin in the bed is referred to as one bed volume and is expressed in cubic feet, gallons, or liters.

Rinse - The passage of water through an ion exchange bed to wash out excess regenerant and residual contaminants. The slow rinse or displacement rinse is generally less than 3 BV and is performed at the same rate as the regenerant flow rate (0.5-1 gal/min ft^3). The fast rinse is generally less than 20 BV, and is performed at the service (exhaustion) flow rate (3-5 gal/min

ft^3).

Run Length - The number of bed volumes (BV) or the exhaustion time (hrs) until the breakthrough point of the contaminant ion of interest, arsenic in this case. For arsenic removal we are interested in Run Length to Arsenic Breakthrough—RLTAsBT.

Salt Loading - Salt loading is the amount of regenerant applied to a resin during the regeneration step. It can be expressed in terms of pounds of NaCl per cubic foot of resin, grams of salt/L of resin, equivalents of salt/L of resin or, more conveniently, in terms of bed volumes of brine (volumes brine/ volumes resin) having a specified concentration of NaCl. Salt loading and regeneration level are equivalent terms.

7.0 Task 1: Selection and Characterization of Feed Water

7.1 Introduction

The Manufacturer must choose either a surface or ground water location to test the ion exchange plant. Generally, a ground water would be chosen because most of the drinking water arsenic problems will be associated with ground waters. On the other hand, if the target market is surface waters, a surface water test site should be chosen because ground water testing may not fully challenge the plant. For example, surface waters will contain higher TOC and particulates, and be subject to significant seasonal variations in temperature, arsenic concentration, algae, turbidity, color, taste and odor, and TOC.

When removing arsenic from water by anion exchange, sulfate present in the water will reduce the capacity of the resin for arsenic. For example, sulfate in excess of 200 mg/L may rule out the ion-exchange process entirely, because run lengths may be less than 250 BV, which some consider to be the lower limit for a practical ion-exchange process for public water supply treatment. Therefore, care should be taken during verification testing to use waters with similar sulfate levels to those expected to be encountered during full scale operation. See Section 2.2.1 - "Effect of Sulfate on Arsenic Removal". If it is the objective of the manufacturer to prove that their unit is widely acceptable for arsenic removal from ground water, test waters with very low sulfate concentration, e.g., less than 20 mg/L should be avoided. If a manufacturer chooses to demonstrate the effectiveness of their plant under a significantly different set of background water conditions, the option exists for a second test period to be carried out at a different site with the same transportable ion-exchange plant.

7.2 Objectives

The first objective of this task is to choose a representative site with water quality and water quality variations that will be similar to locations where the ion exchange process will be implemented. Once the site has been chosen, the second objective is to fully characterize the feed water with respect to the chemical, particulate, and biological parameters that would be expected to influence the ion-exchange process performance.

7.3 Work Plan

This selection and characterization task can be accomplished by using analytical measurements obtained from third party sources (i.e. United States Geological Survey (USGS), USEPA, State Laboratories, and Municipal Laboratories). If sufficient water quality data for the site do not exist, they must be generated by the Manufacturer using at least three sets of samples taken over a period of at least one month or more, during which time the water source is in operation as it would be during Verification Testing. The new data will be included in the Product-Specific Test Plan. The specific parameters and approved methods needed to characterize the water are listed in the Table 2 below:

Sufficient information shall be obtained to illustrate the variations expected to occur in these parameters that will be measured during Verification Testing for a typical annual cycle for the water source. This information will be compiled and shared with NSF so NSF and the Field Testing Organization can determine the adequacy of the data for use as the basis to make decisions on the testing schedule. Failure to adequately characterize the feed water (source water) could result in testing at a site later deemed inappropriate, so the initial characterization will be important to the success of the testing program. Clifford (1990 Chapter 9) has shown that the sulfate concentration in the raw water is a primary determinant of arsenic run length, and Ghurye and Clifford (1998) have recently demonstrated that nitrate peaking before arsenic breakthrough may determine the ion exchange run length.

Table 2. Historical Water Quality Data

Ground Water	Surface Water	Standard Method	EPA Method
As(III) and As(V)	As(III) and As(V)	Methods for analyzing As(III) and As(V) are non-standard.	
Total As	Total As	3500-As, 3113 B, 3120 B, 3114 B	200.7, 200.8, 200.9
Sulfate	Sulfate	4500-Sulfate, 4110 B	300.0, 375.2
Nitrate	Nitrate	4500-NO_3, 4110 B	300.0, 353.2
Chloride	Chloride	4500-Cl^- D, 4110 B	300.0
Total Alkalinity	Total Alkalinity	2320-B	
Fluoride	Fluoride	4500-F, 4110 B	300.0
pH	pH	4500-H^+ B	
TDS	TDS	2540-C	
TOC	TOC	5310-C	
Temperature	Temperature	2550-B	
Iron		3111 B, 3113 B, 3120 B	200.7, 200.9
Manganese		3111 B, 3113 B, 3120 B	200.7, 200.8, 200.9
	Color	2120-B	
	Turbidity	2130-B	180.1
	Algae	10200 and 10900	

The presence of iron above about 0.3 mg/L in a ground water will influence the process design. First, significant iron will signal a reducing water with As(III) the predominant species present,

and the As(III) must be oxidized to As(V) prior to ion exchange treatment. Second, when exposed to the air, which inevitably occurs during treatment, some ferrous iron will be oxidized to ferric and will form a precipitate, which may adsorb significant arsenic. Research (Ghurye and Clifford, 1998) has shown that the precipitated iron will largely pass through the anion resin and cause high arsenic in the column effluent. Thus, iron above about 0.3 mg/L should be removed by oxidation and precipitation prior to anion exchange. When this situation occurs, one should consider a coagulation-filtration or a coagulation-microfiltration process rather than ion exchange for arsenic removal.

If the source water is surface water, a brief description of the watershed that provides the feed water shall be provided to aid in predicting water quality variability and characterizing the feed water. The watershed description should include:

(1) approximate size,

(2) topography (i.e. flat, gently rolling, hilly, mountainous),

(3) types of human activities that take place (i.e. mining, manufacturing, cities or towns, farming),

(4) potential sources of pollution influencing water quality, especially potential sources for arsenic discharge, and

(5) nature of the water source, such as stream, river, lake, wells, or man-made reservoir.

A primary consideration when using anion exchange to treat surface water is the natural organic matter (NOM), measured as TOC, present in the source water. Because a significant portion of the NOM comprises large anions with aromatic character and multiple negative charges, some NOM will be irreversibly adsorbed by the resin and may eventually lead to organic fouling (Clifford et. al., 1998, TOC IX Chapter in DBP Book). To clean the resins, a regenerant mixture of NaOH and NaCl will occasionally be used, and this complicates the process significantly. Thus, anion exchange for removing arsenic from surface water will not be commonly applied, but is sometimes used. For example, chloride anion exchange for nitrate removal, which is very similar to arsenate removal, has been installed in Des Moines, Iowa, to remove nitrate from the Des Moines river water. This process has been reported to be successful and serious organic fouling has not occurred (Benjamin, Des Moines, IA, 1998). For surface water treatment, the test plan must include the season with the highest expected TOC values, and a sufficient number of ion exchange runs must be made so that conclusions about the potential for organic fouling may be made. Alternatively, the manufacturer may provide resin testing data on the water to be treated that indicates that serious fouling will not occur during the projected life of the resin.

7.4 Schedule

In many cases, sufficient water quality data may already exist such that the determination of the suitability of a source water for use as feed water in an ion-exchange process Verification Testing program might be made without further testing. If historical data is insufficient, sampling and analysis of the proposed test water must be undertaken. As a minimum, the water should be sampled three times over a period of one month to characterize one test period. If the

water is expected to vary from season to season, e.g., a surface water, one additional test period must be defined and characterized.

7.5 Evaluation Criteria

Feed water quality will be evaluated in the context of the Manufacturer's statement of performance objectives. The feed water should challenge the capabilities of the equipment but should not be beyond the range of water quality suitable for treatment for the equipment in question. For example, if the Manufacturer's equipment is designed for source water containing less than 500 mg/L TDS, and 200 mg/L sulfate, it would not be appropriate to test it on waters with greater than these levels of TDS and sulfate.

Because the ion exchange breakthrough point of a trace-level contaminant will not be significantly affected by its concentration, the arsenic level in the raw water will generally not be a determinant of process success or failure. Nevertheless, because increasing the feed water arsenic level will lead to proportionately higher arsenic leakage, it would not be reasonable to spike the feed water with more than the highest expected level of arsenic in the waters to treated. The minimum arsenic level in the test water should be the lesser of 20 µg/L or three times the applicable EPA-specified MCL.

If the manufacturer wants to As(III) removal to be part of its performance objective, the unit must be challenged with an As(III)-containing test water, otherwise an As(V) challenge water will be acceptable. When challenging the unit with As(V), sufficient chlorine or an alternative oxidant may be added to the to insure the oxidation of any As(III) present to As(V).

8.0 TASK 2: PREPARATION, COORDINATION, AND STARTUP

8.1 Introduction

One or more meetings will be held regarding the tasks and scheduling of tasks between the manufacturer and the NSF-approved testing organization regarding the tasks described in the NSF approved manufacturer’s PSTP. This task will also include the plant start up if it is not already in operation. If possible, the Manufacturer and the Field Testing Organization representative(s) should be present together during the plant start up for purposes of training the testing personnel in plant operation and maintenance.

8.2 Objective

The objective of the meeting(s) is to train the Field Testing representative(s) to operate the plant and to provide an opportunity for the Manufacturer and the Field Testing Organization personnel to reach a common understanding of the objectives and execution of the testing plan. Further, the meeting(s) will provide an opportunity to clarify any areas of concern by either party. Initial start up data may be collected if the plant is not already in operation. Other interested parties such as the owner/operator and local or state health officials should attend at least a portion of the meeting.

8.3 Work Plan

The Manufacturer will explain the material included in the PSTP; in particular, the plant design, operations, outstanding and distinguishing features and especially the treatment objectives and other secondary performance goals claimed for the plant performance.

The treatment objectives shall include the following:

(1) The process effluent shall always be less than 10 parts per billion (ppb).

(2) The process effluent pH shall be within the specified design range (typically 7.0-9.0).

(3) The process effluent nitrate-N shall never exceed 10 mg/L.

(4) The volume of wastewater, including brine and rinses, discharged from the process shall be equal to or less than the Manufacturer's objectives (typically $\leq$2% of product water volume).

(5) The regenerant salt consumption, e.g., lbs NaCl/1000 gal product water, shall meet the Manufacturer's objectives (typically $\leq$3 lbs/1000 gal). The Manufacturer will also report the resin-regeneration salt loading in the units of lbs regenerant/ft^3 resin.

The Manufacturer will use diagrams, drawings, plans and the actual equipment to illustrate the design, operation and control of the ion-exchange system being tested. Special attention will be given to critical equipment such as alarms, controls, and safety devices. Emergency shut down procedures will be carefully reviewed.

8.4 Schedule

Prior to the meeting(s), the Manufacturer will provide the Testing Organization with any drawings, plans, site plans, operation manuals, and similar helpful materials. Sufficient time should be allowed prior to the meeting to allow the testing organization to develop their testing plans and methods to quantify the evaluation criteria. The orientation meeting(s) will be held just before the next task: Initial Plant Characterization.

9.0 Task 3: Initial Plant Characterization

9.1 Introduction

Shortly after the orientation and training meetings between the Manufacturer and the Testing Organization, Initial Plant Characterization Tests will be conducted by the Field Testing Organization or the Manufacturer and the base line performance data will be recorded. During these tests, a preliminary assessment of plant performance will be made. If the plant doesn't perform to specification, adjustments can be made prior to the actual Verification Testing. Furthermore, the performance data obtained during these preliminary tests will provide base line data for comparison with future plant performance. When Verification Testing is complete, a comparison between the early and late plant performance can be made to determine if

performance has deteriorated over time.

This Initial-Plant-Characterization-Test phase is a logical time for NSF to carry out a field inspection of equipment operations and sampling and field analysis procedures. If problems are found with the operation and/or data collection procedures, they may be corrected before the Verification Testing begins. Also, these preliminary test results should be reported to the Manufacturer, which may choose to make NSF-approved changes in operating procedures prior to Verification Testing.

9.2 Objective

The objectives of this task are to establish the initial plant performance characteristics and to permit NSF and the Manufacturer to make approved changes in the PSTP prior to Verification Testing. The approved preliminary data may be used as base-line data for comparison with future plant performance.

9.3 Work Plan

9.3.1 Arsenic Spiking

If there is insufficient arsenic naturally present in the feed water, spiked arsenic may be used at a concentration sufficient to permit the most-stressed operation claimed by the Manufacturer. The minimum arsenic level in the test water should be the lesser of 20 µg/L or three times the applicable EPA-specified MCL. If the manufacturer wants As(III) removal as part of its objective, the unit must be challenged with an As(III)-containing test water, otherwise an As(V) challenge water will be acceptable. When challenging the unit with As(V), sufficient chlorine or an alternative oxidant may be added to the feed water to insure the oxidation of any As(III) present to As(V). When spiking the feed water, the following guidelines are suggested:

(1) Arsenic spiking of the feed water shall begin at least 24 hours prior to any actual data collection so that the spiking system is at steady state and has stabilized.

(2) Arsenic (III) feed solution will be prepared by diluting the arsenic into dilution water that is distilled or deionized and oxidant free. Arsenic (V) feed solution will also be prepared in distilled or deionized water, which may contain an oxidant.

(3) To spike arsenic (III), use Analytical Reagent Grade sodium arsenite, $NaAsO_2$.

(4) To spike arsenic (V), use Analytical Reagent Grade sodium arsenate, Na_2HAsO_4,•$7H_20$.

(5) The feed reservoir for the arsenic spike solution shall be made of chemically inert material such as polyethylene, polypropylene, or stainless steel, which will not adsorb arsenic.

(6) The reservoir will be mixed continuously throughout the experiment.

(7) The arsenic spike solution will be fed using an adjustable rate chemical feed pump.

(8) Use an in-line static mixer or a rapid mixing chamber to mix this solution into the feed water.

If Manufacturers wish to prove that their process will oxidize and remove As(III), spiking with As(III) will be necessary. When feeding As(III) to a plant, Manufacturers and Field Testing Organizations need to be aware of potential difficulties in preventing conversion of As (III) to As (V) as the spiking solution is held in its storage container. Further conversion to the higher valence state could occur during passage of spiked water through the system. This is very significant because As(III) is not removed by chloride anion exchange (Clifford et. al. 1998). Thus, pre-oxidation to convert As(III) to As (V), with an oxidant such as free chlorine is mandatory if As(III) is present at levels near or above the MCL for total arsenic (Frank and Clifford, 1986).

9.3.2 Attainment of Steady State Operation

The recording of data for the Initial Plant Characterization Tests should begin only after the arsenic ion exchange plant has reached steady state operation, which occurs when the mass of arsenic removed by the resin equals the mass of arsenic eluted from the resin during regeneration. The acceptable QA/QC error range for arsenic analysis and flow rate measurements will determine the acceptable range of error for the mass balance on arsenic. For arsenic removal, steady state should be reached within 3-5 exhaustion-regeneration cycles because arsenic is easily eluted from the resin during regeneration. To first set the controls on the system, an estimate of arsenic run length may be obtained from small-column lab data or by using predictive equations based on equilibrium multicomponent chromatography theory (Clifford, 1995; Tirupanangadu, 1997; Guter, Cathedral Peak Software Computer Program.).

Balancing the arsenic adsorbed with that eluted during regeneration may be accomplished as follows: Calculate the mass of arsenic adsorbed by measuring the area between the influent and effluent arsenic curves. Measure the mass of arsenic eluted during regeneration by sampling and analyzing the composite sample of collected regenerant and rinse waters.

In the event that a single ion-exchange column exhaustion cycle would require more than 2,000 BV to exhaust a column on the water to be tested, steady state will be defined as the completion of three exhaustion-regeneration cycles of at least 2,000 BV. For systems with multiple parallel columns operating simultaneously, this rule shall apply to each operating column in the system, i.e., each column must be subjected to three exhaustion-regeneration cycles of at least 2,000 BV. A carousel system will be defined as having reached steady state when all the following conditions have been met: (a) at least three rotations have been completed, (b) the regenerant mass and volumetric flow rates have been stable (±25%) for two days, and (c) the effluent concentrations of the target contaminants, e.g., arsenic, and nitrate have been stable (±25%) for two days.

Note: The Verification Testing Runs must be performed at the same operating

conditions that were used to define steady state operation during the Initial Plant Characterization Tests.

9.3.3 Collection of Preliminary Data

Feed and Product Water Analyses: At least two feed water (raw water) and 10 product water (process effluent water) samples should be collected and analyzed during the preliminary exhaustion runs. It is recommended that complete preliminary data be collected for at least one Initial Characterization run, which shall consist of at least one exhaustion-regeneration cycle for each column in the operating system. For a two-column system with one column designed to be operating while a second column is in standby mode, the Initial Characterization Run would consist of only one exhaustion-regeneration cycle. For a four-column system designed to have three columns operating in parallel at different stages of exhaustion while a fourth column is in standby mode, the Initial Characterization Run would consist of three exhaustion-regeneration cycles. The samples should be appropriately labeled as to Run No., Cycle No., BV and sampling time. Ground waters and surface waters should be analyzed for pH, arsenic, nitrate, sulfate, chloride, and bicarbonate according to the methods listed in Table 1.

Operating Data: The following operating data should be recorded by time of day during the preliminary run(s):

(1) controller set points for each bed including:
- flow rate of product water,
- start time, finish time, and volume to exhaustion,
- flow rate and volume of backwash water,
- mass of salt and volume of regenerant used for each regeneration,

(2) pressure readings for each column and pre-filter device
(3) number of vessels in exhaustion, regeneration, and standby
(4) visual observations of piping leaks, scaling and fouling problems, resin condition

9.3.4 Determination of Variable Effluent Quality and Arsenic Peaking Potential

Effluent Histories: For systems that operate with only one or two ion-exchange columns in service at a time, concentration vs. bed volume plots (effluent histories) should be plotted on the same graph for pH, arsenic, nitrate, sulfate, chloride and bicarbonate. At least one complete set of effluent history curves ($\geq$6 data points for each curve) for one column should be plotted during the Initial Plant Characterization Tests. It is not necessary to plot the single-column effluent histories if the system consists of three or more multiple parallel columns, operating simultaneously.

Arsenic Peaking Potential: The potential for arsenic peaking should be determined to quantify the danger of exceeding arsenic breakthrough when only one or two simultaneously exhausted columns are employed for arsenic treatment. The arsenic peaking potential can be determined during the construction of the effluent history curves

by running the column to a point 500 BV beyond the known breakthrough point for arsenic. Collect at least 10 samples for arsenic analysis at appropriate intervals, especially just before and after the anticipated arsenic breakthrough point, so that an effluent history can be constructed showing the arsenic peak that would occur if the run is not terminated at the proper time.

9.3.5 Preliminary Assessment of Plant Performance:

The preliminary data collected during the Initial Plant Characterization Tests should be summarized and analyzed by the Field Testing Organization and reported to the Manufacturer and NSF. If the plant doesn't meet its performance objectives, the tests may be re-run with improved operating conditions as approved and/or suggested by the Manufacturer. Alternatively, the Manufacturer may wish to cancel the remainder of the Verification Testing program. If there are no significant problems with the performance data and no objections to the preliminary testing procedures, the Verification Testing may proceed as planned. If problems arise, they must be resolved to the satisfaction of NSF before Verification Testing begins.

9.4 Schedule

Task 3, the Initial Plant Characterization Tests will be performed as soon as possible after Task 2, Preparation, Coordination and Startup. Unless the arsenic run lengths are exceptionally long ($\geq$ 2,000 BV), steady state operation should be achieved within one week after starting the preliminary tests. For a three-parallel-column system operating at 2,000 BV run length, steady state should be achieved within 10-12 days. The collection of preliminary data and the arsenic peaking tests should be completed within two more weeks and the preliminary assessment of plant performance should take no more than one week. Thus, one month should be sufficient for the Initial Plant Characterization Tests.

10.0 TASK 4: VERIFICATION TESTING RUNS

10.1 Introduction

This task, which comprises the actual Verification Testing Runs, is the core of the Verification Testing Plan. During this task, the arsenic-removal ion exchange plant shall be operated for at least 240 hours over a period of at least 14 days during one testing period to collect data on equipment performance and water quality for purposes of performance verification. If a manufacturer chooses to demonstrate the effectiveness of their plant under a significantly different set of background water conditions, the option exists for a second test period to be carried out at a different site with the same transportable ion-exchange plant.

10.2 Objectives

The objectives of the Verification Testing Runs are to (a) to observe and record the plant operating conditions and equipment performance, (b) determine the overall feed water and finished water quality, and (c) establish the arsenic-removal performance of the plant.

10.3 Work Plan

10.3.1 Plant Operating Conditions and Equipment Performance

If the treatment equipment is being used for production of potable water and treats a water that naturally contains concentrations of arsenic appropriate for Verification Testing, so that arsenic spiking is not needed, routine operation for water production is anticipated in the time intervals between verification runs. The operating and water quality data collected and furnished to the Safe Drinking Water Act (SDWA) primacy agency during these times shall also be supplied to the Field Testing Organization.

The plant shall be operated for at least 240 hours during a period of 14 days or longer using the set point conditions determined in the Initial Plant Characterization Tests.

Table 3 indicates the operating and performance data to be collected during the Verification Testing Runs.

10.3.2 Feed Water and Product Water Quality

Water Quality Measurements: Water quality data shall be collected for the feed water, column influent water, and product water, as shown in Table 4, during Verification Testing. At a minimum, the required sampling schedule shown in Table 4 shall be observed by the Field Testing Organization. Water quality goals and target removal goals for the water treatment equipment shall be recorded in the Product-Specific Test Plan in the statement of objectives.

Table 3. Operating and Performance Data from Verification Test Runs

Parameter	Frequency
For the Entire Plant	
Instantaneous product water flow rate, gpm	Twice daily
Cumulative product water flow rate, gal	Twice daily
Cumulative waste water flow, gal	Daily
Brine consumption, gal	Daily
NaCl consumption, lbs and lbs/1000 gal product water	Daily
[&]Volume of arsenic-contaminated sludge, gal	Daily
[&]Solids conc. of arsenic-contaminated sludge, wt% solids	Daily
[&]Mass of arsenic contaminated sludge, lbs	Daily
[†]Diluted brine concentration, wt% NaCl	Daily
[†]Brine flow rate, gpm	Twice Daily
[†]Average time in exhaustion zone, hrs & BV of feed water	Daily
[†]Average time in regeneration zone, hrs & BV of regenerant	Daily
[†]Average time in rinse zone, hrs & BV of rinse water	Daily
[†]Carousel rotation time, hrs	Daily
Number of columns exhausted	Daily
Number of columns regenerated	Daily
Electrical energy consumption, kwhr	Daily
Energy cost, $/day	Daily
Equipment malfunctions, description of each malfunction and its result on plant performance.	As they occur
For Each Column in a Fixed-Bed Plant	
Instantaneous feed water flow rate, gpm	Twice daily
Pressure drop, psig	Twice daily
Cumulative feed water flow, gal	Daily
Exhaustion start and stop times, time of day	Each exhaustion
Regeneration start and stop times, time of day	Each regeneration
Displacement rinse start and stop times, time of day	Each rinse
Brine consumption, gal	Each Regeneration
Brine flow rate, gpm	Daily
NaCl consumption, lbs	Each Regeneration
**Diluted brine concentration, wt% NaCl	Daily
Visual inspection of resin level through site glass	Daily

[&]Only those plants with Fe(III) precipitation of brine will produce a sludge to be disposed of. Some plants will not produce an arsenic sludge.

†For a carousel plant

**If more than one dilution device exists in a plant, each device will be sampled and analyzed daily.

Some of the water quality parameters described in Table 4 will be measured on-site by the Field Testing Organization (see Table 5). Analysis of the remaining water quality parameters will be performed by a state-certified or third party or EPA-accredited analytical laboratory. The methods to be used for measurement of water quality parameters in the field are described in Table 5. The analytical methods utilized in this study for on-site monitoring of feed water and filtered water qualities are discussed in Task 6, Quality Assurance/Quality Control (QA/QC).

Table 4. Water Quality Sampling and Measurement Schedule

Parameter	Minimum Frequency*
pH	Continuous Monitoring of feed water and product water, daily on-site verification
Conductivity	Continuous Monitoring of product water, daily on-site verification
TDS	Daily on composite samples of feed water and product water
¶Residual Cl_2	Once per six hours on column inlet water, daily composite on product water
†Arsenic, Total	Once per six hours on product water, daily composite on feed water
§Arsenic(III)	At least four times on column inlet water during the course of the verification testing runs.
†Sulfate	Daily on composite samples of feed water and product water
†Nitrate	Daily on composite samples of feed water and product water
†Chloride	Daily on composite samples of feed water and product water
†Total Alkalinity	Daily on composite samples of feed water and product water

*All the above measurements assume a multiple column plant with at least three columns operating simultaneously, or a carousel plant. For one or two columns operating singly or in parallel, more frequent water quality analyses will be required because the water quality will be more variable. See note † below.

¶If another oxidant is used, the residual concentration of that oxidant should be measured.

†In addition to the daily composite samples, when one or two columns is operating singly or in parallel, the product water during one complete exhaustion cycle of at least one column must be analyzed once per 50 bed volumes based on the volume of resin in service at any given time. For an EBCT of 1.5 min, a 50 BV frequency translates to one sample per 75 min.

§As(III) speciation will only be required when objectives are established regarding the ability of the plant to remove As(III). The assessment of arsenic-removal performance shall not be dependent on the form of arsenic fed to the plant. Regardless of whether As(III) or As(V) or a mixture of the two is fed, the performance requirements will be determined by the measurement of As(total) in the product water. For purposes of determining the reasons for high arsenic in the product water, the Manufacturer and the Field Testing Organization are encouraged to measure the As(III) concentration in the product water whenever 10 ppb is closely approached or exceeded.

Water Quality Sample Collection: Water quality data shall be collected during each of the specified periods of Verification Testing. Before the any data is collected, the plant must have reached steady state, which has been previously defined in Section 9.3.1. Additional sampling and data collection may be performed at the discretion of the Manufacturer. Sample collection frequency and protocol shall be defined in the Product-Specific Test Plan.

In the case of water quality samples that will be shipped to the state-certified or third party or EPA-accredited analytical laboratory for analysis, the samples shall be collected in appropriate containers (containing preservatives as applicable) prepared by the state-

certified or third party or EPA-accredited, analytical laboratory. These samples shall be preserved, stored, shipped and analyzed in accordance with appropriate procedures and holding times, as specified by the analytical laboratory.

Table 5. Analytical Methods

Parameter	**Analysis Location**	**Standard Method**	**EPA Method**
Arsenic concentration	Lab	3500-As, 3113 B, 3114 B, 3120 B	200.7, 200.8, 200.9
Arsenic species	Field	Modified anion exchange method for field speciation.[a]	
pH	On-Site	4500-H^+	
Conductivity	On-Site	2510-B	
Sulfate	On-Site or Lab	Test Kit 4500-Sulfate, 4110 B	300.0, 375.2
Chloride	On-Site or Lab	Test Kit or Electrode 4500-Chloride, 4110 B	300.0
Total alkalinity	On-Site or Lab	Test Kit-Digital Titrator 2320-B	
Nitrate	On-Site or Lab	Test Kit 4500-Nitrate, 4110 B	300.0, 353.2
Total organic carbon[b]	Lab	5310-C	
Turbidity[b]	On-Site or Lab	2130-B	180.1
Iron	On-Site or Lab	Test Kit 3111 B, 3113 B, 3120 B	200.7, 200.9
Manganese	On-Site or Lab	Test Kit 3111 B, 3113 B, 3120 B	200.7, 200.8, 200.9

[a]Methods for analyzing As(III) and As(V) are non-standard but the modified anion exchange method for field speciation as described in Edwards et al., 1999, may be used or another method may be submitted to NSF for consideration.

[b]Turbidity and TOC measurement will only be required for surface waters or unusual ground waters. When turbidity is a problem, pressure prefiltration will be employed as a pretreatment for ion exchange.

10.3.3 Arsenic Removal Performance

Evaluation of arsenic removal shall be performed by analyzing arsenic in the feed and product waters, and in the blended water if applicable. If arsenic spike testing is required, the feed water arsenic measurement will be made after appropriate arsenic species—either arsenate (As(V)) or arsenite (As(III))—have been added to the feed water. If

arsenic spiking of feed water is employed, the ion-exchange system with spiking should have been tested and have reached steady state operation during the Initial Plant Characterization Tests (see Task 3, Section 9.3.1). Arsenic sampling and analysis shall be performed as specified in Table 5.

Arsenic Sample Collection: Water quality data shall be collected during each of the specified periods of Verification Testing. Before the any data is collected, the plant must have reached steady state, which has been previously defined as five exhaustion-regeneration cycles for each column in the fixed bed or carousel system.

10.4 Schedule

The plant shall be operated for at least 240 hours during a period of 14 days or longer using the set point conditions determined in the Initial Plant Characterization Tests. **Note:** According to the initial plant characterization tests, the longest run length will be 2,000 BV. At a typical EBCT of 1.4 minutes (1000 BV/day), the exhaustion of a column will require 48 hours, thus, at least five exhaustion-regeneration cycles for each column in an operating system will be completed during the 240-hour Verification Test Period.

10.5 Evaluation Criteria

Performance of ion exchange systems shall be evaluated in the context of the Manufacturer's statement of performance objectives with respect to (1) treatment equipment performance, (2) finished water quality, and (3) arsenic removal performance.

10.5.1 Treatment Equipment Performance

The goal of this sub-task was to operate the plant within the mechanical, electrical, and cost constraints for at least 240 hours during the Verification Testing Runs. To complete the Treatment Equipment Performance test, the plant must meet all the criteria specified in the PSTP. These would include criteria such as (1) advertised capacity in terms of total daily treated water production, waste water discharges, sludge production, NaCl consumption, electrical costs, maintenance costs, total cost of treatment in terms of $/1000 gallons product water, and other relevant equipment performance criteria.

10.5.2 Product Water Quality

Because an ion-exchange bed produces a variable water quality as it is exhausted, care must be exercised to ensure that the variable effluent quality doesn’t exceed the finished water quality objectives at any time. For example, the effluent pH may be lower than 7.0 during the early portions of a run. This variable water quality problem is generally addressed by simultaneously operating three or more columns in parallel or by using a carousel system. It is recommended that at least 95% of the product water samples be within the pH range of 7.0-9.0 and have a nitrate concentration below water quality objectives, in addition to meeting the objectives for arsenic.

10.5.3 Arsenic Removal Performance

A properly operated ion exchange process can easily achieve an effluent arsenic concentration below 1.0 µg/L, a level below any likely MCL adopted by EPA. However, if the resin is not rinsed properly following regeneration or if the column is allowed to run beyond breakthrough, arsenic MCL violations might occur. To maintain the Arsenic Removal Performance objective, the plant must consistently deliver a finished water which is below 10 ppb, i.e., 95% of the product water samples must be below 10 ppb. Furthermore, no product water samples may exceed the feed water concentrations of arsenic (total) or nitrate.

The assessment of arsenic-removal performance shall not be dependent on the form of arsenic fed to the plant. Regardless of whether As(III) or As(V) or a mixture of the two is fed, the performance requirements will be determined by the measurement of As(total) in the product water. For purposes of determining the reasons for high arsenic in the product water, the Manufacturer and the Field Testing Organization are encouraged to measure the As(III) concentration in the product water whenever the 10 ppb is closely approached or exceeded.

11.0 TASK 5: DATA MANAGEMENT

11.1 Introduction

The data management system used in the verification testing program shall involve the use of computer spreadsheet software and manual recording of operational parameters for the water treatment equipment on a daily basis.

11.2 Objectives

The objective of this task is to establish a viable structure for the recording and transmission of field testing data such that the Field Testing Organization provides sufficient and reliable operational data for verification purposes. A second objective is to develop a statistical analysis of the data, as described in "Protocol for Equipment Verification Testing for Arsenic Removal."

11.3 Work Plan

11.3.1 Data Handling

SCADA Systems: The following protocol has been developed for data handling and data verification by the Field Testing Organization. Where possible, a Supervisory Control and Data Acquisition (SCADA) system should be used for automatic entry of testing data into computer databases.

(1) Specific parcels of the computer databases for operational and water quality parameters should be downloaded by manual importation into Excel (or similar spreadsheet software) as a comma delimited file.

(2) Specific database parcels will be identified based on discrete time spans and monitoring parameters.

(3) The data will be manipulated into a convenient framework to allow analysis of ion-exchange equipment operation in a spreadsheet form.

(4) Backup of the computer databases to diskette should be performed on a monthly basis at a minimum.

Non-SCADA Systems: In the case when a SCADA system is not available:

(1) Field testing operators will record data and calculations by hand in laboratory notebooks. (Daily measurements will be recorded on specially-prepared data log sheets as appropriate.)

(2) Laboratory notebook will contain carbon copies of each page (to ease referencing the original data and offer protection of the original record of results).

(3) Original notebooks will be stored on-site; the carbon-copy sheets will be forwarded to the project engineer of the Field Testing Organization at least once per week.

(4) Operating logs shall include a description of the process equipment (description of test runs, names of visitors, description of any problems or issues, etc.); such descriptions shall be provided in addition to experimental calculations and other items.

Spreadsheets:

(1) The data for the project will be recorded in custom-designed spreadsheets.

(2) The spreadsheets will be capable of storing and manipulating each monitored water quality and operational parameter from each task, sampling location, and sampling time.

(3) All data from the laboratory notebooks and data log sheets will be entered into the appropriate spreadsheet.

(4) Data entry will be conducted on-site by the designated field testing operators, with all recorded calculations checked at this time.

(5) Following data entry, the spreadsheet will be printed out and the printout will be checked against the handwritten data sheet.

(6) Any corrections will be noted on the hard-copies and corrected on the screen, and a corrected version of the spreadsheet will be printed out.

(7) Each step of the verification process will be initialed by the field testing operator or engineer performing the entry or verification step.

Data Tracking:

(1) Each experiment (e.g., each ion-exchange test run) will be assigned a run number which will then be linked to the data from that experiment through each data entry and analysis step.

(2) Data will be tracked by use of the same system of run numbers as samples are collected and sent to state-certified or third party or EPA-accredited analytical laboratories.

(3) Data from the analytical laboratories will be received and reviewed by the Field Testing Organization.

(4) These data will be entered into the data spreadsheets, corrected, and verified in the same manner as the field data.

11.3.2 Statistical Analysis

Arsenic data developed from grab samples collected during filter runs according to the Analytical Schedule in Task 4 of this Test Plan shall be analyzed for statistical uncertainty. The Field Testing Organization shall calculate 95% confidence intervals for the arsenic data obtained during Verification Testing as described in "Protocol for Equipment Verification Testing for Arsenic Removal." A separate statistical analysis shall be carried out for each testing condition for which the required 11 or more sets of arsenic samples were collected and analyzed.

The statistics developed will be helpful in demonstrating the degree of reliability with which the water treatment equipment can attain quality goals under the treatment conditions tested. The results of the statistical analysis also shall be used to determine if the performance of the equipment was equal to or better than that given in the statement of performance objectives.

12.0 TASK 6: Quality Assurance/Quality Control

12.1 Introduction

Quality assurance and quality control (QA/QC) of the operation of the ion exchange equipment and the measured water quality parameters shall be maintained during the Verification Testing program.

12.2 Objectives

The objective of this task is to maintain strict QA/QC methods and procedures during the Equipment Verification Testing Program. Maintenance of strict QA/QC procedures is important, in that if a question arises when analyzing or interpreting data collected for a given experiment, it will be possible to verify exact conditions at the time of testing.

12.3 Work Plan

Equipment flow rates and associated signals should be verified and recorded on a routine basis. A routine daily walk-through during testing will verify that each piece of equipment or instrumentation is operating properly. Particular care will be taken to verify the water, brine, and arsenic spiking (if applicable) flow rates are correct. In-line monitoring equipment, such as flow meters and conductivity meters, will be checked to verify that the readout matches with the actual measurement (i.e. flow rate, specific conductance) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods.

12.3.1 Daily QA/QC Verifications

The product water pH meter should be checked and calibrated daily.

The following parameters should be verified by weight or by volume:

(1) Chlorine or oxidant consumption

(2) NaCl consumption

(3) Concentrated arsenic spiking solution flow rate

(4) Saturated brine flow rate

(5) Diluted brine flow rate

12.3.2 Bi-weekly QA/QC Verifications

In-line flow meters and/or rotameters: clean equipment to remove any debris or biological buildup and verify flow volumetrically to avoid erroneous readings.

12.3.3 QA/QC Verifications for Each Test Period

(1) In-line conductivity meters

(2) Differential pressure transmitters (verify gauge readings and electrical signal using a pressure meter)

(3) Tubing (verify good condition of all tubing and connections, replace if necessary)

12.4 On-Site Analytical Methods

The analytical methods utilized in this study for on-site monitoring of raw water and treated water quality are described in the section below. Use of either bench-top or in-line field analytical equipment will be acceptable for the verification testing; however, in-line pH and conductivity meters (located on each column effluent in a fixed-bed plant) are recommended for ease of operation.

12.4.1 pH

(1) pH analysis shall be performed according to Standard Method 4500-H^+.

(2) A three-point calibration of the pH meter shall be performed once per day when the instrument is in use.

(3) Certified pH buffers in the expected range shall be used.

(4) The pH probe shall be stored in the appropriate solution defined in the instrument manual.

(5) The water is poorly buffered, pH measurement in a confined vessel is recommended to minimize the effects of carbon dioxide exchange with the atmosphere.

12.4.2 Sulfate, Nitrate, Chloride and Alkalinity by Test Kits

Sulfate, nitrate, chloride, and alkalinity (bicarbonate) are not target contaminants for arsenic removal by ion exchange, but they can give indication as to the degree of exhaustion of a column and the approach of arsenic breakthrough. Thus, they may be measured on-site by properly calibrated test kits. Nitrate may be a special case; if the Initial Plant Characterization tests indicate that nitrate will potentially exceed its MCL, nitrate analysis becomes a primary measure of plant performance and nitrate should be determined at a state-certified or third-party or EPA-accredited laboratory, although on-site test kits may also be used to indicate the plant performance.

All test kits used on site should be calibrated daily using known standards at two or more concentration levels. Data obtained with test kits, which utilize non-standard methods shall not be used to determine if the plant meets the applicable performance criteria.

12.4.3 Conductivity

Electrical conductivity (µS or microSiemens) is continuously measured at the outlet of each ion exchange column to indicate when the unit is in exhaustion, regeneration, or rinse mode. Its most important function is to indicate the degree of rinsing of a column following regeneration. If the column is put back into service too soon, arsenic from the spent regenerant salt solution remaining in the column may get into the plant effluent. Thus, it is necessary to check and calibrate the conductivity probes at least once per test period. Conductivity shall be measured using Standard Method 2510 B.

12.4.4 Temperature (Optional for Ion Exchange)

Temperature is not a very important variable in ion exchange providing that the water is less than about 80°C to prevent damage to the strong-base anion resin. If however, the ground water is naturally hot and has been cooled prior to ion exchange treatment and distribution, temperature measurement may be required. Generally, temperature is an optional measurement for the ion exchange process. If required, readings for temperature shall be conducted in accordance with Standard Method 2550. Raw water temperatures

should be obtained at least once daily. The thermometer shall have a scale marked for every 0.1^{o}C, as a minimum, and should be calibrated weekly against a precision thermometer certified by the National Institute of Standards and Technology (NIST).

12.4.5 Color

If a surface water is being treated by ion exchange, color measurement may be required. Normally, however, color would be an optional measurement. If it is required, true color shall be measured with a spectrophotometer at 455 nm, using a Hach Company adaptation of the *Standard Methods* 2120 procedure. Samples should be collected in clean plastic or glass bottles and analyzed as soon after collection as possible. If samples can not be analyzed immediately they should be stored at 4°C for up to 24 hours, and then warmed to room temperature before analysis. The filtration system described in *Standard Methods* 2120 C should be used, and results should be expressed in terms of PtCo color units.

12.5 Chemical and Biological Samples Shipped Off-Site for Analyses

Inorganic chemical samples, including arsenic, alkalinity, iron, and manganese, shall be collected and preserved in accordance with Standard Method 3010B, paying particular attention to the sources of contamination as outlined in Standard Method 3010C. The samples should be refrigerated at approximately 2 to 8°C immediately upon collection, shipped in a cooler, and maintained at a temperature of approximately 2 to 8°C. Samples shall be processed for analysis by a state-certified or third party or EPA-accredited laboratory within 24 hours of collection. The laboratory shall keep the samples at approximately 2 to 8°C until initiation of analysis.

TOC samples shall be collected in glass bottles supplied by the state-certified or third party or EPA-accredited laboratory and shipped at 4 ^{o}C to the analytical laboratory as soon as practical. The TOC samples shall be collected and preserved in accordance with Standard Method 5010B.

Algae samples shall be preserved with Lugol's solution after collection, stored and shipped in a cooler at a temperature of approximately 2 to 8°C, and held at that temperature range until counted.

13.0 OPERATIONS & MAINTENANCE (O&M)

The Field Testing Organization shall obtain the Manufacturer-supplied O&M Manual to evaluate the instructions and procedures for their applicability during the verification testing period. The following are recommendations for criteria for O&M Manuals for systems employing ion exchange.

13.1 Maintenance

The Manufacturer should provide readily understood information on the recommended or required maintenance schedule for each piece of operating equipment such as:

(1) Ion-exchange beds containing strong-base anion resin

(2) Multiple parallel fixed beds

(3) Carousel ion-exchange system, if applicable

(4) Pumps

(5) NaCl Brine saturator

(6) Brine dilutor

(7) Flow control valves

(8) Chemical feeders

(9) Mixers

(10) Motors

(11) Instruments, such as continuous pH monitors or conductivity meters

(12) Integrating Flow meters

(13) In-line static mixers

(14) Tanks and basins, especially brine storage tanks

13.2 Operation

13.2.1 Operation Manuals:

The Manufacturer should provide readily understood recommendations for procedures related to proper operation of the equipment. Among the operating aspects that should be discussed are the following:

Automated Ion Exchange Systems

(1) Fixed beds

(2) Multiple fixed beds in parallel, typically three in service and one in standby or regeneration

(3) Carousels (multiple rotating beds in parallel)

Automated single ion exchange column operation

(1) Begin exhaustion (service) cycle

(2) End exhaustion cycle

(3) Start Backwash

(4) End Backwash

(5) Start regeneration

(6) End regeneration

(7) Start slow (displacement) rinse

(8) End slow rinse

(9) Start fast rinse

(10) End fast rinse

(11) Return to service

Chemical feeders (e.g. for NaCl brine preparation and delivery)

(1) Dilution of brine -- proper procedures

(2) Calibration check

(3) Settings and adjustments -- how they should be made

Mixers (if arsenic spiking is employed)

(1) Purpose

(2) Changing intensity (RPM), if available

Pressure Filtration (if prefiltration before ion-exchange columns is required)

(1) Control of filtration rate

(2) Observation and measurement of head loss during filter run

(3) Automatic backwashing

13.2.2 Troubleshooting Guide:

The Manufacturer should provide a troubleshooting guide; a simple check-list of what to do for a variety of problems including:

(1) No raw water (feed water) flow to plant

(2) Carousel will not turn

(3) Master carousel valve not functioning

(4) Ion exchange column effluent pH too low

(5) No brine flow

(6) No ion-exchange column backwash flow

(7) Can't control rate of flow of water through system

(8) No chemical feed (brine, chlorine, or arsenic spiking solution)

(9) Calibration and maintenance of on-line pH monitoring instruments, problems of erratic pH or drifting pH readings

(10) No reading on pH meter and/or conductivity meter

(11) Product water conductivity too high

(12) No electric power

(13) Mixer (for arsenic spiking) will not operate

(14) Pressure prefilter can't be backwashed or backwash rate of flow can't change

(15) Automatic operation (if provided) not functioning

(16) No ion-exchange column head loss readings

(17) Flow control valve stuck or will not operate

13.2.3 History of Ion Exchange Equipment Operability:

During Verification Testing, attention shall be given to equipment operability aspects. These aspects of plant operation should be included to the extent practical in reports of equipment testing when the testing is done under the ETV Verification Program. Among the factors that should be considered are the following:

(1) How successful is a SCADA system, i.e., complete automation and computer control with data acquisition as a means of operating an arsenic ion-exchange plant?

(2) How does one ensure that arsenic has not broken through the column without actually making a continuous on-line arsenic measurement, which is impractical.

(3) Is there any easy-to-measure parameter such as pH or sulfate concentration that would signal the breakthrough of arsenic from a column?

(4) How does the operator ensure that the regenerant brine has actually been fed to the spent resin column?

(5) What is the preferred means of measuring or estimating brine consumption?

(6) How many times can the brine be reused without treatment

(7) How does one automate the precipitation of arsenic from the spent brine?

(8) Does reuse of the brine cause any precipitation problems?

(9) How often is it necessary to reset the brine flow rate?

(10) How can plant operator check on condition and depth of ion-exchange media?

(11) Can ion exchange columns be mothballed in the summer without microbiological growth on the resin?

(12) What are the special problems encountered in treating surface water using ion exchange for arsenic removal, and it really feasible to use arsenic ion exchange for surface water treatment?

The reports on Verification Testing should address the above questions in the written reports. The issues of operability should be dealt with in the portion of the reports that are written in response to Section 10.3.1 Plant Operating Conditions and Equipment Performance.

14.0 REFERENCES

Clifford, D. & Lin, C.C. 1991. Arsenic (III) and Arsenic (V) Removal From Drinking Water in San Ysidro, New Mexico, EPA/600/52-91/001. Cincinnati, Ohio (June).

Clifford, D. A. & C. C. Lin, "Arsenic Removal from Groundwater in Hanford, California—A Preliminary Report," University of Houston, Department of Civil/Environmental Engineering, 1986.

Clifford, D. A. & Ghurye, G. Ion Exchange With Spent Brine Recycling As A Viable Treatment Technology For Arsenic Removal From Drinking Water, In preparation for submission to J. AWWA, April, 1998.

Clifford, D.A. & Bilimoria, M. Mobile Drinking Water Treatment Research Facility for Inorganic Removal. EPA-600/S2-84/018 (1978).

Clifford, D.A. & Lin, C.C. Ion Exchange, Activated Alumina, and Membrane Processes For Arsenic Removal From Groundwater. Proc. 45th Annual Environmental Engineering Conf. Univ. of Kansas (1995).

Clifford, D.A. 1990. Ion Exchange and Inorganic Adsorption. *Water Supply and Treatment: A Handbook of Community Water Supplies, 4th ed.* McGraw-Hill, New York.

Cullen, W.R., & Reimer, K. J. 1989. "Arsenic Speciation in the Environment." *Chemistry Review*, 89:713.

Eaton, A.D. 1994, "Determining the Practical Quantitation Level for Arsenic," *Journal AWWA*, 86:2:100 (February).

Edwards, Marc, Sapna Patel, Laurie McNeill, Hsiao-wen Chen, Michelle Frey, Andrew Eaton, Ronald C. Antweiler, and Howard E. Taylor. 1998. "Considerations in As Analysis and Speciation," *Journal AWWA*, 90:3:103.

Ferguson, J. F. & Gavis, J. A., 1972, " A Review of the Arsenic Cycle in Natural Waters." *Water Research*, 6:1259.

Fox, K.R., & Sorg, T.J. 1987. "Controlling Arsenic, Fluoride, and Uranium by Point-of-Use Treatment," *Journal AWWA*, 79:10:81.

Frank, P. & D. A. Clifford, *Arsenic(III) Oxidation and Removal from Drinking Water*, PB 86-158 607/ NTIS, Springfield, Va., 1986; *Summary Report*, EPA/600/5286/021, U.S. EPA, Cincinnati, April 1986.

Frey, M. M., M. A. Edwards, et al. (1997). National Compliance assessment and costs for the regulation of arsenic in drinking water. Denver CO, American Water Works Association.

Ghurye, G. L., D. A. Clifford, et al. (1998). "Combined Arsenic and Nitrate removal by ion exchange and KDF media." American Water Works Assoc.

Gulledge, J.H. & O'Connor, J.T. 1973, "Removal of Arsenic From Water by Adsorption on Aluminum and Ferric Hydroxides," *Journal AWWA*, 65:8:548 (August).

Gupta, S.K. & Chen, K.Y. 1978, "Removal of Arsenic From Water by Adsorption on Aluminum and Ferric Hydroxides," *Journal WPCF*, 50:493 (March).

Guter, G. (1998). IX Windows Pro. Bakersfield, California, Cathedral Peak Software.

Hach Water Analysis Handbook, 2nd Ed. Hach Company, Loveland, Colorado 1992.

Hathaway, S. and F. Rubel Jr. (1987). "Removing arsenic from drinking water." American Water Works Association Journal 79 (No. 8): 61-65.

Horng, L. L. and D. A. Clifford (1997). "The behavior of polyprotic anions in ion exchange resins." Reactive and Functional Polymers 35 (1/2): 41-54.

Irgolic, K. J., *Speciation of Arsenic Compounds in Water Supplies*, EPA 600/S1-82010, Cincinnati, Ohio, November 1982.

Malcolm Pirnie, Inc. 1993. Treatment and Occurrence, Arsenic in Potable Water Supplies. Drinking Water Treatment Branch, Office of Groundwater and Drinking Water, US Environmental Protection Agency, Washington, D.C., September.

Pontius, F. W. (1995). "An update of the federal drinking water regulations." Journal of the American Water Works Association 87 (2): 48-58.

Smith, A.H. et al. Cancer Risks From Arsenic In Drinking Water. *Environmental Health Perspective*, 97:259 (1992).

Sorg, T. J., & Logsdon, G. S. 1978. "Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics: Part 2," *Journal AWWA*, 70:7:379.

Standard Methods for the Examination of Water and Wastewater, 1999. APHA, AWWA, and WPCF, 20th ed., Washington, D.C.

Thompson, M.A., And Chowdhury, Z.K. 1993. Evaluating Arsenic Removal Technologies. Proceedings 1993 AWWA Annual Conference, Water Resources. AWWA, Denver, Colorado, pp. 321-342.

Tirupanangadu, M. (1996). A visual basic application for multicomponent chromatography in ion exchange columns. Environmental Engineering Program. Houston, University of Houston**:** 179.

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CHAPTER 3

EPA/NSF ETV EQUIPMENT VERIFICATION TESTING PLAN COAGULATION AND/OR CO-PRECIPITATION AND FILTRATION FOR REMOVAL OF ARSENIC

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TABLE OF CONTENTS

Page

1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN 3-5

2.0 INTRODUCTION 3-5

3.0 GENERAL APPROACH 3-6

4.0 OVERVIEW OF TASKS 3-6
4.1 Task A: Characterization of Feed Water 3-7
4.2 Task B: Initial Tests Runs 3-7
4.3 Task 1: Verification Testing Runs 3-7
4.4 Task 2: Feed Water and Finished Water Quality 3-7
4.5 Task 3: Operating Conditions and Treatment Equipment Performance 3-7
4.6 Task 4: Arsenic Removal 3-7
4.7 Task 5: Data Management 3-8
4.8 Task 6: Quality Assurance and Quality Control 3-8

5.0 TESTING PERIODS 3-8

6.0 DEFINITIONS 3-8
6.1 Coagulation 3-8
6.2 Conventional filtration treatment 3-8
6.3 Direct filtration 3-8
6.4 Filtration 3-8
6.4.1 Granular media filtration 3-8
6.4.2 Membrane filtration 3-8
6.4.3 Precoat filtration 3-9
6.4.4 Bag filtration 3-9
6.4.5 Cartridge filtration 3-9
6.5 Flocculation 3-9
6.6 Sedimentation 3-9
6.7 Dissolved air flotation 3-9
6.8 Contact clarification 3-9
6.9 Surface water 3-9
6.10 Groundwater 3-9

7.0 TASK A: CHARACTERIZATION OF FEED WATER 3-10
7.1 Introduction 3-10
7.2 Objective 3-10
7.3 Work Plan 3-10
7.4 Analytical Schedule 3-11
7.5 Evaluation Criteria 3-11

8.0 TASK B: INITIAL TEST RUNS 3-11
8.1 Introduction 3-11

TABLE OF CONTENTS (continued)

Page

8.2 Objective 3-11
8.3 Work Plan 3-11
8.4 Analytical Schedule 3-12
8.5 Evaluation Criteria 3-12

9.0 TASK 1: VERIFICATION TESTING RUNS 3-13
9.1 Introduction 3-13
9.2 Experimental Objective 3-13
9.3 Work Plan 3-13
9.3.1 Verification Testing Runs 3-13
9.3.2 Routine Equipment Operation 3-14
9.4 Schedule 3-14
9.5 Evaluation Criteria 3-15

10.0 TASK 2: FEED WATER AND FINISHED WATER QUALITY 3-15
10.1 Introduction 3-15
10.2 Experimental Objectives 3-15
10.3 Work Plan 3-15
10.3.1 Water Quality Sample Collection 3-16
10.4 Analytical Schedule 3-16
10.5 Evaluation Criteria 3-17

11.0 TASK 3: OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE 3-18
11.1 Introduction 3-18
11.2 Objective 3-18
11.3 Work Plan 3-18
11.4 Schedule 3-19
11.5 Evaluation Criteria 3-19

12.0 TASK 4: ARSENIC REMOVAL 3-20
12.1 Introduction 3-20
12.2 Experimental Objective 3-20
12.3 Work Plan 3-20
12.3.1 Background Arsenic Levels 3-21
12.3.2 Spiked Arsenic 3-21
12.4 Analytical Schedule 3-22
12.5 Evaluation Criteria 3-23

13.0 TASK 5: DATA MANAGEMENT 3-23
13.1 Introduction 3-23
13.2 Experimental Objectives 3-23
13.3 Work Plan 3-24

TABLE OF CONTENTS (continued)

Page

13.3.1 Data Handling 3-24
13.3.2 Statistical Analysis 3-25

14.0 TASK 6: Quality Assurance/Quality Control 3-26
14.1 Introduction 3-26
14.2 Experimental Objectives 3-26
14.3 Work Plan 3-26
14.3.1 Daily QA/QC Checks 3-26
14.3.2 QA/QC Checks Performed Every Two Weeks 3-26
14.3.3 QA/QC Checks for Each Test Period 3-26
14.4 On-Site Analytical Methods 3-27
14.4.1 pH 3-27
14.4.2 Turbidity 3-27
14.4.2.1 Bench-Top Turbidimeters 3-27
14.4.2.2 In-Line Turbidimeters 3-28
14.4.3 Temperature 3-28
14.4.4 True Color 3-28
14.4.5 Chlorine Residual 3-29
14.4.6 Chlorine Dioxide Residual 3-29
14.4.7 Dissolved Ozone and Gas Phase Ozone 3-29
14.5 Chemical and Biological Samples Shipped Off-Site for Analyses 3-29
14.5.1 Total Organic Carbon and UV254 Absorbance 3-29
14.5.2 Arsenic 3-30
14.5.3 Other Inorganic Samples 3-30
14.5.4 Algae 3-30

15.0 OPERATIONS & MAINTENANCE 3-30
15.1 Maintenance 3-31
15.2 Operation 3-31

16.0 REFERENCES 3-34

TABLES

Page

Table 1. Generic Schedule for Verification Testing 3-37
Table 2. Water Quality Sampling and Measurement Schedule 3-38
Table 3. Analytical Methods 3-39
Table 4. Equipment Operating Data 3-40

APPENDICES

Appendix A Arsenic Speciation Method Developed by Battelle for EPA

1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN

This document is the Environmental Technology Verification (ETV) Technology Specific Test Plan (TSTP) for evaluation of water treatment equipment for arsenic removal utilizing chemical coagulation and filtration processes. This TSTP is to be used as a guide in the development of Product Specific Test Plan (PSTP) procedures for testing coagulation and filtration equipment, within the structure provided by the "EPA/NSF ETV Protocol for Equipment Verification Testing For Arsenic Removal: Chapter 1, Requirements for All Studies." This TSTP was originally developed for use with granular media filtration processes that rely upon chemical coagulation to effectively condition the feed water for effective filtration. Other approaches to arsenic removal by coagulation and filtration may be utilized, including oxidation and co-precipitation of naturally occurring iron and arsenic in water, to facilitate removal by coagulation and filtration. Furthermore, filtration processes other than granular media might be utilized. For these reasons the original TSTP for removal of arsenic by coagulation and filtration has been modified to reflect the numerous options for treatment that exist. Where appropriate, other TSTPs are referenced.

To participate in the equipment verification process for coagulation and filtration, the equipment manufacturer shall employ the procedures and methods described in this TSTP and in the referenced ETV protocol document as guidelines for the development of the PSTP. The procedures shall generally follow those tasks related to verification testing that are outlined herein, with changes and modification made for adaptations to specific equipment. At a minimum, the format of the procedures written for each task should consist of the following sections:

- Introduction;
- Objectives;
- Work Plan;
- Analytical Schedule; and
- Evaluation Criteria.

Each PSTP shall include Tasks 1 through 6.

2.0 INTRODUCTION

Various types of water treatment equipment employing processes of coagulation and filtration are used for a wide number of applications, including removal of turbidity from surface waters; removal of pathogens such as bacteria, viruses, *Giardia* and *Cryptosporidium;* removal of algae, color, and other natural organic matter from surface waters; and removal of inorganic constituents such as arsenic. Some equipment process trains use only chemical coagulation, mixing, and granular media filtration while others employ a solids separation or clarification step between coagulation and filtration. Clarification processes may include one of the following:

- Sedimentation;
- Sedimentation aided by tubes or plates;

- Downflow contact clarification;
- Upflow contact clarification; and
- Dissolved air flotation (DAF).

Filtration processes that could be tested include the following:

- Granular media filters;
- Membrane filters;
- Precoat filters;
- Bag filters;
- Cartridge filters; and
- Backwashable depth filters.

This TSTP is applicable to the testing of water treatment equipment utilizing a coagulation and filtration process train, which may include a clarification step before filtration. Two phases of testing are discussed. The first phase is initial operations, which consists of a series of tests that will be used to determine the optimum chemical pretreatment scheme at a specific geographic location. The second phase is verification testing, which will evaluate performance of the equipment under different raw water quality conditions. Verification tests will be performed for relatively short time intervals during one or more periods when the source water or feed water quality is appropriate for testing the range of water quality conditions that need to be evaluated.

Several of the arsenic studies referenced in this TSTP have shown that As (V) removal by coagulation and filtration is much more effective than As (III) removal. Thus, a preferred approach to arsenic treatment may involve pre-oxidation to convert all arsenic to As (V) so the most effective results will be attained. This optional additional treatment procedure is discussed where appropriate.

3.0 GENERAL APPROACH

Testing of equipment covered by this TSTP will be conducted by a Field Testing Organization (FTO) that is qualified by NSF International (NSF) and is selected by the manufacturer. Water quality analytical work to be carried out as a part of this TSTP shall be contracted with a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA.

4.0 OVERVIEW OF TASKS

The following section provides a brief overview of the recommended tasks that may be included in initial operations and of the tasks required to be included in the coagulation and filtration verification testing program.

4.1 Task A: Characterization of Feed Water

The objective of this recommended initial operations task is to obtain a chemical and physical characterization of the feed water. A brief description of the watershed that provides the feedwater shall be provided to aid in interpretation of feedwater characterization.

4.2 Task B: Initial Tests Runs

During initial operations, a manufacturer may want to evaluate equipment operation and determine the chemical dosages and other pretreatment conditions that result in effective treatment of the feed water. This is a recommended initial operations task.

4.3 Task 1: Verification Testing Runs

Water treatment equipment shall be operated for at least 320 hours during one or more testing periods to collect data on equipment performance and water quality for purposes of performance verification. Length of operation depends on the filtration process used.

4.4 Task 2: Feed Water and Finished Water Quality

During verification testing, feed water and treated water samples shall be collected, and appropriate sample analysis shall be undertaken. For example, turbidity samples are needed to determine the efficiency of surface water treatment, in addition to arsenic analyses for the evaluation of arsenic removal.

4.5 Task 3: Operating Conditions and Treatment Equipment Performance

During verification testing, operating conditions and performance of the water treatment equipment shall be documented. Operating conditions include pretreatment chemistry for coagulation, a listing of treatment processes used, and their operating conditions. If pre-oxidation is used, performance of this equipment shall be documented. Equipment performance information includes data such as rate of filter head loss gain, duration of filter runs and volume of water filtered per run, frequency and duration of filter cleaning, filter changing or replacement, and need for cleaning of pretreatment clarifiers. The operating conditions shall include plant flow rates and chemical dosages.

4.6 Task 4: Arsenic Removal

The objective of this task is to evaluate arsenic removal during verification testing by measuring arsenic in the feed water and in the treated water. If the arsenic concentration naturally present in the feed water is not sufficiently high for testing, arsenic spiking is needed. In addition detailed data on coagulant dosages and pre-oxidants, if used, are to be collected.

4.7 Task 5: Data Management

The objective of this task is to establish an effective field protocol for data management at the field operations site and for data transmission between the FTO and NSF for data obtained during the verification testing, plus the requirement for statistical analysis of the data.

4.8 Task 6: Quality Assurance and Quality Control

An important aspect of verification testing is the protocol developed for quality assurance and quality control (QA/QC). The objective of this task is to assure accurate measurement of operational and water quality parameters during coagulation and filtration equipment verification testing.

5.0 TESTING PERIODS

The required tasks in this TSTP (Tasks 1 through 6) are designed to be carried out over one or more testing periods having a duration of at least 320 hours, not including the time required for mobilization, start-up, and initial operations. Length of operation depends on the filtration process used. A schedule describing the duration of testing periods for various filtration processes is provided in Table 1.

6.0 DEFINITIONS

Definitions that apply for coagulation and filtration processes and that were given in the Surface Water Treatment Rule, as published in the *Federal Register* on June 29, 1989, are:

6.1 Coagulation: A process using coagulant chemicals and mixing by which colloidal and suspended materials are destabilized and agglomerated into flocs.

6.2 Conventional filtration treatment: A series of processes including coagulation, flocculation, sedimentation, and filtration resulting in substantial particulate removal.

6.3 Direct filtration: A series of processes including coagulation and filtration but excluding sedimentation which results in substantial particulate removal.

6.4 Filtration: A process for removing particulate matter from water by passage through porous media.

> **6.4.1 Granular media filtration:** Filtration through a bed of granular material such as sand, anthracite coal, garnet, ilmenite, granular activated carbon, or other material suitable for use as filter media.
>
> **6.4.2 Membrane filtration:** Filtration using a microfiltration or ultrafiltration membrane.

6.4.3 Precoat filtration: A process resulting in substantial particulate removal in which (1) a cake of precoat filter media is deposited on a support membrane (septum), and (2) while the water is filtered by passing through the cake on the septum, additional filter media known as body feed is continuously added to the filter cake to maintain the permeability of the filter cake.

6.4.4 Bag filtration: Filtration using a non-rigid, disposable, fabric filter in which flow generally is from the inside of the bag to the outside. One or more filter bags are contained within a pressure vessel designed to facilitate rapid change of the filter bags when the filtration capacity has been used up.

6.4.5 Cartridge filtration: Filtration using a rigid or semi-rigid, disposable, self-supporting filter element in which flow generally is from the outside of the cartridge to the inside. One or more filter cartridges are contained within a pressure vessel designed to facilitate rapid change of the cartridges when the filtration capacity has been used up.

6.5 Flocculation: A process to enhance agglomeration or collection of smaller floc particles into larger, more easily settleable particles through gentle stirring by hydraulic or mechanical means.

6.6 Sedimentation: A process for removal of solids before filtration by gravity or separation.

Other definitions include:

6.7 Dissolved air flotation: A process in which coagulated, flocculated water is introduced into the bottom of a chamber, along with recycled water containing microscopic air bubbles. The bubbles attach to the floc and rise to the water surface, carrying the floc up, while the clarified water leaves the chamber near the bottom.

6.8 Contact clarification: A process in which coagulated water is applied to a bed of coarse granular media. Flow may be downward from the top of the media bed to the bottom, or upward from the bottom of the media bed to the top. The bed of coarse media acts both as a flocculator by causing the division and recombination of flow streams of coagulated water, and as a clarifier, by trapping and removing some of the floc that forms as water flows through the bed. The coarse granular media may consist of natural mineral material or man-made materials such as plastic.

6.9 Surface water: All water which is open to the atmosphere and subject to surface runoff. For purposes of this document, surface water includes water from surface sources such as lakes, reservoirs, canals, rivers, or streams; and it also includes ground water under the direct influence of surface water.

6.10 Groundwater: For purposes of this testing program, groundwater is defined by *The Drinking Water Dictionary* as: The water contained in interconnected pores located (1) below the water table in an unconfined aquifer or (2) in a confined aquifer.

7.0 TASK A: CHARACTERIZATION OF FEED WATER

7.1 Introduction

The initial operations task is needed to determine if the chemical, biological and physical characteristics of the feed water are appropriate for the water treatment equipment to be tested.

7.2 Objective

The objective of this task is to obtain a complete chemical, biological, and physical characterization of the source water or the feed water that will be entering the treatment system being tested.

7.3 Work Plan

This task can be accomplished by using analytical measurements obtained from third party sources (i.e. United States Geological Survey (USGS), U.S. EPA, State Laboratories, Municipal Laboratories). The specific parameters needed to characterize the water will depend on the equipment being tested but information on the following characteristics should be compiled:

- Water temperature, pH, turbidity, and arsenic concentration and species;
- Total alkalinity, calcium hardness, iron, manganese, sulfate, silica and fluoride; and
- Algae, color, and total organic carbon (TOC).

Sufficient information should be obtained to illustrate the variations expected to occur in the water source during an annual cycle for the parameters that will be measured during verification testing. . This information will be compiled and shared with NSF so NSF and the FTO can determine the adequacy of the data for use as the basis to make decisions on the testing schedule. Failure to adequately characterize the feed water (source water) could result in testing at a site later deemed inappropriate, so the initial characterization will be important to the success of the testing program. Hering et al. (1997) have shown that under certain conditions, source water composition can influence arsenic removal by coagulation and filtration, so a good understanding of source water composition could be important to the outcome of verification testing. If removal of arsenic by pre-oxidation and co-precipitation with naturally occurring iron is contemplated, careful documentation of the concentrations of arsenic and iron in the feed water prior to verification testing are essential.

A brief description of the watershed that provides the feedwater shall be provided to aid in interpretation of feedwater characterization. The watershed description should include:

- Approximate size;
- Topography (i.e. flat, gently rolling, hilly, mountainous);
- Types of human activities that take place (i.e. mining, manufacturing, cities or towns, farming);
- Potential sources of pollution influencing water quality, especially potential sources for arsenic discharge; and

- Nature of the water source, such as stream, river, lake, wells, or man-made reservoir.

7.4 Analytical Schedule

In many cases, sufficient water quality data may already exist in the determination of the suitability of a source water for use as feedwater in a coagulation and filtration verification testing program.

7.5 Evaluation Criteria

Feed water quality will be evaluated in the context of the manufacturer's statement of performance objectives. The feed water should challenge the capabilities of the equipment but should not be beyond the range of water quality suitable for treatment for the equipment in question. For example, if the manufacturer's equipment is only capable of treating a maximum arsenic influent concentration of 200 μg/L, it would not be appropriate to test a feedwater containing an influent arsenic concentration of 300 μg/L.

8.0 TASK B: INITIAL TEST RUNS

8.1 Introduction

During initial operations, a manufacturer may want to evaluate equipment operation and determine the chemical dosages and other pretreatment conditions that result in effective treatment of the feed water. This is a recommended initial operations task. An NSF field inspection of equipment operations and sampling and field analysis procedures may be carried out during the initial test runs.

8.2 Objective

The objective of the test runs is to determine the proper chemical pretreatment scheme for treatment of the feedwater during verification testing. The chemical pretreatment requirements may be different for feedwaters from different test sites, different sources, or for the feedwater from the same site during testing periods when water quality has changed from the quality encountered during an earlier testing period. Therefore, conducting initial test runs is strongly recommended.

8.3 Work Plan

Before runs are made in which coagulant is used, the equipment shall be operated with uncoagulated feed water (spiked with arsenic if necessary) for one 24-hour run, and samples shall be collected from the feed water, clarifier effluent, and the filter effluent at 6, 12, 18, and 24 hours of operation to determine if arsenic losses occur through the system. Even though this test run is made during the initial operations, the data shall be presented in the verification testing report.

Conducting jar tests is often a cost effective means of developing data on coagulant chemical dosages and pH that give effective coagulation. The use of jar tests is recommended before filtration testing is initiated. The American Water Works Association's (AWWA) Manual M37 (1992) contains a chapter that describes procedures for using jar tests to optimize coagulation. Tests conducted for the effectiveness of both alum and iron as inorganic coagulants may be appropriate. The effect of polymer addition as a coagulant aid, and the effect of pH adjustment (acid or base addition) could also be examined through jar tests. Extensive bench-scale coagulation studies of arsenic removal have been performed previously at different test sites to determine arsenic removal, as demonstrated by various researchers (Sorg and Logsdon, 1978; Cheng, *et al*., 1994).

After jar tests have identified effective treatment conditions, several test runs may be needed to further refine appropriate chemical pretreatment conditions. At the end of these tests, an effective chemical pretreatment scheme should have been defined. During initial operations, the filters should be operated for a period of 24 hours, or for filter run times as long as those anticipated during verification testing. The use of bench-scale tests followed by pilot-scale coagulation tests, using alum and ferric chloride, is documented in a study performed by Cheng, *et al*. (1994), and may be used as a guide for performing this phase of testing.

For equipment that uses naturally occurring iron in groundwater as the coagulant chemical for attaining arsenic removal, initial test runs should include frequent measurement of iron and arsenic in the source water to indicate the extent of variability of these constituents. Sorg (2002) has described a range of arsenic and iron concentrations in which removal of iron can result in effective arsenic removal by coagulation and filtration. Sorg suggested that for effective removal of arsenic by natural iron, the natural iron concentration should be at least 0.3 mg/L, and the ratio of iron to arsenic (the Fe:As ratio) should be 20:1 or greater.

Filters will be operated until either terminal headloss is reached or effluent turbidity increases above a value recommended by the manufacturer (but not higher than 5 NTU).

8.4 Analytical Schedule

Because these runs are being conducted to define operating conditions for verification testing, a strictly defined schedule for sampling and analysis may not need to be followed. Adhering to the schedule for sampling and analyses to be followed during verification testing would be wise so that the operator can gain familiarity with the time requirements that will be applicable later on in the test program. Also, during the initial operations phase, NSF may conduct an initial on-site inspection of field operations and sampling activities. The sampling and analysis schedule for verification testing shall be followed during the on-site inspection.

8.5 Evaluation Criteria

The manufacturer should evaluate the data produced during the initial operations to determine if the water treatment equipment performance met or exceeded expectations based on the statement of performance objectives. If the performance was not as good as the statement of performance

objectives, the manufacturer may wish to conduct more initial operations or to cancel the testing program.

9.0 TASK 1: VERIFICATION TESTING RUNS

9.1 Introduction

Drinking water treatment equipment employing coagulation and filtration shall be operated for verification testing purposes, with the approach to coagulation based on the results of the initial operations testing. If pre-oxidation is included in the equipment being tested and pre-oxidation is necessary for effective equipment performance, that process equipment shall be operated also.

9.2 Experimental Objective

The objective of this task is to operate the treatment equipment provided by the manufacturer and to assess its ability to meet the water quality goals and any other performance characteristics specified by the manufacturer in the statement of performance objectives.

9.3 Work Plan

9.3.1 Verification Testing Runs

The verification testing runs in this task consist of continued evaluation of the treatment system, using the most successful treatment parameters defined in initial operations. To obtain a perspective on the influence of feed water quality on arsenic removal by coagulation and filtration, and on the overall performance of the equipment, one or more verification testing periods, each lasting for a minimum of 320 hours (the equivalent of 13 full days plus one 8-hour shift), are anticipated for evaluating the performance of a treatment system. During each of these testing periods, Tasks 2 through 5 shall be conducted within the time frame for carrying out Task 1. Table 1 lists filtration processes that might be used, and states requirements for minimum duration of operation for verification testing for different filtration processes.

Operation under a variety of water quality conditions is recommended because of the differences in water quality that occur over time in many source waters. For coagulation and filtration treatment equipment, factors that can influence treatment performance include:

- Cold water, encountered in winter or at high altitudes in mountainous regions;
- High turbidity, often occurring in spring, encountered in rivers carrying a high sediment load or in surface waters during periods of high runoff resulting from heavy rains or snowmelt;
- Algae, which may bloom on a seasonal basis such as in summer or fall;
- Natural organic matter (NOM), which may be higher in some waters in the fall;
- pH, alkalinity, and hardness, which may vary over time; and

- Sulfate can influence arsenic removal (Hering et al. 1997).

It is highly unlikely that all of the above problems would occur in a surface water during a single test period. Although one testing period satisfies the minimum requirement of ETV, manufacturers are encouraged to use additional testing periods to cover a wider range of water quality conditions. Testing a water which has little change in quality over time could result in acceptance of equipment for use only in water having a narrow range of water quality.

For evaluation of arsenic removal by coagulation and filtration using a process other than granular media, information on factors to evaluate in the verification testing runs can be obtained by referring to the "ETV Protocol for Equipment Verification: Testing for Physical Removal of Microbiological and Particulate Contaminants" and a TSTP for one of the following:

- Membrane Filtration for the Removal of Microbiological and Particulate Contaminants;
- Bag Filters and Cartridge Filters for the Removal of Microbiological and Particulate Contaminants;
- Precoat Filtration for the Removal of Microbiological and Particulate Contaminants; or
- Backwashable Depth Filtration for the Removal of Microbiological and Particulate Contaminants.

9.3.2 Routine Equipment Operation

If the water treatment equipment is being used for production of potable water and treats a water that naturally contains concentrations of arsenic appropriate for verification testing, so that arsenic spiking is not needed, routine operation for water production is anticipated in the time intervals between verification runs. The operating and water quality data collected and furnished to the Safe Drinking Water Act (SDWA) primacy agency during these times shall also be supplied to the FTO.

9.4 Schedule

To meet the goals of the verification testing for equipment employing coagulation and granular media filtration, the following conditions shall be met:

- Water treatment equipment shall be operated continuously for a minimum of 320 hours (the equivalent of 13 full days plus one 8-hour work shift);
- During this time, treatment equipment shall be operated continuously from start-up until turbidity breakthrough or terminal head loss is attained;
- Interruptions in filtration shall occur only as needed for backwashing of the filters or contact clarification pretreatment unit;
- Filter runs shall not be stopped before turbidity breakthrough or terminal head loss is achieved, with the exception of equipment failure or power interruption;

- The duration of each filter run and the number of gallons of water produced per square foot of filter area shall be recorded in the operational results; and
- During routine equipment operation, the water treatment equipment should be operated to meet the system demands and water quality requirements.

Schedules for operation of other filtration processes are found in the TSTPs that have been developed for evaluation of those processes.

9.5 Evaluation Criteria

The goal of this task is to operate the coagulation and filtration equipment for the time required in Table 1, including time for filter cleaning and other necessary operating activities, during verification testing. Data shall be provided to substantiate the operation for the required time.

10.0 TASK 2: FEED WATER AND FINISHED WATER QUALITY

10.1 Introduction

Water quality data shall be collected for the feedwater and filtered water as shown in Table 2, during verification testing. At a minimum, the required sampling schedule shown in Table 2 shall be observed by the FTO. Water quality goals and target removal goals for the water treatment equipment shall be recorded in the PSTP in the statement of objectives.

10.2 Experimental Objectives

A list of the minimum number of water quality parameters to be monitored during equipment verification testing is provided in the analytical schedule section below and in Table 3. The actual water quality parameters selected for testing shall be stipulated in the PSTP procedures and shall include all those necessary to permit verification of the statement of performance objectives.

10.3 Work Plan

The FTO will be responsible for establishing the equipment operating parameters on the basis of the initial operations testing. The filter shall be operated continuously until turbidity breakthrough or terminal headloss is attained, at which time it shall be backwashed.

Some of the water quality parameters described in this task will be measured on-site by the FTO (refer to Table 3). Analysis of the remaining water quality parameters will be performed by a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA. The methods to be used for measurement of water quality parameters in the field are described in Table 3. The analytical methods utilized in this study for on-site monitoring of feedwater and filtered water qualities are discussed in Task 6, Quality Assurance/Quality Control. Where appropriate, the *Standard Methods* reference numbers for water quality parameters are provided for both the field and laboratory analytical procedures.

10.3.1 Water Quality Sample Collection

Water quality data shall be collected during each period of filtration testing, as noted in this section. Additional sampling and data collection may be performed at the discretion of the manufacturer. Sample collection frequency and protocol shall be defined in the PSTP.

In the case of water quality samples that will be shipped to the State or EPA-accredited analytical laboratory for analysis, the samples shall be collected in appropriate containers (containing preservatives as applicable) prepared by the state or EPA-accredited analytical laboratory. These samples shall be preserved, stored, shipped and analyzed in accordance with appropriate procedures and holding times, as specified by the analytical laboratory.

10.4 Analytical Schedule

During verification testing for coagulation and filtration treatment equipment, the feed water (raw water) quality, filtered water quality, (and if applicable, the clarified water quality) shall be characterized by measurement of the following water quality parameters. For pH samples, the treated water pH must be the pH of the coagulated water because coagulation pH can have a strong influence on arsenic removal. If any pH adjustment is made after coagulation, this also must be noted. Water quality samples, whether designated for collection at maximum intervals of once per day or once per week shall be obtained during each arsenic challenge test that involves distinct treatment conditions, even if this increases the water quality sample collection frequency to greater than once per week.

- Temperature (daily);
- pH (daily and in conjunction with arsenic sample collection);
- Total alkalinity (daily);
- Hardness (weekly or once during each set of treatment conditions for which arsenic sampling is done);
- TOC (weekly or once during each set of treatment conditions for which arsenic sampling is done);
- UV_{254} absorbance (weekly or once during each set of treatment conditions for which arsenic sampling is done);
- Turbidity (daily at bench to check continuous turbidimeters);
- Aluminum (daily if an aluminum salt coagulant is used and each time when arsenic sampling is done and alum is the coagulant chemical; sampled weekly if aluminum coagulant not used.);
- Iron (daily if iron coagulant is used and each time when arsenic sampling is done and iron is the coagulant chemical; sampled weekly if iron is not used to co-precipitate with arsenic.);
- Manganese (weekly or once during each set of treatment conditions for which arsenic sampling is done if above 0.05 mg/L in feed water);
- Algae, number and species (weekly or once during each set of treatment conditions for which arsenic sampling is done);

- True color (weekly or once during each set of treatment conditions for which arsenic sampling is done);
- Sulfate (weekly);
- Dissolved oxygen concentration in feed water (daily);
- Dosage of pre-oxidation chemical and residual concentration after filter (if a preoxidation chemical was used) (only in Task 4, every 6 hours to coincide with arsenic sampling); and
- Arsenic (see Task 4).

The above water quality parameters are listed to provide verification report readers with background data on the quality of the feed water being treated and the quality of the filtered water. These data are to be collected to enhance the usefulness of the verification testing data to a wide range of verification report readers. Data on feed water need to be obtained because of the possibility that feed water composition could influence arsenic removal performance for some operating variables, including coagulation pH, coagulant chemical used, and valence state of the arsenic.

Additionally, at the end the verification test, samples of the sludge generated shall be collected to assess the chemical content for disposal purposes. At least one representative sample of the sludge shall be collected and sent to the laboratory for the Toxicity Characteristic Leaching Procedure (TCLP) and the California Waste Extraction Test (WET). The FTO shall describe the sampling procedures that will be used to ensure that a representative sample of the sludge is collected for these analyses. The sample that is collected for TCLP and California WET shall have the following metals analyzed in the leachate from these procedures: As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Se, Ag, and Zn.

10.5 Evaluation Criteria

Performance shall be evaluated in the context of the manufacturer's statement of performance objectives.

If iron coagulant is used or if natural iron is oxidized so it can act as a coagulant, the filtered water data shall be tabulated and the concentration of iron in filtered water shall be compared to the secondary Maximum Contaminant Level (MCL) of 0.3 mg/L. If aluminum coagulant is used, the residual aluminum concentration in filtered water samples shall be tabulated.

Also, turbidity results for systems treating surface waters or ground water under the influence of surface water shall be analyzed to determine the percentage of turbidity data in the range of 0.10 NTU or lower, the percentage in the range of 0.11 NTU to 0.20 NTU, the percentage in the range between 0.21 NTU and 0.34 NTU, the percentage between 0.35 NTU and 0.54 NTU, and the percentage that equaled or exceeded 0.55 NTU. The percentage of filtered water turbidity results that exceed 1.0 NTU shall also be noted. In addition, the frequency of occurrence in which the filter was placed into service after backwashing and subsequently produced filtered water turbidity exceeding 0.5 NTU after a four hour ripening period (i.e. the turbidity did not fall to below 0.5 NTU within four hours of starting the filter) shall be noted. The time intervals used for determining turbidity values shall be the same for all data analyzed, and because continuous

turbidimeters are to be used to collect turbidity data, the intervals shall be between 5 and 15 minutes.

For systems treating ground water, turbidity results shall be analyzed to determine the percentage of turbidity data in the range of 0.50 NTU or lower, the percentage in the range of 0.51 NTU to 1.0 NTU, the percentage in the range between 1.1 NTU and 2.0 NTU, and the percentage exceeding 2.0 NTU.

11.0 TASK 3: OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE

11.1 Introduction

Operating conditions shall be documented during each day of verification testing. This shall include descriptions of chemicals used for coagulation, pretreatment chemistry for coagulation, treatment processes used, and operating conditions. In addition, the performance of the water treatment equipment shall be documented, including rate of filter head loss gain, frequency and duration of filter cleaning, and need for cleaning of pretreatment clarifiers.

11.2 Objective

The objective of this task is to accurately and fully document the operating conditions applied during treatment and the equipment performance. This task is intended to result in operational data describing the operation of the equipment, which can be used to develop cost estimates.

11.3 Work Plan

A description of the testing equipment shall include:

- Complete description of each process, with data on volume and detention time of each process basin at rated flow;
- Data on each layer of the granular media filtering and support material, including:
  - Depth
  - Material type
  - Effective size
  - Uniformity coefficient;
- Manufacturer's data describing characteristics of membrane filter, precoat filter, cartridge filter, bag filter, or backwashable depth filter; and
- Location of each chemical or polymer addition point.

During verification testing, the following items shall be monitored, collected, recorded, or analyzed:

- Treatment equipment operating parameters for both pretreatment and filtration, including:
  - Pretreatment chemistry,

- Pre-oxidation operating parameters, if pre-oxidation is used,
- Mixing and flocculation intensities,
- Operating parameters for clarification ahead of filtration; rate of flow; and filtration rate, and
- Process detention times.

- Filter head loss and backwashing data, cleaning data, precoating data, or data on changing filter cartridges or filter bags.

- Chemical dosages for all chemicals used, including oxidants. If oxidation is used, oxidant dosage and residual oxidant shall be measured each time an arsenic sample is taken. In addition, the supplier and manufacturer of the coagulant chemical, the strength of solution for liquid coagulants, the specific gravity for liquid coagulants, and the chemical formula and percentage of impurities for dry coagulants shall be documented and included in the report of the testing. If ozone is used, the ozone system should be monitored according to Table 3 in the "The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes", except that frequency should be once per day for all parameters that are listed, on days when arsenic samples are not collected. Ozone monitoring shall be performed for parameters listed in Table 3 in the "The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes" each time when an arsenic sample is obtained.

- Quantities of filter aid used for precoating and body feed if precoat filtration equipment is used.

- Electrical energy consumed by the treatment equipment or aggregate horsepower of all motors supplied with the equipment for estimating the maximum power consumption during operation. If ozonation is used in pre-oxidation, measurement of watt-hours of energy used is the recommended method for determination of energy usage. The energy use for the ozone system should be monitored according to Table 3 in the "The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes", except that the frequency should be once per day for the energy parameters that are listed.

11.4 Schedule

Table 4 presents the schedule for observing and recording coagulation and filtration equipment operating and performance data.

11.5 Evaluation Criteria

Where applicable, the data developed from this task will be compared to statements of performance objectives with respect to filter head loss, frequency and duration of filter cleaning or filter replacement, and the need for pretreatment clarifier cleaning.

If no relevant statement of performance objectives exists for each set of conditions employed in arsenic challenge testing, the results of operating and performance data shall be tabulated for inclusion in the verification report, and shall include:

- Average rate of flow for equipment, gallons/day;
- Average filtration rate, expressed in units appropriate for the filtration process used;
- Average run length, hours, and volume of water treated per filter run;
- Average daily chemical usage and cost factors for treatment chemicals, including filter aid for precoat filters, if used;
- Average daily energy cost factors;
- Average daily wash water production, if appropriate;
- Average daily sludge or floated solids production, and;
- Cleaning efficiency for membrane filters as described in Task 2 of the ETV Membrane Filtration Test Plan for the Removal of Microbiological and Particulate Contaminants, if applicable.

12.0 TASK 4: ARSENIC REMOVAL

12.1 Introduction

Arsenic removal may be a primary purpose of coagulation and filtration of some surface and ground waters. Consequently, the effectiveness of coagulation and filtration treatment processes for arsenic removal will be evaluated in this task. Additionally, turbidity removal is needed to ensure that water quality goals are met when treating surface waters. Therefore, assessment of treatment efficacy will be made on the basis of turbidity measurements (as described in Task 3) and arsenic removal for surface water treatment. For ground water treatment, assessment of treatment efficacy will be made on the basis of arsenic removal.

12.2 Experimental Objective

The objective of this task is to evaluate arsenic removal during verification testing by measuring arsenic naturally present in the feed water or by spiking the feed water with arsenic in the treated water.

12.3 Work Plan

Task 4 shall be carried out during the verification testing runs conducted in Task 1. The treatment equipment shall be operated using the chemical pretreatment conditions that provide effective clarification (if used) and filtration.

Evaluation of arsenic removal shall be performed by analyzing arsenic in the feed and filtered waters. If arsenic spike testing is required, the appropriate arsenic species [either arsenate (V) or arsenite (III)] will be added to the feedwater.

A minimum of 48 hours of operation involving collection of 11 or more arsenic samples shall be conducted to provide statistically verifiable arsenic removal data for each condition of coagulant chemical type and dosage, coagulation pH, feed water arsenic species, and feed water arsenic concentration tested.

12.3.1 Background Arsenic Levels

If sufficient arsenic concentration is naturally present in the feed water to meet the manufacturer's stated operating range for arsenic removal, the treatment equipment shall be operated as usual in verification testing runs, and sampling shall be done as stipulated in the analytical schedule.

12.3.2 Spiked Arsenic

Spiked arsenic shall be used in concentrations sufficient to permit the most-stressed operations for the manufacturer's equipment, following the recommended guidelines:

- Arsenic spiking shall begin at start-up of the treatment equipment.
- Arsenic feed solution will be prepared by diluting the arsenic into dilution water that is distilled or deionized and oxidant free.
- To spike arsenic (III), use commercially-prepared arsenic trioxide. (In cold water, at 2°C, the solubility of this chemical is about 1.2 g/100 g water.)
- To spike arsenic (V), use commercially-prepared arsenic pentoxide.
- Feed reservoir for the arsenic spike solution shall be made of chemically inert material (i.e., not reactive or adsorbable to the arsenic).
- The reservoir will be mixed continuously throughout the experiment.
- The arsenic spike solution will be fed using an adjustable rate chemical feed pump.
- Use an in-line static mixer to mix this solution into the feedwater.
- Arsenic samples of at least 250 mL shall be collected in bottles prepared for holding such samples.

If testing with Arsenic (III) is contemplated, manufacturers and FTOs need to be aware of potential difficulties in preventing conversion of As (III) to As (V) as the spiking solution is held in its storage container. Further conversion to the higher valence state could occur during passage of spiked water through the equipment. Several of the arsenic studies referenced in this TSTP have shown that As (V) removal by coagulation and filtration is much more effective than As (III) removal. Thus, a preferred approach to arsenic

treatment may involve pre-oxidation to convert all arsenic to As (V) so the most effective results will be attained. If pre-oxidation is done, the conditions need to be documented.

12.4 Analytical Schedule

Turbidity in feed water samples may be measured on a batch or a continuous basis. For facilities treating surface waters, if batch measurements are used, they shall be performed every six hours during each working day in the verification testing. Filtered water analysis shall be conducted using continuous flow turbidimeters equipped with recording capability so data can be collected on a 24-hour-per-day basis during verification testing.

Chemistry samples shall be collected from the plant influent (feed water after spiking, if arsenic is spiked), clarifier effluent if a clarification step is employed ahead of filtration, and the filter effluent. Samples shall not be collected until the treatment plant has been in operation for a total of three (3) theoretical detention times (the theoretical detention time is the volume of water held in the treatment equipment, divided by the rate of flow) as measured through the pretreatment process up to the filter. For arsenic sampling purposes, the time of operation when three pretreatment detention times have elapsed shall be considered time zero. Arsenic samples shall be collected at time zero and at 1, 3, and 6 hours past time zero. Thereafter, arsenic samples shall be collected once every 6 hours until the end of the filter run or until the filter run has lasted 48 hours from time zero. This would result in collection of 11 sets of arsenic samples in a 48-hour filter run. Because four sets of arsenic samples are to be collected during the first 6 hours of a filter run, conducting more than one filter run during the 48 hour period required for a given set of treatment conditions would result in collection of more than 11 sets of arsenic samples. During each sampling event, one 250-mL sample will be collected at each sampling location. The exact time of sampling will be recorded so turbidity measurements can be determined at the time of sampling. When Task 4 is carried out, if pre-oxidation is done, the pre-oxidant dosage and the pre-oxidant residuals are to be determined at time zero and at 6-hour intervals through the 48-hour time period required for this task. The total concentration of iron or aluminum acting as a coagulant to co-precipitate arsenic shall be determined in each feed water sample and filtered water sample for which the arsenic concentration is determined.

For filtration process equipment other than granular media filters, eleven (11) sets of feed water and filtered water arsenic samples shall be collected, but the timing for collection of those samples shall be as indicated in the PSTP, specific to the filtration process equipment being evaluated, with reference to the timing for sample collection during microbial contaminant challenges. Regardless of the wording related to the number of microbiological or microbe surrogate challenge samples to be collected, no fewer than eleven sets of arsenic samples shall be collected.

The FTO shall then submit collected water samples to a state or EPA-accredited analytical laboratory for arsenic testing. The laboratory shall have a minimum detection limit for arsenic of 2 μg/L.

12.5 Evaluation Criteria

Performance evaluation shall be conducted in a number of ways, depending on the types of data collected during testing. Performance of coagulation and filtration equipment shall be evaluated in the context of the manufacturer's statement of performance objectives with respect to arsenic removal and the filtered water turbidity goals, if surface water was treated. For arsenic removal by coagulation and filtration, the following information shall be provided:

- Valence of the arsenic being treated by coagulation and filtration, i.e. As (III) or As (V);
- pH of coagulated water;
- Coagulant chemical used;
- Coagulant dosage or concentration of coagulant such as iron naturally present in the feed water; and
- Concentration of oxidant added, if an oxidant is used.

An example of a statement of performance objectives for arsenic removal might be, "Coagulation and filtration in the pH range of 7.0 to 8.0 can reduce arsenate [Arsenic (V)] concentration by 90 percent when the initial arsenic concentration is in the range of 20 to 100 μg/L and a 30 mg/L dose of ferric sulfate is used for coagulation." To provide data to verify such a performance statement, testing would have to be done at pH 7.0 for feed water with arsenic at 20 μg/L and with arsenic at 100 μg/L. Testing at both arsenic concentrations also would be required at pH 8.0. If a statement of performance objectives specifies the type of coagulant and the dosage that is effective, both the coagulant type and dosage would also be required to be used for all conditions tested.

13.0 TASK 5: DATA MANAGEMENT

13.1 Introduction

The data management system used in the verification testing program shall involve the use of computer spreadsheet software and manual recording of operational parameters for the water treatment equipment on a daily basis.

13.2 Experimental Objectives

The objective of this task is to establish a viable structure for the recording and transmission of field testing data such that the FTO provides sufficient and reliable operational data for verification purposes. A second objective is to develop a statistical analysis of the data, as described in "Protocol for Equipment Verification Testing for Arsenic Removal."

13.3 Work Plan

13.3.1 Data Handling

The following protocol has been developed for data handling and data verification by the FTO. Where possible, a Supervisory Control and Data Acquisition (SCADA) system should be used for automatic entry of testing data into computer databases.

- Specific parcels of the computer databases for operational and water quality parameters should be downloaded by manual importation into Excel (or similar spreadsheet software) as a comma delimited file.

- Specific database parcels will be identified based on discrete time spans and monitoring parameters.

- The data will be manipulated into a convenient framework to allow analysis of coagulation and filtration equipment operation in a spreadsheet form.

- Backup of the computer databases to diskette should be performed on a monthly basis at a minimum.

In the case when a SCADA system is not available:

- Field testing operators will record data and calculations by hand in laboratory notebooks. (Daily measurements will be recorded on specially-prepared data log sheets as appropriate.)

- Laboratory notebook will contain carbon copies of each page (to ease referencing the original data and offer protection of the original record of results).

- Original notebooks will be stored on-site; the carbon copy sheets will be forwarded to the project engineer of the FTO at least once per week.

- Operating logs shall include a description of the process equipment (description of test runs, names of visitors, description of any problems or issues, etc.); such descriptions shall be provided in addition to experimental calculations and other items.

Spreadsheets:

- The data for the project will be recorded in custom-designed spreadsheets.

- The spreadsheets will be capable of storing and manipulating each monitored water quality and operational parameter from each task, sampling location, and sampling time.

- All data from the laboratory notebooks and data log sheets will be entered into the appropriate spreadsheet.

- Data entry will be conducted on-site by the designated field testing operators, with all recorded calculations checked at this time.

- Following data entry, the spreadsheet will be printed out and the printout will be checked against the handwritten data sheet.

- Any corrections will be noted on the hard-copies and corrected on the screen, and a corrected version of the spreadsheet will be printed out.

- Each step of the verification process will be initialed by the field testing operator or engineer performing the entry or verification step.

Data tracking:

- Each experiment (e.g., each filtration test run) will be assigned a run number which will then be linked to the data from that experiment through each data entry and analysis step.

- Data will be tracked by use of the same system of run numbers as samples are collected and sent to State or EPA-accredited analytical laboratories.

- Data from the analytical laboratories will be received and reviewed by the FTO.

- These data will be entered into the data spreadsheets, corrected, and checked in the same manner as the field data.

13.3.2 Statistical Analysis

Arsenic data developed from grab samples collected during filter runs according to the analytical schedule in Task 4 of this TSTP shall be analyzed for statistical uncertainty. The FTO shall calculate 95% confidence intervals for the arsenic data obtained during verification testing as described in Chapter 1 of the "Protocol for Equipment Verification Testing for Arsenic Removal." A separate statistical analysis shall be carried out for each testing condition for which the required 11 or more sets of arsenic samples were collected and analyzed.

The statistics developed will be helpful in demonstrating the degree of reliability with which the water treatment equipment can attain quality goals under the treatment conditions tested. The results of the statistical analysis also shall be used to determine if the performance of the equipment was equal to or better than that given in the statement of performance objectives.

14.0 TASK 6: Quality Assurance/Quality Control

14.1 Introduction

QA/QC of the operation of the coagulation and filtration equipment and the measured water quality parameters shall be maintained during the verification testing program.

14.2 Experimental Objectives

The objective of this task is to maintain strict QA/QC methods and procedures during the equipment verification testing program. When specific items of equipment or instruments are used, the objective is to maintain the operation of the equipment or instructions within the ranges specified by the manufacturer or by *Standard Methods*. Maintenance of strict QA/QC procedures is important, in that if a question arises when analyzing or interpreting data collected for a given experiment, it will be possible to confirm exact conditions at the time of testing.

14.3 Work Plan

Equipment flow rates and associated signals should be documented and recorded on a routine basis. A routine daily walk-through during testing will check that each piece of equipment or instrumentation is operating properly. Particular care will be taken to confirm the water and chemicals flow rates to ensure that the chemical feed concentrations are correct. In-line monitoring equipment, such as flow meters and turbidimeters, will be checked to confirm that the readout matches with the actual measurement (i.e. flow rate, turbidity) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods.

14.3.1 Daily QA/QC Checks

- Chemical feed pump (if used) flow rates (checked volumetrically over a specific period of time to confirm instrument reading);
- In-line turbidimeters flow rates (checked volumetrically over a specific period of time to confirm instrument reading); and
- In-line turbidimeters readings checked against a properly calibrated bench model.

14.3.2 QA/QC Checks Performed Every Two Weeks

- In-line flow meters/rotameters (clean equipment to remove any debris or biological buildup and check flow volumetrically over a specific period of time to confirm instrument reading).

14.3.3 QA/QC Checks for Each Test Period

- In-line turbidimeters (clean out reservoirs, if necessary, and recalibrate);
- Differential pressure transmitters (check gauge readings and electrical signal using a pressure meter); and

- Tubing (check condition of all tubing and connections, replace if necessary).

14.4 On-Site Analytical Methods

The analytical methods utilized in this study for on-site monitoring of raw water and treated water quality are described in the section below. If new methods are published and approved or current methods updated, the most current methods shall be used. In-line equipment is recommended for its ease of operation and because it limits the introduction of error and the variability of analytical results generated by inconsistent sampling techniques. In-line equipment is recommended for measurement of turbidity and particle counting for feed water, and is required for measurement of turbidity and particle counting for filtered water.

14.4.1 pH

pH analysis shall be performed according to *Standard Method* 4500-H^+ or EPA Methods 150.1 and 150.2. A three-point calibration of the pH meter shall be performed once per day when the instrument is in use. Certified pH buffers in the expected range shall be used. The pH probe shall be stored in the appropriate solution defined in the instrument manual. Transport of carbon dioxide across the air-water interface can confound pH measurement in poorly buffered waters. If this is a problem, pH measurement in a confined vessel is recommended to minimize the effects of carbon dioxide loss to the atmosphere.

14.4.2 Turbidity

Turbidity analyses shall be performed according to *Standard Method* 2130 B or EPA Method 180.1 with either a bench-top or in-line turbidimeter. In-line turbidimeters shall be used for measurement of turbidity in the filtrate waters, and either an in-line or bench-top may be used for measurement of the feedwater.

During each verification testing period, the bench-top and in-line turbidimeters will be left on continuously. Once each turbidity measurement is complete, the unit will be switched back to its lowest setting. All glassware used for turbidity measurements will be cleaned and handled using lint-free tissues to prevent scratching. Sample vials will be stored inverted to prevent deposits from forming on the bottom surface of the cell.

The FTO shall document any problems experienced with the monitoring turbidity instruments, and shall also document any subsequent modifications or enhancements made to monitoring equipment.

14.4.2.1 Bench-Top Turbidimeters. Grab samples shall be analyzed using a bench-top turbidimeter. Readings from this instrument will serve as reference measurements throughout the study. The bench-top turbidimeter shall be calibrated within the expected range of sample measurements at the beginning of equipment operation and on a weekly basis using primary turbidity standards of 0.1, 0.5, and 3.0 NTU. Secondary turbidity standards shall be obtained and checked against the primary standards. Secondary

standards shall be used on a daily basis to check calibration of the turbidimeter and to recalibrate when more than one turbidity range is used.

The method for collecting grab samples will consist of running a slow, steady stream from the sample tap, triple-rinsing a dedicated sample beaker in this stream, allowing the sample to flow down the side of the beaker to minimize bubble entrainment, double-rinsing the sample vial with the sample, carefully pouring from the beaker down the side of the sample vial, wiping the sample vial clean, inserting the sample vial into the turbidimeter, and recording the measured turbidity.

For the case of cold water samples that cause the vial to fog preventing accurate readings, allow the vial to warm up by submersing partially into a warm water bath for approximately 30 seconds.

14.4.2.2 In-Line Turbidimeters. In-line turbidimeters are required for filtered water monitoring during verification testing and must be calibrated and maintained as specified in the manufacturer's operation and maintenance manual. It will be necessary to check the in-line readings using a bench-top turbidimeter at least daily; although the mechanism of analysis is not identical between the two instruments, the readings should be comparable. Should these readings suggest inaccurate readings, then all in-line turbidimeters should be recalibrated. In addition to calibration, periodic cleaning of the lens should be conducted, using lint-free paper, to prevent any particle or microbiological build-up that could produce inaccurate readings. Periodic check of the sample flow rate should also be performed using a volumetric measurement. Instrument bulbs should be replaced on an as-needed basis. The LED readout shall be checked that it matches the data recorded on the data acquisition system, if the latter is employed.

14.4.3 Temperature

Readings for temperature shall be conducted in accordance with *Standard Method* 2550. Raw water temperatures should be obtained at least once daily. The thermometer shall have a scale marked for every 0.1^{o}C, as a minimum, and should be calibrated weekly against a precision thermometer certified by the National Institute of Standards and Technology (NIST). (A thermometer having a range of -1°C to +51°C, subdivided in 0.1^{o} increments, would be appropriate for this work.)

14.4.4 True Color

True color shall be measured with a spectrophotometer at 455 nm, using a Hach Company adaptation of the *Standard Method* 2120 B procedure. Samples should be collected in clean plastic or glass bottles and analyzed as soon after collection as possible. If samples can not be analyzed immediately, they should be stored at 4°C for up to 24 hours, and then warmed to room temperature before analysis. The filtration system described in *Standard Method* 2120 C should be used, and results should be expressed in terms of PtCo color units.

14.4.5 Chlorine Residual

Because free chlorine in aqueous solutions is unstable, the free chlorine concentration in treated water samples will decrease rapidly. Exposure to sunlight or other strong light, or agitation, will accelerate free chlorine loss. Therefore, analysis of free and total chlorine samples shall begin immediately after sampling, and excessive light and agitation shall be avoided. Samples to be analyzed for free or total chlorine shall not be stored prior to analysis.

Glassware to be used for chlorine analyses shall be chlorine demand free. Chlorine demand free glassware will be prepared by soaking glassware in a 50 mg/L chlorine bath for a period of 24 hours. At the end of this time, all glassware will be rinsed three times with organic-free water that has a TOC concentration of less than 0.2 mg/L. Glassware will then be dried at room temperature for a period of 24 hours. During the drying process, bottle openings will be covered with aluminum foil to prevent contamination.

The method for collecting samples for chlorine analyses shall consist of the following procedure: running a slow, steady stream from the sample tap, triple-rinsing a chlorine demand free sample beaker in this stream; allowing the sample to flow down the side of the beaker to minimize agitation; performing the free and total chlorine analyses; and recording the measured chlorine concentrations.

14.4.6 Chlorine Dioxide Residual

Similar to chlorine, chlorine dioxide in aqueous solutions is unstable. Exposure to sunlight or other strong light, or agitation, will accelerate chlorine dioxide loss. Therefore, analysis of chlorine dioxide samples shall begin immediately after sampling, and excessive light and agitation shall be avoided. Samples to be analyzed for chlorine dioxide shall not be stored prior to analysis. Glassware for chlorine dioxide analyses shall be chlorine demand free, as described above in Section 14.4.5. The method for collecting samples for chlorine dioxide residual shall be identical to that described above for chlorine residual.

14.4.7 Dissolved Ozone and Gas Phase Ozone

For dissolved and gas phase ozone analyses, refer to the "The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes" section 14.4.7 for dissolved ozone measurement and section 14.4.8 for gas phase ozone analysis.

14.5 Chemical and Biological Samples Shipped Off-Site for Analyses

14.5.1 Total Organic Carbon and UV_{254} Absorbance

Samples for analysis of TOC and UV_{254} absorbance shall be collected in glass bottles supplied by the state-certified or third party- or EPA- accredited laboratory and shipped

at 4°C to the analytical laboratory. These samples shall be preserved, held, and shipped in accordance with *Standard Method* 5010B. Storage time before analysis shall be minimized, according to *Standard Methods*.

14.5.2 Arsenic

Laboratory analyses for arsenic shall be performed in accordance with EPA Method 200.8. These analyses are the most critical for the entire ETV procedure. When arsenic species are to be analyzed, the samples shall be collected and preserved in accordance with the Protocol for Arsenic Speciation developed by Battelle for the EPA, as found in Appendix A of this protocol. EPA Method 200.8 has been specified because of the need to achieve low detection limits (0.002 to 0.004 mg/L) with good accuracy and precision for this verification test. Other EPA approved drinking water methods that can achieve these low laboratory reporting limits with comparable accuracy and precision may be proposed by the FTO. Please note when using this method that ultra-pure (optimum) grade sulfuric acid must be used (not reagent grade) to avoid the trace amounts of arsenic that can be present in reagent grade sulfuric acid.

14.5.3 Other Inorganic Samples

Inorganic chemical samples, including arsenic, alkalinity, hardness, aluminum, iron, and manganese, shall be collected, preserved, shipped, and held in accordance with *Standard Method* 3010B, paying particular attention to the sources of contamination as outlined in *Standard Method* 3010C. The samples shall be refrigerated at approximately 4°C immediately upon collection, shipped in a cooler, and maintained at a temperature of approximately 4°C during shipment. Samples shall be processed for analysis by a state-certified or third party- or EPA- accredited laboratory within 24 hours of collection. The laboratory shall keep the samples at approximately 4°C until initiation of analysis.

14.5.4 Algae

Algae samples shall be preserved with Lugol's solution after collection, stored and shipped in a cooler at a temperature of approximately 4°C, and held at that temperature range until counted.

15.0 OPERATIONS & MAINTENANCE

The FTO shall obtain the manufacturer-supplied Operations and Maintenance (O&M) manual to evaluate the instructions and procedures for their applicability during the verification testing period. The following are recommendations for criteria for O&M manuals for equipment employing coagulation and filtration.

Most of the recommendations in this section are for equipment employing granular media filtration. For arsenic removal equipment using other filtration processes, refer to the TSTP developed for the filtration process being used as a source of guidance on other O&M aspects to consider.

15.1 Maintenance

The manufacturer should provide readily understood information on the recommended or required maintenance schedule for each piece of operating equipment such as:

- Pumps;
- Valves;
- Pressure gauges;
- Flow meters;
- Chemical feeders;
- Mixers;
- Motors;
- Instruments, such as continuous pH monitors or turbidimeters;
- Water meters, if provided; and
- Ozonation system, if provided (per requirements in section 15.1 of "The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes").

The manufacturer should provide readily understood information on the recommended or required maintenance for non-mechanical or non-electrical equipment such as:

- Tanks and basins;
- In-line static mixers; and
- Filter vessels.

15.2 Operation

The manufacturer should provide readily understood recommendations for procedures related to proper operation of the equipment. Among the operating aspects that should be discussed are:

Pre-oxidant generation/feed:

- Measurement of pre-oxidant concentration generated;
- Measurement of pre-oxidant concentration fed into treatment equipment; and
- Ozonation system, if provided (per requirements in section 15.2 of "The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes").

Chemical feeders:

- Calibration check;
- Settings and adjustments -- how they should be made; and
- Dilution of chemicals and polymers -- proper procedures.

Mixers and flocculators:

- Purpose and
- Changing intensity (RPM), if available.

Filtration:

- Control of filtration flow and rate and
- Observation and measurement of head loss during filter run.

Filter backwashing, if applicable:

- End of filter run;
- Use of auxiliary water scour (surface wash) or air scour;
- Start of backwash;
- Appropriate backwash rates;
- Conclusion of filter backwashing; and
- Return of filter to service.

Filter cleaning for membrane filters, if applicable or for backwashable depth filters, if applicable.

Filter cleaning and precoating for precoat filters, if applicable.

Changing filter cartridges or filter bags, if applicable.

Monitoring and observing operation:

- Observation of floc;
- Pretreated water turbidity, if appropriate;
- Filtered water turbidity;
- Filter head loss;
- What to do if turbidity breakthrough occurs; and
- Measuring and controlling pH of coagulated water.

Coagulant dose selection:

It is strongly recommend that manufacturer include a copy of AWWA's Manual M37, "Operational Control of Coagulation and Filtration Processes" with each coagulation and filtration package plant, as an AWWA committee of experts has prepared an excellent manual that would be very helpful to plant operators.

The manufacturer should provide a troubleshooting guide; a simple check-list of what to do for a variety of problems including:

- No raw water (feed water) flow to plant;

- Can’t control rate of flow of water through equipment;
- No chemical feed;
- Loss of pre-oxidant feed;
- Calibration and maintenance of in-line pH monitoring instruments, problems of erratic pH or drifting pH readings;
- Mixer or flocculator will not operate (won’t rotate);
- Filter can’t be backwashed or backwash rate of flow can’t change;
- No reading on turbidimeter or streaming current monitor;
- Automatic operation (if provided) not functioning;
- Filtered water turbidity too high;
- Filter head loss builds up excessively rapidly;
- No head loss readings;
- Valve stuck or won’t operate; and
- No electric power.

The following are recommendations regarding operability aspects of equipment employing coagulation and filtration. These aspects of plant operation should be considered, if possible, in reviews of historical data and should also be included to the extent practical in verification reports.

During verification testing and during compilation of historical equipment operating data, attention shall be given to equipment operability aspects. Among the factors that should be considered are:

- Fluctuation of chemical feed rate from desired value -- the time interval at which re-setting is needed (i.e., how long can feed pumps hold on a set value for the feed rate?).

- Ability to maintain desired pre-oxidant feed rate.

- Presence of devices to aid the operator with chemical dosage selection:
  - streaming current monitor provided?
  - influent and filtered water continuous turbidimeters provided?
  - in-line pH meter provided?

- Can backwash be done automatically?

- If automatic backwash provided, could it be initiated by:
  - reaching a set value for head loss?
  - reaching a set value for filtered water turbidity?

- Does remote notification to operator occur when backwash happens?

- Can operator observe filter backwash?

- How can plant operator check on condition and depth of filter media?

- Can flocculation energy be varied?

- Does plant have multiple feed points for chemicals:
  - for pH adjustment?
  - for coagulant chemical feed?
  - for polymer feed?
  - for oxidants?

- Is head loss measurement provided?

- Is rate of flow of raw water measured?

- Is chemical feed paced with raw water flow?

- Can coagulation pH be maintained automatically if raw water flow changes?

- Is backwash rate of flow measured and variable?

- Is backwash duration (time) variable?

Does the equipment have sensors or monitoring equipment that can detect an equipment malfunction, unsatisfactory treated water quality, or operating conditions that exceed allowable limits, and if so, during such situations can the equipment be automatically shut down? Upon automatic shutdown, can a means of operator notification be provided, if the operator is not present on the site where the equipment is located?

Both the reviews of historical data and the reports on verification testing should address the above questions in the written reports. The issues of operability should be dealt with in the portion of the reports that are written in response to Task 3: Operating Conditions and Treatment Equipment Performance, in this TSTP.

16.0 REFERENCES

American Water Works Association. 1992. Operational Control of Coagulation and Filtration Processes, Manual of Water Supply Practices, AWWA M37, Denver, CO.

Amirtharajah, A., and O'Melia, C. R. 1990. Coagulation Processes: Destabilization, Mixing, and Flocculation. *Water Supply and Treatment: A Handbook of Community Water Supplies, 4th ed.* McGraw-Hill, New York.

Bowers, D. A., Bowers, A. E., and Newkirk, D. D. 1982. Development and Evaluation of a Coagulation Control Test Apparatus for Direct Filtration. 1982 AWWA WQTC, Nashville, TN.

Chen, C. J., et al, 1992. "Cancer Potential in Liver, Lung, Bladder, and Kidney Due to Ingested Inorganic Arsenic in Drinking Water," *British Journal of Cancer*, 66:888.

Cheng, R. C., Liang, S., Wang, H. C., and Beuhler, M. D. 1994. "Enhanced Coagulation for Arsenic Removal," *Journal AWWA*, 86:9:79 (September).

Clifford, D. A. 1990. Ion Exchange and Inorganic Adsorption. *Water Supply and Treatment: A Handbook of Community Water Supplies, 4th ed.* McGraw-Hill, New York.

Clifford, D., and Lin, C. C. 1991. Arsenic (III) and Arsenic (V) Removal From Drinking Water in San Ysidro, New Mexico, EPA/600/52-91/001. Cincinnati, Ohio (June).

Cullen, W. R., and Reimer, K. J. 1989. "Arsenic Speciation in the Environment." *Chemistry Review*, 89:713.

Eaton, A. D. 1994. "Determining the Practical Quantitation Level for Arsenic." *Journal AWWA*, 86:2:100 (February).

Ferguson, J. F., and Davis, J. A. 1972. "A Review of the Arsenic Cycle in Natural Waters." *Water Research*, 6:1259.

Fox, K. R., and Sorg, T. J. 1987. "Controlling Arsenic, Fluoride, and Uranium by Point-of-Use Treatment." *Journal AWWA*, 79:10:81.

Gulledge, J. H., and O'Connor, J. T. 1973. "Removal of Arsenic From Water by Adsorption on Aluminum and Ferric Hydroxides." *Journal AWWA*, 65:8:548 (August).

Gupta, S. K., and Chen, K. Y. 1978. "Removal of Arsenic From Water by Adsorption on Aluminum and Ferric Hydroxides." *Journal WPCF*, 50:493 (March).

Hach Water Analysis Handbook. 2nd Ed. Hach Company, Loveland, Colorado 1992.

Hathaway, S. W., and Rubel, F., Jr. 1987. "Removing Arsenic from Drinking Water." *Journal AWWA*, 79:8:161.

Hering, J. G., Pen-Yuan Chen, Wilkie, J. A., and Elimelech, M. 1997. "Arsenic Removal from Drinking Water During Coagulation." *Journal of Environmental Engineering*, 123:8:800.

Huxstep, J. R. and Sorg, T. J. 1988. Reverse Osmosis Treatment to Remove Inorganic Contaminants From Drinking. EPA/600/51-87/109. Cincinnati, Ohio (March).

Malcolm Pirnie, Inc. 1993. Treatment and Occurrence, Arsenic in Potable Water Supplies. Drinking Water Treatment Branch, Office of Groundwater and Drinking Water, US Environmental Protection Agency, Washington, D.C., September.

National Academy of Sciences. 1977. Arsenic-Medical and Biological Effects of Environmental Pollutants. US Government Printing Office, Washington, D.C.

Northington, D. J., Hovanec, B. M., and Reich, K. 1993. Arsenic in Groundwater by ICPMS and Hydride Generation-ICPMS. Proceedings 1993 AWWA WQTC, Miami, FL.

Office of Environmental Health Hazard Assessment. 1991. Arsenic in Drinking Water: Questions and Answers CAL-EPA. (May).

Shen, Y. S. 1973. "Study of Arsenic Removal From Drinking Water." *Journal AWWA*, 65:8:543 (August).

Smith, A. H. et. al., 1992 "Cancer Risks from Arsenic in Drinking Water," *Environmental Health Perspectives*, 97:259.

Sorg, T. J. 2002. "Iron Treatment for Arsenic Removal Neglected." *Opflow*, 28:11:15.

Sorg, T. J., and Logsdon, G. S. 1978. "Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics: Part 2." *Journal AWWA*, 70:7:379.

Standard Methods for the Examination of Water and Wastewater. 1999. APHA, AWWA, and WPCF, 20th ed., Washington, D.C.

Symons, J. M. 2000. *The Drinking Water Dictionary*. AWWA, Denver, CO.

Thayer, J. S. 1984. *Organometallic Compounds and Living Organisms*. Academic Press, Orlando, FL.

Thompson, M. A., and Chowdhury, Z. K. 1993. Evaluating Arsenic Removal Technologies. Proceedings 1993 AWWA Annual Conference, Water Resources. AWWA, Denver, Colorado, pp. 321-342.

Table 1. Generic Schedule for Verification Testing	
A period of initial operations is required for all filtration process equipment. This initial operations testing may require from 1 to 6 weeks.	
Filtration Process	**Required Duration of Verification Testing Period**
Granular Media	320 hours
Precoat Filtration	320 hours
Bag Filters, Cartridge Filters, Backwashable Depth Filters	320 hours minimum; however verification testing must be performed for a period of time sufficiently long to attain one change/replacement of bag or cartridge. If such a change has not occurred at 29 days due to lack of terminal head loss development, the bag/cartridge shall be replaced and the equipment shall be operated for at least 24 hours longer, with the total operating time to be at least 30 days
Membrane Filtration Equipment	30 days

Table 2. Water Quality Sampling and Measurement Schedule	
Parameter	**Minimum Frequency**
Temperature	Daily
pH[1]	Once per day during runs with no arsenic sampling. Measure pH of coagulated water each time arsenic samples are collected.
Total Alkalinity	Daily
Hardness	Weekly[2]
Total Organic Carbon	Weekly[2]
UV254 Absorbance	Weekly[2]
Turbidity	Daily at bench to check continuous turbidimeters
Aluminum	Weekly[2,3]
Iron	Weekly[2,3]
Manganese	Weekly[2] if present in concentration of 0.05 mg/L or greater
Total Suspended Solids in backwash water	See Task 4
Arsenic	See Task 4
Sulfate	Weekly
Dissolved Oxygen in feedwater	Daily
Algae, number and species	Weekly or once during each set of treatment conditions for which arsenic sampling is done
True Color	Weekly[2]
Dosage of pre-oxidation chemical and pre-oxidation chemical residual in filtered water	Only in Task 4, every 6 hours beginning at time zero

Sampling points: feed water, clarified water (if applicable) and filtered water.
During arsenic challenge testing, collection of weekly and daily samples shall be coordinated with arsenic sampling so other water quality data can be related to arsenic results.

[1] For pH samples, filtered water pH values are valid only if no pH adjusting chemicals are added after coagulation. The pH of filtered water is intended to represent the pH of coagulation.

[2] When used as the coagulant to co-precipitate arsenic, measure daily when arsenic samples are not taken on a given day.

[3] When used as the coagulant to co-precipitate arsenic, measure influent to filter and filtered water each time arsenic is sampled.

Table 3. Analytical Methods			
Parameter	**Facility**	***Standard Methods*[1] number or Other Method Reference**	**EPA Method[2]**
Temperature	On-Site	2550	
pH	On-Site	4500-H^+ B	150.1, 150.2
Total Alkalinity	On-Site	2320 B	
Total Hardness	Lab or On-Site[3]	2340 C	
Total Organic Carbon	Lab	5310 C	
UV_{254} absorbance	Lab	5910 B	
Turbidity	On-Site	2130 B	180.1
Aluminum	Lab	3120 B	200.7, 200.8, 200.9
Iron	Lab	3120 B	200.7, 200.9
Manganese	Lab	3120 B	200.7, 200.8, 200.9
Total Suspended Solids in backwash water	Lab	2450 D	
Algae, number and species	Lab	10200 and 10900	
Sulfate	Lab	4110 B, 4500-SO_4^{2-} C, D, E, & F	300.0, 375.2
Dissolved Oxygen	On-Site	4500-O C or G	
True Color	On-Site	2120 B (Hach Company modification of SM 2120 measured in spectrophotometer at 455 nm)	
Arsenic	Lab		200.8
Arsenic Speciation	Lab		Battelle Speciation Method and Arsenic by 200.8[4]
Pre-oxidants: Ozone Residual Chlorine Chlorine Dioxide Potassium Permanganate (if used to oxidize Arsenic III)	 On-Site On-Site On-Site Lab	 4500-O_3 B; HACH Indigo Blue Method[5] 4500-Cl 4500-ClO_2 3111	
TCLP	Lab		1311 and metals analysis by SW-846 6010 and 7470a[6]
California Waste Extraction Test (WET)	Lab		Special CA method and metals analysis by SW-846 6010 and 7470a[6]

[1] Standard Methods Source: 20th Edition of *Standard Methods for the Examination of Water and Wastewater*, 1999, AWWA.
[2] EPA Methods Source: EPA Office of Ground Water and Drinking Water. EPA Methods are available from the National Technical Information Service (NTIS).
[3] On-Site or at Laboratory, must meet short holding time requirements.
[4] Speciation Method developed by Battelle for EPA (see Appendix A).
[5] Dissolved ozone residual measurements can also be from a properly calibrated and installed dissolved ozone monitor.
[6] Metals analyses shall include As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Se, Ag, Zn.

Table 4. Equipment Operating Data	
Operating Data	**Action**
Chemicals Used	Record on a daily basis: type; supplier; commercial strength (e.g. as percent Fe or Al, specific gravity of liquid coagulants or percent purity and chemical formula of dry coagulants); and dilution for stock solution to be fed (if diluted).
Chemical Type, Feed Volume and Dosage	Check and record each 2 hours. Refill as needed, note volumes and times of refill. Maintain all calculations on coagulant chemical solution preparation and all data on coagulant chemicals as purchased from supplier or chemical manufacturer. Calculate the chemical dosage for each filter run in which arsenic challenge testing was carried out.
Ozonation System	See Section 15.2 and Table 3 of "The ETV Protocol for Inactivation of Microbiological Contaminants, Chapter 2, Test Plan for Ozone and Advanced Oxidation Processes"
RPM of Rapid Mix and Flocculator	Check once/day and record
Feedwater Flow and Filter Flow	Check and record each two hours Adjust when flow >10% above or below goal Record flows before and after adjustment.
Filter Head Loss	Record initial clean bed total head loss at start of filter run Record total head loss every two hours. Record terminal head loss at end of filter run.
Filtered Water Production	Record gallons of water produced per square foot of filter area, for each filter run. [This figure is the product of filtration rate (gpm/sf) and length of filter run in minutes for a filter run performed at constant rate.]
Filter Backwash	Record time and duration of each filter backwashing. Record water volume used to wash filter.
Sludge Production	If sludge is drawn off, record volume of sludge.
Suspended solids in washwater	Determine suspended solids in washwater for each set of arsenic removal testing conditions.
Clarifier/flocculator or other similar process ahead of filter	If clarifier/flocculator is backwashed separately from backwashing of filter, record the time of every backwash for this process, and volume of water used.
DAF flotate removal	Record frequency of flotate removal action each day.

Table 4. Equipment Operating Data (continued)	
Operating Data	**Action**
DAF recycle flow	Record recycle water flow rate each 8 hours.
DAF saturator pressure	Record DAF saturator vessel pressure each 8 hours.
Electric Power	Record meter reading once per day
Hours operated per day	Record in logbook at end of day or at beginning of first shift on the following workday.

All parameters will be checked only during times when the equipment is staffed.

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CHAPTER 4

EPA/NSF ETV EQUIPMENT VERIFICATION TESTING PLAN - ELECTRODIALYSIS PROCESSES FOR THE REMOVAL OF ARSENIC: See Test Plan for Removal of Inorganic Constituents by Electrodialysis and Electrodialysis Reversal

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CHAPTER 5

EPA/NSF ETV EQUIPMENT VERIFICATION TESTING PLAN - REVERSE OSMOSIS PROCESSES FOR THE REMOVAL OF ARSENIC: See Test Plan for Removal of Inorganic Constituents by Reverse Osmosis

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CHAPTER 6

EPA/NSF ETV EQUIPMENT VERIFICATION TESTING PLAN
ADSORPTIVE MEDIA PROCESSES
FOR THE REMOVAL OF ARSENIC

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TABLE OF CONTENTS

Page

1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN 6-5

2.0 INTRODUCTION 6-5
2.1 Adsorption Process 6-6
2.2 Adsorbents 6-7
2.3 Capacity 6-7
2.4 Intermittent Operation 6-8

3.0 GENERAL APPROACH 6-8

4.0 OVERVIEW OF TASKS 6-9
4.1 Task 1: System Integrity Verification Testing 6-9
4.2 Task 2: Adsorption Capacity and Regeneration Verification Testing 6-9
4.2.1 Task 2A: Adsorption Capacity Verification Testing 6-9
4.2.2 Task 2B: Regeneration Verification Testing (Optional) 6-10
4.3 Task 3: Documentation of Operating Conditions and Treatment Equipment Performance 6-10
4.4 Task 4: Data Management 6-11
4.5 Task 5: Quality Assurance/Quality Control 6-11

5.0 TESTING PERIODS 6-11

6.0 DEFINITIONS 6-11
6.1 Adsorb 6-11
6.2 Adsorptive Media, Granular 6-11
6.3 Adsorptive Media, Powdered 6-11
6.4 Bed Volume 6-12
6.5 Breakthrough 6-12
6.6 Desorb 6-12
6.7 Empty Bed Contact Time (EBCT) 6-12
6.8 Filtrate 6-12
6.9 Ground Water 6-12
6.10 Regenerate 6-12
6.11 Supernatant 6-12
6.12 Surface Water 6-12
6.13 Treatment 6-12
6.14 Treatment Band 6-12
6.15 Treatment Bed 6-12

7.0 TASK 1: SYSTEM INTEGRITY VERIFICATION TESTING 6-12
7.1 Introduction 6-12
7.2 Experimental Objectives 6-12

TABLE OF CONTENTS (continued)

Page

7.3 Work Plan 6-13
7.3.1 Spiked Arsenic (Optional) 6-14
7.4 Analytical Schedule 6-15
7.5 Evaluation Criteria and Minimum Reporting Requirements 6-15

8.0 TASK 2A: ADSORPTION CAPACITY VERIFICATION TESTING 6-16
8.1 Introduction 6-16
8.2 Experimental Objective 6-16
8.3 Work Plan 6-17
8.4 Analytical Schedule 6-21
8.5 Evaluation Criteria and Minimum Reporting Requirements 6-22

9.0 TASK 2B: REGENERATION VERIFICATION TESTING (OPTIONAL) 6-22
8.1 Introduction 6-22
8.2 Experimental Objectives 6-22
8.3 Work Plan 6-23
8.4 Analytical Schedule 6-24
8.5 Evaluation Criteria and Minimum Reporting Requirements 6-25

10.0 TASK 3: DOCUMENTATION OF OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE 6-25
10.1 Introduction 6-25
10.2 Experimental Objectives 6-26
10.3 Work Plan 6-26
10.4 Schedule 6-26
10.5 Evaluation Criteria 6-26

11.0 TASK 4: DATA MANAGEMENT 6-26
11.1 Introduction 6-26
11.2 Experimental Objective 6-27
11.3 Work Plan 6-27

12.0 TASK 5: QUALITY ASSURANCE/QUALITY CONTROL 6-28
12.1 Introduction 6-28
12.2 Experimental Objectives 6-28
12.3 Work Plan 6-28
12.3.1 Daily QA/QC Checks 6-29
12.3.2 Weekly QA/QC Checks 6-29
12.3.3 QA/QC Checks Performed Each Testing Period 6-29
12.4 Analytical Methods 6-29
12.4.1 Arsenic 6-30
12.4.2 pH 6-31
12.4.3 Alkalinity 6-31

TABLE OF CONTENTS (continued)

Page

12.4.4 Fluoride 6-31
12.4.5 Chloride 6-31
12.4.6 Sulfate 6-31
12.4.7 Silica 6-31
12.4.8 Aluminum 6-31
12.4.9 Sodium (Optional) 6-31
12.4.10 Calcium 6-32
12.4.11 Hardness 6-32
12.4.12 Magnesium 6-32
12.4.13 Iron 6-32
12.4.14 Manganese 6-32
12.4.15 Turbidity 6-32
12.4.15.1 Bench-top Turbidimeters 6.32
12.4.15.2 In-line Turbidimeters 6-33
12.4.16 Temperature 6-33
12.4.17 TCLP 6-33
12.4.18 California WET 6-33
12.5 Tests and Data Specific to Adsorptive Media Type Evaluated 6-33

13.0 OPERATIONS & MAINTENANCE 6-34
13.1 Operation 6-34
13.2 Maintenance 6-35

14.0 REFERENCES 6-35

TABLES

Page

Table 1. Required Water Quality Analyses and Minimum Sample Frequencies for Task 1 System Integrity Verification Testing 6-37
Table 2. Schedule for Observing and Recording Equipment Operating and Performance 6-38
Table 3. System Integrity Verification Test Chemical Consumption Data Report 6-39
Table 4. Tests and Data Specific to Adsorptive Media Type Evaluated 6-40
Table 5. Required Water Quality Analyses and Minimum Sample Frequencies for Task 2A Adsorption Capacity Verification Testing 6-41
Table 6. Adsorption Capacity Verification Data Report 6-42

APPENDICES

Appendix A Arsenic Speciation Method Developed by Battelle for EPA

1.0 APPLICATION OF THIS VERIFICATION TESTING PLAN

This document is the Environmental Technology Verification (ETV) Technology Specific Test Plan (TSTP) for evaluation of water treatment equipment for arsenic removal utilizing the adsorptive media process. This TSTP is to be used as a guide in the development of Product Specific Test Plan (PSTP) procedures for testing adsorptive media equipment, within the structure provided by, "Protocol for Equipment Verification Testing for Arsenic Removal: Chapter 1, General Requirements." This TSTP is applicable only to granular adsorptive media processes that use a material, such as activated alumina, that attracts arsenic ions to adsorption sites, with or without pH adjustment in fixed or moving packed beds. Powdered adsorptive media may also be effectively utilized in combination with chemicals in Coagulation and Filtration Arsenic Removal Processes. Since performance of powdered adsorptive media is to be included in that equipment category it is not included in this TSTP.

To participate in the equipment verification process for adsorptive media, the equipment manufacturer and its designated Field Testing Organization (FTO) shall employ the procedures and methods described in this TSTP and in the referenced ETV protocol document as guidelines for the development of the PSTP. The procedures shall generally follow those tasks related to verification testing that are outlined herein, with changes and modification made for adaptations to specific equipment. At a minimum, the format of the procedures written in the PSTP for each task should consist of the following sections:

- Introduction;
- Objectives;
- Work Plan;
- Analytical Schedule; and
- Evaluation Criteria.

Each PSTP shall include Tasks 1 through 5. An overview of Tasks 1 through 5 is provided in Section 4.0 of this TSTP.

2.0 INTRODUCTION

This TSTP is applicable to the testing of package and modular water treatment equipment utilizing an adsorptive media process, which may include a pretreatment pH adjustment step. Verification testing shall evaluate performance of the equipment under at least one feed water quality condition. Waters containing naturally occurring arsenic are preferable to synthetic water "spiked" with arsenic. Use of feed water artificially spiked with arsenic, a product of a non-standard method, might provide inaccurate performance data, which will not reflect performance data acquired with use of natural water. Verification tests will be performed during time periods when the source water or feed water quality is appropriate for testing the full range of water quality conditions that need to be evaluated.

Adsorption can be an effective treatment technique for removing arsenic prior to disinfection application. Adsorptive media processes are operated as filters usually containing a 28x48 US

standard mesh size. Typical empty bed contact times (EBCTs) are 5 to 10 minutes. Arsenic removal is typically greater than 99 percent at the beginning of adsorptive media vessel operation for EBCTs greater than 5 minutes. Over time, effluent concentrations increase, yielding a characteristic breakthrough curve that is unique to the water source, pretreatment conditions, EBCT, and type of adsorptive media used. Thus, the adsorptive media vessel run time for a given treated water criterion can be determined from the appropriate breakthrough curve. Once effluent criteria are exceeded, the adsorptive media must be regenerated or replaced with new adsorptive media.

This TSTP is not intended to be used for the evaluation of ability of adsorptive media to serve as a particulate matter (turbidity) filter. The TSTP for Coagulation and Filtration should be used in conjunction with this TSTP when verification of particulate matter filtration performance is required.

2.1 Adsorption Process

The adsorption process is the physical attraction of the ion to be adsorbed to the surface of the adsorbent material. The adsorbed ion (adsorbate) gathers on to the surface of the adsorbent. The process is sensitive to the concentration of the adsorbate, the surface area of the adsorbent, the physical characteristics of both the adsorbent and/or the adsorbate, competing ions, time, and flow characteristics of the medium conducting the adsorbate into the treatment bed of adsorbent. In this case, arsenic is the adsorbate.

Arsenic occurs in water in two valence states (As III and As V.) The valence state can be modified by oxidation and reduction processes. The toxicology of arsenic varies depending upon its concentration and valence. Since arsenic valence can change while in aqueous solution, the objective of arsenic removal treatment is to remove all of the arsenic regardless of valence. The higher the arsenic concentration is in the feed water, the higher the adsorptive driving force that results in a higher arsenic capacity of the adsorptive media.

The adsorptive capacity of the treatment media is also a function of the surface area (adsorption sites) and the access to those sites. An adsorptive media's surface area is a function of its porosity. An adsorptive treatment media contains an extensive network of fine (small diameter) pores, which extend throughout the body of a grain of media. The adsorptive attraction force is a function of the pore size, the ion size, the pH and other physical conditions. The arsenic ion requires time to migrate into a pore within the grain of the adsorbent. As the surface area of each adsorbent grain becomes saturated with arsenic ions, the time required for additional adsorption becomes longer.

The adsorptive media is normally in a packed bed and contained in a pressure vessel. The water to be treated flows in one direction through the treatment bed (normally downflow). Gravity flow is feasible; but if pH adjustment is employed, gravity flow is not as effective because in gravity flow the pressure required to retain the CO_2 in solution does not exist. Therefore, the free CO_2 is released resulting in the pH rising to higher than the desired level. As the feed water flows through the adsorptive media, the arsenic ions are adsorbed onto the available adsorption sites. As the adsorption sites are being occupied, the arsenic ion concentration decreases in the

water. As the water flows through the bed, its arsenic concentration decreases until no longer detectable. The water continues to flow through the media until it exits the treatment vessel as treated water. As the feed water continues to flow through the treatment media, the media which first contacts the feed water becomes saturated with arsenic ions. A treatment band then progresses through the treatment bed until breakthrough occurs. At that point, traces of arsenic appear in the treated water. As flow continues, the treatment band progresses through the treatment media until the media is saturated; the arsenic concentration in the treated water is then the same as that in the feed water. Since the arsenic concentration in the treated water is the contaminant of concern, the arsenic concentration must be controlled to the desired level.

There are various methods of sequencing multiple treatment beds (parallel and/or series arrangements) which allow the entire (or almost the entire) adsorptive media capacity to be utilized. When the adsorptive media becomes saturated with arsenic ions, it is removed from service for regeneration or disposal. Normally the economic feasibility of the adsorptive process requires reuse of the treatment media. This is accomplished by means of chemical regeneration requiring adjustment of pH (or other methods) to a level at which adsorptive conditions no longer exist. At those pH levels the adsorptive treatment media desorbs the adsorbate. The arsenic is released and flushed from the adsorptive media as a high concentration arsenic wastewater. Upon completion of regeneration, the pH of the treatment media is to be adjusted back to the treatment pH at which point the media is reused for a subsequent treatment cycle. During regeneration, some adsorptive media may be consumed (attrition); if that occurs, replacement adsorptive media is to be added to the treatment bed. In small treatment systems and/or in treatment systems in which the arsenic concentration in the feed water is not excessively high, economic feasibility might dictate replacement of spent media in lieu of regeneration.

2.2 Adsorbents

The following is a list of adsorbents that may be included in the use of this TSTP. This list is not an all-inclusive list since other types of adsorbent materials are currently being developed.

- Activated alumina;
- Ferric Media; and
- Greensand.

2.3 Capacity

Capacities and performance of different adsorptive media do vary. Some adsorptive media may be capable of regeneration while others may not. Those adsorptive media that have regeneration capability also may vary in performance during subsequent treatment runs. The arsenic removal capacity diminishes until it is determined that adsorptive media replacement is required. Other adsorptive media experience attrition during each regeneration requiring addition of makeup adsorptive media prior to commencement of the next arsenic removal treatment run. The latter type of adsorptive media may not experience reduction of arsenic removal capacity during subsequent treatment runs. The treatment system manufacturer may choose to include verification of the regeneration process in its PSTP.

2.4 Intermittent Operation

In full-scale operation, adsorptive media arsenic removal water treatment systems may operate intermittently. The smaller the system the higher the probability that the operation will experience more frequent starts and stops. The performance of adsorptive treatment media is usually not degraded when operated on an intermittent basis. In fact, the performance of this form of treatment media may exhibit a short period of improved performance during startup after a shutdown of the process. The reason for the improved performance is that arsenic ions adsorbed during continuous operation occupy adsorption sites that are most accessible. During process shutdown, the arsenic ions migrate from the most accessible adsorption sites to less accessible sites located deep in the pores of the media thereby re-exposing the most accessible adsorption sites for reuse. At the time the treatment process restarts, the arsenic removal process exhibits increased capacity for a short period after which time the performance returns to the level occurring at time of treatment process shutdown. The treatment system manufacturer may include optional intermittent operational steps in its PSTP.

Adsorptive media treatment systems experiencing extended shutdowns (several weeks) might require a backwash step to expand the media bed to eliminate performance degradation. Degradation will vary due to channeling, biological activity, cementing of media, and other types of process fouling for which potential exists due to characteristics of either the adsorptive media or the water to be treated.

3.0 GENERAL APPROACH

This TSTP is directed to the completion of two main tasks: System Integrity Verification Testing and Adsorption Capacity Verification Testing. An optional third task applies to media that can be regenerated: Regeneration Verification Testing.

System Integrity Verification Testing is a two-week field operation of the equipment with monitoring to ensure the system is functional and to identify any major systemic problems such as channeling, insufficient media, excessive headloss buildup, etc. This TSTP includes sampling and monitoring requirements for System Integrity Verification Testing. Adsorption Capacity Verification Testing is intended to evaluate the capability of adsorptive media at a set contact time to remove arsenic to the level established by the manufacturer. For media that is regenerated, this task includes a mandatory regeneration of the media and a short post regeneration monitoring period. An optional Regeneration Verification Testing task is intended to evaluate the performance of the media through at least two regeneration cycles. This optional task can be important in determining the impact on treatment efficiency, as some media may show a decrease in performance after one or more regeneration cycles.

The manufacturer's statement of performance capabilities is used to establish data quality objectives (DQOs) to develop the experimental design of the verification test. The broader the performance capabilities, the more comprehensive the PSTP must be to achieve the DQOs. An example of a performance capability statement that may be included in an PSTP is: "This system, when operated at an adsorption media EBCT of 5 minutes or more, is capable of

achieving an effluent arsenic concentration of 10 parts per billion or less for at least 10,000 bed volumes for influent arsenic concentrations up to 0.12 mg/L (species of arsenic must be indicated if applicable, i.e., arsenic III or arsenic V)."

Testing shall be conducted by an FTO that is qualified by NSF International (NSF) and is selected by the manufacturer. Water quality analytical work to be completed as part of this TSTP shall be contracted with a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA.

The influent water quality chosen for Adsorption Capacity Verification Testing should be appropriate for the performance capabilities outlined by the manufacturer. Multiple capabilities based on the ability of a system to treat a variety of influent water quality conditions must be supported by Adsorption Capacity Verification Testing performed under conditions representative of this range of water quality. Adsorption Capacity Verification Testing must be conducted at least once using the equipment. Additional testing may be performed to demonstrate performance capabilities that include higher or lower influent arsenic concentrations.

The manufacturer shall stipulate which pretreatment processes are necessary prior to the adsorptive media. The recommended pretreatment processes shall then be employed as pretreatment during equipment verification testing. Adsorptive media performance will be evaluated based on influent water quality, sampled after any pretreatment processes.

4.0 OVERVIEW OF TASKS

The following section provides a brief overview of the tasks included in this adsorptive media TSTP.

4.1 Task 1: System Integrity Verification Testing

The objectives of this task are to demonstrate that the equipment is (1) able to initially produce a finished water as described in the manufacturer's performance objectives, and (2) able to reliably operate under field conditions. The equipment is operated, monitored, and sampled for approximately two weeks.

4.2 Task 2: Adsorption Capacity and Regeneration Verification Testing

4.2.1 Task 2A: Adsorption Capacity Verification Testing

The objective of this task is to evaluate the ability of the adsorptive media equipment to remove arsenic, based upon the water quality performance capabilities specified by the manufacturer. The performance of the adsorptive media package is a function of the type of adsorptive media used and the feed water quality. Task 2A, Adsorption Capacity Verification Testing, must be performed at least once using the equipment and may be repeated, as necessary, using different water sources to verify the ability of the equipment

to meet multiple treated water quality performance capabilities stated by the manufacturer. Adsorptive media influent and effluent analyses performed include arsenic, pH and other ions that are identified in the feed water. The duration of testing will depend on treatment performance capabilities stated by the manufacturer. If the media is normally regenerated, it must be regenerated after reaching capacity. For media requiring regeneration, one regeneration cycle will be monitored and a post-regeneration monitoring period will be included for this task.

4.2.2 Task 2B: Regeneration Verification Testing (Optional)

This task applies only to media that is regenerated as part of the normal treatment process and is an optional task. The objective of this task is to evaluate the impact of the regeneration process on the ability of the media to meet the water quality performance capabilities specified by the manufacturer. Regeneration of media is specific to the media type and the regeneration process. Some media experience a decrease in performance or capacity after one or more regeneration steps. If this optional task is performed, a minimum of two full regeneration cycles must be monitored, including a post-regeneration monitoring period after the second regeneration cycle. Task 2B can be expected to be twice as long as Task 2A, with the first regenerative cycle being included as part of Task 2A. Adsorptive media influent and effluent analyses performed include arsenic, pH and other ions that are identified in the feed water and any specific ions that may be important to the regeneration process. The duration of testing will depend on treatment performance capabilities supplied by the manufacturer and the volume of water that can be treated between regeneration cycles.

It may be possible to perform this verification task using existing data and experience from a similar site. Given the long run times between regenerations for some media, the ETV Program will consider the use of well-documented data and operating records from installations that have years of information. The source water will need to be similar and the treatment system must use the same media and treatment process. Acceptance of existing data will be on a case-by-case basis. The use of existing data may be reviewed by the ETV Program and included in ETV verification reports and statements as separate and distinct from verified data.

4.3 Task 3: Documentation of Operating Conditions and Treatment Equipment Performance

The objective of this task is to observe, measure, and document the operating conditions throughout the verification test. During each day of verification testing, operating conditions shall be documented. This shall include descriptions of any pretreatment processes and their operating conditions. The volumetric flow rate through adsorptive media vessels is a critical parameter, and shall be frequently monitored, recorded, and adjusted if necessary. Adsorptive media performance is affected by the EBCT, which is a function of the volumetric flow rate through the adsorptive media vessel. If media regeneration is applicable, the volume and flow rate of regenerative fluids shall be monitored and recorded. Operating conditions immediately following the completion of the regeneration process shall be monitored and recorded to

determine if any changes have occurred within the treatment system.

4.4 Task 4: Data Management

This task will establish effective field protocol for data management at the field operations site and for data transmission between the FTO and NSF.

4.5 Task 5: Quality Assurance/Quality Control

The objective of this task is to ensure accurate measurement of operational and water quality parameters during verification testing.

5.0 TESTING PERIODS

Task 1, System Integrity Verification Testing, is designed to be carried out in conjunction with Tasks 3 through 5 in a two-week period, not including mobilization and start-up. When verifying package plants or module components for small systems and very small systems, the equipment shall be operated for a minimum of two hours or longer depending on the actual application, and then the flow to the equipment shall be stopped and operations resumed the next day. After the completion of Task 1, subsequent testing may use the normal intermittent or continuous flow pattern that is typical for the test site. Task 2A, Adsorption Capacity Verification Testing, is designed to be carried out in conjunction with Tasks 3 through 5. The duration of Task 2A is dependent on the volume of water required (as specified in the manufacturer's statement of performance capabilities), the flow rate processed through the system, the run time, the source water quality, and other factors that may affect media capacity. Task 2B is designed to be carried out in conjunction with Tasks 3 through 5. This task will include a minimum of two full regeneration cycles, so the duration of the test will be dependent on the same factors as Task 2A. Task 2B can be expected to be twice as long as Task 2A, with the first regenerative cycle being included as part of Task 2A.

6.0 DEFINITIONS

Definitions that may apply to adsorptive media processes include:

6.1 **Adsorb:** To adhere on a surface in a condensed layer.

6.2 **Adsorptive Media, Granular:** Particles retained on a 100 mesh screen that have ability to adsorb. During the treatment process, these materials are contained in a treatment vessel.

6.3 **Adsorptive Media, Powdered:** Particles that pass through a 100 mesh screen that have ability to adsorb. During the treatment process, these particles are added into and mixed with the water to be treated. The particles are removed from the treated water by sedimentation and/or filtration.

6.4 **Bed Volume:** The volume of adsorptive media including voids between particles contained in a treatment vessel.

6.5 **Breakthrough:** The point in adsorptive media run time when the effluent arsenic concentration reaches a predetermined value, such as the detection limit, the maximum contaminant level (MCL), some fraction of the MCL, etc.

6.6 **Desorb:** To remove an adsorbate from an adsorptive media surface.

6.7 **Empty Bed Contact Time (EBCT):** The volume of the media divided by the flow rate. For example, the time (EBCT) required for feed water flowing at 150 gpm through an adsorptive treatment media volume of 100 ft^3 (750 gallons) is 5 minutes.

6.8 **Filtrate:** Liquid that has passed through a filter.

6.9 **Ground Water:** Water located below grade, which is not under the influence of surface water. The source of water in wells and springs.

6.10 **Regenerate:** To renew or restore treatment capacity to adsorptive media.

6.11 **Supernatant:** Liquid above a sludge layer.

6.12 **Surface Water:** All water that is open to the atmosphere and subject to surface runoff. For purpose of this document, surface water includes lakes, reservoirs, canals, rivers, streams, and ground water under the influence of surface water.

6.13 **Treatment:** To subject to some agent or action to bring about a particular result.

6.14 **Treatment Band:** The portion of a bed of adsorptive media in which treatment takes place.

6.15 **Treatment Bed:** The space occupied by the adsorptive media.

7.0 TASK 1: SYSTEM INTEGRITY VERIFICATION TESTING

7.1 Introduction

This task will evaluate the short-term ability of the equipment to produce water of acceptable quality. This task is not designed to evaluate the long-term ability of the equipment to remove arsenic.

7.2 Experimental Objectives

The objectives of this task are to demonstrate that the equipment is (1) able to produce a treated

water within performance capabilities, and (2) able to reliably operate under field conditions.

7.3 Work Plan

The manufacturer and its designated FTO shall specify in the PSTP the operating conditions to be evaluated during verification testing and shall supply written procedures on the operation and maintenance of the treatment system. To complete the System Integrity Test, for applications where the treatment system is expected to operate continuously, the equipment shall be operated continuously for a minimum of 320 hours (13 full days plus one 8-hour work shift). For applications where the treatment system is expected to operate intermittently, such as for very small systems, the equipment shall be operated for a minimum of two hours continuously each day throughout the 13 full days plus one 8-hour work shift period. For adsorptive media vessels operated as post-filter adsorbers, the media filters on-line upstream of the adsorptive media vessels shall be operated from start-up until turbidity breakthrough or terminal head loss is attained, at which time the media filters shall be backwashed and operation shall resume.

System Integrity Verification Testing shall include at least one backwashing event, as determined by turbidity breakthrough or terminal head loss. For adsorptive media filters that are not operated as post-filter adsorbers, but specify that a backwash cycle is part of normal operation, at least one backwashing event at the end of the System Integrity Verification Test shall be included in the test. This backwash shall be performed even if the backwash criteria (volume treated, headloss or pressure drop, etc.) are not experienced or met. Interruptions in the treatment system shall be documented and are allowed only for backwashing events and required equipment maintenance. Since adsorptive media performance is a function of EBCT, which is dependent on the volumetric flow rate, it is critical that verification testing be conducted at a set flow rate that is maintained within 5 percent of the design value.

Water Quality Sample Collection. Water quality data shall be collected at regular intervals as described in the analytical schedule (see Table 1). Additional or more frequent analyses may be stipulated at the discretion of the FTO. Sample collection frequency and protocol shall be defined by the FTO in the PSTP.

The arsenic species (III or V) present in the feed water can have a direct impact on the performance of adsorptive processes. It is important that the distribution of arsenic species be determined as part of the verification test. At a minimum, two samples of source water, collected before or during startup and shakedown, and three samples of the feed water and treated water, collected during the Integrity Test, shall be speciated. More frequent arsenic speciation may be needed depending on the actual distribution of the arsenic species in the feed water, and the importance of the arsenic species (III or V) to the performance of a specific treatment process. If the feed water has only one species of arsenic present, then the minimum frequency may be appropriate. However, if the source water has significant concentrations of both species present, and/or the media performance is dependent on the arsenic species, then more frequent or daily arsenic speciation should be proposed by the FTO to properly monitor the system performance.

Sample collection procedures for intermittent flow systems must ensure that freshly treated water is collected and not water that was stagnant in the bed. For intermittent flow systems, sample

collection should occur during a continuous flow period, after a minimum of 10 bed volumes has passed through the system or after one hour of continuous flow.

In the case of water quality samples to be shipped to the laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA for analysis, the samples shall be collected in appropriate containers (containing preservatives as applicable) prepared by the laboratory. These samples shall be preserved, stored, shipped, and analyzed in accordance with appropriate procedures and holding times, as specified by the analytical laboratory. Acceptable methods for the required analytical procedures are described in Task 5, Quality Assurance/Quality Control. All PSTPs shall include, at a minimum, a table(s) showing all parameters to be analyzed, the analytical methods, the laboratory reporting limits or quantitation limits, sample volume, bottle type, preservation method, and holding time.

7.3.1 Spiked Arsenic (Optional)

If the feed water does not contain the level of arsenic concentration required to verify the manufacturer's performance capabilities, arsenic spiking may be employed. Spiked arsenic may be used in concentrations sufficient to permit the most-stressed operations for the manufacturers' equipment, following the recommended guidelines:

- Arsenic spiking shall begin at start-up of the treatment equipment.
- Arsenic feed solution will be prepared by diluting the arsenic into dilution water that is distilled or deionized and oxidant free.
- To spike arsenic (III), use commercially-prepared arsenic trioxide. (In cold water, at 2°C, the solubility of this chemical is about 1.2 g/100 g water.).
- To spike arsenic (V), use commercially-prepared arsenic pentoxide.
- Feed reservoir for the arsenic spike solution shall be made of chemically inert material (i.e., not reactive or adsorbable to the arsenic).
- The reservoir will be mixed continuously throughout the experiment.
- The arsenic spike solution will be fed using an adjustable rate chemical feed pump.
- Use an in-line static mixer to mix this solution into the feedwater.
- Arsenic samples of at least 250 mL shall be collected in bottles prepared for holding such samples.

If testing with Arsenic (III) is contemplated, manufacturers and FTOs need to be aware of potential difficulties in preventing conversion of As (III) to As (V) as the spiking solution is held in its storage container. Further conversion to the higher valence state could occur during passage of spiked water through the equipment. Manufacturers and FTOs should also be aware that there are professional opinions that are opposed to arsenic spiking for adsorptive media verification testing.

If arsenic (III) is spiked, then speciation tests shall be conducted to verify that the arsenic (III) is being fed to the treatment system. The application test that was developed by Battelle for the EPA shall be employed (see Appendix A). Also, if the adsorptive media to be tested does not efficiently remove Arsenic (III), the speciation test developed by

Battelle shall be employed. Please note when using this method that ultra-pure (optimum) grade sulfuric acid must be used (not reagent grade) to avoid the trace amounts of arsenic that can be present in reagent grade sulfuric acid.

7.4 Analytical Schedule

Operational Data Collection. The FTO shall provide written procedures describing the operational parameters that should be monitored, monitoring points, and the frequency of monitoring. Such operational parameters shall include, at a minimum, system flow rates and head loss or pressure. Operational data monitoring frequencies are described in Table 2. The FTO shall include acceptable values and ranges for all operational parameters monitored. Data organization and recording is important. An example of chemical consumption data recording is illustrated in Table 3.

Water Quality Data Collection. During System Integrity Testing, the adsorptive media feed water quality and adsorptive media treated water quality shall be characterized by analysis of the water quality parameters listed in Table 1. For applications where the treatment system is expected to operate intermittently, such as for very small systems, the samples shall be collected during the minimum two hours of operation (see *Water Quality Sample Collection Section* above). Additional or more frequent analyses may be stipulated at the discretion of the FTO.

The first sampling for each required analyte shall be performed by means of grab samples one day after plant operation start-up, and then by the frequency given in Table 1 or in the PSTP. Although many parameters may be analyzed off-site, pH, temperature, and turbidity must be analyzed on-site.

It is important when selecting the analytical methods for the various parameters that the procedures achieve detection and reporting limits that are appropriate to meet the objectives of the test. As an example, some arsenic test methods can only detect arsenic above 0.010 mg/L. If the performance of the technology is being verified to meet drinking water standards of 0.010 mg/L, and the capacity test is based on a maximum treated water level of 0.010 or 0.012 mg/L, then a method with a detection limit of 0.010 mg/L would not be appropriate or useful. The selection of each test method must consider how the data will be used, the objectives of the PSTP, and the ability of the method to meet the accuracy and precision objectives specified in the PSTP.

The water quality parameters, listed in Table 1, are selected to provide state drinking water regulatory agencies with background data on the quality of the feed water being treated and the quality of the treated water. These data are to be collected to enhance the acceptability of the System Integrity Verification Testing to a wide range of drinking water regulatory agencies.

7.5 Evaluation Criteria and Minimum Reporting Requirements

The results of System Integrity Verification Testing shall be evaluated based on arsenic removal. Time series plots shall be generated describing adsorptive media influent and effluent arsenic.

The System Integrity Verification Testing should demonstrate the initial ability of the adsorptive media to remove arsenic concentration below detectable levels in the treated water. Detectable levels of arsenic or immediate breakthrough of arsenic are indicative of failure of the treatment system, possibly due to hydraulic channeling, insufficient media, very low adsorptive media capacity, or inappropriate adsorptive media design for the water quality tested. Long-term arsenic removal will be evaluated during Task 2A (Adsorption Capacity Verification Testing) and during optional Task 2B (Regeneration Verification Testing).

8.0 TASK 2A: ADSORPTION CAPACITY VERIFICATION TESTING

8.1 Introduction

The purpose of Task 1 System Integrity Verification Testing is to quickly and efficiently test the basic ability of the adsorptive media vessel (1) to initially yield a treated water of acceptable water quality and (2) to reliably operate under field conditions. After Task 1 has been performed, the long-term effectiveness of the treatment system to remove arsenic shall be evaluated by Task 2A Adsorption Capacity Verification Testing. For a tabulation of physical data requirements for the adsorption media being evaluated, see Table 4.

The breakthrough of arsenic for a given water source is characteristic of the treatment system and will depend on design, EBCT, the type of adsorptive media used, and feed water quality. Breakthrough is highly dependent on the concentration and adsorptive characteristics (isotherm) of the arsenic to be treated by the adsorptive media. Since adsorptive media performance is dependent on feed water quality, the manufacturer may have multiple performance capabilities on the arsenic removal ability of the equipment. Adsorption Capacity Verification Testing shall be performed at least once for a system, but may be performed multiple times utilizing different water qualities to verify multiple performance capabilities. To verify multiple performance capabilities, the FTO shall repeat Adsorption Capacity Verification Testing, utilizing multiple water qualities representative of those described in the performance capabilities, as described below in the work plan.

Some adsorptive media require regeneration when the media becomes saturated with arsenic or other ions, and removal efficiency declines (See discussion in Section 2.1 and 2.4). It is important to assess the regeneration process and its impact on media performance following the regeneration step. Some regeneration processes can cause reduced system performance, as compared to fresh media. Therefore, Task 2A shall include an evaluation of the regeneration process (minimum of one regeneration of the media), and a short post-regeneration monitoring period to assess system performance. A more complete evaluation of the regeneration process and possible impacts on performance is incorporated into optional Task 2B, if the manufacturer chooses to verify the long-term effects of regeneration.

8.2 Experimental Objective

The objective of this task is to evaluate the ability of the adsorptive media employed in the treatment system to demonstrate the water quality performance capabilities specified by the

manufacturer.

The FTO shall identify in the PSTP the treated water quality objectives to be achieved in the statement of performance capabilities of the equipment to be demonstrated during verification testing. The statement of performance capabilities prepared by the manufacturer shall indicate the range of water quality under which the equipment can be challenged, while successfully treating the adsorptive media feed water. One example of a statement of water treatment performance capabilities is provided below:

"This system, when operated at an adsorption media EBCT of 5 minutes or more, is capable of achieving an effluent arsenic concentration less than 10 parts per billion for at least 10,000 bed volumes for influent arsenic concentrations up to 0.12 mg/L (species of arsenic must be indicated if applicable, i.e., arsenic III or arsenic V)."

8.3 Work Plan

Task 2A, Adsorption Capacity Verification Testing, may begin simultaneously with Task 1, System Integrity Verification Testing. Subsequent sessions of Task 2A, Adsorption Capacity Verification Testing, will not require Task 1, System Integrity Verification Testing. The manufacturer shall estimate or specify to the FTO the run time criteria for each Adsorption Capacity Verification Testing period and shall supply written procedures on the operating conditions and maintenance of the treatment system. Run time criteria can be based on treated water quality conditions, or expected capacity of the media. For example, the manufacturer may specify that the equipment be operated until the treated arsenic concentration reaches 0.010 mg/L, or the current MCL. In this example, the manufacturer shall provide the FTO with an estimated volume of water or bed volumes that are expected to be processed before the treated water concentration rises to the target level or slightly above the target level. These estimates are usually based on the known capacity and characteristics of the media, and the concentration of arsenic in the feed water. The manufacturer and FTO will use this information in conjunction with the flow rates that will be used at the site and historical arsenic concentrations at the site to estimate the run time to reach the capacity or manufacturer's performance capabilities. Alternatively, the manufacturer may specify a maximum run time, after which the media needs to be changed or regenerated.

The Adsorption Capacity Verification Testing shall be run for a minimum of sixty (60) days (this includes Tasks 1 and 2A). A combination of treated water quality and maximum run time criteria may also be utilized. The selection of a specified maximum run time should be carefully considered, as the use of a specified run time may result in significantly underestimating (or not verifying) the capacity of a media. If the specified run time option is selected, then the verification test will only be conducted for that specified time, and the test will be either terminated or regeneration will occur (if appropriate), whether or not the media has reached capacity. A specified run time that is short could result in a significant cost disadvantage for a system being compared to similar systems with longer service life between media change out or regeneration. The run time criteria chosen should reflect the specified treatment capability of the system, based on the adsorptive media feed water quality.

Water sources must be chosen carefully so that water qualities are representative of that on which the manufacturer's performance capabilities are based. The arsenic concentration in the feed water should be in the same range as the concentration used to develop the performance capabilities statement. This ensures that Adsorption Capacity Verification Testing adequately tests the equipment's ability to meet manufacturer's performance capabilities for a given water quality. Multiple Adsorption Capacity Verification Testing periods may be necessary to provide verification testing on multiple treatment capabilities. For example, multiple Adsorption Capacity Verification Testing runs may be needed to verify water treatment capabilities if the performance capabilities are stated to cover a wide concentration range, such as 0.02 to 0.20 mg/L. If the feed water does not contain the level of arsenic concentration required to verify the manufacturer's removal capability, arsenic spiking may be employed (refer to procedures outlined in Section 7.3.1).

Media requiring regeneration shall be regenerated at least once at the end of the Adsorption Capacity Verification Test. The manufacturer's recommended procedures shall be followed for regeneration of the media. The FTO shall provide the operating procedures that will be used for regeneration of the media, including specifying the chemicals, solution concentrations, and other pertinent information for regeneration. At the completion of media regeneration, the system shall be placed back to normal service and monitoring shall continue for a minimum of four weeks for comparison to the initial performance data obtained using fresh media.

Any residuals produced during in-place regeneration of the adsorptive media shall be fully characterized and documented with respect to quantity and composition. The information from this residuals characterization task shall be used to determine the efficiency of regeneration. For example, if a low pH solution is used to remove arsenic from the media, this solution shall be monitored for arsenic content and other ions of interest. If a rinsing solution is used, then this liquid will also be measured for arsenic concentration and other ions of interest. A mass balance approach shall be used to determine whether all the arsenic was removed during the regeneration process. The regeneration efficiency and the adsorbent usage rate shall be reported.

Water Quality Sample Collection. Water quality data shall be collected at regular intervals as described in the analytical schedule (see Table 5) and as described below. Additional or more frequent analyses may be stipulated at the discretion of the FTO. Sample collection frequency and protocol shall be defined by the FTO in the PSTP.

The sample collection schedule will be dependent upon the run time estimate developed for the specific media. The FTO will develop a sample collection and analytical schedule that collects sufficient data to define the breakthrough or capacity curve. The actual total number of samples collected for this task will be dependent on the run time estimate and the actual length of time to reach the capacity of the media. Frequent sampling (e.g. daily or 3 times per week) could result in 100 samples or more being collected, if the run time is several months. This large number of samples may not be cost effective. It is important, however, that several sets of data are available near the breakthrough point to properly define the capacity of the media, and that regular monitoring occurs throughout the test period. Table 5 provides minimum sampling intervals that should be considered by the FTO.

In the case of water quality samples to be shipped to the laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA for analysis, the samples shall be collected in appropriate containers (containing preservatives as applicable) prepared by the laboratory. These samples shall be preserved, stored, shipped, and analyzed in accordance with appropriate procedures and holding times, as specified by the analytical laboratory. Acceptable methods for the required analytical procedures are described in Task 5, Quality Assurance/Quality Control. All PSTPs shall include, at a minimum, a table(s) showing the parameters to be analyzed, analytical method, the laboratory reporting limit or quantitation limit, sample volume, bottle type, preservation method, and holding time.

The FTO shall develop an overall sampling plan and schedule for all parameters based on the guidance in this document, the estimated length of the test based on the manufacturer's run time estimate, and any other media specific issues. The FTO shall prepare an arsenic specific sampling plan that addresses collection of several samples near the breakthrough point and considers the frequency of arsenic speciation analysis.

The FTO must consider collecting samples for arsenic measurement on a regular basis (e.g. weekly) during the beginning and middle portions of the Adsorption Capacity Verification Test, and then more frequently as the media approaches capacity. One option is to use field test kits to monitor arsenic, which can provide immediate information on the arsenic concentrations in the treated water. These kits are not acceptable for final verification data, but can be used to indicate when arsenic is increasing in the treated water and the media is nearing capacity. This information can be used to indicate that increased sampling frequency should be initiated in anticipation of breakthrough. If the use of arsenic test kits is planned, it is important to select a kit that has a detection limit, accuracy, and precision that will provide meaningful data at the concentrations expected in the treated water. The FTO may also consider collecting samples for arsenic on a more frequent basis (daily or three times per week) as the media approaches capacity, but not analyzing all the samples. Arsenic samples can be preserved and held (for total arsenic, as well as soluble arsenic and speciated arsenic if field speciated and preserved) for later analysis. In this approach, only selected samples (e.g. one per week) would be analyzed. Once the results are received, additional samples could be scheduled for analysis to "fill in" the data, as the breakthrough curve begins to rise and capacity is approached. A "sample and hold" plan can be a cost effective approach for long run time tests. The FTO sampling and analysis plan for arsenic should incorporate a schedule that will provide a minimum of five samples to represent the 80 to 100 percent portion of the breakthrough curve. It is recommended that the sampling plan include increased sampling frequency as the media approaches 70 percent of the predicted capacity.

The arsenic sampling plan shall also include a schedule for collection of samples for arsenic speciation. As described in Section 7.3, the species of arsenic (III or V) present in the feed water can have a direct impact on the performance of adsorptive processes. The frequency of performing arsenic speciation will depend on the source water and the specific media. At a minimum, three samples of the feed water and treated water, collected at regular intervals over the duration of the Adsorption Capacity Verification Test, shall be speciated. More frequent arsenic speciation may be needed depending on the actual distribution of the arsenic species in the feed water, and the importance of the arsenic species (III or V) to the performance of a

specific treatment process. If the feed water has only one species of arsenic present, then the minimum frequency may be appropriate. However, if the source water has significant concentrations of both species present, and/or the media performance is dependent on the arsenic species, then more frequent arsenic speciation should be proposed by the FTO to properly monitor the system performance. If both species of arsenic (III and V) are present in the source water, then it is expected that at least 25 percent of the samples collected during the Adsorption Capacity Verification Test will be speciated.

Sample collection procedures for intermittent flow systems must ensure that freshly treated water is collected and not water that was stagnant in the bed. For intermittent flow systems, sample collection should occur during a continuous flow period after a minimum of 10 bed volumes has passed through the system or after one hour of continuous flow. If a system is not normally operated for at least 10 bed volumes or one hour (such as an intermittent system that is only "on" for a few minutes each hour), then the system shall be operated manually during sample collection to meet this requirement.

For media that requires regeneration, the FTO shall specify the sample collection frequency and sample type to characterize the regeneration process. At a minimum, sampling of the regenerative water for the parameters listed in Table 5 shall be done on a composite sample. The composite should be a flow weighted composite sample of the regeneration fluid. If grab samples are being taken to make a composite, a minimum of six samples should be collected over the regeneration period. It is important that the sample be representative of the entire regeneration fluid volume so that an accurate determination of the mass of arsenic recovered in the regeneration process can be determined. Other parameters may be important for monitoring the effectiveness of the regenerative liquid, or the performance of the regeneration step. These additional parameters should be added as appropriate to the specific media being verified.

Following the completion of media regeneration, the system shall be operated for at least four weeks. The sampling plan developed for all parameters and specifically for arsenic should include this post-regeneration operating period. The sampling plan should include the collection of sufficient samples to provide a basis for comparison to the original performance of the media, and determine if the media has been impacted by regeneration. The post-regeneration monitoring plan shall specify the collection of samples at the same frequency as for the Adsorption Capacity Verification Test (Table 5) or more frequently if needed to characterize the water after regeneration. In addition, total arsenic samples will be collected at a minimum of three times during the first week of the post regeneration period test. More frequent monitoring of selected parameters may be needed and proposed by the FTO. As an example, certain activated alumina media can release elevated levels of aluminum after regeneration. In this case, sampling for aluminum every four hours for the first day and daily for a week may be appropriate. An arsenic speciation test shall be performed at least once during the post regeneration test period. More frequent speciation shall be performed if more frequent arsenic speciation was part of the arsenic speciation plan, as described earlier in this section.

At the end of Task 2A, samples of the media shall be collected to assess the chemical content for disposal purposes. At least one representative sample of the media shall be collected and sent to the laboratory for the Toxicity Characteristic Leaching Procedure (TCLP) and the California

Waste Extraction Test (WET). The sample of the media shall be collected in a manner that ensures that a cross section of all the media (a composite sample over the entire depth of the column) is included in the sample sent to the laboratory. It may be necessary to place the media from the column in a container and mix it prior to sampling, or it may be necessary to "core" the column to collect a representative sample. The FTO shall describe the sampling procedures that will be used to ensure that a representative sample of the media is collected for these analyses.

8.4 Analytical Schedule

Operational Data Collection. The FTO shall provide written procedures describing the operational parameters that should be monitored, monitoring points, and the frequency of monitoring. Such operational parameters shall include at a minimum flow rates, head loss (or pressure), chemicals used (including feed volume and dosage), and hours of operation per day. Operational data monitoring frequencies are described in Table 2. The FTO shall include acceptable values and ranges for all operational parameters monitored.

Operational parameters shall also be specified for the regeneration requirements for the system. Operational parameters shall include at a minimum, regenerate solution composition, flow rate and volume of regenerate, rinse solution composition, flow rate, and volume, measurement of media quantity before and after regeneration, and any operating parameters specified by the manufacturer for control of the regenerative process. The FTO shall include acceptable values and ranges for these operational parameters and monitoring requirements.

Water Quality Data Collection. During Adsorption Capacity Verification Testing , the adsorptive media feed water quality and treated water quality shall be characterized by analysis of the water quality parameters listed in Table 5. The sampling frequency described in Table 5 and as discussed in the previous section, is intended to provide sufficient water quality data to effectively characterize the breakthrough profile for arsenic. Additional or more frequent analyses may be stipulated at the discretion of the FTO.

As described earlier in Section 7.4, it is important when selecting the analytical methods for the various parameters that the procedures can achieve detection and reporting limits that are appropriate to meet the objectives of the test. As an example, some arsenic test methods can only detect arsenic above 0.010 mg/L. If the performance of the technology is being verified to meet drinking water standards of 0.010 mg/L, and the capacity test is based on a maximum treated water level of 0.010 or 0.012 mg/L, then a method with a detection limit of 0.010 mg/L would not be appropriate or useful. The selection of each test method must consider how the data will be used, the objectives of the PSTP, and the ability of the method to meet the accuracy and precision objectives specified in the PSTP.

The sample of media that is collected for TCLP and California WET shall have the following metals analyzed in the leachate from these procedures: As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Se, Ag, and Zn.

8.5 Evaluation Criteria and Minimum Reporting Requirements

At a minimum, breakthrough curves (adsorptive media effluent concentrations versus bed volumes) for arsenic concentrations should be presented. Include plotted adsorptive media influent parameter concentrations versus bed volumes on the same plot. Calculate and tabulate average influent parameter concentrations. A sample form for reporting data is illustrated in Table 6. For media requiring regeneration, the data from the post regeneration period will be compared to the first four weeks of operation with fresh media. The data will be evaluated for evidence of reduced performance after regeneration.

Tabular records for the adsorptive media influent and effluent arsenic, pH, pressure, and all other monitored parameters and constituents shall be maintained and presented. Results shall include adsorptive media influent and effluent average, minimum, and maximum; and for sample sets of eight or more the results shall also include the standard deviation and confidence interval for each analyte.

9.0 TASK 2B: REGENERATION VERIFICATION TESTING (OPTIONAL)

9.1 Introduction

This task is applicable only to adsorption treatment systems that use adsorptive media that can be regenerated in-place and that incorporate regeneration capability as an integral part of the equipment being tested. If the manufacturer wishes to evaluate the in-place regeneration capability of the equipment, verification testing must include, as a minimum, two complete cycles: an initial loading cycle, followed by a regeneration cycle (which is part of Task 2A), and then a second loading cycle, followed by a second regeneration cycle. This allows for a comparison of adsorptive media performance before and after regeneration. Furthermore, the regeneration efficiency shall be determined based on the second regeneration cycle.

Verification of in-place regeneration based on two or more complete loading/regeneration cycles is recommended, if possible. However, the length of time between regeneration cycles may preclude multiple cycles being tested.

Guidelines for modified testing to evaluate an in-place regeneration are described within this task. The regeneration step, regeneration fluids used, and regeneration procedure shall be documented as part of the Equipment Characteristics (Chapter 1, Section 4.2).

9.2 Experimental Objectives

The objectives of this task are to evaluate adsorptive media performance after regeneration, evaluate regeneration efficiency, evaluate operational details of media regeneration, and characterize any residuals produced during regeneration.

The FTO shall identify in the PSTP the treated water quality performance to be achieved after regeneration of the media, and any specific criteria concerning the regeneration process, such as

quantity of regenerate used, time to regenerate the media, etc.

9.3 Work Plan

To verify a manufacturer's stated performance capability regarding the in-place regeneration capability of adsorption equipment, verification testing shall be conducted as described in Task 2A, Section 8, combined with the additional requirements or modifications as described in this task. The testing period shall include, as a minimum, two complete cycles: an initial loading cycle, followed by a regeneration cycle, and then a second loading cycle, followed by a second regeneration cycle. During each loading period, the adsorptive media system must be operated at least until breakthrough of arsenic, based on the treatment capability defined in the manufacturer's statement of performance as described in Section 8.2.

The source water arsenic concentration shall be the same during both loading cycles. The testing conditions shall also be identical during both loading cycles. All other experimental parameters, such as water source, pretreatment, etc. shall be as similar as possible during the two (or more, if necessary) loading cycles. If the four-step cycle is completed in less than 60 days, additional loading/regeneration cycles shall be performed until the total run time is at least 60 days.

The work plan for this task shall follow the same approach as for Task 2A, Section 8.3 and will run in conjunction with Task 2A. The results from the first loading and regeneration cycle for this task will be the same as Task 2A. Under this task, the second loading cycle will begin after the first regeneration of the media and continue until the second loading and regeneration cycles are complete. All aspects of the work plan for Tasks 2A, Section 8.3, shall be incorporated into the work plan for this task.

If possible, incorporation of additional cycles into the testing program would increase the amount of data on regeneration effectiveness and retention of adsorption capacity over time. Whether or not additional cycles are completed, the FTO must make a statement about the long-term efficiency of regeneration for the adsorptive media tested. If the long-term efficiency of regeneration is not studied as part of this testing program, or not available from other studies, a statement by the FTO is required indicating that the long-term regeneration efficiency is unknown. For adsorptive media that has been well studied, a statement on the long-term regeneration efficiency can be based on the results of previous peer-reviewed published studies. See Section 4.2.2. for information on using available data.

Any residuals produced during in-place regeneration of the adsorptive media shall be fully characterized and documented with respect to quantity and composition. The information from this residuals characterization task shall be used to determine the efficiency of regeneration. For example, if a low pH solution is used to remove arsenic from the media, this solution shall be monitored for arsenic content and other ions of interest. If a rinsing solution is used, then this liquid will also be measured for arsenic concentration and other ions of interest. A mass balance approach shall be used to determine whether all the arsenic was removed during the regeneration process. The regeneration efficiency and the adsorbent usage rate for each cycle shall be reported.

Under Task 2A a sample of the media shall be taken for TCLP and California WET testing at the end of the verification period. If Task 2B is part of the verification process, the sample of the media for this testing will be deferred until the end of the regeneration verification process. The same sampling and analysis plan shall be followed as outlined in Task 2A, Section 8.3

Operational Data Collection. The FTO shall provide written procedures, the same as under Task 2A, Section 8.3, describing the operational parameters that should be monitored, monitoring locations, and the frequency of monitoring. Such operational parameters shall include at a minimum flow rates, and head loss (or pressure), chemicals used (including feed volume and dosage), and hours of operation per day. Operational data monitoring frequencies are described in Table 2. The FTO shall include acceptable values and ranges for all operational parameters monitored. The collection of operational data shall continue during the second and any subsequent loading cycles, following the same procedures as set forth for Task 2A, Adsorption Capacity Verification Test.

Operational parameters shall also be specified for the regeneration requirements for the system. Operational parameters shall include at a minimum, regenerate solution composition, flow rate and volume of regenerate, rinse solution composition, flow rate, and volume, measurement of media quantity before and after regeneration, and any operating parameters specified by the manufacturer for control of the regenerative process. The FTO shall include acceptable values and ranges for these operational parameters and monitoring requirements.

Water Quality Data Collection. During the Regeneration Verification Testing, the adsorptive media feed water quality and treated water quality shall be characterized during all loading cycles by analysis of the water quality parameters listed in Table 5 and in accordance with sampling schedule and approach given in Section 8.3. The sampling frequency described in Table 5 and in the Section 8.3 is intended to provide sufficient water quality data to effectively characterize the breakthrough profile for arsenic for each loading and regeneration cycle. Additional or more frequent analyses stipulated at the discretion of the FTO for Task 2A shall also apply to additional loading cycles under this task.

It is possible that the results obtained on media capacity and source water variability during the first loading cycle may indicate that a reduced or more focused sampling program could be used in subsequent loading cycles. The FTO can propose a reduced sampling frequency for some or all parameters based on the results from Task 2A. This request will be reviewed by NSF and, if appropriate, NSF may approve the change in sampling frequency. However, the FTO shall incorporate the same testing plan as planned for Task 2A, Section 8.3 in the PSTP. Only after the first loading and regenerative cycles are complete, and the results available, will a request for a change in the sampling plan be considered. If the sampling plan for Task 2A is modified during the first loading cycle, then the modification will also apply to this task and to subsequent loading cycles.

9.4 Analytical Schedule

Influent and effluent sampling and analysis requirements described in Section 8.4 for Task 2A and Table 5 shall be applied to *each* loading cycle to assess arsenic breakthrough and other water

quality parameters. For characterization of regeneration residuals, a sampling and analytical plan shall be developed by the FTO in the PSTP to thoroughly characterize the content of the residual stream(s). Selection of parameters, in addition to arsenic and pH, for monitoring the regenerative liquids and solids will be specific to the media and the regeneration process. The FTO shall include in the PSTP a discussion of the basis for the parameter selection for the regeneration residuals. The analytical program shall meet all of the Quality Assurance/Quality Control (QA/QC) requirements that apply to the previous Tasks (1 and 2A).

9.5 Evaluation Criteria and Minimum Reporting Requirements

Verification testing of adsorption treatment systems with in-place regeneration includes the same types of data analysis and interpretation as described previously in Section 8.5. In addition, a comparative analysis of adsorption characteristics before and after media regeneration shall be performed. The purpose of the comparative analysis is to assess and quantify whether any reduction in adsorptive media service life or adsorption capacity occurs because of in-place regeneration. This shall be evaluated by determining the media service life (operation time, throughput in bed volumes of water treated, and adsorbent usage rate until breakthrough), for the initial and subsequent loading periods and quantitatively comparing the results. Similarly, the adsorption capacity before and after regeneration can be determined and compared. In addition, a mass balance for arsenic should be developed to evaluate the regeneration efficiency. A general equation that describes the regeneration efficiency is:

$$E_R = \frac{q \cdot m_A}{m_R} \quad (1)$$

where: E_R is the regeneration efficiency,
q is the adsorption capacity,
m_A is the mass of adsorbent, and
m_R is the mass arsenic recovered in the regeneration stream.

The regeneration efficiency shall be calculated after each regeneration cycle.

10.0 TASK 3: DOCUMENTATION OF OPERATING CONDITIONS AND TREATMENT EQUIPMENT PERFORMANCE

10.1 Introduction

During each day of verification testing, operating conditions shall be documented. This shall include descriptions of any pretreatment processes and their operating conditions. In addition, the performance of the water treatment equipment shall be documented, including rate of head loss gain. The volumetric flow rate through an adsorptive media vessel is a critical parameter, and must be monitored and documented. Adsorptive media performance is affected by the EBCT, which varies directly with the volumetric flow rate through the vessel.

10.2 Experimental Objective

The objective of this task is to accurately and fully document the operating conditions during treatment, and the performance of the equipment. This task is intended to result in data that describe the operation of the equipment and data that can be used to develop cost estimates for operation of the equipment.

This task shall be performed in conjunction with Task 1, System Integrity Verification Testing, and in conjunction with Task 2A, Adsorption Capacity Verification Testing. This task will also be performed in conjunction with Task 2B, Regeneration Verification Testing, if applicable.

10.3 Work Plan

During each day of verification testing [Task 1, System Integrity Verification Testing; Task 2A, Adsorption Capacity Verification Testing; and Task 2B, Regeneration Verification Testing (if applicable)], treatment equipment operating parameters for both pretreatment and adsorptive media shall be monitored and recorded on a routine basis. This shall include a complete description of pretreatment chemistry and all other applicable data.
Electrical energy consumed by the treatment equipment shall be measured, or as an alternative, the aggregate horsepower of all motors supplied with the equipment could be used to develop an estimate of the maximum power consumption during operation. Performance shall be evaluated to develop data on chemical dosages needed and on energy needed for operation of the process train being tested.

A complete description of the treatment process shall be given, with data on points of chemical addition, and volume and detention time of each process vessel at rated flow if applicable. Data on the adsorptive media vessel shall be provided and shall include the EBCT, depth, effective size, and uniformity coefficient of each layer of adsorptive media and support material. The type and source of adsorptive media used and the type of support material used shall be stated.

10.4 Schedule

Tables 2 and 3 present the schedule for observing and recording equipment operation and performance data. The schedule applies to System Integrity Verification Testing, Adsorption Capacity Verification Testing, and Regeneration Verification Testing.

10.5 Evaluation Criteria

Operating conditions and performance data will be tabulated for inclusion in the ETV verification report.

11.0 TASK 4: DATA MANAGEMENT

11.1 Introduction

The data management system used in the verification testing program shall involve the use of

computer spreadsheet software and manual recording of operational parameters for the adsorptive media and pretreatment equipment on a daily basis.

11.2 Experimental Objective

The objective of this task is to establish a viable structure for the recording and transmission of field testing data such that the FTO provides sufficient and reliable operational data for verification purposes.

11.3 Work Plan

The following section has been developed for data handling and data verification by the FTO. Where possible, a Supervisory Control and Data Acquisition (SCADA) system should be used for automatic entry of testing data into computer databases. Specific parcels of the computer databases for operational and water quality parameters should then be downloaded by manual importation into Excel (or similar spreadsheet software) as a comma delimited file. These specific database parcels shall be identified based upon discrete time spans and monitoring parameters. In spreadsheet form, the data shall be manipulated into a convenient framework to allow analysis of adsorptive media operation. At a minimum, backup of the computer databases to diskette should be performed on a weekly basis.

In the case when a SCADA system is not available, field testing operators shall record data and calculations by hand in laboratory notebooks. (Daily measurements shall be recorded on specially-prepared data log sheets as appropriate.) The laboratory notebook shall provide carbon copies of each page. The original notebooks shall be stored on-site; the carbon copy sheets shall be forwarded to the project engineer of the FTO at least once per week during testing period. This protocol will not only ease referencing the original data, but offer protection of the original record of results. Operating logs shall include a description of the treatment equipment (description of test runs, names of visitors, description of any problems or events, etc.); such descriptions shall be provided in addition to experimental calculations and other items.

The database for the project shall be set up in the form of custom-designed spreadsheets. The spreadsheets shall be capable of storing and manipulating each monitored water quality and operational parameter from each task, each sampling location, and each sampling time. All data from the laboratory notebooks and data log sheets shall be entered into the appropriate spreadsheet. Data entry shall be conducted on-site by the designated field testing operators. All recorded calculations shall also be checked at this time. Following data entry, the spreadsheet shall be printed out and the print out shall be checked against the handwritten data sheet. Any corrections shall be noted on the hard copies and corrected on the screen, and then a corrected version of the spreadsheet shall be printed out. Each step of the verification process shall be initialed by the field testing operator or engineer performing the entry or verification step.

Each experiment (i.e., System Integrity Verification Testing runs, Adsorption Capacity, and Regeneration Verification Testing runs) shall be assigned a run number which will then be permanently associated to the data from the experiment through each step of data entry and analysis. As samples are collected and sent to a laboratory that is certified, accredited or

approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA, the data shall be tracked by use of the same system of run numbers. Data from the outside laboratories shall be received and reviewed by the field testing operator. These data shall be entered into the data spreadsheets, corrected, and checked in the same manner as the field data.

12.0 TASK 5: QUALITY ASSURANCE/QUALITY CONTROL

12.1 Introduction

QA/QC of the operation of the water treatment system, adsorptive media vessels, instrumentation, and the measured water quality parameters shall be maintained during the verification test.

12.2 Experimental Objective

The objective of this task is to maintain strict QA/QC methods and procedures during the equipment verification testing program. Maintenance of strict QA/QC procedures is important, in that if a question arises when analyzing or interpreting data collected for a given experiment, it will be possible to determine exact conditions at the time of testing.

12.3 Work Plan

When developing the Quality Assurance Project Plan (QAPP) within the PSTP, the FTO should refer to Chapter 1, Section 6.0 Quality Assurance Project Plan in addition to the information provided herein. All of the requirements and guidelines described in Chapter 1 shall be included in the development of the PSTP. In addition to the general ETV Program QA/QC described in Chapter 1, the PSTP shall incorporate the specific adsorptive media QA items detailed in this section.

Equipment flow rates and associated signals should be checked and recorded on a routine basis. A routine daily walk through during testing shall be established to confirm that each piece of equipment or instrumentation is operating properly. Particular care shall be taken to confirm that any chemicals are being fed at the defined flow rate into a flowstream that is operating at the defined flow rate, such that the chemical concentrations are correct. In-line monitoring equipment such as flowmeters, etc. shall be calibrated to confirm that the readout matches with the actual measurement (i.e. flow rate) and that the signal being recorded is correct. The items listed are in addition to any specified checks outlined in the analytical methods or specified by the FTO.

It is extremely important that system flow rates are maintained at set values and monitored frequently. Doing so allows a constant and known EBCT to be maintained in the adsorptive media vessel. Adsorptive media performance is directly affected by the EBCT, which in turn is proportional to the volumetric flow rate through the contactor. Therefore, an important QA/QC objective shall be the maintenance of a constant volumetric flow rate through the adsorptive media vessel by frequent monitoring and documentation. Documentation shall include an

average and standard deviation of recorded flow rates through the adsorptive media vessel.

12.3.1 Daily QA/QC Checks

- Chemical feed pump flow rates, if applicable;
- In-line pH, pressure and temperature (check calibration);
- System adsorptive media vessel flow rate (checked volumetrically over a specific period of time to confirm instrument reading at least two times daily, approximately four hours apart for applications where the treatment system is expected to operate continuously, or once daily where the treatment system is expected to operate intermittently);
- In-line turbidimeter flow rate checked daily by volumetric measurement over a specific period of time to confirm instrument reading; and
- In-line turbidimeter readings checked daily against a properly calibrated bench-top model.

12.3.2 Weekly QA/QC Checks

- In-line flow meters/rotameters (confirm flow rate volumetrically over a specific period of time to confirm instrument reading, and if necessary, clean equipment to remove any foulant buildup);
- In-line turbidimeters (clean out reservoirs, if necessary, and recalibrate);
- Differential pressure transmitters (check gauge readings and electrical signal using a dead weight calibration tester); and
- Tubing (check condition of all tubing and connections, replace if necessary).

12.3.3 QA/QC Checks Performed Each Testing Period

- Performance evaluation check of the resin columns used during arsenic speciation procedures (see Appendix A).

12.4 Analytical Methods

The analytical methods utilized in this study for on-site and off-site monitoring of adsorptive media influent and effluent water quality are described in the sections below and presented in Tables 1 and 5. If new methods are published and approved or current methods updated, the most current methods shall be used. Use of either bench-top or in-line field analytical equipment will be acceptable for on-site analyses for the verification testing; however, in-line equipment is recommended for ease of operation. Use of in-line equipment is also preferable because it reduces the introduction of error and the variability of analytical results generated by inconsistent sampling techniques.

Temperature, pH, alkalinity, and turbidity must be analyzed on-site immediately after sample collection. Other parameters, such as calcium, magnesium, hardness and fluoride can be performed either on-site or in the laboratory, as long as the holding time requirements are met.

All other analyses shall be performed in a laboratory that is certified, accredited or approved by a state, a third-party organization (i.e., NSF), or the U.S. EPA. All samples collected for laboratory analysis, including arsenic chloride, sulfate, silica, aluminum, sodium, iron, manganese and additional parameters, shall be collected and preserved in accordance with *Standard Method* 3010 B, paying particular attention to the sources of contamination as outlined in *Standard Method* 3010 C. The samples should be refrigerated at approximately 2 to 8°C immediately upon collection, shipped in a cooler, and maintained at a temperature of approximately 2 to 8°C. Samples shall be processed for analysis within EPA approved holding times, which must be included in the PSTP. The laboratory shall keep the samples at approximately 2 to 8°C until initiation of analysis.

Arsenic speciation using the Battelle method (Appendix A) is an important part of the verification test. In addition to all normal QA requirements for handling field samples and for arsenic determination, a special check of the resin used for the speciation procedure is required. The resin must be prepared properly in accordance with the procedures given in the method, and the capability of the resin to properly separate arsenic III from V must be demonstrated. It cannot be assumed that a batch of resin has been properly prepared without validating the separation process using water spiked with known concentrations of arsenic III and V. This QC check should include having the laboratory make a solution with a mixture of arsenic III and V, having the field staff perform the separation using their standard procedures, and then having the laboratory analyze the samples for arsenic III and V. The results of the QC check sample must demonstrate the separation procedure is working properly. This check must be done for each new batch of resin used during the verification test.

The FTO shall prepare tables summarizing the pertinent QA information and the objectives/acceptance limits for accuracy and precision. These tables shall show at minimum, the methods to be used, the method detection limits, the number of field and lab duplicates, the number of laboratory spikes/blanks, the acceptable precision as a percent, the acceptable accuracy as a percent recovery range, and calibration information that impacts accuracy, such as frequency and method for calibrating the pH meter, the turbidimeter, etc.

12.4.1 Arsenic

Laboratory analyses for arsenic shall be performed in accordance with EPA Method 200.8. These analyses are the most critical for the entire ETV procedure. When arsenic species are to be analyzed, the samples shall be collected and preserved in accordance with the Protocol for Arsenic Speciation developed by Battelle for the EPA, as found in Appendix A of this protocol. EPA Method 200.8 has been specified because of the need to achieve low detection limits (0.002 to 0.004 mg/L) with good accuracy and precision for this verification test. Other EPA approved drinking water methods that can achieve these low laboratory reporting limits with comparable accuracy and precision may be proposed by the FTO. Minimum analytical turn around time is required to achieve optimum process control. Please note when using this method that ultra-pure (optimum) grade sulfuric acid must be used (not reagent grade) to avoid the trace amounts of arsenic that can be present in reagent grade sulfuric acid.

12.4.2 pH

Analyses for pH shall be performed on-site according to *Standard Method* 4500-H^+ B (Electrometric Method) or EPA Methods 150.1 and 150.2. A three-point calibration of the pH meter used in this study shall be performed once per day when the instruments are in use. Certified pH buffers in the expected range shall be used. The pH probes shall be stored in the appropriate solution defined in the instrument manual. If pH is adjusted in the process, pH readings are required before and after each pH adjustment.

12.4.3 Alkalinity

Analyses for alkalinity shall be performed on-site according to *Standard Method* 2320 B (Titration Method).

12.4.4 Fluoride

Analyses for fluoride shall be performed on-site or in the lab according to *Standard Method* 4110 B, 4500-F^- B, 4500-F^- C (Ion-Selective Electrode Method), 4500-F^- D, or EPA Method 300.0.

12.4.5 Chloride

Analyses for chloride shall be performed in the lab according to *Standard Method* 4110 B, 4500-Cl^- B (Argentometric Method) or 4500-Cl^- D (Mercuric Nitrate Method) or EPA Method 300.0.

12.4.6 Sulfate

Analyses for sulfate shall be performed in the lab according to *Standard Methods* 4110 B, 4500 SO_4^{2-}C, 4500 SO_4^{2-}D, 4500 SO_4^{2-}E (Turbidimetric Method), or 4500 SO_4^{2-}F, or EPA Methods 300.0 or 375.2.

12.4.7 Silica

Analyses for silica shall be performed in the lab according to *Standard Method* 3120 B, 4500-Si C, 4500-Si D (Molybdosilicate Method), or 4500-Si E, or EPA Method 200.7.

12.4.8 Aluminum

Analyses for aluminum shall be performed in the lab according to *Standard Method* 3120 B or EPA Methods 200.7, 200.8, or 200.9.

12.4.9 Sodium (Optional)

Analyses for sodium shall be performed in the lab according to EPA Method 200.7.

12.4.10 Calcium

Analyses for calcium shall be performed on-site or in the lab according to *Standard Methods* 3120 B or 3500-Ca B (EDTA Titrimetric Method), or EPA Method 200.7.

12.4.11 Hardness

Analyses for hardness shall be performed on-site or in the lab according to *Standard Method* 2340 C (EDTA Titrimetric Method).

12.4.12 Magnesium

Analyses for magnesium shall be performed on-site or in the lab according to *Standard Method* 3120 B or 3500-Mg B (Calculation Method), or EPA Method 200.7.

12.4.13 Iron

Analyses for iron shall be performed in the lab using *Standard Method* 3120 B or EPA Methods 200.7, 200.9.

12.4.14 Manganese

Analyses for manganese shall be performed in the lab using *Standard Method* 3120 B or EPA Methods 200.7, 200.8, 200.9.

12.4.15 Turbidity

Turbidity analyses shall be performed on-site according to *Standard Method* 2130 B or EPA Method 180.1 with either an in-line or a bench top turbidimeter. In-line turbidimeters shall be used for measurement of turbidity in the treated waters, and either an in-line or bench-top turbidimeter may be used for measurement of the feedwater.

During each verification testing period, the in-line and bench-top turbidimeters shall be left on continuously. Once each turbidity measurement is complete, the unit shall be switched back to its lowest setting. All glassware used for turbidity measurements shall be cleaned and handled using lint-free tissues to prevent scratching. Sample vials shall be stored inverted to prevent deposits from forming on the bottom surface of the cell. The FTO shall document any problems experienced with the monitoring turbidity instruments, and shall also document any subsequent modifications or enhancements made to monitoring instruments.

12.4.15.1 Bench-top Turbidimeters. Grab samples shall be analyzed using a bench-top turbidimeter. Readings from this instrument shall serve as reference measurements throughout the study. The bench-top turbidimeter shall be calibrated within the expected range of sample measurements at the beginning of verification testing and on a weekly basis using primary turbidity standards of 0.1, 0.5, and 3.0 NTU. Secondary turbidity

standards shall be obtained and checked against the primary standards. Secondary standards shall be used on a daily basis to check calibration of the turbidimeter and to recalibrate when more than one turbidity range is used.

The method for collecting grab samples shall consist of running a slow, steady stream from the sample tap, triple-rinsing a dedicated sample beaker in this stream, allowing the sample to flow down the side of the beaker to minimize bubble entrainment, double-rinsing the sample vial with the sample, carefully pouring from the beaker down the side of the sample vial, wiping the sample vial clean, inserting the sample vial into the turbidimeter, and recording the measured turbidity. For the case of cold water samples that cause the vial to fog preventing accurate readings, the vial shall be allowed to warm up by partial submersion in a warm water bath for approximately 30 seconds.

12.4.15.2 In-line Turbidimeters. In-line turbidimeters shall be used for measurement of turbidity in the filtrate water during verification testing and must be calibrated and maintained as specified in the manufacturer's operation and maintenance manual. It will be necessary to check the in-line readings using a bench-top turbidimeter at least daily; although the mechanism of analysis is not identical between the two instruments, the readings should be comparable. Should the comparison suggest inaccurate readings, then all in-line turbidimeters should be recalibrated. In addition to calibration, periodic cleaning of the lens should be conducted, using lint-free paper, to prevent any particle or microbiological build-up that could produce inaccurate readings. Periodic check of the sample flow should also be performed using a volumetric measurement. Instrument bulbs should be replaced on an as-needed basis. The LED readout shall be checked that it matches the data recorded on the data acquisition system, if the latter is employed.

12.4.16 Temperature

Temperature shall be analyzed on-site according to *Standard Method* 2550.

12.4.17 TCLP

TCLP shall be performed in the laboratory on the spent media using SW-846 and EPA Method 1311, including method SW-846 6010B for As, Ba, Cd, Cr, Cu, Ni, Pb, Se, Ag, and Zn; and method SW-846 7470A for Hg.

12.4.18 California WET

The California WET shall be performed in the laboratory on the spent media, including method SW-846 6010B for As, Ba, Cd, Cr, Cu, Ni, Pb, Se, Ag, and Zn; and method SW-846 7470A for Hg.

12.5 Tests and Data Specific to Adsorptive Media Type Evaluated

The adsorptive media type used for testing shall be described by providing data on the adsorptive media type characteristics and tests listed in Table 4.

13.0 OPERATIONS AND MAINTENANCE

The following are recommendations for criteria for the evaluation of operations and maintenance (O&M) manuals for equipment employing adsorptive media for arsenic removal.

13.1 Operation

The manufacturer shall provide readily understood information on the required or recommended procedures related to the proper operation of the equipment including, but not limited to, the following:

Monitoring of Preconditioning of Adsorptive Media:

- Utilize manufacturer's procedure, which may vary depending upon adsorptive media selected;
- Backwash Parameters (flow rate, time, backwash water turbidity, etc.);
- Pretreatment chemical application (chemical concentration, time, and flow rate);
- Volume of wastewater; and
- Wastewater disposal requirements (see Regeneration Wastewater Disposal below).

Monitoring Operation:

- Feed water arsenic concentration;
- Feed water pH;
- Feed water adjusted pH;
- Feed water flow rate;
- Feed water pressure;
- Treated water arsenic concentration;
- Treated water pH;
- Treated water adjusted pH;
- Treated water pressure;
- Chemical feed rates;
- Chemical consumption;
- Electrical energy consumption;
- Maintenance and operator labor requirements; and
- Spare parts requirements.

Monitoring Regeneration of Adsorptive Media:

- Utilize manufacturer's procedure for regeneration, which shall vary depending upon selected adsorptive media, equipment, and process variables;
- Backwash parameters (flow rate, time, backwash water turbidity, etc.);
- Regeneration parameters (flow rate, time, regeneration chemical concentration and flow rate, effluent arsenic concentration, effluent pH, etc.);
- Neutralization (or transition to Arsenic Removal Treatment Mode) Parameters (flow rate,

time, neutralization chemical concentration and flow rate, effluent arsenic concentration, effluent pH, adsorptive media depletion, etc.); and
- Adsorptive media makeup requirement.

Monitoring Regeneration Wastewater Disposal:

- Utilize manufacturer's procedure for processing, reclaiming, and/or disposing of regeneration wastewater, adsorptive media preconditioning wastewater, and waste solids, which shall vary depending upon selected adsorptive media, equipment, treatment chemicals and process variables;
- pH adjustment parameters (flow rate, pH, time, pH adjustment chemical consumption, etc.);
- Flocculation/coagulation parameters (flow rate, time, flocculation/coagulation chemical consumption, etc.);
- Liquid/solid separation parameters (flow rate, time, etc.);
- Solids dewatering parameters (flow rate, time, sludge conditioning chemical consumption, dewatered sludge solids, content, toxicity of dewatered solids, etc.);
- Solids disposal parameters (volume, toxicity, permits, transportation of solids to disposal site, costs of transportation and disposal, etc.); and
- Liquid disposal parameters (volume, toxicity, pH, permits, adjustment requirements, costs of disposal, etc.).

13.2 Maintenance

The manufacturer shall provide readily understood information on the required or recommended maintenance schedule for each piece of operating equipment including, but not limited to:

- Pumps;
- Valves;
- All chemical feed and storage equipment; and
- All instruments.

The manufacturer shall provide readily understood information on the required or recommended maintenance schedule for non-mechanical or non-electrical equipment including, but not limited to:

- Adsorptive media vessels;
- Feed lines; and
- Manual valves.

14.0 REFERENCES

"California Code of Regulations." California Office of Administrative Law. 2003. http://ccr.oal.ca.gov.

Hathaway, S. W., and Rubel, F., Jr. 1987. "Removing Arsenic from Drinking Water." *Journal AWWA*, 79:8:161.

Protocol for Arsenic Speciation, developed by Battelle for the EPA (see Appendix A).

Sorg, T. J., and Logsdon, G. S. 1978. "Treatment Technology to Meet the Interim Primary Drinking Water Regulations for Inorganics: Part 2." *Journal AWWA*, 70:7:379.

Standard Methods for the Examination of Water and Wastewater. 1999. 20th edition. APHA, AWWA, and WEF, Washington, D.C.

USEPA. 1996a. ICR Manual for Bench- and Pilot-Scale Treatment Studies. Technical Support Division, Office of Ground Water and Drinking Water, Environmental Protection Agency.

Table 1. Required Water Quality Analyses and Minimum Sample Frequencies for Task 1 System Integrity Verification Testing

Parameter	Frequency	Location	Standard Method[a]	EPA Method[b]
Adsorptive Media Influent and Effluent				
Arsenic	Daily	Lab		200.8
Arsenic Speciation	Three times during this task, twice during Startup and Shakedown	On-Site Prep[c], Lab analyses	Not applicable	Battelle Speciation Method[c] , 200.8
Arsenic Test Kit	Optional by FTO	On-Site	Not applicable	Not applicable
pH	Daily	On-Site	4500-H^+ B	150.1, 150.2
Alkalinity	Daily	On-Site	2320 B	
Fluoride	Daily	On-Site, Lab[d]	4110 B, 4500-F^- B, C, & D	300.0
Chloride	Weekly	Lab	4110 B, 4500-Cl^- B & D	300.0
Sulfate	Weekly	Lab	4110 B, 4500-SO_4^{2-} C, D, E, & F	300.0, 375.2
Silica	Daily	Lab	3120 B, 4500-Si C, D, & E	200.7
Aluminum	Daily	Lab	3120 B	200.7, 200.8, 200.9
Sodium (Optional)	Weekly	Lab		200.7
Calcium	Weekly	On-Site, Lab[d]	3120 B, 3500-Ca B	200.7
Hardness	Weekly	On-Site, Lab[d]	2340 C	
Magnesium	Weekly	On-Site, Lab[d]	3120 B, 3500-Mg B	200.7
Iron	Weekly	Lab	3120 B	200.7, 200.9
Manganese	Weekly	Lab	3120B	200.7, 200.8, 200.9
Turbidity	Daily	On-Site	2130 B	180.1
Temperature	Daily	On-Site	2550	

[a] Standard Methods Source: 20th Edition of *Standard Methods for the Examination of Water and Wastewater*, 1999, American Water Works Association (AWWA).
[b] EPA Methods Source: EPA Office of Ground Water and Drinking Water. EPA Methods are available from the National Technical Information Service (NTIS).
[c] Speciation Method developed by Battelle for EPA (see Appendix A).
[d] On-Site or at Laboratory, must meet short holding time requirements.

Table 2. Schedule for Observing and Recording Equipment Operating and Performance Data

Operational parameter	Action
Feed water and adsorptive media vessel volumetric flow rate	When staffed, check and record every four hours, adjust when >5% above or below target. Record before and after adjustment.
Adsorptive media vessel head loss	Record initial clean bed total head loss at start of run and record total head loss every four hours, when staffed.
Electric power	Record meter daily.
Chemicals used	Record name of chemical, supplier, commercial strength, and dilution used for stock solution to be fed (if diluted) for all chemicals fed during treatment.
Chemical feed volume and dosage	Check and record once per day or more frequently if solution(s) made more frequently. Refill as needed and note volumes and times of refill.
Hours operated per day	Record in logbook at end of day or at beginning of first shift on the following workday. Any stoppage of flow to the adsorptive media vessel shall be recorded. Flow stoppage shall be accounted for by not including it in the cumulative operation time.

Table 3. System Integrity Verification Test Chemical Consumption Data Report[a]

MANUFACTURER _____ PRODUCT NAME _____ MODEL NO.
ADSORPTIVE MEDIA
MANUFACTURER'S CHEMICAL CONSUMPTION OBJECTIVE: Chemical "A"____Gallons/1000gal
_____---------- ____Gallons/1000gal
Chemical "X"____Gallons/1000gal

Event	Date/Time	Meter (gallons)	Meter[b] (gallons)	Chemical "A" Day Tank (gallons)	Chemical "A" Dry Tank (gallons)			Chemical "X"[c] Dry Tank (gallons)	Chemical "X" Dry Tank (gallons)
1) Start Test									
2) Fill Day Tank "A"									
3) Fill Day Tank "X"									
4) Fill Day Tank "A"									
(n-2) Fill Day Tank "X"									
(n-1) Fill Day Tank "A"									
(n) End Test									

[a] Data assembled on this report provides information which yields chemical consumption per thousand gallons of treated water. This in turn is to be converted to cost of each chemical per thousand gallons of treated water.
[b] Flow Totalizing Meter Reading (n) - Meter Reading (n-1) in minutes.
[c] "X" represents the total number of chemicals utilized, therefore, if two chemicals are used, "X" becomes "B", etc.

Table 4. Tests and Data Specific to Adsorptive Media Type Evaluated

Data	Parameter
Raw material used to make adsorptive media	
Method of manufacture:	Chemical processes Thermal processes Sizing / Screening methods Packaging methods
Preconditioning Procedure:	Wetting requirements Defining requirements Waste
Regeneration Procedure:	Backwash Chemical process Return to treatment mode Waste
Regeneration Results:	Adsorption capacity restored Adsorption media attrition Waste
Physical and chemical characteristics**:**	Percent voids Pore size Abrasion number Moisture (weight %) Particle size Sieve size, US sieve series Effective size Uniformity coefficient

Table 5. Required Water Quality Analyses and Minimum Sample Frequencies for Task 2A Adsorption Capacity Verification Testing

Parameter	Frequency	Location	Standard Method[a]	EPA Method[b]
Adsorptive Media Influent and Effluent[c]				
Arsenic	Weekly & more frequent near breakthrough	Lab		200.8
Arsenic Speciation	Minimum of three times during this task	On-Site Prep[d], Lab analyses	Not applicable	Battelle Speciation Method[d] , 200.8
Arsenic Test Kit	Optional by FTO	On-Site	Not applicable	Not applicable
pH	Daily	On-Site	4500-H^+ B	150.1, 150.2
Alkalinity	Daily	On-Site	2320 B	
Fluoride	Daily[f]	On-Site, Lab[e]	4110 B, 4500-F^- B, C, & D	300.0
Chloride	Weekly	Lab	4110 B, 4500-Cl^- B– & D	300.0
Sulfate	Weekly	Lab	4110 B, 4500-SO_4^{2-} C, D, E, & F	300.0, 375.2
Silica	Daily[f]	Lab	3120 B, 4500-Si C, D, & E	200.7
Aluminum	Daily[f]	Lab	3120 B	200.7, 200.8, 200.9
Sodium (Optional)	Weekly	Lab		200.7
Calcium	Weekly	On-Site, Lab[e]	3120 B, 3500-Ca B	200.7
Hardness	Weekly	On-Site, Lab[e]	2340 C	
Magnesium	Weekly	On-Site, Lab[e]	3120 B, 3500-Mg B	200.7
Iron	Weekly	Lab	3120 B	200.7, 200.9
Manganese	Weekly	Lab	3120B	200.7, 200.8, 200.9
Turbidity	Daily	On-Site	2130 B	180.1
Temperature	Daily	On-Site	2550	
TCLP	Once	Lab		1311 Metals analysis by SW-846 6010B and 7470A[g]
CA WET	Once	Lab		Special CA method Metals analysis by SW-846 6010B and 7470A[g]

[a] Standard Methods Source: 20th Edition of *Standard Methods for the Examination of Water and Wastewater*, 1999, AWWA.
[b] EPA Methods Source: EPA Office of Ground Water and Drinking Water. EPA Methods are available from the National Technical Information Service (NTIS).
[c] Influent sampling shall occur at approximately the same time as effluent sampling for each parameter during equipment operation.
[d] Speciation Method developed by Battelle for EPA (see Appendix A).
[e] On-site or laboratory analysis acceptable, as long as short holding time requirement is met.
[f] Sampling and analysis frequency may be reduced if data from Task 1 show influent and effluent are stable.
[g] Metals analyses will include As, Ba, Cd, Cr, Cu, Hg, Ni, Pb, Se, Ag, and Zn.

Table 6. Adsorption Capacity Verification Data Report

MANUFACTURER _____ PRODUCT NAME _____ MODEL NO_____
ADSORPTIVE MEDIA _____ RATED CAPACITY _____ mg/L/FT^3

Date/Time	Minutes[a)]	Flow Rate (gpm)	Meter (gallons)	Meter[b)] (gallons)	Pressure[c)] (psig)	Feed Arsenic (mg/L)	Treated Arsenic (mg/L)	Arsenic Removed[d)] (mg)	Cumulative Arsenic Removed (mg)
Start 1)									
2)									
3)									
4)									
n-3)									
n-2)									
n-1)									
End n)									

[a] Time (n) - Time (n-1) in minutes.
[b] Flow Totalizing Meter Reading (n) - Meter Reading (n-1) in gallons.
[c] Influent pressure - effluent pressure (gauge reading differential pressure).
[d] $\frac{[\text{Feed Arsenic (n)} - \text{Treated Arsenic (n)}] + [\text{Feed Arsenic (n-1)} - \text{Treated Arsenic (n-1)}]}{(2)} \times [\ \text{meter (n)}]$ in mg

Appendix A

Protocol for Arsenic Speciation

PROTOCOL FOR ARSENIC SPECIATION

The following text presents the protocol to be used for arsenic speciation sampling and analysis during this project.

1.0 Scope and Application

Arsenic occurs in natural water in both the organic and inorganic forms. However, inorganic arsenic is predominant in natural water and is the most likely form of arsenic to exist at concentrations that cause regulatory concerns (Edwards et al., 1997). Inorganic arsenic is normally found in water supplies as an anion with acid characteristics in the trivalent [arsenite or As (III)] and pentavalent [arsenate or As (V)] forms. The valence is significant because most arsenic treatment technologies are more effective for the removal of arsenate than for arsenite.

Although total arsenic concentrations can be effectively preserved in field samples, the present status of preserving inorganic arsenic species in field samples is inconclusive. Preservation of total arsenic is accomplished by acidifying the sample to pH < 2 in the field. However, a high level of ambiguity exists when acids such as nitric acid (HNO_3) or hydrochloric acid (HCl) are used to preserve inorganic species of arsenic. Interconversion of As (III) and As (V) in samples preserved with 0.05 *N* HCl has been reported to occur within one day (Andreae, 1977). Another laboratory study conducted by Eaton et al. (1997) examined preservation of arsenic using ascorbic acid and HCl. This study concluded that there were no effective methods for preservation of As (III) and As (V) in water samples. Some researchers have used freezing of samples as a means of preserving the inorganic species of arsenic. However, freezing is not a cost-effective or practical method for field sampling.

Since the present status of preserving arsenic species indicates that there are no completely effective preservation methods, field speciation is required. Research by Clifford et al. (1983), Ficklin (1983), and Edwards et al. (1997) indicate that the use of an anion exchange resin column is an accurate and cost-effective field method for arsenic speciation. As (III) and As (V) recovery was shown to be consistently above 95% using an anion exchange column (Edwards et al., 1997). Therefore, the decision was made to utilize a field speciation technique similar to that used by Edwards et al. (1997).

The field speciation technique described in the following sections uses 0.45-μm pore size filters to remove "particulate" arsenic. Research done by Edwards et al. (1997) also using 0.45-μm pore size filters indicates that particulate arsenic may not be completely removed by this pore size filter. Therefore, the particulate arsenic found using a 0.45-μm pore size filter should be considered the lower bound for arsenic particulate.

The only laboratory analysis required using the field speciation technique is total arsenic. Inductively coupled plasma-mass spectrometry (ICP-MS) was chosen as the method for total arsenic analysis due to its low method detection limit (MDL), proven effectiveness, and relatively low cost.

2.0 Method Summary

The field speciation method described in the subsequent sections utilizes an anion exchange resin column to separate the soluble arsenic species, As (V) and As (III). The soluble portion of the sample is obtained by passing the sample through a 0.45-μm pore size filter. After filtration, the sample is acidified using 0.5 mL of ultra-pure sulfuric acid per L of sample (0.05% [volume/ volume]) to lower the sample pH value to about 2. At this pH range, As (III) will be completely protonated as H_3AsO_3 (see Figure A-1) and As (V) will be present in both the ionic form (i.e., $H_2AsO_4^-$) and protonated form (i.e., H_3AsO_4) (see Figure A-2). As the acidified sample is run through the column, the resin retains the As (V) (Note that the resin will retain only $H_2AsO_4^-$ and that H_3AsO_4, when passing through the column, will be ionized to $H_2AsO_4^-$ due to elevated pH values in the column caused by the buffer capacity of acetate exchanged from the resin) and the As (III) (i.e., H_3AsO_3) passes through the column. The acidified sample and the resin-treated sample are analyzed separately for total arsenic using ICP-MS. As (III) concentration is reflected by the total arsenic concentration of the resin-treated sample. As (V) concentration is the difference of the total arsenic concentration of the acidified sample and the total arsenic concentration of the resin-treated sample.

H_2SO_4 is used to acidify the sample because HCl may create undesirable chloride interference when using the ICP-MS and because there is concern that nitric acid may damage the resin or form nitric acid-arsenic redox couples (Edwards et al., 1997).

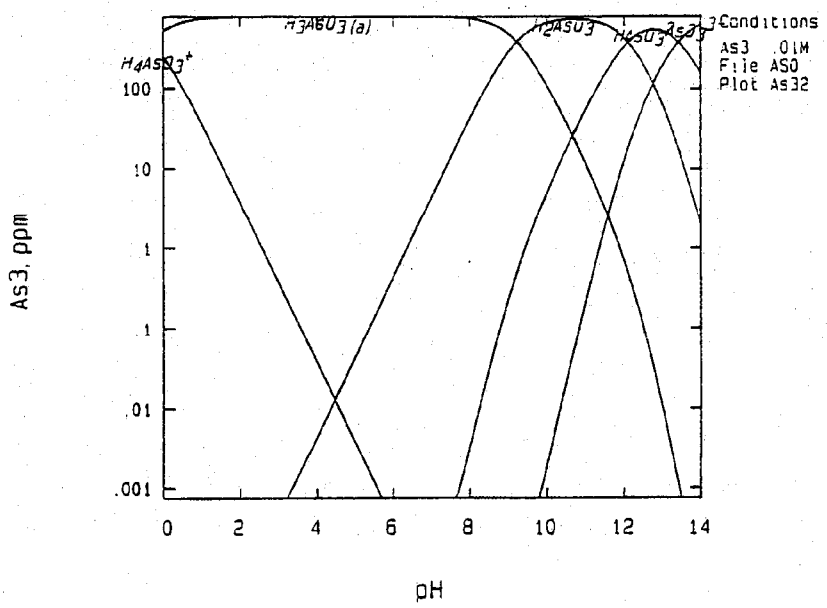

Figure A-1. Solubility Diagram of As (III)

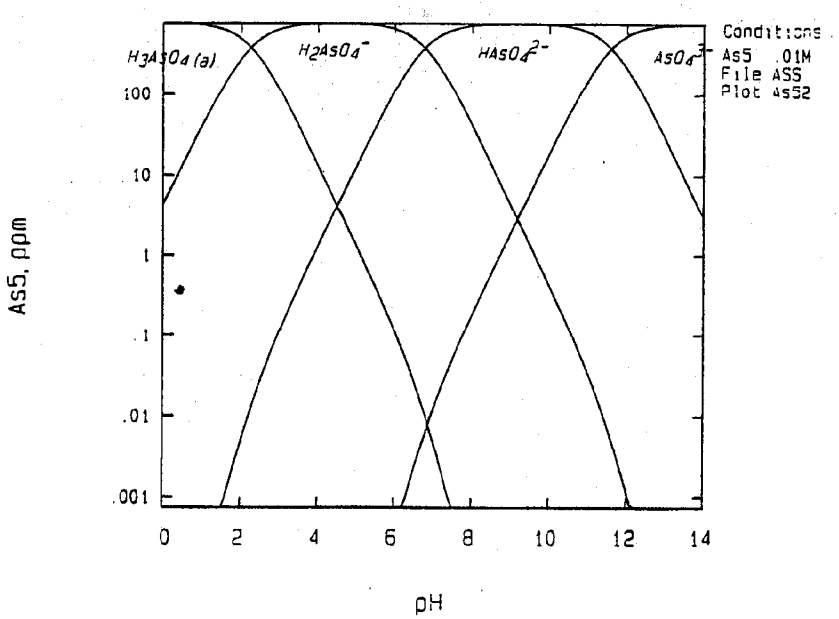

Figure A-2. Solubility Diagram of As (V)

3.0 Reagents

Reagents required for field speciation of arsenic include Dowex 1-X8, 50-100 mesh resin, acetic acid, sodium hydroxide (NaOH), and ultra-pure sulfuric acid and nitric acid. All chemicals are of reagent grade or higher.

3.1 Resin. Dowex 1-X8, 50-100 mesh resin will be used in this study.

3.2 Sodium Hydroxide. One (1) *N* NaOH will be used to prepare the resin.

3.3 Acetic Acid. One (1) *N* acetic acid will be used to prepare the resin.

3.4 Sulfuric Acid. An ultra-pure sulfuric acid (93-98%, sub-boiling distilled in quartz) will be used to acidify samples prior to the resin treatment.

3.5 Nitric Acid. An ultra-pure nitric acid (65%, sub-boiling distilled in quartz) will be used to preserve samples (see Table A-1)

4.0 Equipment/Apparatus

4.1 Resin Preparation. Dowex 1-X8, 50-100 mesh resin will be converted from the chloride form (as supplied by the manufacturer) to the acetate form before packing into columns. The resin will be prepared in batch according to the method used by Edwards et al. (1997). In summary, one kg of the resin will be placed in a 3-L beaker. One liter of 1 *N* NaOH will be added to the resin, stirred for an hour using an overhead stirrer, and drained. This NaOH rinse will be repeated three times in sequence. The NaOH-treated resin will then be rinsed twice with 1 L of deionized (DI) water, followed by an acetic acid rinse. The acetic acid rinse consists of adding 1 L of 1 *N* acetic acid to the resin, stirring for 5 minutes, and draining. The acetic acid rinse will be repeated three times in sequence. Finally, the mixture will be rinsed with 1 L of DI water three times in sequence.

4.2 Anion Exchange Column Preparation. Anion exchange columns will be prepared as described by Edwards et al. (1997). The columns selected for this field speciation method are 12 cm x 15 mm in size and made of polypropylene (Bio-Rad Laboratories, CA). Each column will

be slurry packed with approximately 20 grams (drained weight) of the prepared resin, yielding a resin depth of approximately 10.5 cm. The column will be capped with a plastic cap to prevent contamination prior to use.

4.3 Beaker. Four hundred-mL (400-mL) disposable plastic beakers will be used to collect raw water samples. All disposable beakers will be rinsed with DI water and air-dried before being packed into the sampling kits.

4.4 Syringe and Filter. Sixty-mL (60-mL) disposable plastic syringes with 0.45-μm screw-on filters will be used to filter samples. All disposable syringes and filters will be rinsed with DI water and air-dried before being packed into the sampling kits.

4.5 Sample Bottles. VWRbrand™ TraceClean™ HDPE sample bottles (125 mL) labeled A, B and C will be used to contain unfiltered and acidified samples; filtered and acidified samples; and filtered, acidified, and resin-treated samples, respectively. Bottles A and C will contain appropriate amounts of concentrated ultra-pure nitric acid; whereas bottle B will contain 1.25 mL of 5% (volume/volume) ultra-pure sulfuric acid.

5.0 Sample Preservation, Containers, Handling, and Storage

Sample preservation, containers, handling, and storage requirements are indicated in Table A-1. Arsenic speciation at each sampling point in the water treatment process (e.g., inlet, pre-filtration, and outlet) will require collection of three 125-mL bottles identified as bottles A, B, and C, which are defined as follows:

- Bottle A will contain 125 mL of an unfiltered and acidified sample
- Bottle B will contain 125 mL of a filtered sample acidified with 1.25 mL of 5% H_2SO_4
- Bottle C will contain 20 mL of a sample obtained by passing some bottle B sample through an anion exchange resin column

Table A-1. Sample Preservation, Containers, Handling, and Storage

Sample Bottle Identifier	Sample Size	Container Type	Preservation	Analyte	Holding Time
A	125 mL	Certified HDPE	4°C HNO_3 for pH<2	Total Arsenic by ICP-MS	6 months
B	125 mL	Certified HDPE	4°C 1.25 mL of 5% H_2SO_4	Total Arsenic by ICP-MS	6 months
C	20 mL	Certified HDPE	4°C HNO_3 for pH<2	Total Arsenic by ICP-MS	6 months

6.0 Procedure

The procedure for processing each arsenic speciation sample includes the following steps:

6.1 Raw Water Sample Collection. Completely fill bottle A with the water to be sampled. Cap bottle A and seal the lid with tape.

6.2 Filtered Sample Collection. Fill a 400-mL disposable plastic beaker with the water sampled in Section 6.1. Completely fill the syringe with the water from the plastic beaker. Screw the filter snug onto the end of the syringe and push the sample through the filter. Discard the first 10 drops to rinse the filter. Collect the filtered sample in bottle B. Remove the filter, refill the syringe with raw water, reattach the filter to the syringe, and push the sample through the filter into the bottle B. Repeat this process until bottle B is almost full; however, leave a small air gap at the top. The air gap should be approximately 1 to 5 mL. Cap bottle B tightly and shake the bottle for about 15 seconds to ensure thorough mixing. The air gap in the bottle allows the contents to mix thoroughly.

6.3 Resin-Treated Sample Collection. Remove the protective cap from the top of the resin column and break off the end at bottom of the resin column. Carefully fill the resin column to the top with the water in bottle B and let the column drain completely. Repeat this process until approximately 40 mL of water from bottle B has been passed through the column. Thereafter, position the resin column over bottle C, fill the column to the top, and let the entire column drain

into bottle C. Repeat this process until approximately 20 mL of resin-treated sample has been collected in bottle C. Cap bottles B and C and seal the lids with tape.

6.4 Sample Shipping. After the field speciation is complete, fill out a chain-of-custody form. Place all the sample bottles in a shipper with cold packs and have it shipped to Battelle via FedEx overnight delivery.

6.5 Arsenic Analysis. After the samples are received, Battelle will process the samples and perform arsenic analysis using ICP-MS according to EPA 200.8 method. The sample in bottle A will be digested prior to ICP-MS analysis, whereas the samples in bottles B and C will not be digested.

6.6 Graphic Speciation Procedure. Figure A-3 provides a graphic description of the field speciation procedure which is designed to assist plant POCs to follow the procedure more easily.

7.0 Calculations

For each As speciation sampling event, three sample bottles (A, B, and C) will be produced and the water in these bottles will be analyzed for total arsenic by ICP-MS. Total arsenic (including particulate arsenic), total particulate arsenic, total soluble arsenic, As (III), and As (V) will be calculated as follows:

- **Total Arsenic (including particulate arsenic)** = total arsenic concentration in bottle A
- **Total Soluble Arsenic** = total arsenic concentration in bottle B
- **Total Particulate Arsenic** = total arsenic concentration in bottle A – total arsenic concentration in bottle B
- **As (III)** = total arsenic concentration in bottle C
- **As (V)** = total arsenic concentration in bottle B – total arsenic concentration in bottle C

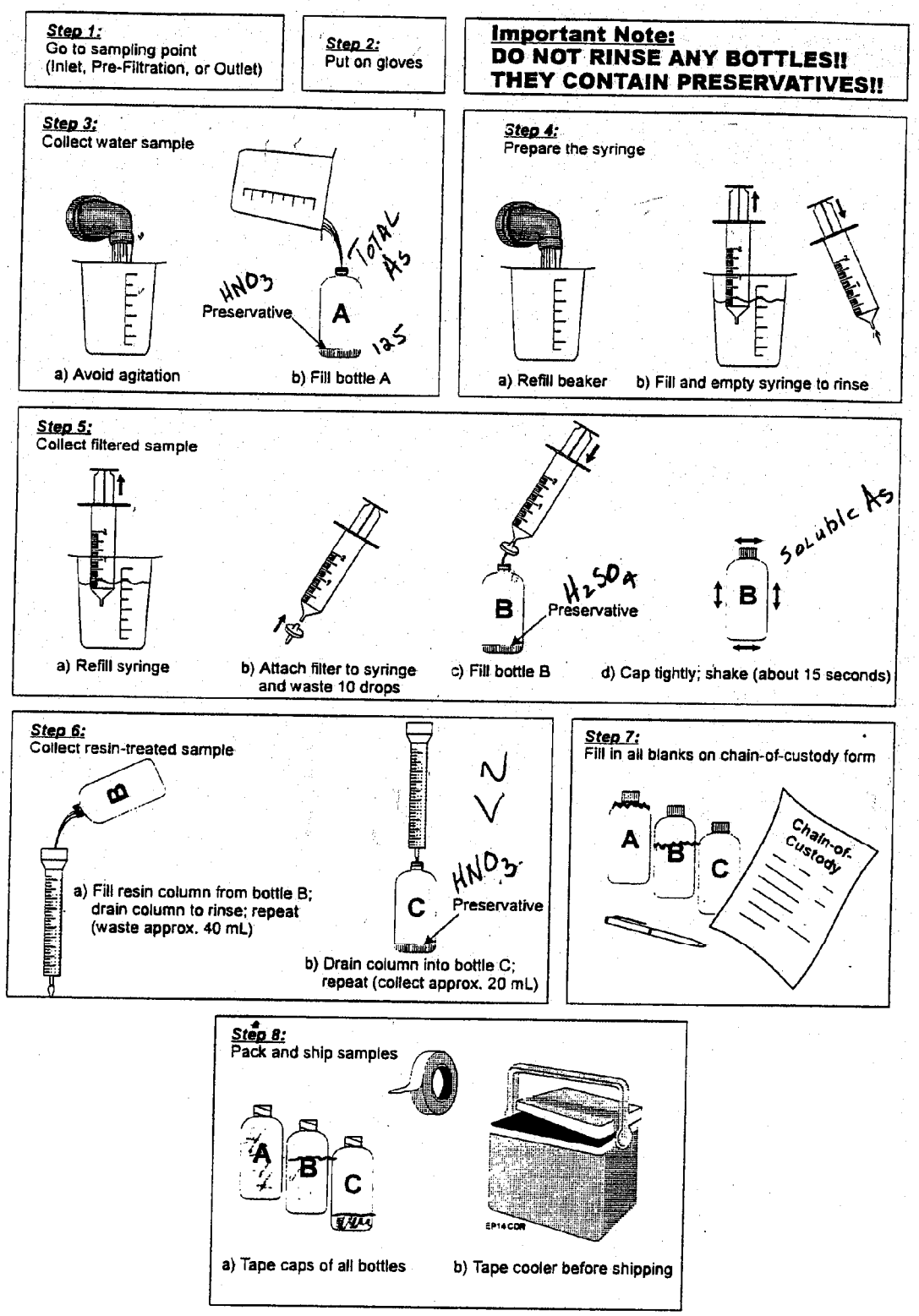

Figure A-3. Arsenic Field Speciation Procedure

8.0 ICP-MS Quality Control

As required by EPA Method 200.8, Battelle's ICP-MS laboratory performed a quality control (QC) check, including an initial demonstration of laboratory capacity and periodic analyses of laboratory reagent blanks, fortified blanks, and calibration solutions as a continuing check on performance. A 5-point calibration was performed using certified As standard solutions with concentrations of 0.1, 5, 10, 30, and 50 μg/L. A linear calibration range of 0.1 to 50 μg/L was established with a correlation coefficient greater than 0.999. A method detection limit (MDL) was established to be 0.02 μg/L.

DI water and two source water samples including a groundwater and a surface water collected from two local water treatment plants were spiked with 10 μg/L of the As standard. A series of samples including QC samples (a calibration blank, calibration standards, quality control standards, and a laboratory fortified blank) were analyzed in a sequence shown in Table A-2. All percentage recoveries and relative percent difference (%RPD) values presented in Table A-2 are within the QC limits required by the Method 200.8.

Table A-2. ICP-MS Quality Control Check

Sample Sequence	Concentration	Percent Recovery	% RPD
Calibration Blank	-0.055		
Calibration Standard 2	4.94	99%	
Calibration Standard 4	29.0	97%	
Quality Control Standard	26.8		
Quality Control Standard	26.4		
Quality Control Standard	26.9		
Average	26.7	107%	0.9%
Laboratory Fortified Blank	8.07	101%	
DI Water (Laboratory Reagent Blank)	0.032		
DI Water Spiked with 10 μg/L As	9.56		
Ground Water	0.725		
Ground Water Spiked with 10 μg/L As	10.7		
Surface Water	1.19		
Surface Water Spiked with 10 μg/L As	9.80		
Quality Control Standard	63.7	106%	
Calibration Blank	-0.018		
Calibration Standard 2	5.22	104%	
Calibration Standard 4	28.9	96%	
Quality Control Standard	26.3	105%	
Laboratory Fortified Blank	7.92	99%	

9.0 Verification of Arsenic Speciation Method

Verification of the arsenic speciation method was performed in Battelle's laboratories using sodium arsenite ($NaAsO_2$) and disodium hydrogen arsenate heptahydrate ($Na_2HAsO_4 \bullet 7H_2O$) as As (III) and As (V) model compounds. The source water used in the ICP-MS QC check was also used in the verification study to more closely mimic field conditions.

DI water was spiked with 10 or 50 μg/L of an As (III) or an As (V) standard solution. Groundwater and surface water were spiked with 10 or 50 μg/L of the As (V) standard. The pH of each solution was adjusted to 2, 3, or 4 using an ultra-pure sulfuric acid. Thereafter, the procedure described in Section 6.0 was followed. The samples before and after the resin column treatment were analyzed for total arsenic by ICP-MS.

The results show that the recoveries of As (III) from the resin columns ranged from 93.2 to 97.3%. The amount of As (V) retained in the resin columns ranged from 91.5 to 100%. The results also indicate that the difference in arsenic recovery/retention between the samples of pH 2 and the samples of pH 4 was less than 6%.

10.0 References

Andreae, M. 1977. *Determination of Arsenic Species in Natural Waters. Anal Chem.* 49: 820-823.

Clifford, D., L. Ceber, and S. Chow. 1983. *Arsenic(III)/Arsenic(V) Separation by Chloride-Form Ion-Exchange Resins.* Proceedings of the XI AWWA WQTC.

Eaton, A.D., H.C. Wang, and J. Northington. 1997. *Analytical Chemistry of Arsenic in Drinking Water.* AWWARF Project 914. In publication.

Edwards, M., S. Patel, L. McNeill, H.-W. Chen, A.D. Eaton, R. C. Antweiler, and H. E. Taylor, 1997. *Considerations in Arsenic Analysis and Speciation.* In publication.

Ficklin, W.H. 1983. *Separation of Arsenic (III) and Arsenic (V) in Groundwaters by Ion Exchange. Talanta,* 30 (5): 371-373.