

# Laboratory Study on the Oxidation of Arsenic III to Arsenic V

As (III) As (V) reduction

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## **Laboratory Study on the Oxidation** of Arsenic III to Arsenic V

by

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E. Timothy Oppelt, Director National Risk Management Research Laboratory

#### **Abstract**

A one-year laboratory study was performed to determine the ability of seven oxidants to oxidize As(III) to As(V). These included chlorine, permanganate, ozone, chlorine dioxide, monochloramine, a solid-phase oxidizing media, and 254 nm ultraviolet light.

Chlorine and permanganate rapidly oxidized As(III) to As(V) in the pH range of 6.3 to 8.3. Dissolved manganese, dissolved iron, sulfide and TOC slowed the rate of oxidation slightly, but essentially complete oxidation was obtained in less than one minute with chlorine and permanganate under all conditions studied.

In the absence of interfering reductants, ozone rapidly oxidized As(III). Although, dissolved manganese and dissolved iron had no significant effect on As(III) oxidation, the presence of sulfide considerably slowed the oxidation reaction. The presence of TOC had a quenching effect on As(III) oxidation by ozone, producing incomplete oxidation at the higher TOC concentration studied.

Only limited As(III) oxidation was obtained using chlorine dioxide, which was probably due to the presence of chlorine (as a by-product) in the chlorine dioxide stock solutions. The reason for the ineffectiveness of chlorine dioxide was not studied.

Preformed monochloramine was ineffective for As(III) oxidation, whereas limited oxidation was obtained when monochloramine was formed in-situ. This showed that the injected chlorine probably reacted with As(III) before being quenched by ammonia to form monochloramine.

Filox, a manganese dioxide-based media, was effective for As(III) oxidation. When dissolved oxygen (DO) was not limiting, complete oxidation was observed under all conditions studied. However, when DO was reduced, incomplete oxidation was obtained in the presence of interfering reductants. The adverse effect of interfering reductants was completely eliminated by either (a) supplying enough DO or (b) increasing the contact time. In addition to oxidizing As(III), the Filox media also removed some arsenic by adsorption, which diminished greatly as the media came into equilibrium with the As(III)-spiked synthetic water.

UV light alone (254 nm) was not very effective for As(III) oxidation. Significant oxidation was observed only at very low flow rates representing 0.6 - 2.5% of the rated capacities of the two UV sterilizer units tested. However, as reported in a patented process, complete oxidation by UV light was observed when the challenge water was spiked with 1.0 mg/L sulfite.

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#### **Abbreviations and Acronyms**

AWWA American Water Works Association

DO Dissolved Oxygen, mg/L

DPD N,N-diethyl-p-phenylenediamine

EBCT Empty Bed Contact Time (media volume/flow rate), min

EPA US Environmental Protection Agency

FIAS Flow Injection Analysis Hydride Generation System

GFAAS Graphite Furnace Atomic Absorption Spectrophotometer

GPM Gallons/min

HDPE High Density Polyethylene IR Interfering Reductant

MCL Maximum Contaminant Level

MDL Method Detection Limit
NPT Nominal Pipe Thread

NRMRL National Risk Management Research Laboratory

PAO Phenyl Arsenic Oxide PRV Pressure Relief Valve QA Quality Assurance

QAPP Quality Assurance Project Plan
QA/QC Quality Assurance/Quality Control

SDWA Safe Drinking Water Act

SM Standard Methods

SR Stoichiometric Ratio, µg oxidant/µg reductant

TOC Total Organic Carbon UH University of Houston

UV Ultraviolet

WAL Work Assignment Leader
WAM Work Assignment Manager

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#### 1. Introduction

#### 1.1 Background

Arsenic (As) is a metalloid that is naturally present in drinking water in a variety of forms (organic and inorganic), oxidation states, and valences (Ferguson Inorganic arsenic and Gavis, 1972). predominates in drinking water and is present as arsenate (As(V)) and arsenite (As(III)). Under pH conditions of 6-9, As(V) exists as an anion while As(III) is fully protonated and exists as an uncharged molecule (Clifford and Zhang, 1994).

While any future revisions in the arsenic MCL will likely target total arsenic, the speciation of arsenic (III or V) is significant because of differences in arsenic removal efficiencies by various treatment techniques. As(V) is generally more efficiently removed than As(III), which is poorly removed using treatment ion processes such as exchange (Clifford, 1999, Clifford et al., 1998a, 1997), iron coagulation followed by microfiltration (Clifford et al., 1998b; Ghurye et al., 1998; Hering et al., 1996a. 1996b), and activated alumina adsorption (Clifford, 1990. 1986: Clifford et al., 1998b; Hathaway and Rubel, 1987). Hence, for drinking water supplies containing significant concentrations of As(III), preoxidation of As(III) to As(V) is mandatory for high arsenic removal.

#### 1.1.1 Previous Studies

Frank and Clifford (1986) studied the oxidation of As(III) to As(V) using chlorine, monochloramine and oxygen. They determined that the oxidation of As(III) by chlorine was very rapid. A

1.0 mg/L free chlorine dose was able to oxidize 100 ug/L As(III) in less than 5 seconds. Monochloramine was able to oxidize only a fraction of the initial present, possibly because As(III) chlorine injected in the presence of an excess of ammonia to form monochloramine, was responsible for As(III) oxidation rather than monochloramine. Oxygen was found to be ineffective for As(III) oxidation. Amy et al. (2000) studied the use of chlorine, ozone and permanganate for As(III) oxidation. This study used excess (over As stoichiometry) ozone and stoichiometric doses of chlorine and permanganate. All three oxidants proved effective although less than 100% As(III) oxidation was obtained with chlorine and permanganate. was probably the result of NOM (0.2 -2.3 mg/L) presenting a competing oxidant demand. Although higher doses of chlorine and permanganate were not tested, the authors concluded that the provision of these oxidants stoichiometric excess would result in complete conversion of As(III) to As(V).

Oxidation of As(III) to As(V) by solidphase oxidants such as birnessite (δ MnO<sub>2</sub>) has also been reported by Oscarson et al. (1983), Moore et al. (1990), Driehaus (1995), and Scott and Morgan (1995). These studies generally concluded that birnessite directly oxidized As(III) to As(V) through a surface mechanism and that adsorption of As(III) to the oxide surface was the rate-limiting step. Additionally, Scott and Morgan (1995) concluded that dissolved oxygen had no effect on the rate of the oxidation reaction. However, they did not study the effect of interfering reductants on As(III) oxidation. As will be shown later in this report, we observed no effect of DO on As(III) oxidation in the absence of interfering reductants. We did, however, observe that the DO level had a significant detrimental effect on As(III) oxidation in the presence of interfering reductants.

As(III) oxidation has also been studied by other researchers using a variety of techniques including electrochemical oxidation (Catherino, 1967), oxidation by electrogenerated iodine (Johnson and Bruckenstein. 1968), oxidation peroxodisulfate (Gupta, et al., 1984 and Nishida and Kimura, 1989), oxidation by perchloric acid (Everett and Skoog, 1971), oxidation by chromic acid (Sen Gupta and Chakladar, 1989), oxidation by hexacyanoferrate(III) (Mohan et al., 1977). These methods were considered unsuitable for As(III) oxidation in drinking water and hence, were not investigated in this study.

#### 1.2 Oxidants Evaluated

Oxidation experiments were performed in the aqueous phase via the addition of oxidants such as chlorine or ozone to a solution containing As(III) or by contacting the As(III)-containing solution with a solid-phase oxidant. A solid-phase oxidant is typically a media that has the oxidant immobilized on its

surface and such media may be used in packed columns through which the As(III)-containing solution is passed at a specified flow rate or empty bed contact time (EBCT). The use of UV radiation to oxidize As(III) to As(V) was also studied at a wavelength of 254 nm, using two commercially available UV disinfection units.

# 1.3 Chemical Oxidant Stoichiometry

Reaction stoichiometries of the various chemical oxidants with As(III) and potentially interfering reductants are summarized below.

#### 1.3.1 Chlorine

#### For As(III):

$$H_3AsO_3 + NaOCl \rightarrow H_2AsO_4^- +$$
 (1)  
 $Na^+ + Cl^- + H^+$ 

In reaction (1), one mole of As(III) requires 1 mole of NaOCl, which is equivalent to one mole of  $Cl_2$ . A 50  $\mu$ g/L As(III) solution contains 0.667  $\mu$ M As(III)/L (AW of As = 74.92). Therefore, the stoichiometric requirement of chlorine is 0.667  $\mu$ M/L or 47.4  $\mu$ g  $Cl_2$ /L, and the stoichiometric ratio (SR) of chlorine needed to oxidize As(III) is 0.95  $\mu$ g  $Cl_2$ / $\mu$ g As(III).

 $SR = 0.95 \,\mu g \,Cl_2/\mu g \,As(III)$ 

#### For Fe(II):

2 Fe<sup>2+</sup> + HOCl + 5 H<sub>2</sub>O 
$$\rightarrow$$
 (2)  
2Fe(OH)<sub>3</sub> (s) +Cl +5H<sup>+</sup>

 $SR = 0.64 \mu g Cl_2/\mu g Fe(II)$ 

#### For Mn(II):

$$Mn^{2+} + HOCl + H_2O \rightarrow$$
 (3)  
 $MnO_2$  (s)  $+Cl^- + 3H^+$ 

 $SR = 1.29 \mu g Cl_2/\mu g Mn(II)$ 

#### For Sulfide:

$$HS^- + HOCl \rightarrow S^0 \downarrow + Cl^- + H_20$$
 (4)

SR =  $2.21 \mu g \text{ Cl}_2/\mu g \text{ S}^2$ pH Range = 5 - 9Optimum pH = 9.0

$$HS^- + 4HOCl \rightarrow SO_4^{2-} + 4HCl + H^+$$
 (5)

SR =  $8.86 \mu g \text{ Cl}_2/\mu g \text{ S}^2$ pH Range = 5 - 9Optimum pH = 6.0

The chemistry of the oxidation of sulfide is extremely complex. Reportedly, the oxidation proceeds to form either elemental sulfur, sulfate, or both (White, 1986). Equations (4) and (5) for the oxidation of sulfur with chlorine were obtained from White (1986). oxidant doses used in the presence of sulfide were either three- or 10-times the stoichiometric requirement based on As(III) alone. Since the As(III) concentration in the presence of

interfering reductants such as sulfide was always  $50~\mu g/L$ , the resultant oxidant doses used were low in relation to the sulfide concentrations of 1.0 and 2.0 mg/L, Oxidation reactions, similar to equation (4) for chlorine dioxide, permanganate, ozone, and monochloramine were derived based on oxidation of sulfide to elemental sulfur only.

#### 1.3.2 Permanganate

#### For As(III):

$$3H_3AsO_3 + 2MnO_4 \rightarrow 3H_2AsO_4 + (6)$$
  
 $2MnO_2 + H_2O + H^+$ 

 $SR = 1.06 \mu g MnO_4/\mu g As(III)$ 

#### For Fe(II):

$$3\text{Fe}^{2+} + \text{MnO}_4^- + 7\text{H}_2\text{O} \rightarrow$$
 (7)  
 $3\text{Fe}(\text{OH})_3 \text{ (s)} + \text{MnO}_2 \text{ (s)} + 5\text{H}^+$ 

 $SR = 0.71 \mu g MnO_4/\mu g Fe(II)$ 

#### For Mn(II):

$$3Mn^{2+} + 2MnO_4^- + 2H_2O \rightarrow$$
 (8)  
 $5MnO_2$  (s) +  $4H^+$ 

 $SR = 1.44 \mu g MnO_4/\mu g Mn(II)$ 

#### For Sulfide:

$$3HS^{-} + 2MnO_{4}^{-} + 5H^{+} \rightarrow 3S^{0} \downarrow +$$
 (9)  
 $2MnO_{2}(s) + 4H_{2}O$ 

 $SR = 2.48 \mu g MnO_4 / \mu g S^{2-}$ 

#### 1.3.3 Ozone

#### For As(III):

$$H_3AsO_3 + O_3 \rightarrow H_2AsO_4 + (10)$$
  
 $O_2 + H^+ (@ pH 6.5)$ 

$$H_3AsO_3 + O_3 \rightarrow HAsO_4^{2-} +$$
 (11)  
 $O_2 + 2H^+$  (@ pH 8.5)

 $SR = 0.64 \mu g O_3/\mu g As(III)$ 

#### For Fe(II):

$$2\text{Fe}^{2+} + \text{O}_3 \text{ (aq)} + 5\text{H}_2\text{O} \rightarrow (12)$$
  
 $2\text{Fe}(\text{OH})_3 \text{ (s)} + \text{O}_2 \text{ (aq)} + 4\text{H}^+$ 

 $SR = 0.43 \mu g O_3/\mu g Fe(II)$ 

#### For Mn(II):

$$Mn^{2+} + O_3 (aq) + H_2O \rightarrow$$
 (13)  
 $MnO_2 (s) + O_2 (aq) + 2H^+$ 

 $SR = 0.88 \ \mu g \ O_3/\mu g \ Mn(II)$ 

#### For Sulfide:

$$HS^- + O_3 (aq) + H^+ \rightarrow S^0 \downarrow +$$
 (14)  
 $O_2 (aq) + H_2O$ 

 $SR = 1.50 \,\mu g \, O_3/\mu g \, S^{2-}$ 

#### 1.3.4 Chlorine Dioxide

Oxidation by chlorine dioxide can occur via a 1- or 5-electron transfer with the conversion of ClO<sub>2</sub> to ClO<sub>2</sub> or Cl, respectively. Knocke (1990) determined that chlorine dioxide oxidized Mn(II) via a 1-electron transfer whereas it oxidized Fe(II) via a 5-electron transfer. When calculating an appropriate chlorine dioxide dose for As(III), a conservative 1-electron transfer was assumed.

However, theoretical stoichiometric ratios for both 1-and 5-electron transfer mechanisms are shown below.

#### For As(III):

$$H_3AsO_3 + 2ClO_2 + H_2O \rightarrow H_2AsO_4$$
 +  $2ClO_2$  +  $3H$  (1-electron transfer) (15)

$$5H_3AsO_3 + 2ClO_2 + H_2O \rightarrow 5H_2AsO_4$$
  
+  $2Cl^2 + 7H^+$  (5-electron transfer) (16)

SR=1.80  $\mu g$  ClO<sub>2</sub>/ $\mu g$  As(III) for 1-electron transfer SR=0.36  $\mu g$  ClO<sub>2</sub>/ $\mu g$  As(III) for 5-electron

#### For Fe(II):

transfer

$$5\text{Fe}^{2+} + \text{ClO}_2 + 13\text{H}_2\text{O} \rightarrow 5\text{Fe}(\text{OH})_3 \text{ (s)} + \text{Cl}^- + 11\text{H}^+$$
 (17)

SR=0.24  $\mu g$  ClO<sub>2</sub>/ $\mu g$  Fe(II) for 5-electron transfer

#### For Mn(II):

$$Mn^{2+} + 2ClO_2 + 2H_2O \rightarrow$$
 (18)  
 $MnO_2(s) + 2ClO_2^- + 4H^+$ 

SR=2.45  $\mu$ g ClO<sub>2</sub>/ $\mu$ g Mn(II) for 1-electron transfer

#### For Sulfide:

$$HS^- + 2ClO_2 \rightarrow S^0 \downarrow + 2ClO_2^- + H^+$$
 (19)  
1 electron transfer

$$5HS^{-} + 2ClO_2 + 3H^{+} \rightarrow 5S^{0} \downarrow +$$
 (20)  
 $2Cl^{-} + 4H_2O$  (5 electron transfer)

SR = 4.21  $\mu g$  ClO<sub>2</sub>/ $\mu g$  S<sup>2-</sup> for 1-electron transfer SR = 0.84  $\mu g$  ClO<sub>2</sub>/ $\mu g$  S<sup>2-</sup> for 5-electron transfer

Chlorine dioxide was prepared according to the general procedure described in Methods with Standard modifications (White, 1986) to increase the yield of chlorine dioxide and decrease the background concentrations of chlorine and chlorite. modifications were (a) doubling the concentrations sodium reagent of chlorite and sulfuric acid and (b) precooling the receiving solution

#### 1.3.5 Monochloramine

#### For As(III):

$$H_3AsO_3 + NH_2Cl + H_2O \rightarrow$$
 (21)  
 $HAsO_4^{2-} + NH_4^{+} + Cl^{-} + 2H^{+}$ 

 $SR = 0.69 \mu g NH_2Cl/\mu g As(III)$ 

#### For Fe(II):

$$2Fe^{2+} + NH_2Cl + 6H_2O \rightarrow$$
 (22)  
 $2Fe(OH)_3 (s) + NH_4^+ + Cl^- + 4H^+$ 

 $SR = 0.46 \mu g NH_2Cl/\mu g Fe(II)$ 

#### For Mn(II):

$$Mn^{2+} + NH_2Cl + 2H_2O \rightarrow$$
 (23)  
 $MnO_2(s) + NH_4^+ + Cl^- + 2H^+$ 

 $SR = 0.94 \mu g NH_2Cl/\mu g Mn(II)$ 

#### For Sulfide:

$$S^{2-} + NH_2Cl + 2H^+ \rightarrow (24)$$
  
 $S^0 \downarrow + NH_4^+ + Cl^-$ 

 $SR = 1.61 \mu g NH_2Cl/\mu g S^2$ 

#### 1.4 Research Objectives

The overall objective of this study was to determine the effectiveness of five chemical oxidants. a solid-phase oxidizing media, and UV radiation in oxidizing As(III) to As(V) under a variety of environmental conditions. Potentially interfering reductants such as dissolved manganese, dissolved iron, sulfide and TOC were studied as they arsenictypically present in contaminated waters. The specific objectives of this study were as follows:

- (1) Study the effectiveness of (a) chlorine (b) permanganate (c) ozone, (d) chlorine dioxide, (e) monochloramine, (f) solid-phase oxidizing media and (g) UV radiation (@254 nm) for the oxidation of As(III) to As(V).
- (2) Determine the effect of pH, in the range of 6.3-8.3, on the oxidation of As(III) to As(V).
- (3) Determine the effect of potentially interfering reductants including dissolved iron, dissolved manganese, sulfide, and TOC, and the effect of low temperature (5 °C) on the oxidation process.

#### 2. Materials and Methods

# 2.1 Synthetic Test Water Composition

The composition of the synthetic test water used to perform the oxidation

experiments is shown in Table 2-1. The synthetic test water contained most of the common ions found in surface and ground waters.

Table 2-1. Composition of Synthetic Test Water.

Cations	meq/L	mg/L	Anions	meq/L	mg/L
Na <sup>+</sup> Ca <sup>2+</sup> Mg <sup>2+</sup>	3.3	75.9	HCO <sub>3</sub> · SO <sub>4</sub> <sup>2</sup> ·	3.0	183.0
Ca <sup>2+</sup>	2.0	40.2	$SO_4^{2-}$	0.5	24.0
$Mg^{2+}$	1.0	12.2	Cl <sup>-</sup>	2.5	88.8
			Silicate as	0.3	20.0
			$\mathrm{SiO}_2$		
Total	6.3	128.3		6.3	315.8

Calculated TDS = 128.3 + 315.8 - 93 mg/L (loss of H<sub>2</sub>CO<sub>3</sub> during evaporation) = 351.1 mg/L

#### 2.2 Interfering Reductants

Synthetic water was amended with potentially interfering reductants and studied for their ability to affect As(III)

oxidation. The various interfering reductants studied are listed in Table 2-2 along with their concentrations.

Table 2-2. Interfering Reductants.

Interfering Reductant	Concentration (mg/L)
Manganese (Mn(II))	0.2
Iron (Fe(II))	0.3, 2.0
Sulfide (S <sup>2</sup> -)	1.0, 2.0
Total Organic Carbon (TOC)	1.4-6.9

#### 2.3 Speciation Method

A 3M Empore anion exchange filter (hereafter referred to simply as IX filter) was used to speciate As(III)/As(V). The filter was preconditioned according to the manufacturers recommendations (See Appendix A). Following the manufacturers preconditioning procedure, the IX filter was further

conditioned (UH Method—See Appendix A) by acid regeneration and 1 M NaCl treatment to ensure that all exchange sites on the filter were in the chloride form prior to initial use or reuse of the filter. Finally, excess 1 M NaCl was rinsed from the filter with 0.005 M NaCl. Analytical reagent grade

chemicals were used throughout the procedure.

# 2.4 Chemical Oxidation Experiments

The procedures developed to design and operate the oxidation reactor are described here. The design of the reactor is described in detail in Section 2.4.1. Before the oxidation reactor could be used to study any of the chemical oxidants, the reactor set-up was tested to (a) prove that the IX filters used in-line oxidation reactor with the could efficiently remove (≥90% retention) As(V), (b) prove that the IX filters caused no inadvertent oxidation of As(III) (≥90% recovery), (c) determine the dead volume in the reactor set-up, and (d) determine the efficiency of oxidant mixing in the reactor. Section 2.4.2 describes these tasks and the procedures used to achieve them. Section 2.4.3 describes the procedures used during routine operation of the oxidation reactor in either high- or low-DO synthetic water. Finally, Section 2.4.4 discusses chemical oxidation experiments performed to study the effect of TOC and low temperature.

The procedures described in Sections 2.4.2 - 2.4.4 have some common steps. irrespective of the objective of the experiments. At the same time, depending on the objective, there were certain inherent differences in the procedures used to operate the reactor. For example, a larger sample volume was desired when testing the reactor setup to determine the capacity of the IX filter whereas a smaller sample volume was required during oxidation experiments. However, in the interest of thoroughness, and at the risk of being repetitive, the procedures are described exactly as they were performed.

#### 2.4.1 Reactor Design

The schematic design of the oxidation reactor is shown in Figure 2-1 and the elevation and plan views are shown in Figures 2-2 and 2-3, respectively. To simplify the drawing, the side port for the pH probe is not shown in the plan view. The reactor was equipped with a pH probe, a nitrogen gas inlet, a pressure relief valve, a septa for injecting the oxidant, and an outlet port. The reactor was made of clear Plexiglas and fabricated at the University of Houston Machine Shop.

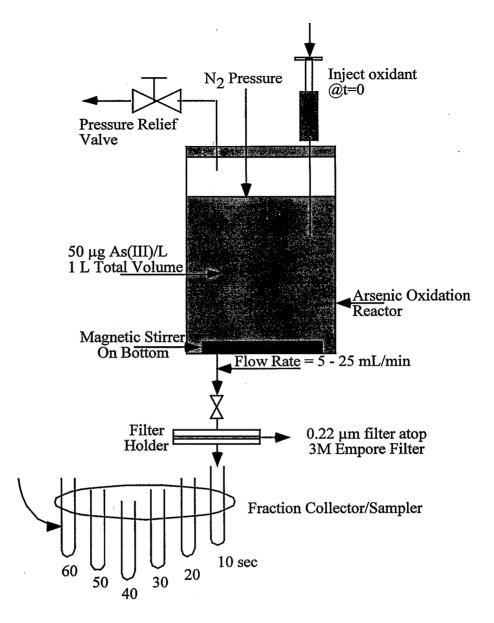


Figure 2-1. Schematic for Oxidation Reactor.

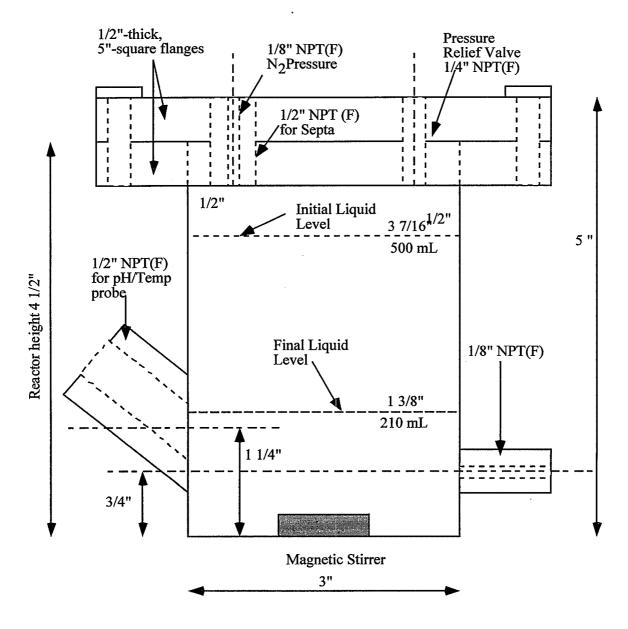


Figure 2-2. Elevation View of Oxidation Reactor. Scale 1:1

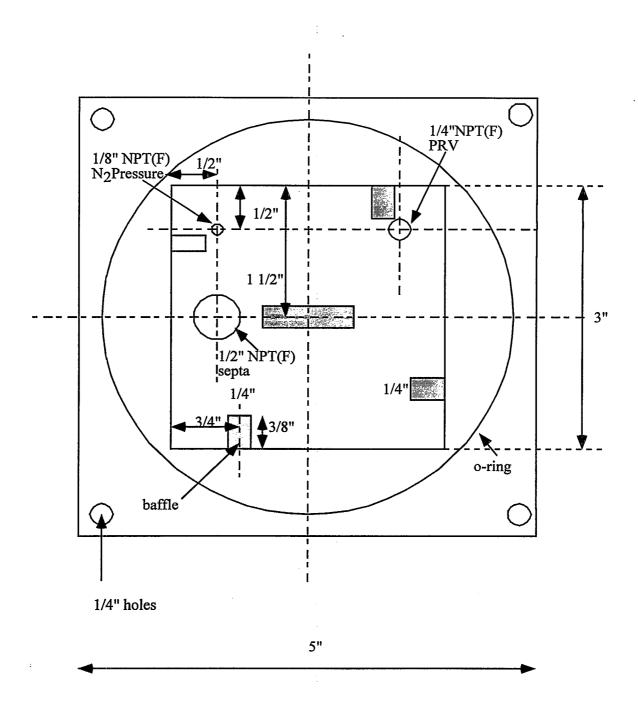


Figure 2-3. Simplified Plan View of Oxidation Reactor. Scale 1:1

#### 2.4.2 Testing Reactor Set-up

#### 2.4.2.1 Arsenic(V) Retention

To ensure that  $\geq 90\%$  As(V) was retained by the IX filter, synthetic test waters containing 50 and 1000 µg As(V)/L were passed through the IX filter. After the passage of a predetermined volume of the As(V)-containing solution, the IX filter was regenerated and reused for further testing. In all, six sequential runs were performed. The first run was performed using a fresh IX filter, whereas, the next five were performed using a regenerated IX filter. The procedures used during testing are described in Appendix B.

#### 2.4.2.2 Arsenic(III) Passage

To ensure that  $\geq$  90% As(III) passed through the IX filter, synthetic waters containing 50 and 1000 µg As(III)/L were tested. The procedures used for the As(III)-passage experiments were the same as those used for the As(V)-retention experiments described in Appendix B.

#### 2.4.2.3 System Dead Volume

The dead volume in the sampling system consisted of the volume of tubing connecting the oxidation reactor and the filter holder plus the dead volume in the filter holder itself. The dead volume inside the filter holder was necessary in to evenly distribute throughout the surface of the filter. This dead volume had to be wasted before the contents of the reactor could be sampled. The dead volume could not be calculated directly because of problems calculating the void space within the filter holder.

The dead volume of the reactor set-up was estimated by introducing a stepincrease in arsenic concentration (from 0-1000 µg/L) into the well-mixed reactor and then plotting the effluent arsenic concentration vs volume passed through the IX filter. Specifically, 500 mL of arsenic-free synthetic test water was placed in the reactor. The reactor was pressurized and the necessary volume of As(III) solution was injected into the reactor at t = 0 to give a final concentration of 1000 µg As(III)/L. The reactor outlet valve was opened immediately at t = 0 (flow rate = 5 mL/min) and samples (0.5 mL) were collected in the fraction collector at an interval of 6 seconds.

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#### 2.4.2.4 Oxidant Mixing Efficiency

When the oxidant was introduced into the reactor, it was important that it mixed instantaneously with the contents of the reactor, so that inefficiencies in mixing did not lead to erroneous conclusions about the kinetics of As(III) oxidation. Mixing of the oxidant was assumed to be adequate if As(III) was immediately oxidized by a large excess (200-fold) of chlorine injected into the mixed reactor. To determine the efficiency of oxidant mixing in the reactor, a 10 µg/L As(III) solution was placed in the reactor. At time t = 0, a chlorine dose of 2 mg/L (200-fold excess over stoichiometric requirement) was added to the reactor. The first 4 mL of reactor effluent was wasted as dead volume and the rest was collected in 2mL increments at 6 second intervals (flow rate = 20 mL/min).

#### 2.4.3 Chemical Oxidation Conditions

Each initial As(III) concentration was tested with at least three concentrations of each oxidant: three-, ten-, and one-hundred times the stoichiometric amount required to oxidize the As(III) initially Two levels of oxidant were used in the presence of interfering reductants: ten times based on As(III) concentration alone, or a higher dose of three-times-stoichiometric based As(III) plus the interfering reductant. However, if the lower dose successfully oxidized greater than 90% of the As(III) initially present, then higher oxidant doses were not tested. Initial As(III) concentration was 50 μg/L, unless mentioned otherwise. Chlorine was the dosed of sodium in form hypochlorite (NaOCl) and reported as mg/L chlorine.

All the chemical oxidation experiments well as the UV oxidation performed experiments) were duplicate. One control experiment was performed for each set of duplicate The control experiment experiments. was performed under identical conditions as the duplicated experiments with the exception that no oxidant was Therefore. added. the control experiment established As(III) losses due to adsorption to the walls of the or other parts, and reactor established any potential As(III) losses due to reaction with the interfering oxidants such as sulfide or dissolved iron. During the course of this study, several such control experiments were performed and no As(III) losses were result of arsenic observed as a adsorption. precipitation or Furthermore, all the oxidation data indicated that when sulfide was present, more rather than less As(III) passed through the IX filter, which suggests that sulfide did not precipitate and remove As(III).

#### 2.4.3.1 pH of Operation

For all of the oxidants studied, the extent of As(III) oxidation was determined for a pH range of 6.3 - 8.3. The effect of interfering reductants was only studied at pH 8.3 because previous studies had suggested that typical As-containing groundwaters would have pH values of  $8.3 \pm 0.6$  (Clifford and Lin, 1986, 1991; Clifford, 1990; Clifford and Zhang, 1994; Clifford, et al., 1991, 1998a, 1998b; Ghurye, et al., 1998, 1999). This may, however, not be true for all Ascontaining waters.

#### 2.4.3.2 High- and Low-DO Experiments Chemical oxidation experiments, in which the effect of dissolved iron on As(III) oxidation was studied, had to be performed in very low DO waters ( $\leq 0.1$ mg/L DO) because dissolved iron (Fe(II)) is very easily oxidized in the presence of DO at greater than neutral pH values (Knocke et al. 1990). Additionally, chemical oxidation experiments with sulfide-spiked synthetic water were also performed in the absence of DO because sulfide can be oxidized by DO. Dissolved oxygen did not present a problem with the other interfering reductants studied.

chemical oxidation The high-DO experiments were performed by raising the DO of the synthetic water to nearsaturation, by sparging with air (from the lab air-distribution system) through a diffuser for about 15 minutes. The procedures used during these experiments are described in Appendix The low-DO chemical oxidation experiments were performed by sparging extra dry grade nitrogen gas (containing approx. 3 ppm  $O_2$ ) through the synthetic water to reduce the DO to  $\leq 0.1$  mg/L as measured by a lab DO meter. The procedures used during the low-DO experiments are described in detail in Appendix C.

2.4.3.3 Oxidation Experiments with TOC In order to determine the effect of TOC on the oxidation of As(III) with the five oxidants, untreated Lake chemical Houston water (not previously exposed to oxidants) was filtered sequentially through a 8.0, 0.45, and 0.22 µm filters and then stored at 4 °C. Prior to an experiment, the filtered Lake Houston water was allowed to come to room temperature (~24 °C). This was either used directly by spiking with an appropriate amount of As(III) or diluted with synthetic water to yield a water with 2.1 mg/L TOC as in the ozone experiments. The TOC in the filtered Lake Houston water was not characterized.

## 2.4.3.4 Low Temperature (5 °C) Oxidation

A limited number of experiments were performed at 5 °C to determine the effect of low temperature on As(III) oxidation. Only those oxidants that were successful in oxidizing As(III) to As(V) were tested at low temperature. The general procedure for performing experiments was the same as the other chemical oxidation experiments. Additionally, the oxidation kinetics reactor, filled with 500 mL of synthetic water containing 50 µg/L As(III), was refrigerated to a temperature of  $5 \pm 1$  °C. Upon attaining the required temperature, the reactor was quickly removed from the refrigerator and dosed with the

oxidant. The appropriate entire experiment was usually completed in less than 6 minutes from the time the was removed the reactor from refrigerator. At the end of the experiment. the reactor water temperature was usually in the range of 5-6 °C.

# 2.5 Solid-Phase Media (Filox) Experiments

The solid-phase oxidizing media used in this project was Filox-R<sup>TM</sup> (Matt-Son Inc, Barrington, IL), which is typically used for iron, hydrogen sulfide and manganese removal. The gray-black granular Filox media (12 x 40 mesh, bulk density 114 lbs/ft<sup>3</sup>) containing 75-85% manganese dioxide, reportedly an oxidation-reduction utilizes filtration process for removal dissolved iron, hydrogen sulfide and manganese. In this study, the media was used to oxidize As(III) to As(V) under a variety of conditions.

#### 2.5.1 Pretreatment of Filox Media

Approximately 100 mL of the Filox media was backwashed with synthetic water (of the composition in Table 1 and without any As(III)) in a 1 in.-i.d. glass column at a flow rate of 285 mL/min (14 gal/min ft<sup>2</sup>) for 30 minutes. backwashing, 12 mL of media was transferred to a 1 cm-i.d. glass column. The bed depth was 6 inches (15 cm) and the flow rate was varied from 16 mL/min (EBCT of 0.75 min) to 2 mL/min (EBCT of 6.0 min). schematic for the Filox experiments is shown in Figure 2-4. All of the Filox experiments were performed with the same 12 mL of media, which was not treated in any way except for periodic backwashing.

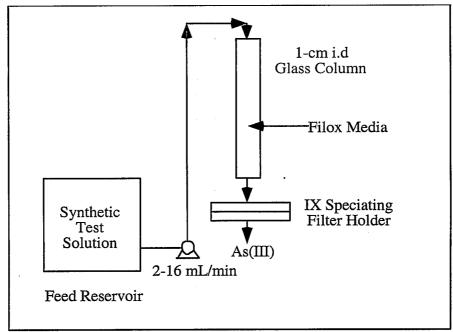


Figure 2-4. Schematic for Solid-Phase (Filox) Oxidizing Experiments.

#### 2.5.2 Preparation of Low- and High-DO Synthetic Water

The high-DO synthetic water (8.2 mg/L DO) was prepared by sparging air through synthetic water for about 15 minutes prior to passage through the Filox column. The low-DO synthetic water (0.1 mg/L DO) was prepared by sparging extra-dry-grade nitrogen for 30 minutes through 500 mL of synthetic water (or filtered Lake Houston water) contained in the oxidation reactor.

## 2.5.3 Procedure for Variable-EBCT and Variable-pH Experiments

The procedures for the variable-EBCT and the variable-pH Filox experiments were identical except for the pH of the synthetic water. All of the variable-EBCT experiments were performed at a pH of 8.3 whereas during the variable-

pH experiments, the pH of the synthetic water was varied at 6.3, 7.3, and 8.3. The procedures are described in detail in Appendix D.

## 2.5.4 Procedure to Stabilize Arsenic Removal by Filox Media

During the variable-EBCT experiments, it was observed that the Filox media, in addition to oxidizing As(III) to As(V), also removed arsenic. To enable the media to come to equilibrium with the As(III)-containing water represent what would occur in a Filox actual field use, column in preequilibration of the media attempted. To achieve equilibrium, 2000 BV (24 L) of pH 8.3 synthetic water containing 50 µg/L As(III) was passed through the media at an EBCT of 0.75 min.

## 2.5.5 Procedure for Low-DO Filox Experiments

As mentioned earlier, the low-DO synthetic water was prepared in the oxidation reactor in the same manner as during the chemical oxidation experiments. The low-DO synthetic water was then pumped directly from the reactor to the Filox column. The

procedures used are described in detail in Appendix D.

#### 2.6 UV Oxidation Experiments 2.6.1 Unit 1: 0.5 gpm UV Sterilizer Unit

A schematic for the UV oxidation experiments is shown in Figure 2-5. The experimental set-up for the UV experiments was the same as for the Filox experiments except that the Filox column was substituted with a UV unit.

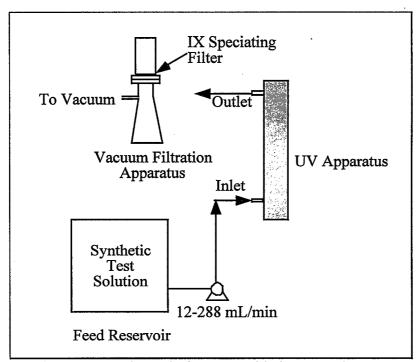


Figure 2-5. Schematic for UV-Oxidation Experiments.

Unit 1 was a 0.5 gpm unit from R-Can Environmental Inc. (Canada), equipped with a low-pressure mercury lamp with an advertised lamp intensity of 32,000  $\mu$ w/cm<sup>2</sup> at 254 nm. The unit was mounted vertically with the electrical connections to the lamp on top to prevent accidental water spillage from damaging the sterilizer assembly. As

seen from Figure 2-5, the lower port was chosen as the inlet and the upper port the outlet. A 4-L HDPE container was filled with synthetic water containing 50  $\mu$ g As(III)/L. Before the UV lamp was turned on, the synthetic test water was pumped through the inactive sterilizer assembly at 288 mL/min (residence time 1.0 min), and the effluent from the

sterilizer unit was collected, speciated, and analyzed for As(III). This served as a control for the UV experiments to ensure that the act of pumping the synthetic water through the inactive sterilizer unit did not cause any inadvertent As(III) oxidation. The flow was then switched to the lowest setting corresponding to the highest residence time employed. The lamp was switched on and allowed to stabilize for 30 minutes, which is much longer than the 3-5 minutes recommended by manufacturer. At the end of 30 minutes, three consecutive 50-mL samples were collected, speciated, and analyzed as As(III). The flow was then increased to the next flow rate and 600 mL (> two times the void space of 288 mL in the sterilizer assembly) of effluent was wasted before three consecutive 50-mL samples were collected, speciated and analyzed for unoxidized As(III). above procedure was repeated until all of the flow rates were studied. temperature of the water exiting the UV unit was not measured.

## 2.6.2 Unit 2: 1.0 gpm UV Sterilizer Unit

Unit 2 was a 1.0 gpm unit from Atlantic Ultraviolet Corp., equipped with a low-

pressure mercury lamp with an advertised lamp intensity of 41,200  $\mu$ w/cm<sup>2</sup> at 254 nm. The experimental set-up and operation were similar to the one used for Unit 1. The void space in Unit 2 was larger, 486 mL, compared with 288 mL for Unit 1.

#### 2.7 QA/QC

#### 2.7.1 Arsenic Standards

Four standards from an arsenic AAS standard solution (Aldrich Chemical Company, Inc.) containing 1000 µg As/mL were employed for routine arsenic analysis. The concentrations of these "WAL standards" were 1.3, 2.8, 6.8, and 11.0 μg/L. Independently, the QA/QC Officer for this project, prepared four separate arsenic standards, which served as internal QA/QC standards. Two such sets of four QA/QC standards were prepared by the QA/QC Officer during the duration of this project. In addition to the standards prepared at UH, we utilized four previous "Water Supply Laboratory Performance Evaluation Study" standards. These standards were preserved in a 0.2 M nitric acid solution. These WS standards and their EPAreported true concentrations are as follows:

Table 2-3. Previous EPA Standards

Table 2-3. Ticylous Li A blandards.					
Standard	Year	EPA-Reported			
		Concentration			
		μg/L			
WS 037	1996	49.3			
WS 038	1997	83.1			
WS 040	1997	102			
WS 041	1998	65.6			

A stock solution containing 88.0 mg/L As(III) was prepared according to the procedure described in Appendix L.

#### 2.7.2 Routine Arsenic Analysis

Routine arsenic analyses were performed by the WAL during the course of this project. Each batch of samples was analyzed according to the following sequence:

- (1) A prep blank (prepared the same as a routine sample with the exception that reagent grade water was substituted for the arsenic sample) was analyzed followed by the four WAL standards. Then, one of the four QA/QC standards was analyzed. This sequence is hereafter referred to as a "set of standards."
- (2) Following measurement of the set of standards, no more than 20 samples were analyzed. This was followed by the analysis of the set of standards. Once again, no more than 20 samples were analyzed followed by the set of standards, and so on until all of the samples had been analyzed.

- (3) Then each of the four WS standards was measured. Each of the WS standards was spiked with  $2.0~\mu g/L$  arsenic and measured to calculate spike recoveries.
- (4) Finally, the set of standards was measured to complete the analyses.

#### 2.7.3 Arsenic Calibration Curve

A calibration curve was developed for arsenic based on the prep blank and the four WAL standards. The OA/OC standard was thus excluded from the points contributing to the calibration curve and its concentration calculated on the basis of the calibration Figure 2-6 shows a typical curve. calibration curve with the QA/QC standard included for comparison. Figure 2-6, each standard was measured eight times. The concentration of the OA/OC standard in Figure 2-6 was 5.97 μg/L and the average of eight measurements of the QA/QC standard was  $5.91 \mu g/L$ .

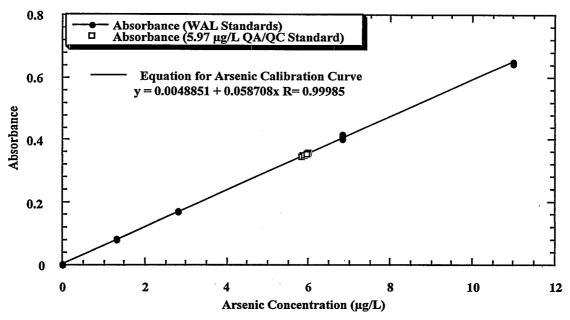


Figure 2-6. Typical Arsenic Calibration Curve.

#### 2.8 Analytical Methods

Table 2-4 shows the various analytical methods used during the course of this project. Only chlorine dioxide was

analyzed by multiple methods for the reasons mentioned in the Results and Discussion section of this report.

Table 2-4. Analytical Methods

Total Arsenic	SM 3114 A (Hydride Generation)
Chlorine, nitrate, sulfate	SM 4110 B (Ion Chromatography)
Total Organic Carbon	SM 5310 B (Combustion-Infrared)
Sulfide	Hach Manual. EPA-approved and adapted from
	SM 4500-S <sup>2</sup> - E (Colorimetric)
Fe and Mn	SM 3111 B (Atomic Absorption)
Chlorine (hypochlorite)	Potentiometric Method of Knocke, et al. (1990)
Chlorine Dioxide	Potentiometric Method of Knocke, et al. (1990)
	SM 4500-ClO <sub>2</sub> -D (DPD Method)
	Hach Method 8138 (Direct UV absorbance @445
	nm)
Ozone	Hach Method 8311 (Colorimetric)
Permanganate	Potentiometric Method of Knocke, et al. (1990)
Monochloramine	SM 4500-Cl G (DPD Method)
	·

#### 3. Results and Discussion

# 3.1 Reactor Set-up Test Results

#### 3.1.1 Arsenic(V) Retention

The IX filter was challenged with synthetic water (composition shown in Table 1) containing As(V) concentrations of 50 and 1000  $\mu$ g/L. The results are shown in Figures 3-1 and 3-2. It can been seen that for the first

100 mL passing through the filter, greater than 98% As(V) retention was obtained with 50  $\mu$ g/L solution and greater than 95% for the 1000  $\mu$ g/L solution. For both As(V) concentrations, at least 100 mL of synthetic water could be put through the IX filter (@ 20 mL/min) before arsenic leakage exceeded 5%.

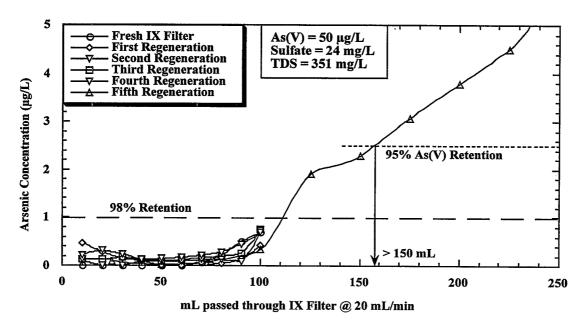


Figure 3-1. 50  $\mu$ g/L-As(V) Retention by IX Filter.

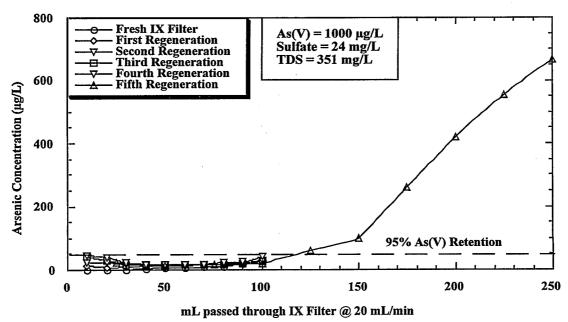


Figure 3-2. 1000 µg/L-As(V) Retention by IX Filter.

#### 3.1.2 Arsenic(III) Recovery

It was also necessary to demonstrate that the unoxidized As(III) that passed from the oxidation reactor through the speciation media was not adsorbed or oxidized by the speciation media. Figures 3-3 and 3-4 show the As(III) recoveries with initial arsenic

concentrations of 50 and 1000  $\mu$ g/L. No significant As(III) oxidation resulted from use of the IX filter, and As(III) recovery averaged 95-105% for the 50  $\mu$ g As(III)/L-spiked water and 90-110% for the 1000  $\mu$ g As(III)/L-spiked water.

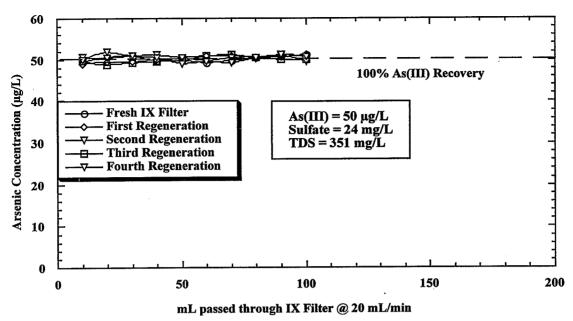


Figure 3-3. 50 μg/L-As(III) Recovery from IX Filter.

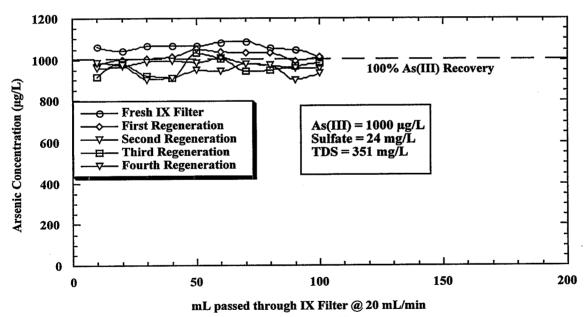


Figure 3-4. 1000 μg/L-As(III) Recovery from IX Filter.

## 3.1.3 Dead Volume in the Oxidation Reactor Set-up

The results of the dead-volume experiment are presented in Figure 3-5, which shows the volume of system

effluent that must pass through the IX filter before the actual reactor effluent is sampled. The response was 50 and 80% after 2 and 4 mL of flow, respectively. The true dead volume is probably closer

to 2 mL, the point at which 50% of the response is achieved. However, due to the presence of water in the dead space above the IX filter in addition to water within the filter itself, and the inevitable mixing (and dilution) that results

between the incoming flow from the reactor and the water in the dead space, it took 4 mL of flow for the response to reach 80% and nearly 8 mL to reach 100%.

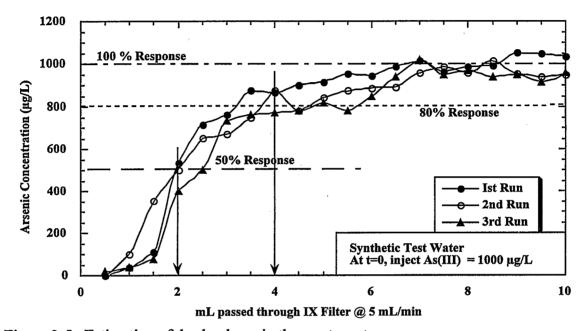


Figure 3-5. Estimation of dead volume in the reactor set-up.

A certain initial volume of effluent from the reactor had to be wasted to compensate for the dead volume in the system, after which the actual contents of the reactor could be sampled. Therefore, if the dead volume was not wasted, then the first few samples would be substantially diluted by the fluid in the dead volume. Also note that during actual oxidation experiments, when fluid exits the reactor, the oxidation reaction continues because the oxidant is still in contact with As(III). Therefore, the time spent to waste the dead volume must be taken into account.

Based on Figure 3-5, it was decided that four mL (corresponding to >80%

response) of the reactor effluent would have to be wasted before the actual reactor contents could be sampled. Thus, for a sampling flow rate of 20 mL/min during actual oxidation experiments, the first sample that represented the dead volume (4 mL) was collected during the 0-12 second interval. The next sampling interval was 12-18 sec (median time 15 sec). Consequently, no reaction time earlier than 15 sec could be studied.

## 3.1.4 Mixing Efficiency in Oxidation Reactor

The results of this experiment showed that the effluent arsenic concentrations (representing unoxidized As(III)) were usually lower than 0.4 µg/L (Figure 3-6). The low effluent As(III) concentrations confirmed the rapidity of As(III) oxidation by chlorine as previously reported by Frank and Clifford (1986) and also showed the efficiency of mixing

in the reactor. If the reactor had provided inadequate mixing, the initial effluent As(III) concentrations (for t = 15 seconds) would have been much higher than was actually observed.

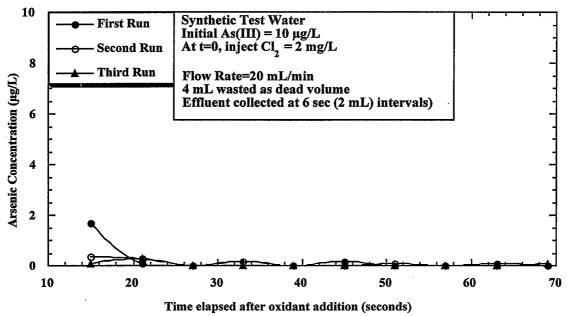


Figure 3-6. Mixing efficiency in oxidation reactor.

#### 3.2 Chlorine Test Results

The results of the chlorine oxidation experiments are summarized in Table 3-1 and discussed below.

### 3.2.1 Effect of pH on Chlorine

Chlorine rapidly oxidized As(III) in the pH range of 6.3-8.3 (Table 3-1, experiments 1-3 and Figure 3-7). Oxidation was slightly slower at pH 6.3 but still complete in 39 seconds. Higher

As(III) concentrations were also completely and rapidly oxidized by chlorine (Table 3-1, experiment 11). The time reported (in Table 3-1 and similar Tables elsewhere) to >95% oxidation was the median time of its sample interval, i.e., if greater than 95% oxidation was observed in the earliest sampling interval, 12-18 sec, then the time was reported as 15 seconds.

Table 3-1. Free Chlorine Experiments.

#	As(III)	Chlorine	SR <sup>2</sup>	SR <sup>3</sup>	pН	Interfering	>95%
	Conc	Conc <sup>1</sup>	$Cl_2/As$	Cl <sub>2</sub> /		Reductant	$Oxid^4$
	(μg/L)	(mg/L)	_	(As+IR)		(IR)	(sec)
1	50	0.14	3	NA	8.3	None	15
2	50	0.14	3	NA	7.3	None	15
3	50	0.14	3	NA	6.3	None	39
4	50	0.48	10	1.55	8.3	Fe (II) (0.3 mg/L)	15
5	50	0.48	10	0.27	8.3	Fe (II) (2.0 mg/L)	15
6	50	0.48	10	1.20	8.3	Mn (II) (0.2 mg/L)	27
7	50	0.48	10	$0.21^{5}$	8.3	$S^{2-}$ (1.0 mg/L)	57
8	50	0.48	10	$0.11^{5}$	8.3	$S^{2-}(2.0 \text{ mg/L})$	57
9	50	0.48	10	NA	8.3	TOC (6.9 mg/L)	15
10	50	0.14	3	NA	8.3	Temperature (5 °C)	15
11	1000	2.84	3	NA	8.3	None	15

<sup>1-</sup>Oxidant dosed as NaOCl, reported as mg/L chlorine

<sup>5—</sup>Based on oxidation of sulfide to elemental sulfur

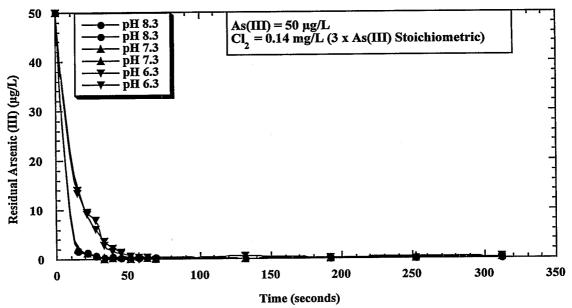


Figure 3-7. Effect of pH on As(III) Oxidation with Free Chlorine.

<sup>2—</sup>Stoichiometric Ratio of Oxidant/As(III)

<sup>3—</sup>Stoichiometric Ratio of Oxidant/(As(III) + Interfering Reductant)

<sup>4—</sup>Average of duplicate runs

### 3.2.2 Effect of Dissolved Manganese and Iron on Chlorine

The results of the dissolved manganese and iron experiments at pH 8.3 are shown in Table 3-1, experiments 4, 5 and 6. Only a slight effect of dissolved manganese was observed on As(III) oxidation where complete oxidation was observed in 27 seconds with Mn(II) present compared with 15 seconds in the absence of Mn(II). Dissolved iron had no effect on As(III) oxidation at pH 8.3.

#### 3.2.3 Effect of Sulfide on Chlorine

The results of the sulfide experiments are shown in Table 3-1, experiments 7 and 8. Although sulfide (1.0 and 2.0 mg/L) slowed the oxidation reaction. complete oxidation was still obtained in less than 1 min (Figure 3-8). However, concentrations sulfide higher further slow As(III) oxidation so that reaction times much greater than 1 min higher oxidant doses become necessary to achieve complete As(III) oxidation.

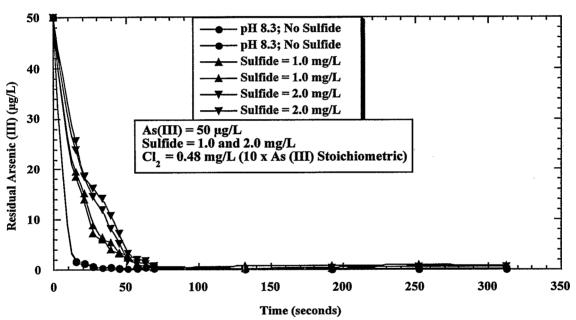


Figure 3-8. Effect of sulfide on As(III) oxidation with free chlorine.

# 3.2.4 Effect of TOC and Temperature on Chlorine

The results of the TOC and temperature experiments are shown in Table 3-1; experiments 9 and 10. Neither the presence of 6.9 mg/L TOC in Lake Houston water nor a low temperature of 5 °C had any significant effect on As(III) oxidation because the time required for

complete oxidation for both conditions was the same as that required when no interfering reductants were present.

# 3.3 Permanganate Test Results

Eleven experiments were conducted using permanganate as an oxidant, and a

summary of the results is shown in Table 3-2

3.3.1 Effect of pH on Permanganate
Permanganate rapidly oxidized As(III) in
the pH range of 6.3-8.3 (Table 3-2,

experiments 1-3 and Figure 3-9). Oxidation was slightly slower at pH 6.3 but still complete in 33 seconds. Higher As(III) concentrations were also completely and rapidly oxidized by permanganate (Table 3-2, experiment 11).

Table 3-2. Permanganate Experiments.

#	As(III)	$MnO_4$	$SR^1$	$SR^2$	pH	Interfering	>95%
	Conc	Conc	$MnO_4$	$MnO_4$		Reductant	Oxid <sup>3</sup>
	(μg/L)	(mg/L)	As	(As+IR)		(IR)	(sec)
1	50	0.16	3	NA	8.3	None	15
2	50	0.16	3	NA	7.3	None	15
3	50	0.16	3	NA	6.3	None	33
4	50	0.53	10	1.99	8.3	Fe (II) (0.3 mg/L)	21
5	50	0.53	10	0.36	8.3	Fe (II) (2.0 mg/L)	15
6	50	0.53	10	1.55	8.3	Mn (II) (0.2 mg/L)	21
7	50	0.53	10	0.214	8.3	$S^{2-}(1.0 \text{ mg/L})$	51
8	50	0.53	10	$0.11^{4}$	8.3	$S^{2-}$ (2.0 mg/L)	51
9	50	0.53	10	NA	8.3	TOC (6.9 mg/L)	15
10	50	0.16	3	NA	8.3	Temperature (5 °C)	15
11	1000	3.20	3	NA	8.3	None	15

<sup>1—</sup>Stoichiometric Ratio of Oxidant/As(III)

<sup>2—</sup>Stoichiometric Ratio of Oxidant/(As(III) + Interfering Reductant)

<sup>3—</sup>Average of duplicate runs

<sup>4—</sup>Based on oxidation of sulfide to elemental sulfur

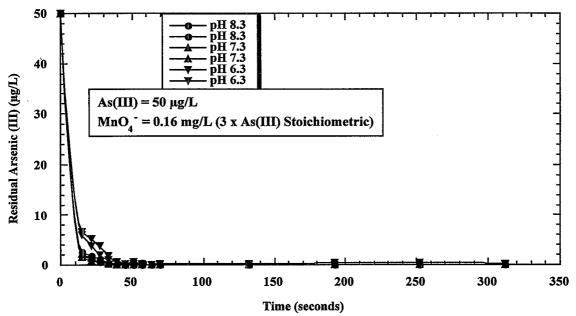


Figure 3-9. Effect of pH on As(III) oxidation with permanganate.

# 3.3.2 Effect of Dissolved Manganese and Iron on Permanganate

The results of the dissolved manganese and iron experiments are shown in Table 3-2, experiments 4, 5 and 6. Neither dissolved manganese nor dissolved iron (Fe(II)) had any significant effect on As(III) oxidation at pH 8.3 with complete oxidation achieved in 21 seconds or less.

# 3.3.3 Effect of Sulfide on Permanganate

The results of the sulfide experiments are shown in Table 3-2, experiments 7 and 8. Although sulfide (1.0 and 2.0 mg/L) slowed the oxidation reaction, complete oxidation was still obtained in less than 1 min (Figure 3-10). However, higher sulfide concentrations may further slow As(III) oxidation such that reaction times much greater than 1 min and/or higher oxidant doses will be required to achieve complete oxidation.

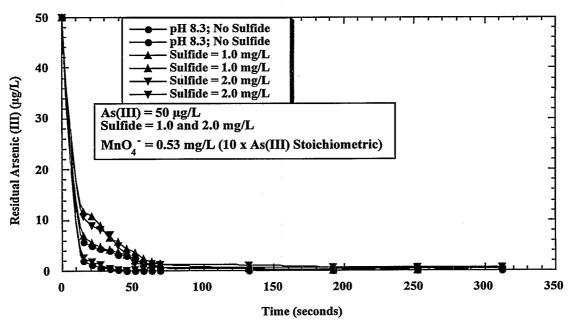


Figure 3-10. Effect of sulfide on As(III) oxidation with permanganate.

# 3.3.4 Effect of TOC and Temperature on Permanganate

The results of the TOC and temperature experiments are shown in Table 3-2, experiments 9 and 10. Neither the presence of TOC nor a low temperature of 5 °C had any significant effect on As(III) oxidation by permanganate.

Complete oxidation was achieved for both the conditions in 15 seconds.

#### 3.4 Ozone Test Results

Eleven experiments were conducted using ozone as an oxidant, and a summary of the results is shown in Table 3-3.

Table 3-3. Ozone Experiments.

#	As(III)	Ozone	$SR^1$	SR <sup>2</sup>	pН	Interfering	>95%
	Conc	Conc	O <sub>3</sub> /As	$O_3/$		Reductant	$Oxid^3$
	$(\mu g/L)$	(mg/L)	-	(As+IR)		(IR)	(sec)
1	50	0.10	3	NA	8.3	None	15
2	50	0.10	3	NA	7.3	None	15
3	50	0.10	3	NA	6.3	None	15
4	50	0.32	10	1.99	8.3	Fe (II) (0.3 mg/L)	15
5	50	0.32	10	0.36	8.3	Fe (II) (2.0 mg/L)	15
6	50	0.32	10	1.55	8.3	Mn (II) (0.2 mg/L)	15
7	50	0.32	10	$0.21^{4}$	8.3	$S^{2-}(1.0 \text{ mg/L})$	51
8	50	0.32	10	$0.11^{4}$	8.3	$S^{2-}$ (2.0 mg/L)	132
9	50	0.32	10	NA	8.3	TOC (2.1 mg/L)	27
10	50	0.32	10	NA	8.3	TOC (6.9 mg/L)	NA <sup>5</sup>
11	50	0.10	3	NA	8.3	Temperature (5 °C)	39

<sup>1—</sup>Stoichiometric Ratio of Oxidant/As(III)

#### 3.4.1 Effect of pH on Ozone

In the range of 6.3-8.3, pH had no effect on As(III) oxidation with complete oxidation achieved in 15 seconds as seen in Table 3-3, experiments 1-3 and Figure 3-11.

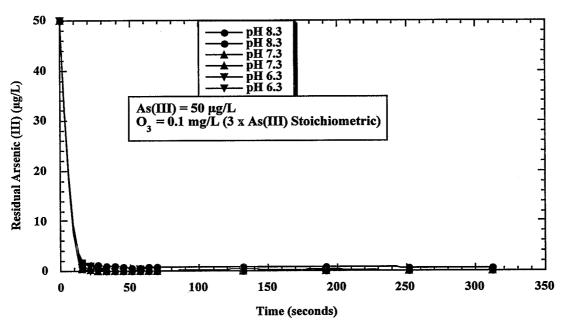


Figure 3-11. Effect of pH on As(III) oxidation with ozone.

<sup>2-</sup>Stoichiometric Ratio of Oxidant/(As(III) + Interfering Reductant)

<sup>3—</sup>Average of duplicate runs

<sup>4-</sup>Based on oxidation of sulfide to elemental sulfur

<sup>5-</sup>Max. oxidation achieved with 6.9 mg/L TOC was 38%

### 3.4.2 Effect of Dissolved Manganese and Iron on Ozone

The results of the dissolved manganese and iron experiments are shown in Table 3-3, experiments 4, 5 and 6. Neither dissolved Mn (0.2 mg/L) nor dissolved Fe (0.3 and 2.0 mg/L) had any effect on As(III) oxidation by ozone at pH 8.3, with complete As(III) oxidation being achieved in 15 seconds.

#### 3.4.3 Effect of Sulfide on Ozone

The results of the sulfide experiments are shown in Table 3-3, experiments 7 and 8. The presence of sulfide at 1.0

and 2.0 mg/L slowed As(III) oxidation by ozone at pH 8.3. At sulfide concentrations of 1.0 and 2.0 mg/L, greater than 95% oxidation was achieved in 51 and 132 seconds, respectively (Figure 3-12). By comparison, in the absence of sulfide, >95% oxidation was achieved in just 15 seconds and at a much lower ozone dose of three-times the stoichiometric requirement. however, that in the presence of 1.0 and 2.0 mg/L sulfide (SR = 0.21 and 0.11, respectively), there was insufficient ozone to oxidize both As(III) and sulfide.

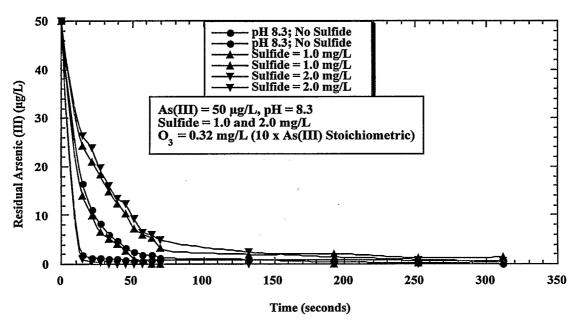


Figure 3-12. Effect of sulfide on As(III) oxidation with ozone.

# 3.4.4 Effect of TOC and Temperature on Ozone

The results of the TOC and temperature experiments are shown in Table 3-3, experiments 9 and 10. The presence of TOC had a significant quenching effect

on the ability of ozone to oxidize As(III) in filtered Lake Houston water (Figure 3-13). With 6.9 mg/L TOC, there was insufficient ozone present to oxidize both As(III) and the TOC. Since most arsenic-contaminated groundwaters are

unlikely to contain such high TOC, the Lake Houston water was diluted with synthetic water (composition shown in Table 2-1) to yield a TOC of about 2.1 mg/L. In the presence of this lower TOC

concentration, ozone was able to efficiently oxidize As(III), with greater than 95% oxidation achieved in 27 seconds.

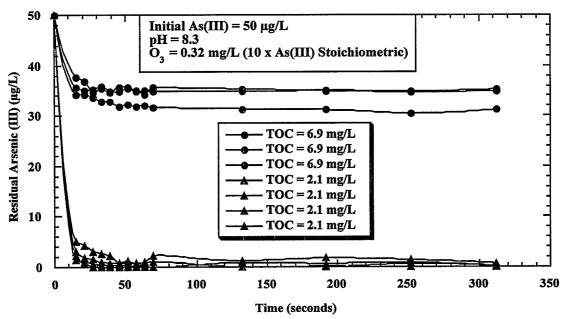


Figure 3-13. Effect of TOC on As(III) oxidation with ozone.

# 3.5 Chlorine Dioxide Test Results

Thirteen arsenic oxidation experiments with chlorine dioxide were performed assuming a conservative one-electron transfer mechanism. i.e., chlorine dioxide is converted to ClO<sub>2</sub> while oxidizing As(III) to As(V). The fiveelectron transfer mechanism was only used in calculating chlorine dioxide Fe(II)-oxidation doses for the experiments (Knocke, et al., 1990). The results of the thirteen tests summarized in Table 3-4.

### 3.5.1 Effect of pH on Chlorine Dioxide

In the pH range of 6.3-8.3, chlorine dioxide produced limited oxidation (20-30%) in 21 seconds and produced no oxidation (Table further experiments 1, 2, 3 and 9). In order to verify that the IX filter was undamaged by chlorine dioxide and functioning normally, two more experiments were performed, which included a three-times stoichiometric amount of chlorine injected at 117 seconds. If filter integrity was maintained, the unoxidized As(III) concentration would be in the range of 35-40 µg/L after chlorine dioxide addition, and then quickly drop to zero due to complete As(III) oxidation range of 35-40 µg/L after chlorine dioxide addition, and then quickly drop to zero due to complete As(III) oxidation after the addition of chlorine. The results of these experiments are shown in Figure 3-14, which shows that only 20-30% oxidation was obtained with

chlorine dioxide, but complete oxidation was achieved after the addition of chlorine. This test confirmed that the IX filter, which separates As(III) from As(V), was still effective after exposure to chlorine dioxide.

Table 3-4. Chlorine Dioxide Experiments.

				O DIOMIGO E			
#	As(III)	ClO <sub>2</sub> Conc	$SR^1$	$SR^2$	pН	Interfering	>95%
	Conc (µg/L)	(mg/L)	ClO <sub>2</sub> /As	ClO <sub>2</sub> /		Reductant	$Oxid^3$
				(As+IR)		(IR)	(sec)
1	50	0.27	3	NA	8.3,	None	>323
2	50	0.27	3	NA	7.3	None	>312
3	50	0.27	3	NA	6.3	None	>312
4	50	0.90	10	5.56	8.3	Fe (II) (0.3 mg/L)	>312
5	50	0.90	10	1.58	8.3	Fe (II) (2.0 mg/L)	>312
6	50	0.90	10		8.3	Mn (II) (0.2 mg/L)	>312
7	0	1.08	NA	1.12	8.3	$Fe(II) (4.0 \text{ mg/L})^4$	15
						Without silica	
8	0	1.08	NA	1.12	8.3	$Fe(II) (4.0 \text{ mg/L})^4$	15
9	50 <sup>5</sup>	0.27	3	NA	8.3	None	>312
10	50	$ClO_2 = 0.27$	3	NA	8.3	None	$>NA^6$
		$Cl_2=0.14$	3				
11	50	0.27	3	NA	8.3	Deaerated	>312
						synthetic water	
12	50	0.90	10	NA	8.3	None	>312
13	50	9.00	100	NA	8.3	None	>312

<sup>1—</sup>Stoichiometric Ratio of Oxidant/As(III)

<sup>2—</sup>Stoichiometric Ratio of Oxidant/(As(III) + Interfering Reductant) based on a 1-electron transfer mechanism, except for Fe(II) which is oxidized by chlorine dioxide by a 5-electron transfer mechanism

<sup>3—</sup>Average of duplicate runs

<sup>4—</sup>Experiments 7 and 8 were performed to duplicate the Fe(II) oxidation experiments of Knocke (1990). Silica was eliminated from #7 as it is known to complex Fe.

<sup>5—</sup>Repeat of experiment # 1

<sup>6—</sup>Complete Oxidation was achieved only after the addition of chlorine

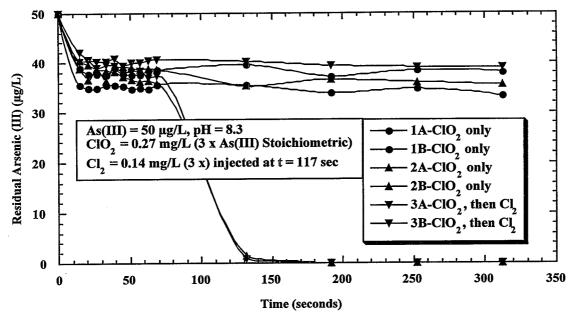


Figure 3-14. Arsenic(III) oxidation with chlorine dioxide. Chlorine injected at 117 sec to verify IX filter performance in experiments 3A and 3B.

The ineffectiveness of chlorine dioxide was surprising as it is known to be a powerful oxidant. Moreover, the phenomenon of 20-30% oxidation in 21 seconds with no further oxidation could not be explained. The scope of research, and time constraints the budget, preempted further investigation into the reasons for this ineffectiveness. Possibly, the initial As(III) oxidation seen in the chlorine dioxide experiments was due to the presence of chlorine in the chlorine dioxide stock solutions. Knocke et al. (1990) reported the formation of about 20 mg/L HOC1 (27 mg/L as chlorine) along with 750 mg/L ClO<sub>2</sub> (390 mg/L as chlorine). possible that the rapid initial As(III) oxidation observed in these experiments was the result of the presence of a very small fraction of chlorine in the ClO2 stock solutions, and was not due to chlorine dioxide itself. It should also be noted that this fraction of chlorine probably varied from one batch to another. Therefore, an increase in the concentration of chlorine dioxide dose does not necessarily imply a proportionate increase in the chlorine fraction as well.

# 3.5.2 Verifying Chlorine Dioxide Stock Concentrations.

In order to verify the ineffectiveness of dioxide chlorine and rule measurement errors, the chlorine dioxide stock solution was assayed to ensure that the proper oxidant dose was delivered. Three different methods were used: (1) Potentiometric method from Knocke et al. (1990), (2) Standard Method 4500-ClO<sub>2</sub>-D (DPD Method), and (3) Hach Method 8138, a direct-reading method with a range of 0-700 mg/L. Both the Potentiometric and DPD methods gave excellent agreement while the Hach method underestimated the chlorine

Table 3-5. Chlorine Dioxide Assays.

2002000		
Method	Observed	Difference <sup>1</sup>
	Value (mg/L)	%
SM 4500- ClO <sub>2</sub> -D	458	<b>-</b> ·
Potentiometric	453	-1.1
Hach 8318	430	-6.1

1—Difference from value obtained using the Standard Method assay.

### 3.5.3 Fe(II) Oxidation with Chlorine Dioxide

Knocke et al. (1990) reported essentially instantaneous oxidation of Fe(II) to Fe(III) by chlorine dioxide at a dose of 105% of stoichiometric requirement. These experiments were repeated for an initial Fe(II) concentration of 4 mg/L. The results of these experiments are shown in Table 3-4, experiments 7 and 8. With a chlorine dioxide dose of 1.08 mg/L (1.12 times stoichiometric), an initial Fe(II) concentration of 4 mg/L was completely oxidized in 15 seconds. To eliminate dissolved oxygen as a potential cause for the ineffectiveness of chlorine dioxide for As(III) oxidation, tests were performed in low-DO (0.1 mg/L) synthetic water. The absence of DO did not improve the performance of chlorine dioxide for As(III) oxidation.

# 3.5.4 Increasing Stoichiometric Dose of Chlorine Dioxide

The chlorine dioxide dose was increased to ten- and one-hundred-times the stoichiometric amount required for As(III) oxidation. These results are shown in Table 3-4, experiments 12 and 13. Even at a chlorine dioxide dose of 9.0 mg/L (100 x stoichiometric), only

about 76% As(III) oxidation was observed at the end of 5 minutes.

### 3.5.5 Effect of Dissolved Manganese and Iron on Chlorine Dioxide

The results of the dissolved manganese and iron experiments are shown in Table 3-4, experiments 4, 5 and 6. The presence of dissolved manganese and iron in the synthetic water resulted in somewhat lower As(III) concentration in the reactor effluent compared with synthetic water without interfering reductants present. The lower residual As(III) concentrations observed were due to adsorption of As(III) and As(V) onto the manganese and iron hydroxide precipitates that formed upon chlorine dioxide addition.

# 3.5.6 Effect of Sulfide, TOC and Temperature on Chlorine Dioxide

Because of the ineffectiveness of chlorine dioxide as an oxidant in the absence of interfering reductants, As(III) these experiments were deemed unnecessary.

# 3.6 Monochloramine Results

**Test** 

Four experiments were performed with monochloramine as oxidant. The results are summarized in Table 3-6.

Table 3-6. Monochloramine Experiments.

#	As(III) Conc (μg/L)	NH <sub>2</sub> Cl Conc (mg/L)	SR¹ NH₂Cl/ As	SR <sup>2</sup> NH <sub>2</sub> Cl/ (As+IR)	pН	Interfering Reductant (IR)	>95% Oxid <sup>3</sup> (sec)
1	50	0.10	3	NA	8.3	None	>312
2	50	0.10	3	NA	7.3	None	>312
3	50	0.10	3	NA	6.3	None	>312
4	50	$0.10^{4}$	3	NA	8.3	None	>312

<sup>1—</sup>Stoichiometric Ratio of Oxidant/As(III)

# 3.6.1 Effect of pH on Monochloramine

In the pH range of 6.3-8.3, limited oxidation (40%) was produced by *in*-

situ-formed monochloramine in the first 21 seconds with no oxidation observed thereafter.

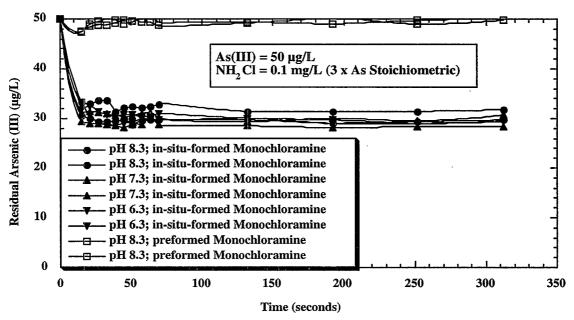


Figure 3-15. Arsenic(III) oxidation with monochloramine.

<sup>2—</sup>Stoichiometric Ratio of Oxidant/(As(III) + Interfering Reductant)

<sup>3-</sup>Average of duplicate runs

<sup>4-</sup>With preformed monochloramine

These results are in agreement with the findings of Frank and Clifford (1986) who speculated that the occurrence of rapid initial As(III) oxidation was due to free chlorine before it reacted with ammonia to form monochloramine. To test this hypothesis, a 10 mg/L monochloramine solution was prepared, assayed, and used as a stock solution. When preformed monochloramine was added to the reactor, no As(III) oxidation was observed (Figure 3-15). Because a three-times-stoichiometric amount of monochloramine failed to produce any As(III) oxidation, it was not studied further.

# 3.7 Solid-Phase Oxidizing Media (Filox)

Twenty-four experiments were conducted with the Filox media and the test results are summarized in Table 3-7.

The variables studied for their effect on As(III) oxidation included EBCT, pH, DO, dissolved Mn, dissolved Fe, sulfide, TOC and initial As(III) concentration. All of the Filox experiments described in this report were performed with the same 12 mL of Filox Media. The media was backwashed after each experiment, but was otherwise untreated.

# 3.7.1 Filox: Effect of Empty Bed Contact Time with High-DO

The effect of EBCT, from 0.75 to 6 min, on As(III) oxidation is shown in Figure 3-16 and Table 3-7, experiments 1-4. Even at the shortest EBCT of 0.75 min, greater than 95% As(III) oxidation was obtained. The media also removed arsenic, in addition to oxidizing it, as seen in Figure 3-16. Arsenic removal increased from 45 to 64% as the EBCT increased from 0.75 to 6.0 min.

Table 3-7. Filox Experiments.

# As(III)		Table 3-7. Filox Experiments.										
Page   Reductant (IR, mg/L)   Removal	#	As(III)	Interfering	pН	$DO^1$	$EBCT^2$	% As(III)	% As				
Columbia   Columbia		* *	Reductant	_		(min)	Oxidation	Removal				
Variable EBCT		, 0	(IR, mg/L)		(mg/L)	, ,						
1   50							· · · · · · · · · · · · · · · · · · ·	h., ,				
1   50		Variable	EBCT									
2 50 None 8.3 8.2 1.5 98.7 48.2 3 50 None 8.3 8.2 3.0 98.7 55.0 4 50 None 8.3 8.2 3.0 98.7 55.0 4 50 None 8.3 8.2 6.0 99.4 63.6   Variable pH  5 50 None 7.3 8.2 1.5 99.8 66.2 6.0 50 None 6.3 8.2 1.5 100.0 75.3   Interfering Reductants, Low-DO, Low EBCT 7 50 None 8.3 0.1 1.5 78.2 12.4 9 50 Fe(II)—0.2 8.3 0.1 1.5 80.9 19.1 10 50 Fe(II)—2.0 8.3 0.1 1.5 81.3 13.9 11 50 Sulfide—1.0 8.3 0.1 1.5 61.5 5.0 12 50 Sulfide—2.0 8.3 0.1 1.5 55.7 9.4 13 50 TOC—1.4 8.3 0.1 1.5 98.3 36.5   Interfering Reductants, Low-DO, High EBCT 15 50 Mn(II)—0.2 8.3 0.1 1.5 98.3 36.5   Interfering Reductants, Low-DO, High EBCT 16 50 Sulfide—1.0 8.3 0.1 1.5 99.3 36.5   Interfering Reductants, Low-DO, High EBCT 17 50 Sulfide—1.0 8.3 0.1 1.5 99.6 57.4 17 50 Sulfide—1.0 8.3 0.1 6.0 99.6 57.4 18 50 TOC—1.4 8.3 0.1 6.0 99.9 47.5   High Initial Arsenic(III) Concentration 19 1000 None 8.3 0.1 6.0 99.9 47.5   High Initial Arsenic(III) Concentration 19 1000 None 8.3 8.2 1.5 95.0 50.3   Interfering Reductants, High-DO, Low EBCT 2 50 Sulfide—1.0 8.3 8.2 1.5 98.4 50.8 22 50 Sulfide—1.0 8.3 8.2 1.5 98.3 76.1 23 50 Sulfide—1.0 8.3 8.2 1.5 98.3 76.1 23 50 Sulfide—1.0 8.3 8.2 1.5 98.3 76.1 23 50 Sulfide—2.0 8.3 8.2 1.5 98.3 76.1 23 50 Sulfide—2.0 8.3 8.2 1.5 98.3 76.1 24 50 TOC—1.4 8.3 8.2 1.5 97.5 55.4	1		_	8.3	8.2	0.75	95.4	45.3				
So			None	8.3	8.2	1.5	98.7	48.2				
Variable pH         8.3         8.2         6.0         99.4         63.6           Variable pH         5         50         None         7.3         8.2         1.5         99.8         66.2           6         50         None         6.3         8.2         1.5         190.0         75.3           Interfering Reductants, Low-DO, Low EBCT           7         50         None         8.3         0.1         1.5         98.9         36.1           8         50         Mn(II)—0.2         8.3         0.1         1.5         78.2         12.4           9         50         Fe(II)—0.3         8.3         0.1         1.5         80.9         19.1           10         50         Fe(II)—2.0         8.3         0.1         1.5         80.9         19.1           10         50         Fe(II)—2.0         8.3         0.1         1.5         81.3         13.9           11         50         Sulfide—1.0         8.3         0.1         1.5         61.5         5.0           12         50         Sulfide—2.0         8.3         0.1         1.5         79.2         7.2           14         50 <td></td> <td></td> <td>i '</td> <td>8.3</td> <td>8.2</td> <td>3.0</td> <td>98.7</td> <td>55.0</td>			i '	8.3	8.2	3.0	98.7	55.0				
Variable pH   5   50				8.3	8.2	6.0	99.4	63.6				
5         50         None         7.3         8.2         1.5         99.8         66.2           6         50         None         6.3         8.2         1.5         100.0         75.3           Interfering Reductants, Low-DO, Low EBCT           7         50         None         8.3         0.1         1.5         98.9         36.1           8         50         Mn(II)—0.2         8.3         0.1         1.5         78.2         12.4           9         50         Fe(II)—0.3         8.3         0.1         1.5         80.9         19.1           10         50         Fe(II)—0.3         8.3         0.1         1.5         81.3         13.9           11         50         Fe(II)—2.0         8.3         0.1         1.5         81.3         13.9           11         50         Sulfide—1.0         8.3         0.1         1.5         51.5         5.0           12         50         Sulfide—2.0         8.3         0.1         1.5         79.2         7.2           14         50         None/8 °C         8.3         0.1         6.0         99.8         51.1           15         <			•	•		•	•					
Interfering Reductants, Low-DO, Low EBCT		Variable	pH									
Interfering Reductants, Low-DO, Low EBCT	5	50	None		8.2	1.5	99.8	66.2				
7         50         None         8.3         0.1         1.5         98.9         36.1           8         50         Mn(II)—0.2         8.3         0.1         1.5         78.2         12.4           9         50         Fe(II)—0.3         8.3         0.1         1.5         80.9         19.1           10         50         Fe(II)—2.0         8.3         0.1         1.5         81.3         13.9           11         50         Sulfide—1.0         8.3         0.1         1.5         61.5         5.0           12         50         Sulfide—2.0         8.3         0.1         1.5         55.7         9.4           13         50         TOC—1.4         8.3         0.1         1.5         79.2         7.2           14         50         None/8 °C         8.3         0.1         1.5         98.3         36.5           Interfering Reductants, Low-DO, High EBCT           15         50         Sulfide—1.0         8.3         0.1         6.0         99.8         51.1           16         50         Sulfide—2.0         8.3         0.1         6.0         99.9         57.4           17 <td>6</td> <td>50</td> <td>None</td> <td>6.3</td> <td>8.2</td> <td>1.5</td> <td>100.0</td> <td>75.3</td>	6	50	None	6.3	8.2	1.5	100.0	75.3				
7         50         None         8.3         0.1         1.5         98.9         36.1           8         50         Mn(II)—0.2         8.3         0.1         1.5         78.2         12.4           9         50         Fe(II)—0.3         8.3         0.1         1.5         80.9         19.1           10         50         Fe(II)—2.0         8.3         0.1         1.5         81.3         13.9           11         50         Sulfide—1.0         8.3         0.1         1.5         61.5         5.0           12         50         Sulfide—2.0         8.3         0.1         1.5         55.7         9.4           13         50         TOC—1.4         8.3         0.1         1.5         79.2         7.2           14         50         None/8 °C         8.3         0.1         1.5         98.3         36.5           Interfering Reductants, Low-DO, High EBCT           15         50         Sulfide—1.0         8.3         0.1         6.0         99.8         51.1           16         50         Sulfide—2.0         8.3         0.1         6.0         99.9         57.4           17 <td></td> <td></td> <td>•</td> <td>•</td> <td></td> <td>=</td> <td>-</td> <td></td>			•	•		=	-					
8       50       Mn(II)—0.2       8.3       0.1       1.5       78.2       12.4         9       50       Fe(II)—0.3       8.3       0.1       1.5       80.9       19.1         10       50       Fe(II)—2.0       8.3       0.1       1.5       81.3       13.9         11       50       Sulfide—1.0       8.3       0.1       1.5       61.5       5.0         12       50       Sulfide—2.0       8.3       0.1       1.5       55.7       9.4         13       50       TOC—1.4       8.3       0.1       1.5       79.2       7.2         14       50       None/8 °C       8.3       0.1       1.5       98.3       36.5         Interfering Reductants, Low-DO, High EBCT         15       50       Mn(II)—0.2       8.3       0.1       6.0       99.8       51.1         16       50       Sulfide—1.0       8.3       0.1       6.0       99.6       57.4         17       50       Sulfide—2.0       8.3       0.1       6.0       99.9       47.5         High Initial Arsenic(III) Concentration         19       1000       None       8.3		Interferin	ng Reductants, Low	-DO, Lo	ow EBCT			_				
9 50 Fe(II)—0.3 8.3 0.1 1.5 80.9 19.1 10 50 Fe(II)—2.0 8.3 0.1 1.5 81.3 13.9 11 50 Sulfide—1.0 8.3 0.1 1.5 61.5 5.0 12 50 Sulfide—2.0 8.3 0.1 1.5 55.7 9.4 13 50 TOC—1.4 8.3 0.1 1.5 79.2 7.2 14 50 None/8 °C 8.3 0.1 1.5 98.3 36.5   Interfering Reductants, Low-DO, High EBCT  15 50 Mn(II)—0.2 8.3 0.1 6.0 99.8 51.1 16 50 Sulfide—1.0 8.3 0.1 6.0 99.6 57.4 17 50 Sulfide—2.0 8.3 0.1 6.0 99.9 47.5   High Initial Arsenic(III) Concentration  19 1000 None 8.3 0.1 6.0 99.9 47.5   High Initial Arsenic(III) Concentration  19 1000 None 8.3 0.1 1.5 96.7 44.8 20 1000 None 8.3 8.2 1.5 95.0 50.3   Interfering Reductants, High-DO, Low EBCT  21 50 Mn(II)—0.2 8.3 8.2 1.5 98.4 50.8 22 50 Sulfide—1.0 8.3 8.2 1.5 98.3 76.1 23 50 Sulfide—2.0 8.3 8.2 1.5 96.2 77.1 24 50 TOC—1.4 8.3 8.2 1.5 97.5 55.4	7	50	None	8.3	0.1	1.5	98.9	36.1				
10         50         Fe(II)—2.0         8.3         0.1         1.5         81.3         13.9           11         50         Sulfide—1.0         8.3         0.1         1.5         61.5         5.0           12         50         Sulfide—2.0         8.3         0.1         1.5         55.7         9.4           13         50         TOC—1.4         8.3         0.1         1.5         79.2         7.2           14         50         None/8 °C         8.3         0.1         1.5         98.3         36.5           Interfering Reductants, Low-DO, High EBCT           15         50         Mn(II)—0.2         8.3         0.1         6.0         99.8         51.1           16         50         Sulfide—1.0         8.3         0.1         6.0         99.6         57.4           17         50         Sulfide—2.0         8.3         0.1         6.0         97.0         42.4           18         50         TOC—1.4         8.3         0.1         1.5         96.7         44.8           20         1000         None         8.3         8.2         1.5         95.0         50.3 <td col<="" td=""><td>8</td><td>50</td><td>Mn(II)0.2</td><td>8.3</td><td>0.1</td><td>1.5</td><td>78.2</td><td>12.4</td></td>	<td>8</td> <td>50</td> <td>Mn(II)0.2</td> <td>8.3</td> <td>0.1</td> <td>1.5</td> <td>78.2</td> <td>12.4</td>	8	50	Mn(II)0.2	8.3	0.1	1.5	78.2	12.4			
11         50         Sulfide—1.0         8.3         0.1         1.5         61.5         5.0           12         50         Sulfide—2.0         8.3         0.1         1.5         55.7         9.4           13         50         TOC—1.4         8.3         0.1         1.5         79.2         7.2           14         50         None/8 °C         8.3         0.1         1.5         98.3         36.5           Interfering Reductants, Low-DO, High EBCT           15         50         Mn(II)—0.2         8.3         0.1         6.0         99.8         51.1           16         50         Sulfide—1.0         8.3         0.1         6.0         99.6         57.4           17         50         Sulfide—2.0         8.3         0.1         6.0         97.0         42.4           18         50         TOC—1.4         8.3         0.1         6.0         99.9         47.5           High Initial Arsenic(III) Concentration           19         1000         None         8.3         8.2         1.5         96.7         44.8           20         1000         None         8.3         8.2         1.5	9	50	Fe(II)—0.3	8.3	0.1	1.5	80.9	19.1				
12   50   Sulfide—2.0   8.3   0.1   1.5   55.7   9.4     13   50   TOC—1.4   8.3   0.1   1.5   79.2   7.2     14   50   None/8 °C   8.3   0.1   1.5   98.3   36.5     Interfering Reductants, Low-DO, High EBCT     15   50   Mn(II)—0.2   8.3   0.1   6.0   99.8   51.1     16   50   Sulfide—1.0   8.3   0.1   6.0   99.6   57.4     17   50   Sulfide—2.0   8.3   0.1   6.0   97.0   42.4     18   50   TOC—1.4   8.3   0.1   6.0   99.9   47.5      High Initial Arsenic(III) Concentration     1000   None   8.3   0.1   1.5   96.7   44.8     20   1000   None   8.3   8.2   1.5   95.0   50.3      Interfering Reductants, High-DO, Low EBCT     21   50   Mn(II)—0.2   8.3   8.2   1.5   98.4   50.8     22   50   Sulfide—1.0   8.3   8.2   1.5   98.3   76.1     23   50   Sulfide—2.0   8.3   8.2   1.5   96.2   77.1     24   50   TOC—1.4   8.3   8.2   1.5   97.5   55.4	10	50	Fe(II)—2.0	8.3	0.1	1.5	81.3	13.9				
13         50         TOC—1.4         8.3         0.1         1.5         79.2         7.2           14         50         None/8 °C         8.3         0.1         1.5         98.3         36.5           Interfering Reductants, Low-DO, High EBCT           15         50         Mn(II)—0.2         8.3         0.1         6.0         99.8         51.1           16         50         Sulfide—1.0         8.3         0.1         6.0         99.6         57.4           17         50         Sulfide—2.0         8.3         0.1         6.0         97.0         42.4           18         50         TOC—1.4         8.3         0.1         6.0         99.9         47.5           High Initial Arsenic (III) Concentration           19         1000         None         8.3         0.1         1.5         96.7         44.8           20         1000         None         8.3         8.2         1.5         95.0         50.3           Interfering Reductants, High-DO, Low EBCT           21         50         Sulfide—1.0         8.3         8.2         1.5         98.3         76.1           23         5	11	50	Sulfide—1.0	8.3	0.1	1.5	61.5	5.0				
14         50         None/8 °C         8.3         0.1         1.5         98.3         36.5           Interfering Reductants, Low-DO, High EBCT           15         50         Mn(II)—0.2         8.3         0.1         6.0         99.8         51.1           16         50         Sulfide—1.0         8.3         0.1         6.0         99.6         57.4           17         50         Sulfide—2.0         8.3         0.1         6.0         97.0         42.4           18         50         TOC—1.4         8.3         0.1         6.0         99.9         47.5           High Initial Arsenic(III) Concentration           19         1000         None         8.3         8.2         1.5         96.7         44.8           20         1000         None         8.3         8.2         1.5         95.0         50.3           Interfering Reductants, High-DO, Low EBCT           21         50         Sulfide—1.0         8.3         8.2         1.5         98.4         50.8           22         50         Sulfide—2.0         8.3         8.2         1.5         96.2         77.1           24         <	12	50	Sulfide—2.0	8.3	0.1	1.5	55.7	9.4				
Interfering Reductants, Low-DO, High EBCT   15   50   Mn(II)—0.2   8.3   0.1   6.0   99.8   51.1   16   50   Sulfide—1.0   8.3   0.1   6.0   99.6   57.4   17   50   Sulfide—2.0   8.3   0.1   6.0   97.0   42.4   18   50   TOC—1.4   8.3   0.1   6.0   99.9   47.5	13	50	TOC-1.4	8.3	0.1	1.5	79.2	7.2				
15         50         Mn(II)—0.2         8.3         0.1         6.0         99.8         51.1           16         50         Sulfide—1.0         8.3         0.1         6.0         99.6         57.4           17         50         Sulfide—2.0         8.3         0.1         6.0         97.0         42.4           18         50         TOC—1.4         8.3         0.1         6.0         99.9         47.5           High Initial Arsenic(III) Concentration           19         1000         None         8.3         0.1         1.5         96.7         44.8           20         1000         None         8.3         8.2         1.5         95.0         50.3           Interfering Reductants, High-DO, Low EBCT           21         50         Sulfide—1.0         8.3         8.2         1.5         98.4         50.8           22         50         Sulfide—1.0         8.3         8.2         1.5         98.3         76.1           23         50         Sulfide—2.0         8.3         8.2         1.5         96.2         77.1           24         50         TOC—1.4         8.3         8.2 <t< td=""><td>14</td><td>50</td><td>None/8 °C</td><td>8.3</td><td>0.1</td><td>1.5</td><td>98.3</td><td>36.5</td></t<>	14	50	None/8 °C	8.3	0.1	1.5	98.3	36.5				
15         50         Mn(II)—0.2         8.3         0.1         6.0         99.8         51.1           16         50         Sulfide—1.0         8.3         0.1         6.0         99.6         57.4           17         50         Sulfide—2.0         8.3         0.1         6.0         97.0         42.4           18         50         TOC—1.4         8.3         0.1         6.0         99.9         47.5           High Initial Arsenic(III) Concentration           19         1000         None         8.3         0.1         1.5         96.7         44.8           20         1000         None         8.3         8.2         1.5         95.0         50.3           Interfering Reductants, High-DO, Low EBCT           21         50         Sulfide—1.0         8.3         8.2         1.5         98.4         50.8           22         50         Sulfide—1.0         8.3         8.2         1.5         98.3         76.1           23         50         Sulfide—2.0         8.3         8.2         1.5         96.2         77.1           24         50         TOC—1.4         8.3         8.2 <t< td=""><td></td><td></td><td>•</td><td>-</td><td>-</td><td>-</td><td></td><td>•</td></t<>			•	-	-	-		•				
16         50         Sulfide—1.0         8.3         0.1         6.0         99.6         57.4           17         50         Sulfide—2.0         8.3         0.1         6.0         97.0         42.4           18         50         TOC—1.4         8.3         0.1         6.0         99.9         47.5           High Initial Arsenic(III) Concentration           19         1000         None         8.3         0.1         1.5         96.7         44.8           20         1000         None         8.3         8.2         1.5         95.0         50.3           Interfering Reductants, High-DO, Low EBCT           21         50         Mn(II)—0.2         8.3         8.2         1.5         98.4         50.8           22         50         Sulfide—1.0         8.3         8.2         1.5         98.3         76.1           23         50         Sulfide—2.0         8.3         8.2         1.5         96.2         77.1           24         50         TOC—1.4         8.3         8.2         1.5         97.5         55.4		Interferir		DO, Hi	gh EBCT	_	_	_				
17         50         Sulfide—2.0         8.3         0.1         6.0         97.0         42.4           18         50         TOC—1.4         8.3         0.1         6.0         99.9         47.5           High Initial Arsenic(III) Concentration           19         1000         None         8.3         0.1         1.5         96.7         44.8           20         1000         None         8.3         8.2         1.5         95.0         50.3           Interfering Reductants, High-DO, Low EBCT           21         50         Mn(II)—0.2         8.3         8.2         1.5         98.4         50.8           22         50         Sulfide—1.0         8.3         8.2         1.5         98.3         76.1           23         50         Sulfide—2.0         8.3         8.2         1.5         96.2         77.1           24         50         TOC—1.4         8.3         8.2         1.5         97.5         55.4	15	50	Mn(II)0.2	8.3	0.1	1	ł .	I				
18         50         TOC—1.4         8.3         0.1         6.0         99.9         47.5           High Initial Arsenic(III) Concentration           19         1000         None         8.3         0.1         1.5         96.7         44.8           20         1000         None         8.3         8.2         1.5         95.0         50.3           Interfering Reductants, High-DO, Low EBCT           21         50         Mn(II)—0.2         8.3         8.2         1.5         98.4         50.8           22         50         Sulfide—1.0         8.3         8.2         1.5         98.3         76.1           23         50         Sulfide—2.0         8.3         8.2         1.5         96.2         77.1           24         50         TOC—1.4         8.3         8.2         1.5         97.5         55.4	16	50	Sulfide—1.0	8.3	0.1		1	1				
High Initial Arsenic(III) Concentration  19	17	50	Sulfide—2.0	8.3	0.1	6.0	97.0					
19     1000     None     8.3     0.1     1.5     96.7     44.8       20     1000     None     8.3     8.2     1.5     95.0     50.3       Interfering Reductants, High-DO, Low EBCT       21     50     Mn(II)—0.2     8.3     8.2     1.5     98.4     50.8       22     50     Sulfide—1.0     8.3     8.2     1.5     98.3     76.1       23     50     Sulfide—2.0     8.3     8.2     1.5     96.2     77.1       24     50     TOC—1.4     8.3     8.2     1.5     97.5     55.4	18	50	TOC1.4	8.3	0.1	6.0	99.9	47.5				
19     1000     None     8.3     0.1     1.5     96.7     44.8       20     1000     None     8.3     8.2     1.5     95.0     50.3       Interfering Reductants, High-DO, Low EBCT       21     50     Mn(II)—0.2     8.3     8.2     1.5     98.4     50.8       22     50     Sulfide—1.0     8.3     8.2     1.5     98.3     76.1       23     50     Sulfide—2.0     8.3     8.2     1.5     96.2     77.1       24     50     TOC—1.4     8.3     8.2     1.5     97.5     55.4												
20         1000         None         8.3         8.2         1.5         95.0         50.3           Interfering Reductants, High-DO, Low EBCT           21         50         Mn(II)—0.2         8.3         8.2         1.5         98.4         50.8           22         50         Sulfide—1.0         8.3         8.2         1.5         98.3         76.1           23         50         Sulfide—2.0         8.3         8.2         1.5         96.2         77.1           24         50         TOC—1.4         8.3         8.2         1.5         97.5         55.4		_	_ ` ` `	-	-							
Interfering Reductants, High-DO, Low EBCT  21			8	1	1	4	1	1				
21     50     Mn(II)—0.2     8.3     8.2     1.5     98.4     50.8       22     50     Sulfide—1.0     8.3     8.2     1.5     98.3     76.1       23     50     Sulfide—2.0     8.3     8.2     1.5     96.2     77.1       24     50     TOC—1.4     8.3     8.2     1.5     97.5     55.4	20	1000	None	8.3	8.2	1.5	95.0	50.3				
21     50     Mn(II)—0.2     8.3     8.2     1.5     98.4     50.8       22     50     Sulfide—1.0     8.3     8.2     1.5     98.3     76.1       23     50     Sulfide—2.0     8.3     8.2     1.5     96.2     77.1       24     50     TOC—1.4     8.3     8.2     1.5     97.5     55.4												
22     50     Sulfide—1.0     8.3     8.2     1.5     98.3     76.1       23     50     Sulfide—2.0     8.3     8.2     1.5     96.2     77.1       24     50     TOC—1.4     8.3     8.2     1.5     97.5     55.4				-			1 .aa.:	1				
23     50     Sulfide—2.0     8.3     8.2     1.5     96.2     77.1       24     50     TOC—1.4     8.3     8.2     1.5     97.5     55.4		1	• •		l .	1						
24 50 TOC—1.4 8.3 8.2 1.5 97.5 55.4			1	1	1	4	3	1				
				1	1	1	1	l .				
			· · · · · · · · · · · · · · · · · · ·	4	8.2	1.5	97.5	55.4				

<sup>1—</sup>High DO = 8.2 mg/L; Low DO = 0.1 mg/L 2—EBCT of 0.75, 1.5, 3.0 and 6.0 equal 4.9, 2.5, 1.2 and 0.6 gpm/ft<sup>2</sup>, respectively.

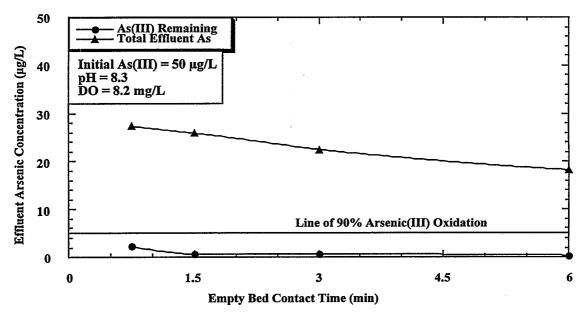


Figure 3-16. Effect of EBCT on Filox Media.

effort to stabilize arsenic In an adsorption, attempts were made to equilibrate the Filox media with As(III)spiked synthetic water before any further experiments were performed. 2000 BV (24 L) of 50 μg/L As(III)spiked synthetic water was passed through the Filox media at a flow rate of 16 mL/min corresponding to an EBCT of 0.75 min and a total equilibration time of 25 hours of interrupted flow over a three-day period. The results are shown in Figure 3-17. Arsenic oxidation rate started out at 96% (2 µg/L As(III) remaining) and decreased slightly to 93% (4 µg/L As(III) remaining) at 2000 BV. Arsenic removal by the Filox media decreased significantly as the run progressed. From an initial removal rate of 26%, arsenic removal decreased to 8% at 2000 BV, indicating that the media's capacity for arsenic adsorption was nearly exhausted. Figure 3-17 also shows that the Filox media will initially oxidize As(III) and remove it, but will eventually come to equilibrium with the influent arsenic and provide no further arsenic removal while still oxidizing As(III) to As(V). It should also be noted that no arsenic was dumped from the media in the equilibration experiment or subsequent in any experiments.

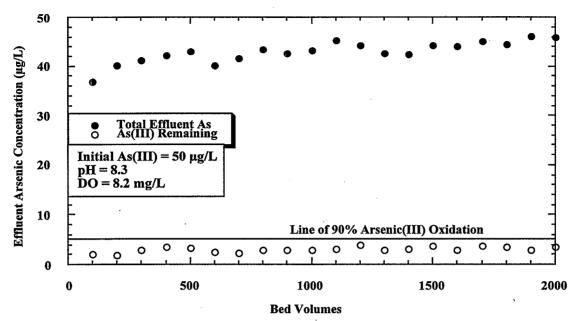


Figure 3-17. Filox media equilibration with 2000 BV of synthetic test water at an EBCT of 0.75 min.

### 3.7.2 Filox: Effect of pH with High-DO

The results on the pH tests in the range of 6.3-8.3 showed that pH had no significant effect on arsenic oxidation by the Filox media (Figure 3-18). Greater than 98% As(III) oxidation was achieved in the pH range of 6.3-8.3. Total arsenic (As(III) + As(V)) removal, however, increased with decreasing pH, with removals increasing from 48% at pH 8.3 to 75% at pH 6.3. It should be noted that in Figure 3-18, arsenic removal by the Filox media was much higher than at the

of the previously performed equilibration experiments. This was probably due to a relaxation in the concentration gradient that occurs when flow through adsorbent-packed media bed is interrupted and then resumed. Morevover, the longer contact time of 1.5 min used in the post-equilibration experiments, compared with the 0.75 contact time used the min in equilibration experiments, will result in increased arsenic adsorption by the Filox media as seen in Figure 3-16.

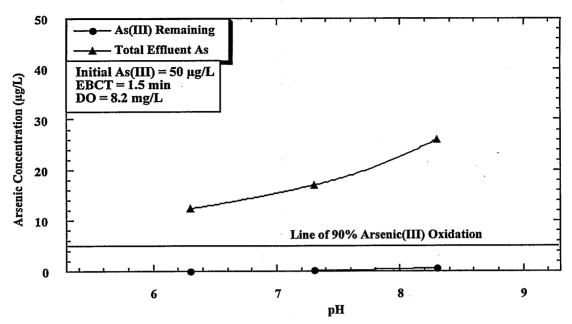


Figure 3-18. Effect of pH on As(III) oxidation with Filox media.

# 3.7.3 Filox: Effect of DO in the absence of interfering reductants

In the absence of interfering reductants, the concentration of dissolved oxygen in the synthetic water had no effect on As(III) oxidation by the Filox media (Table 3-7, experiments 1-7). Similar results were obtained for the higher initial As(III) concentration of 1000  $\mu$ g/L (Table 3-7, experiments 19 and 20). This lack of effect is supported by the studies of Scott and Morgan (1995) who concluded that DO had no effect on As(III) oxidation by  $\delta$ -MnO<sub>2</sub>.

### 3.7.4 Filox: Effect of Interfering Reductants

# 3.7.4.1 Low-DO (0.1 mg/L) Synthetic Water at 1.5 min EBCT

All of the interfering reductants studied had an adverse effect on As(III) oxidation in low-DO synthetic water at pH 8.3 and EBCT of 1.5 min (Table 3-7, experiments 8-13). Sulfide had the greatest effect on As(III) oxidation,

which decreased from 99% with no sulfide present to 62 and 56% at sulfide levels of 1.0 and 2.0 mg/L, respectively. Similarly, in the presence of 1.4 mg/L TOC, As(III) oxidation was reduced to 79% compared with 99% when no TOC was present.

# 3.7.4.2 Low-DO (0.1 mg/L) Synthetic Water at 6.0 min EBCT

To attenuate the effect of interfering reductants in low-DO water, the EBCT was increased from 1.5 to 6.0 min. At an EBCT of 6.0 min, the effects of all of the interfering reductants on As(III) oxidation were completely attenuated (Table 3-7, experiments 15-18), and As(III) oxidation results matched those when no interfering reductants were present.

# 3.7.4.3 High-DO (8.2 mg/L) Synthetic Water at 1.5 min EBCT

Near-complete arsenic oxidation was also obtained in the presence of

interfering reductants when the synthetic test water contained sufficient dissolved oxygen as seen from Table 3-7, experiments 21-24. When 8.2 mg/L DO was present, As(III) oxidation results matched those when no interfering reductants were present.

# 3.7.5 Filox: Effect of Low Temperature in low-DO Synthetic Water

Lowering the temperature of the synthetic water from 24 °C (approximate room temperature) to 8 °C had no effect

on arsenic oxidation with an oxidation efficiency of 98.3% achieved at 8°C compared with 99% at 24 °C (Table 3-7, experiments 7 and 14).

#### 3.8 UV Oxidation Results

Two UV units from different manufacturers were tested for their ability to oxidize As(III). Fifteen experiments were performed using UV to oxidize As(III) and the results are summarized in Table 3-8.

Table 3-8. UV Oxidation Experiments.

#	UV Dose	Flow Rate	Contact	pН	%As(III)
	W-sec/cm <sup>2</sup>	mL/min	Time (min)		Oxidation
UV U	nit 1: 32,000 μ	w/cm² at a des	ign flow rate of 1	890 mL/mii	$\overline{n}$
1 -	1.9	288	1	8.3	4
2	5.8	96	3	8.3	14
3	11.5	48	6	8.3	27
4	23.0	24	12	8.3	58
5	46.1	12	24	8.3	73
6	46.1	12	24	7.3	71
7	46.1	12	24	6.3	64
8	1.8 <sup>a</sup>	310	0.9	8.3	100

UV Unit 2:  $41,200 \,\mu\text{w/cm}^2$  at a design flow rate of 3785 mL/min

9	3.9	310	1.6	8.3	2
10	5.8	209	2.3	8.3	5
11	11.5	105	4.7	8.3	12
12	23.0	52	9.3	8.3	29
13	46.1	26	18.7	8.3	43
14	46.1	26	18.7	7.3	40
15	46.1	26	18.7	6.3	27

a—Spiked with 1.0 mg/L sulfite, SO<sub>3</sub>, to verify reported catalytic effect of sulfite on UV oxidation of As(III).

#### 3.8.1 Unit 1

Unit 1 (R-Can Environmental Inc., Canada) had a design flow rate of 0.5

gpm (1890 mL/min) and provided a UV intensity of 32,000  $\mu$ W/cm<sup>2</sup>. At a flow rate of 288 mL/min (contact time of 1

min), i.e., about 15% of the rated flow, no significant oxidation was observed (Table 3-8, experiments 1-7). A maximum of 73% As(III) oxidation was obtained at 12 mL/min flow rate (contact time of 24 min), i.e., 0.6% of the rated flow. This translates to an extremely high energy input of 46,080,000 μw-sec/cm², whereas only 6,500 μw-sec/cm² is required to achieve a 99.9% destruction level of *E.Coli*.

To verify the reported catalytic effect of sulfite on As(III) oxidation by UV (MSE Technology Applications, Inc., Montana and ANSTO, Australia (1997; Khoe et al. (1997) and Khoe et al. (2000)), the synthetic water was spiked with 1.0 mg/L of sulfite and allowed to stand for 30 minutes. The sulfite-spiked synthetic water was then passed through Unit 1 where complete oxidation of As(III) was obtained, whereas virtually no oxidation occurred in the unspiked synthetic water under the same conditions (Table 3-8, Thus, sulfite played a experiment 8). role in facilitating the oxidation of The mechanism of sulfite-As(III). facilitated As(III) oxidation is a matter of speculation. Sulfite is not an oxidizing agent and control tests performed with the sulfite-spiked water, with the UV lamp turned off, showed no It is possible that As(III) oxidation. sulfite catalyzed the formation of free radicals and thus assisted in the oxidation of As(III). The role of sulfite in facilitating As(III) oxidation merits further research.

#### 3.8.2 Unit 2

Qualitatively, Unit 2 (Atlantic Ultraviolet Corp.) with a design flow rate of 1 gpm (3,785 mL/min) gave results similar to those obtained using Unit 1 (Table 3-8, experiments 9-15). However, for the same UV doses, Unit 2 produced less oxidation than Unit 1. The reasons for the difference in performance between the two UV units was not studied.

It should be noted that the off-the-shelf UV units studied were designed for the primary purpose of disinfection and, therefore, were not optimized for As(III) oxidation. Arsenic shows a strong absorbance at 193.7 nm, which is the wavelength used in AA units for arsenic analysis. Therefore, a more appropriate wavelength to study UV-oxidation of As(III) would be near 193.7 nm. UV systems, with peak intensity at 185 nm, are commercially available and may be more appropriate for such a study.

It should also be noted that the difference in arsenic-oxidation performance of the two UV units does not imply that they would perform differently for a disinfection-type application.

### 4. Summary and Conclusions

Bench-scale studies were performed to assess the feasibility of using three- and ten-times stoichiometric amounts (based As(III) concentration) of five chemical oxidants, a solid-phase oxidant, and UV radiation for As(III) oxidation to The effects of interfering As(V). reductants including dissolved manganese (0.2 g/L), dissolved iron (0.3 and 2.0 mg/), sulfide (1.0 and 2.0 mg/L) and TOC (2.1 and 6.9 mg/L) on the effectiveness of these oxidants was examined. The conclusions of the oneyear lab study on As(III) oxidation performed at the University of Houston are summarized below.

- (1) Chlorine rapidly oxidized As(III) to As(V) under all the conditions tested. Iron and manganese had no measurable effect on As(III) oxidation. Although and TOC sulfide slowed As(III)oxidation by chlorine. complete oxidation was still obtained in less than one minute. Lowering the temperature from 25 to 5 °C had no measurable effect on As(III) oxidation in the absence of interfering reductants.
- (2) Permanganate also rapidly oxidized As(III) to As(V). Even in the presence of interfering reductants, greater than 95% As(III) oxidation was achieved by permanganate in  $\leq$  51 seconds. Lowering the temperature from 25 to 5 °C had no measurable effect on As(III) oxidation in the absence of interfering reductants.
- (3) In the absence of interfering reductants, ozone rapidly oxidized

As(III) in the pH range of 6.3-8.3. No adverse effect was observed in the presence of either dissolved manganese or dissolved iron. Although complete oxidation was obtained, the rate of As(III) oxidation was considerably slower in the presence of sulfide.

TOC had the greatest adverse effect on As(III) oxidation by ozone. In the presence of 6.9 mg/L TOC in As(III)-spiked Lake Houston water, only 34% As(III) oxidation was produced in 21 seconds. Thus, the presence of TOC had a quenching effect on ozone. When the TOC in the Lake Houston was reduced by dilution with synthetic test water to 2.1 mg/L, complete oxidation of As(III) was observed in 27 seconds. Lowering the temperature from 25 to 5 °C had no measurable effect on As(III) oxidation in the absence of interfering reductants.

- (4) Chlorine dioxide was, surprisingly, ineffective for As(III) oxidation. three-fold stoichiometric dose of chlorine dioxide produced only 20-30% oxidation in 21 seconds and produced no additional oxidation thereafter. Even a 100-times stoichiometric dose produced only 76% oxidation in 5 minutes. The limited oxidation that was observed was probably due to the presence of chlorine as a contaminant in the chlorine dioxide stock solutions as chlorine is known to be a by-product of the chlorine dioxide generation process.
- (5) Monochloramine was ineffective as an oxidant for As(III) confirming the findings of other researchers. While

limited As(III) oxidation resulted when monochloramine was formed in-situ, no oxidation was observed when preformed monochloramine was used. This suggests that when chlorine is dosed into an As(III)-containing solution in the presence of excess ammonia, a fraction of that chlorine reacts with As(III) before it is completely quenched by ammonia to form monochloramine.

(6) Filox media was found to be very effective for As(III) oxidation under most of the conditions tested. In the absence of interfering reductants, greater than 95% As(III) oxidation was achieved in both low-and high-DO waters at contact times as short as 1.5 min (15 gpm/ft² in a 3-ft deep bed). In addition to As(III) oxidation, the Filox media also removed arsenic by adsorption onto the media, but the adsorption decreased as the media came into equilibrium with the feed water.

As(III) oxidation by Filox was adversely affected in the presence of all

of the interfering reductants tested in low-DO water at an EBCT of 1.5 min (2.4 gpm/ft²) with sulfide exhibiting the greatest effect. The effects of interfering reductants were completely attenuated by either increasing the contact time to 6 min or by increasing the DO to 8.2 mg/L. As(III) concentrations as high as 1000 µg/L were efficiently oxidized (≥ 95%) in both low- and high-DO waters at pH 8.3 in the absence of interfering reductants.

(7) UV radiation alone was ineffective for As(III) oxidation unless extremely high UV doses, (7000 times the UV dose required for *E.Coli* inactivation) were used. Even with such a high UV dose, only 73% As(III) oxidation was observed. However, as described in a patented process, the presence of sulfite provided for the rapid and quantitative oxidation of As(III). The mechanism by which sulfite promotes the oxidation of As(III) was not studied here.

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### Appendix A. Preconditioning and Regeneration of IX Filter

### A.1 Manufacturer-Recommended Preconditioning

- (1) Center the filter on the base of a vacuum filter holder.
- (2) Wet the filter with 10 mL of acetone for 30 sec, and then apply vacuum to dry the filter.
- (3) Add 10 mL of isopropanol and allow filter to soak for 30 sec. Apply vacuum to dry the filter.
- (4) Finally, add 10 mL of methanol. Draw approximately 3-4 mL of methanol through the filter under vacuum. Vent vacuum and allow filter allowed to soak in methanol for 60 seconds. Reapply vacuum and add 30 mL of reagent grade water to rinse methanol from the filter. Ensure that the filter does not dry by leaving 3-5 mL of reagent grade water on the filter.

# A.2 IX Filter Regeneration— UH Method

All preconditioned and used filters were regenerated (converted to the chloride form) according to the procedure outlined below.

(5) Mount the filter on the base of a vacuum filtration apparatus and place a 0.22 μm filter (Millipore, 47 mm, Type GS) on top of the IX

- Empore filter. Add 20 mL of 1 M HCl and pull approximately 3-4 mL of HCl through the filter under vacuum. Vent the vacuum and allow the filter to soak for about 60 seconds. Reapply vacuum to draw the remaining acid through the filter at a flow rate of 20 mL/min or less.
- (6) Add 20 mL of 1 M NaCl and pull approximately 3-4 mL of the salt solution through the filter. Vent the vacuum and allow the filter to soak for about 60 seconds. Reapply vacuum and draw the remaining salt solution through the filter at a flow rate of 20 mL/min or less.
- (7) To rinse the concentrated NaCl out of the filter, add 20 mL of 0.005 M NaCl and draw about 15 mL through the filter at a flow rate of 20 mL/min or less. The IX filter is now ready to use for the As(III)/(V) speciation tests.
- (8) Once preconditioned and regenerated, the filter should not be allowed to dry for an extended period of time. One way to prevent drying is to place the filter in a beaker or a sealed plastic bag containing a 0.005 M NaCl solution.

### Appendix B. Testing Oxidation Reactor Set-up

The procedures followed for testing the reactor set-up for As(V)/As(III) separation are described in this section.

- (1) Pour 500 mL of the synthetic water containing either As(III) or As(V) into the oxidation reactor. Close the reactor.
- (2) Place the IX filter in the filter holder. Place a 0.22 μm filter on top of the IX filter and assemble the online filter holder.
- (3) Pressurize the reactor to 15 psi using nitrogen gas. Open outlet valve and allow the test solution to flow through the filters.
- (4) Discard the first 10 mL of the effluent. Collect the rest of the effluent in 10 (or 25) mL aliquots. Acidify the 10 mL aliquots using 50 μL of conc. nitric acid and store at 4 °C until ready for analysis. After collecting the desired volume of the filter effluent, close the outlet valve.

The test is now completed. To prepare for the next test, perform the following procedures.

(5) Vent the nitrogen gas pressure and disassemble the filter holder. Transfer the IX filter along with the 0.22 μm filter atop it to a vacuum filtration apparatus.

- (6) Regenerate the IX filter as outlined in the Filter Regeneration Method described in Appendix A.
- (7) Simultaneously, clean the reactor by rinsing four times with 250 mL of DI water. Then fill the reactor with 500 mL of DI water. Close the reactor and pressurize to 15 psi. approximately 100 mL of flow from the reactor through an empty filter This rinses out the tubing between the reactor and the filter holder, the filter holder itself, and the final section of tubing between the filter holder and the fraction collector.
- (8) Discard the used 0.22 μm filter from step 7 and transfer the regenerated IX filter into the rinsed in-line filter holder. Place a new 0.22 um filter on top of the IX filter. Assemble the filter holder together and connect to oxidation reactor. approximately 200 mL of the DI water to pass through the assembled filter holder. This is an additional rinse of all the tubing, the filters, and the filter holder. The IX filter is now ready to speciate As(III)/As(V). Discard the remaining DI water in the reactor. The reactor is now ready to receive a fresh test solution.

### Appendix C. Variable-DO Experiments

# C.1 High-DO Chemical Oxidation Experiments

The experimental procedure for the high-DO oxidation experiments, which were run in duplicate, is outlined below. Briefly, each experiment was performed in duplicate along with a control experiment for each set of duplicates. The control experiment was performed in exactly the same manner as the oxidation experiment except that no oxidant was present.

- (1) Prepare 2 L of the test solution with the appropriate concentration of As(III). Rinse the reactor twice with 50 mL of the test solution. Then place 500 mL of the test solution in the reactor. Close the reactor and pressurize to 15 psi with nitrogen gas. Start the magnetic stirrer.
- (2) Place a conditioned, chloride-form IX filter, fresh or regenerated, into the in-line filter holder. Place a 0.22 µm filter on top of the IX filter, and assemble the in-line filter holder. Set the timer on the fraction collector at 0.1 min, i.e., 6 seconds.
- (3) Inject the required quantity of the oxidant. Immediately, open the outlet valve allowing the test solution to flow through the IX filter into one of the 15-mL sample tubes in the fraction collector. (The flow rate obtained using 15 psi nitrogen gas pressure was approximately 20 mL/min).
- (4) Discard the first 4 mL (12 seconds) of the effluent. Start the fraction collector and collect samples (~ 2 mL aliquots) every six seconds for

the first minute of the reaction. (Samples were collected in the intervals of 12-18, 18-24, 24-30 sec, etc. were labeled with the median time of sampling as 15, 21, 27 sec and so on). Then stop the flow by closing the outlet valve and stop the fraction collector. Restart the flow by opening the outlet valve at 1 min 57 sec and allow flow to waste up to 2 min 07 sec. Collect flow for the next 10 sec, i.e., from 2 min 07 sec to 2 min 17 sec (median sample time of 2 min 12 sec (132 sec) from the start of the reaction). Stop the flow and repeat to get samples at 192, 252, and 312 sec. Acidify the 2.0 mL aliquots using 10 μL of conc. nitric acid and store at 4 °C until ready for analysis.

- (5) At the end of 317 sec, close the outlet valve. The experiment is complete at this point.
- To prepare for the duplicate, follow the procedure described below.
- (6) Vent the nitrogen gas pressure and disassemble the filter holder. Transfer the IX filter along with the 0.22 μm filter atop it to a vacuum filtration apparatus.
- (7) Regenerate the IX filter as outlined in the IX Regeneration Method in Appendix A.
- (8) Clean the reactor by rinsing four times with 250 mL of DI water. Then fill the reactor with 500 mL of DI water. Close the reactor and pressurize. Allow approximately

100 mL of flow from the reactor through an empty filter holder.

- (9) Transfer the regenerated IX filter into the in-line filter holder. Place a new 0.22 mm filter on top of the IX filter. Assemble the filter holder together and connect to the oxidation reactor. Allow approximately 200 mL of the DI water to pass through the assembled filter holder. Collect the last 10 mL of rinse and analyze as reactor blank. Discard the remaining DI water in the reactor. The reactor is now ready to receive a fresh test solution.
- (10) Duplicate the same experiment by following steps 1 through 5.

After completing the repeat experiment, a control run was performed to verify that no oxidation occurred in the absence of oxidant and that no residual oxidant was left in the reactor, i.e., to verify that the rinsing procedures used were effective in purging the entire reactor set-up of any leftover oxidant.

(10) Once again, clean the reactor as described before and fill with 500 mL of test solution spiked with Close the reactor and As(III). nitrogen pressurize with gas. Regenerate and place the IX filter in the filter holder. Start the magnetic stirrer. Start the timer and allow 5 minutes to pass before opening the outlet valve and allowing flow through the filter holder. Waste the first 4 mL and collect the next 10 mL of flow and analyze for arsenic. This sample served as the control for the set of repeat experiments.

# C.2 Low-DO Chemical Oxidation Experiments

The low-DO experiments were necessary only when dissolved iron or sulfide was added to the synthetic test water. The low-DO experiments were performed in the same manner as the high-DO experiments except that the rinse water and the synthetic water was sparged with extra-dry-grade nitrogen gas to produce a low-DO synthetic water containing ≤ 0.1 mg/L of dissolved oxygen).

The additional steps (to the procedure for the high-DO oxidation experiments) necessary to perform the low-DO experiments are described below.

- (1) Add 500 mL of the test solution to the reactor and close the reactor. Sparge with extra dry grade nitrogen gas for 30 minutes.
- (2) Briefly stop sparging and add the appropriate dose of dissolved iron (Fe(II)) or sulfide. In the case of dissolved iron, resume sparging for about 5 minutes and then close the reactor while maintaining nitrogen However, pressure. after the addition of sulfide, resume sparging very briefly (no more than 5-15 seconds to prevent sulfide stripping) and immediately close the reactor. Pressurize with nitrogen gas to 15 psi. Perform the oxidation experiment as described before.

### Appendix D. Solid-Phase (Filox) Experiments

The procedures used for the various Filox experiments are described in detail in this appendix. The procedures used for the variable-EBCT and variable-pH experiments was the same. In order to perform Filox experiments with low-DO, the oxidation reactor was used. Essentially, as in the chemical oxidation experiments, the low-DO synthetic water was prepared in the oxidation reactor as described in Appendix C and instead of adding any chemical oxidant to the reactor, the reactor was maintained under nitrogen pressure and the low-DO synthetic water was pumped from the reactor to the Filox column.

# D.1 Variable-EBCT and Variable-pH Experiments

- Two liters (2L) of synthetic water (previously sparged with air for 15 min) containing 50 μg/L of As(III) was prepared in a 2-L volumetric flask. The average DO of this synthetic water was 8.2 mg/L.
- (2) The high-DO synthetic water was then pumped from the volumetric flask through the Filox column. The flow rate was adjusted to the desired setting (starting with 16 mL/min, EBCT of 0.75 min) following which 5 BV (60 mL) of the synthetic water was passed through the column. Then, approximately 25 mL of the Filox column effluent was collected, acidified, and analyzed as Total Flow was then Effluent As. switched to the IX filter holder and three consecutive 1-BV intervals speciated, acidified. analyzed for unoxidized As(III).

To prepare the filter for the next EBCT or pH, the IX filter was regenerated according to the procedure described in Appendix A. To test the next variable, the flow rate was reset to the desired value and steps (1) - (2) were repeated.

The procedure for the variable-pH experiments was the same as for the variable-EBCT experiments except that the pH of the feed solution was adjusted to the desired level (6.3, 7.3, and 8.3) using 1M HCl solution.

After the desired experiments were completed, flow through the Filox column was stopped. The remaining contents of the volumetric flask were then speciated for As(III)/As(V) to ensure that all of the arsenic that was fed to the Filox column was As(III).

### D.2 Low-DO Filox Experiments

(1) 500 mL of synthetic water, without any sulfate, was sparged for 30 extra-dry-grade minutes with nitrogen gas to strip out the dissolved oxygen. It was then pumped through the Filox-media column and through the IX filter connected to the outlet After purging the of the column. media and the filter holder with approximately 350 mL of the low-DO water, the reactor was emptied refilled with the and composition synthetic water (Table 1). Sulfate was excluded because the Empore filter has a finite speciation capacity of approximately 100-150

- mL before it is exhausted, primarily by sulfate, and requires regeneration.
- After 30 minutes, nitrogen sparging was briefly stopped and the appropriate amount of As(III) and reductant were added to the sparged water. Sparging was resumed and continued for 15-20 more minutes and the low-DO water was then pumped through the Filox media column with continued sparging. When testing the nitrogen-sparged synthetic water in the presence of sulfide, no sparging was performed after sulfide had been added to the test water. Rather the reactor was sealed and maintained under a nitrogen atmosphere. Once sulfide was introduced into the synthetic water, sparging was stopped to avoid stripping sulfide from the synthetic water.
- (3) After 5 BV (60 mL) had passed through the Filox media, an effluent sample collected at the outlet of the Filox column, was acidified and analyzed for "Total Effluent As" exiting the Filox column. The flow was then switched to the IX filter. The first 5 mL of flow from the IX

- filter was wasted and then three consecutive 1-BV samples were collected, acidified with conc nitric acid, and analyzed for arsenic. A 25-mL sample from the closed reactor was collected, acidified, and analyzed for feed As. The reactor was then emptied and rinsed with DI water and prepared for the next experiment.
- (4) To verify that all of the arsenic fed to the Filox column was As(III). the oxidation reactor was filled with synthetic water and sparged for 30 minutes followed by the addition of an appropriate amount of As(III) and reductant, if any. Sparging was continued for a further 15-20 minutes (except in the presence of sulfide) and the synthetic water containing 50 ug/L As(III) was pumped from the reactor straight to the IX filter. The effluent from the IX filter was collected, acidified, and analyzed as Control As(III). Such controls were (one control/set performed duplicates) for the varying pH and EBCT experiments as well as each of the interfering reductant experiments.

### Appendix E. Chlorine Oxidation Data

```
Run # Description
E15.01-15.02: No interfering reductants: Dose = 3 x As(III); pH = 8.3
E15.03-15.04: No interfering reductants: Dose = 3 x As(III); pH = 7.3
E15.05-15.06: No interfering reductants: Dose = 3 x As(III); pH = 6.3
E15.07-15.08: Mn(II) = 0.2 mg/L; Dose = 10 x As(III); pH = 8.3
E15.09-15.10: Fe(II) = 0.3 mg/L; Dose = 10 x As(III); pH = 8.3
E15.11-15.12: Fe(II) = 2.0 mg/L; Dose = 10 x As(III); pH = 8.3
E15.13-15.14: Sulfide = 1.0 mg/L; Dose = 10 x As(III); pH = 8.3
E15.17-15.16: Sulfide = 2.0 mg/L; Dose = 10 x As(III); pH = 8.3
E15.17-15.18: TOC = 6.9 mg/L; Dose = 10 x As(III); pH = 8.3; Lake Houston Water
E15.19-15.20: No interfering Reductants As(III) = 1000 μg/L; Dose = 3 x As(III); pH = 8.3
E15.21-15.22: No interfering reductants: 5 °C; Dose = 3 x As(III); pH = 8.3
```

Table E-1. Residual As(III) Conc. vs Time for Chlorine Experiments.

Sample	Median		Residual As(III) Conc., μg/L for Run #								
Interval	Time										
(sec)	(sec)	15.01	15.02	15.03	15.04	15.05	15.06	15.07	15.08	15.09	15.10
	0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
12-18	15	1.6	1.6	2.2	2.1	14.0	14.0	4.0	4.6	0.5	1.3
18-24	21	1.2	1.2	1.3	1.3	9.1	9.6	2.5	3.1	0.1	0.2
24-30	27	0.6	0.6	0.7	0.6	6.1	8.1	2.0	1.4	0.1	0.1
30-36	33	0.5	0.5	0.1	0.3	3.7	2.9	1.6	1.6	0.1	0.3
36-42	39	0.3	0.3	0.5	0.2	2.3	1.6	1.3	1.1	0.1	0.1
42-48	45	0.5	0.5	0.6	0.3	1.4	1.3	1.1	0.1	0.1	0.1
48-54	51	0.2	0.2	0.5	0.1	0.7	0.7	0.8	0.5	0.1	0.1
54-60	57	0.5	0.5	0.5	0.6	0.1	0.3	0.6	0.1	0.1	0.1
60-66	63	0.3	0.3	0.2	0.2	0.3	0.5	0.3	0.1	0.1	0.1
66-72	69	0.5	0.5	0.2	0.1	0.1	0.1	0.3	0.3	0.1	0.1
127-137	132	0.1	0.1	0.1	0.1	0.0	0.6	0.3	0.3	0.1	0.1
187-197	192	0.2	0.2	0.1	0.2	0.2	0.2	0.1	0.3	0.2	0.1
247-257	252	0.1	0.1	0.1	0.5	0.1	0.1	0.3	0.6	0.8	0.1
307-317	312	0.2	0.2	0.2	0.2	0.3	0.1	0.3	0.3	0.3	0.1

Table E-1. Continued.

	Table 2 1. Commade.										
Sample	Median		Residual As(III) Conc., µg/L for Run #								
Interval	Time										
(sec)	(sec)	15.11	15.12	15.13	15.14	15.15	15.16	15.17	15.18	15.19	15.20
	0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50	1000	1000
12-18	15	0.8	1.2	18.0	20.0	24.0	26.0	1.5	2.8	10.0	7.5
18-24	21	0.2	0.1	14.0	15.0	19.0	19.0	1.5	2.8	3.7	1.7
24-30	27	0.1	0.1	7.2	8.9	15.0	16.0	1.2	1.9	1.1	5.3
30-36	33	0.1	0.1	6.1	6.4	12.0	14.0	1.2	1.3	3.1	3.3
36-42	39	0.1	0.1	5.5	4.0	8.2	11.0	1.0	1.0	4.1	2.5
42-48	45	0.1	0.1	3.5	3.2	5.3	7.2	1.2	0.1	4.3	2.9
48-54	51	0.1	0.1	2.7	2.4	1.7	3.2	1.3	1.3	3.5	4.9
54-60	57	0.1	0.1	1.0	1.1	1.5	2.1	1.2	2.1	3.7	0.9
60-66	63	0.1	0.1	0.8	0.8	1.1	1.7	1.2	2.8	4.5	3.5
66-72	69	0.1	0.1	0.4	0.6	0.5	0.9	1.2	3.6	3.3	1.5
127-137	132	0.1	0.1	0.8	0.3	0.3	0.3	2.3	4.1	3.5	3.1
187-197	192	0.1	0.1	0.8	0.3	0.5	0.1	1.5	2.8	2.1	2.5
247-257	252	0.1	0.1	1.0	0.8	0.6	0.3	2.3	3.7		
307-317	312	0.1	0.1	0.6	0.8	0.6	0.1	1.0	3.6		

Table E-1. Continued.

I GOLO ID	I dolo 11. Commude.										
Sample	Median	Ru									
Interval	Time	μд	/L								
(sec)	(sec)	15.21	15.22								
	0	50	50								
12-18	15	0.1	0.1								
18-24	21	0.1	0.1								
24-30	27	0.1	0.1								
30-36	33	0.1	0.1								
36-42	39	0.1	0.1								
42-48	45	0.1	0.1								
48-54	51	0.1	0.1								
54-60	57	0.1	0.1								
60-66	63	0.1	0.1								
66-72	69	0.1	0.1								
127-137	132	0.1	0.1								
187-197	192	0.1	0.1								
247-257	252	0.1	0.1								
307-317	312	0.1	0.1								

### Appendix F. Permanganate Oxidation Data

Run#	Description
E16.01-16.02:	No interfering reductants: Dose = $3 \times As(III)$ ; pH = $8.3$
E16.03-16.04:	No interfering reductants: Dose = $3 \times As(III)$ ; pH = $7.3$
E16.05-16.06:	No interfering reductants: Dose = $3 \times As(III)$ ; pH = $6.3$
E16.07-16.08:	Mn(II) = 0.2  mg/L; Dose = 10  x As(III); pH = 8.3
E16.09-16.10:	Fe(II) = 0.3  mg/L; Dose = 10  x As(III); pH = 8.3
E16.11-16.12:	Fe(II) = 2.0  mg/L; $Dose = 10  x As(III)$ ; $pH = 8.3$
E16.13-16.14:	Sulfide = $1.0 \text{ mg/L}$ ; Dose = $10 \text{ x As(III)}$ ; pH = $8.3$
E16.15-16.16:	Sulfide = $2.0 \text{ mg/L}$ ; Dose = $10 \text{ x As(III)}$ ; pH = $8.3$
E16.17-16.18:	TOC = 6.9  mg/L; $Dose = 10  x As(III)$ ; $pH = 8.3$
E16.19-16.20:	No interfering Reductants; As(III) = $1000 \mu g/L$ ; Dose = $3 x$
	As(III); pH = 8.3
E16.21-16.22:	No interfering reductants: $5  ^{\circ}\text{C}$ ; Dose = $3  \text{x As(III)}$ ; $pH = 8.3$

Table F-1. Residual As(III) Conc. vs Time for Permanganate Experiments.

Sample	Median	Residual As(III) Conc., μg/L for Run #									
Interval	Time										
(sec)	(sec)	16.01	16.02	16.03	16.04	16.05	16.06	16.07	16.08	16.09	16.10
	0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
12-18	15	1.9	2.6	2.1	1.7	6.0	6.7	2.4	3.0	3.1	3.2
18-24	21	1.2	1.8	1.4	0.8	3.9	5.3	1.5	1.3	1.5	1.8
24-30	27	0.7	1.2	0.7	0.6	2.0	3.9	0.7	0.4	0.7	0.6
30-36	33	0.3	0.5	0.2	0.3	0.9	1.9	0.3	0.1	0.1	0.1
36-42	39	0.2	0.2	0.1	0.2	0.7	0.6	0.1	0.1	0.1	0.1
42-48	45	0.1	0.1	0.1	0.2	0.2	0.2	0.1	0.3	0.1	0.1
48-54	51	0.1	0.2	0.1	0.1	0.7	0.2	0.1	0.1	0.1	0.1
54-60	57	0.1	0.3	0.1	0.2	0.1	0.2	0.1	0.1	0.1	0.1
60-66	63	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
66-72	69	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1
127-137	132	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.1
187-197	192	0.1	0.1	0.1	0.1	0.1	0.3	0.3	0.1	0.1	0.1
247-257	252	0.1	0.1	0.1	0.1	0.1	0.5	0.3	0.1	0.1	0.1
307-317	312	0.1	0.1	0.1	0.1	0.1	0.2	0.3	0.1	0.1	0.1

Table F-1. Continued.

Table F-1. Continued.											
Sample	Median	Residual As(III) Conc., μg/L for Run #									
Interval	Time										
(sec)	(sec)	16.11	16.12	16.13	16.14	16.15	16.16	16.17	16.18	16.19	16.20
	0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	1000	1000
12-18	15	0.1	0.1	5.7	6.9	11.8	10.7	1.5	0.4	8.9	13.0
18-24	21	0.1	0.1	5.0	5.5	10.7	9.0	0.0	0.4	1.5	0.9
24-30	27	0.1	0.1	4.3	4.7	9.0	8.2	1.4	0.2	1.9	2.5
30-36	33	0.1	0.1	4.0	4.1	6.5	7.2	1.5	0.1	2.9	3.7
36-42	39	0.1	0.1	3.2	3.8	5.7	5.1	1.0	0.1	3.3	1.7
42-48	45	0.1	0.1	2.9	3.1	4.4	3.2	0.4	0.1	2.5	1.3
48-54	51	0.1	0.1	2.6	2.1	3.7	1.5	3.4	0.1	1.7	2.9
54-60	57	0.0	0.1	1.4	1.4	2.4	1.4	0.2	0.1	2.9	0.9
60-66	63	0.1	0.1	1.0	1.3	1.8	1.4	1.5	0.2	2.9	0.9
66-72	69	0.1	0.1	0.6	0.6	1.4	1.3	1.9	0.1	2.3	3.5
127-137	132	0.1	0.1	0.3	0.6	0.4	1.1	1.6	1.2	0.9	1.7
187-197	192	0.1	0.1	0.3	0.6	0.1	0.6	1.4	1.5	0.9	2.9
247-257	252	0.1	0.1	0.4	0.1	0.5	0.6	2.1	2.1		
307-317	312	0.1	0.1	0.4	0.6	0.6	0.6	0.8	2.8		

Table F-1. Continued.

Sample	Median	Ru							
Interval	Time	μg/L							
(sec)	(sec)	16.21	16.22						
	0	50.0	50.0						
12-18	15	0.1	0.1						
18-24	21	0.1	0.1						
24-30	27	0.1	0.1						
30-36	33	0.1	0.1						
36-42	39	0.1	0.1						
42-48	45	0.1	0.1						
48-54	51	0.1	0.1						
54-60	57	0.1	0.1						
60-66	63	0.1	0.1						
66-72	69	0.1	0.1						
127-137	132	0.1	. 0.1						
187-197	192	0.1	0.1						
247-257	252	0.1	0.1						
307-317	312	0.1	0.1						

# Appendix G. Chlorine Dioxide Oxidation Data

Run #	Description
E17.01-17.02:	No interfering reductants: pH 8.3
E17.03-17.04:	No interfering reductants: pH 7.3
E17.05-17.06:	No interfering reductants: pH 6.3
E17.07-17.08:	Mn(II) = 0.2  mg/L; Dose = 3  x As(III); pH = 8.3
E17.09-17.10:	Fe(II) = 0.3  mg/L; Dose = 3  x As(III); pH = 8.3
E17.11-17.12:	Fe(II) = 2.0  mg/L; Dose = 3  x As(III); pH = 8.3
E17.13-17.18:	Oxidation of Fe(II); Repeat of Knocke (1990) experiments
	Not included in Table G-1
E17.19-17.20:	Repeat of E17.01-17.02; No interfering reductants: pH 8.3
E17.21-17.22:	No interfering reductants: pH 8.3; 3 x Cl <sub>2</sub> @ t=1'45"
E17.23-17.24:	No interfering reductants: pH 8.3; Deaerated Test Solution
E17.25-17.26:	No interfering reductants: pH 8.3; Dose = $10 \times As(III)$
E17.27-17.28:	No interfering reductants: pH 8.3; Dose = 100 x As(III)

Table G-1. Residual As(III) Conc. vs Time for Chlorine Dioxide Experiments.

Sample	Median			F	Residual A	s(III) Co	nc., μg/L	for Run #	#		
Interval	Time										
(sec)	(sec)	17.01	17.02	17.03	17.04	17.05	17.06	17.07	17.08	17.09	17.10
	0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
12-18	15	38.9	42.0	47.0	48.4	47.0	49.0	37.2	36.3	30.8	29.4
18-24	21	37.7	40.6	46.8	49.0	47.3	49.0	35.6	35.8	29.3	26.8
24-30	27	37.9	40.3	46.8	46.8	46.5	48.7	35.3	35.3	28.4	26.3
30-36	33	37.5	40.3	47.5	47.0	46.1	48.4	31.7	33.9	27.0	26.7
36-42	39	38.9	40.8	46.6	47.3	45.6	48.0	35.1	33.6	26.7	27.0
42-48	45	37.7	39.4	47.3	47.0	47.7	48.0	34.4	33.9	27.2	26.7
48-54	51	37.5	39.9	46.3	47.2	48.4	47.0	34.3	33.2	27.5	26.0
54-60	57	37.5	39.9	46.8	47.2	46.8	47.0	34.1	31.2	26.7	25.8
60-66	63	38.4	40.5	46.5	47.5	46.5	46.8	34.3	32.7	26.5	24.9
66-72	69	38.6	40.6	47.2	47.0	46.7	46.3	34.6	32.9	27.0	25.5
127-137	132	39.6	40.3	47.8	46.3	47.5	46.3	34.3	33.2	27.0	28.0
187-197	192	37.2	39.4	47.3	46.3	47.7	44.6	33.7	33.4	27.0	26.7
247-257	252	38.4	39.1	47.5	45.8	46.3	44.6	33.6	32.2	28.0	27.0
307-317	312	38.0	39.1	47.3	45.8	48.2	45.4	34.6	33.2	26.7	27.0

Table G-1. Continued.

14010	Table G-1. Continued.										
Sample	Median		Residual As(III) Conc., µg/L for Run #								
Interval	Time										
(sec)	(sec)	17.11	17.12	17.19	17.20	17.21	17.22	17.23	17.24	17.25	17.26
	0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50	50
12-18	15	23.9	21.8	35.4	38.8	40.4	40.2	40.2	41.1	35.5	36.0
18-24	21	21.7	19.8	34.8	36.6	39.6	40.4	39.6	40.5	36.0	35.9
24-30	27	21.5	19.4	34.8	38.8	38.8	39.0	39.2	40.2	35.2	36.2
30-36	33	20.8	17.7	35.4	36.4	38.4	39.6	38.4	40.0	35.2	34.8
36-42	39	20.1	18.0	35.4	39.2	38.2	39.4	38.4	39.6	33.6	31.8
42-48	45	20.3	18.4	35.2	39.2	37.2	38.0	37.6	38.4	33.4	32.0
48-54	51	19.8	18.6	34.6	39.0	36.6	38.2	37.8	38.6	32.0	32.9
54-60	57	20.8	19.1	34.8	38.6	36.2	38.4	37.1	38.6	31.0	34.3
60-66	63	20.8	18.6	34.6	38.8	36.4	37.0	37.3	38.2	31.5	31.1
66-72	69	21.0	19.4	35.4	38.6	35.8	37.4	37.3	38.4	29.9	30.6
127-137	132	21.0	19.4	35.4	35.2	1.5	0.9	37.1	38.4	30.6	31.8
187-197	192	20.6	19.1	33.8	36.6	0.1	0.1	38.0	38.4	29.6	30.4
247-257	252	21.8	18.9	34.6	36.0	0.1	0.1	38.0	38.6	29.9	29.0
307-317	312	19.8	19.1	33.3	35.4	0.1	0.1	37.4	39.0	30.1	28.5

Table G-1. Continued.

Table 0-1. Continued.								
Sample	Median	Run#						
Interval	Time	μд	/L					
(sec)	(sec)	17.27	17.28					
	0	50.0	50.0					
12-18	15	26.1	25.2					
18-24	21	24.2	25.9					
24-30	27	24.0	24.5					
30-36	33	23.6	24.3					
36-42	39	22.8	23.5					
42-48	45	22.2	21.9					
48-54	51	22.1	22.8					
54-60	57	22.4	20.7					
60-66	63	21.2	18.9					
66-72	69	20.8	18.4					
127-137	132	15.6	14.7					
187-197	192	13.2	14.0					
247-257	252	12.5	10.9					
307-317	312	12.1 12.1						

## Appendix H. Monochloramine Oxidation Data

Run #	Description	•
E18.01-18.0	2: No interfering reductar	ts: pH 8.3: in situ monochloramine
E18.03-18.0	4: No interfering reductar	ts: pH 7.3: in situ monochloramine
E18.05-18.0	6: No interfering reductar	ts: pH 6.3: in situ monochloramine
E18.07-18.0	8: No interfering reductar	ts: pH 8.3: preformed monochloramine

Table H-1. Residual As(III) Conc. vs Time for Monochloramine Experiments.

Sample	Median	Residual As(III) Conc., µg/L for Run #								
Interval	Time		_	_		_				
(sec)	(sec)	18.01	18.02	18.03	18.04	18.05	18.06	18.07	18.08	
	0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	
12-18	15	30.6	33.3	31.3	29.4	33.3	31.9	47.6	47.4	
18-24	21	30.1	33.1	31.5	29.1	30.6	32.6	48.6	49.1	
24-30	27	29.4	33.6	31.3	29.1	29.1	31.5	48.9	49.6	
30-36	33	29.4	33.6	31.0	28.9	28.7	30.8	48.9	50.1	
36-42	39	29.6	31.5	30.6	28.5	28.7	30.5	49.2	49.9	
42-48	45	29.9	32.2	30.5	28.2	29.1	30.8	49.9	49.1	
48-54	51	28.9	32.4	30.6	28.9	29.2	30.8	50.2	49.6	
54-60	57	29.6	32.2	31.0	28.9	30.1	30.5	49.4	50.1	
60-66	63	29.8	32.4	31.3	30.5	29.8	30.5	49.4	50.6	
66-72	69	29.8	32.9	30.3	28.7	29.8	31.0	48.7	49.4	
127-137	132	29.8	31.5	29.4	28.5	30.1	30.1	49.2	49.4	
187-197	192	29.1	31.5	30.1	28.2	29.1	29.8	50.2	49.1	
247-257	252	29.4	31.5	29.6	28.4	29.1	29.1	49.1	49.7	
307-317	312	29.8	31.9	30.8	28.4	29.4	29.6	49.9	50.2	

## Appendix I. Ozone Oxidation Data

```
Description
Run#
E19.01-19.02: No interfering reductants: Dose = 3 \times As(III); pH = 8.3
E19.03-19.04: No interfering reductants: Dose = 3 \times As(III); pH = 7.3
E19.05-19.06: No interfering reductants: Dose = 3 \times As(III); pH = 6.3
E19.07-19.08: Mn(II) = 0.2 \text{ mg/L}; Dose = 10 x As(III); pH = 8.3
E19.09-19.10: Fe(II) = 0.3 mg/L; Dose = 10 \times As(III); pH = 8.3
E19.11-19.12: Fe(II) = 2.0 \text{ mg/L}; Dose = 10 \text{ x As(III)}; pH = 8.3 \text{ mg/L}
E19.13-19.14: Sulfide = 1.0 \text{ mg/L}; Dose = 10 \text{ x As(III)}; pH = 8.3 \text{ mg/L}
E19.15-19.16: Sulfide = 2.0 \text{ mg/L}; Dose = 10 \text{ x As(III)}; pH = 8.3 \text{ mg/L}
E19.17-19.18: TOC = 6.9 \text{ mg/L}; Dose = 10 \text{ x As(III)}; pH = 8.3
               : Repeat of E19.01-19.02; No interfering reductants: Dose = 3 x As(III);
E19.19
                 pH = 8.3
               : Repeat of E19.17-19.19; TOC = 6.9 \text{ mg/L}; Dose = 10 \text{ x As(III)}; pH = 8.3
E19.20
E19.21-19.22: TOC = 2.1 \text{ mg/L}; Dose = 10 \text{ x As(III)}; pH = 8.3 \text{ mg/L}
E19.23-19.24: No interfering reductants: 5 °C; Dose = 3 x As(III); pH = 8.3
E19.25-19.26: Repeat of E19.21-19.22; TOC = 2.1 \text{ mg/L}; Dose = 10 \text{ x As(III)}; pH = 8.3
```

Table I-1. Residual As(III) Conc. vs Time for Ozone Experiments.

Sample	Median			P	tesidual A	s(III) Co	Residual As(III) Conc., μg/L for Run #							
Interval	Time									_				
(sec)	(sec)	19.01	19.02	19.03	19.04	19.05	19.06	19.07	19.08	19.09	19.10			
	0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0			
12-18	15	1.9	1.1	0.7	0.4	1.6	0.9	0.8	1.2	0.5	0.2			
18-24	21	1.2	0.5	0.7	0.2	1.1	0.1	0.5	0.8	0.2	0.2			
24-30	27	1.2	0.4	0.5	0.1	0.4	0.1	0.5	0.5	0.1	0.2			
30-36	33	1.1	0.1	0.2	0.1	0.2	0.1	0.2	0.3	0.1	0.1			
36-42	39	1.1	0.1	0.1	0.1	0.1	0.1	0.3	0.3	0.2	0.1			
42-48	45	0.9	0.1	0.1	0.1	0.1	0.1	0.5	0.2	0.1	0.2			
48-54	51	0.5	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1			
54-60	57	0.7	0.1	0.1	0.1	0.4	0.1	0.2	0.1	0.1	0.1			
60-66	63	0.9	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.2	0.1			
66-72	69	0.9	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1			
127-137	132	0.9	0.1	0.1	0.4	0.1	0.1	0.3	0.1	0.1	0.1			
187-197	192	0.9	0.1	0.4	0.1	0.2	0.1	0.1	0.2	0.1	0.1			
247-257	252	0.7	0.1	0.1	0.1	0.1	0.1	0.2	0.1	0.1	0.1			
307-317	312	0.7	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1			

Table I-1. Continued.

Table 1 1. Continued.											
Sample	Median		Residual As(III) Conc., µg/L for Run #								
Interval	Time										
(sec)	(sec)	19.11	19.12	19.13	19.14	19.15	19.16	19.17	19.18	19.19	19.20
	0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0	50.0
12-18	15	0.1	0.1	16.4	14.0	24.4	26.4	37.8	34.3	3.1	35.7
18-24	21	0.1	0.1	11.1	9.9	21.1	23.8	36.9	34.3	2.6	35.2
24-30	27	0.1	0.1	8.3	6.6	18.3	19.7	34.7	33.8	2.8	35.3
30-36	33	0.1	0.1	6.1	5.2	14.9	16.1	35.4	32.8	2.4	35.9
36-42	39	0.1	0.1	4.7	4.2	12.5	13.3	34.7	32.8	1.5	35.0
42-48	45	0.1	0.1	3.3	2.6	10.2	12.3	35.8	31.9	2.4	34.8
48-54	51	0.1	0.1	2.5	1.1	7.3	9.2	35.6	32.3	1.5	35.5
54-60	57	0.1	0.1	2.0	0.6	6.1	6.4	34.9	31.9	2.1	35.2
60-66	63	0.1	0.1	2.0	0.1	5.4	5.9	35.1	32.1	1.4	34.3
66-72	69	0.1	0.1	1.3	0.1	3.3	5.1	34.9	31.7	1.2	35.7
127-137	132	0.1	0.1	0.9	0.3	2.0	2.2	34.9	31.4	0.8	35.3
187-197	192	0.1	0.1	0.4	0.1	2.1	1.4	35.1	31.2	0.7	35.0
247-257	252	0.1	0.1	0.2	0.2	1.3	0.9	34.9	30.4	0.1	34.6
307-317	312	0.1	0.1	0.1	0.4	1.4	0.6	35.2	31.2	0.3	35.0

Table I-1. Continued.

Sample	Median		Residual A	As(III) Co	nc., μg/L :	for Run #				
Interval	Time			_	_					
(sec)	(sec)	19.21	19.22	19.23	19.24	19.25	19.26			
	0	50.0	50.0	50.0	50.0	50.0	50.0			
12-18	15	3.1	1.4	3.8	4.3	5.0	2.2			
18-24	21	1.8	1.0	3.1	3.1	4.3	0.7			
24-30	27	1.5	0.7	2.6	3.1	3.1	0.1			
30-36	33	1.0	0.5	2.6	2.8	2.7	0.1			
36-42	39	0.8	0.5	2.4	2.4	2.2	0.1			
42-48	45	0.8	0.5	2.4	2.2	0.9	0.1			
48-54	51	0.8	0.3	2.2	2.1	1.2	0.1			
54-60	57	0.8	0.1	2.4	1.7	0.7	0.1			
60-66	63	0.8	0.1	2.4	1.5	1.1	0.1			
66-72	69	1.0	0.1	2.1	1.0	2.2	0.1			
127-137	132	0.1	0.1	0.1	0.3	1.2	0.9			
187-197	192	0.1	0.1	0.1	0.5	1.8	0.7			
247-257	252	0.1	0.7	0.1	0.8	1.4	0.9			
307-317	312	0.1	0.1	0.1	1.0	0.7	0.2			

## Appendix J. Filox Oxidation Data

```
Run#
                      Description
E20.01:No interfering reductants: pH = 8.3, EBCT = 0.75 min, High DO
E20.02:No interfering reductants: pH = 8.3, EBCT = 1.5 min, High DO
E20.03:No interfering reductants: pH = 8.3, EBCT = 3.0 min, High DO
E20.04:No interfering reductants: pH = 8.3, EBCT = 6.0 min, High DO
E20.05:Repeat of E20.1
E20.06:Repeat of E20.2
E20.07:Repeat of E20.3
E20.08:Repeat of E20.4
E20.09:2000 BV Filox Run, No interfering reductants: pH = 8.3, EBCT = 0.75
       min, High DO
E20.10:No interfering reductants: pH = 7.3, EBCT = 1.5 min, High DO
E20.11:No interfering reductants: pH = 6.3, EBCT = 1.5 min, High DO
E20.12:No interfering reductants: pH = 7.3, EBCT = 1.5 min, Low DO
E20.13:Repeat of E20.12
E20.14:Mn(II) = 0.2 \text{ mg/L}; pH = 8.3, EBCT = 1.5 \text{ min, Low DO}
E20.15:Fe(II) = 0.3 mg/L; pH = 8.3, EBCT = 1.5 min, Low DO
E20.16:Fe(II) = 2.0 mg/L; pH = 8.3, EBCT = 1.5 min, Low DO
E20.17:Sulfide = 1.0 mg/L; pH = 8.3, EBCT = 1.5 min, Low DO
E20.18:Sulfide = 2.0 \text{ mg/L}; pH = 8.3, EBCT = 1.5 \text{ min}, Low DO
E20.19:TOC = 1.4 \text{ mg/L}; pH = 8.3, EBCT = 1.5 \text{ min, Low DO}
E20.20:No interfering Reductants; 5 °C, pH = 8.3, EBCT = 1.5 min, Low DO
E20.21:No interfering Reductants; As(III) = 1000 \mug/L, pH = 8.3, EBCT = 1.5
       min, Low DO
E20.22:No interfering Reductants; As(III) = 1000 \mu g/L, pH = 8.3, EBCT = 1.5
       min, High DO
E20.23:Mn(II) = 0.2 \text{ mg/L}; pH = 8.3, EBCT = 1.5 \text{ min, High DO}
E20.24: Sulfide = 1.0 mg/L; pH = 8.3, EBCT = 1.5 min, High DO
E20.25:Sulfide = 2.0 mg/L; pH = 8.3, EBCT = 1.5 min, High DO
E20.26:TOC = 1.4 \text{ mg/L}; pH = 8.3, EBCT = 1.5 \text{ min, High DO}
E20.27:Mn(II) = 0.2 \text{ mg/L}; pH = 8.3, EBCT = 6.0 \text{ min, Low DO}
E20.28:Sulfide = 1.0 mg/L; pH = 8.3, EBCT = 6.0 min, Low DO
E20.29:Sulfide = 2.0 \text{ mg/L}; pH = 8.3, EBCT = 6.0 \text{ min}, Low DO
E20.30:TOC = 1.4 \text{ mg/L}; pH = 8.3, EBCT = 6.0 \text{ min, Low DO}
```

Table J-1. Residual As(III) vs Effluent As Concentration for Filox Experiments.

Sample	Residual As(III)	Total Effluent						
ID	Concentration	As						
	μg/L	μg/L						
E20.01	2.0	NM						
E20.02	0.1	NM						
E20.03	0.1	NM						
E20.04	0.4	NM						
E20.05	2.6	27.3						
E20.06	1.2	25.9						
E20.07	1.2	22.5						
E20.08	0.3	18.2						
E20.10	0.1	16.9						
E20.11	0.1	12.4						
E20.12	0.3	24.5						
E20.13	0.5	39.4						
E20.14	10.9	43.8						
E20.15	9.5	40.5						
E20.16	9.3	43.1						
E20.17	19.3	47.5						
E20.18	22.1	45.3						
E20.19	10.4	46.4						
E20.20	0.8	31.8						
E20.21	33.2	551.9						
E20.22	49.7	499.3						
E20.23	0.8	24.7						
E20.24	0.8	12.0						
E20.25	1.9	11.4						
E20.26	1.2	22.3						
E20.27	0.1	24.5						
E20.28	0.2	21.3						
E20.29	1.4	28.8						
E20.30	0.1	26.3						
NM: Not	NM: Not Measured							

E20.09	Residual As(III)	Total Effluent
	Concentration	As
BV	μg/L	μg/L
100	2.1	36.8
200	2.0	40.1
300	2.8	41.3
400	3.5	42.1
500	3.3	43.1
600	2.5	40.2
700	2.3	41.6
800	3.0	43.5
900	2.8	42.6
1000	3.0	43.3
1100	3.2	45.3
1200	3.8	44.3
1300	2.8	42.6
1400	3.2	42.5
1500	3.7	44.3
1600	3.0	44.2
1700	3.7	44.2
1800	3.5	44.5
1900	3.0	46.2
2000	3.5	45.9

## Appendix K. UV Oxidation Data

Run #	Description
E21.01:UV	1: Flow Rate = 48 mL/min, Contact Time = 6 min, pH = 8.3
E21.02:UV	1: Flow Rate = 96 mL/min, Contact Time = 3 min, pH = 8.3
E21.03:UV	1: Flow Rate = 288 mL/min, Contact Time = 1 min, pH = 8.3
E21.04:Rep	eat of E21.03
E21.05:Rep	eat of E21.02
E21.06:Rep	eat of E21.01
E21.07:UV	1: Flow Rate = 24 mL/min, Contact Time = 12 min, pH = 8.3
E21.08:UV	1: Flow Rate = 12 mL/min, Contact Time = 24 min, pH = 8.3
	1: Flow Rate = $12 \text{ mL/min}$ , Contact Time = $6 \text{ min}$ , pH = $7.3 \text{ mes}$
	1: Flow Rate = 12 mL/min, Contact Time = 6 min, pH = 6.3
E21.11:UV	1: Flow Rate = 310 mL/min, Contact Time = 0.9 min, pH = 8.3
Sulf	ite = $1.0 \text{ mg/L}$
E22.01:UV	2: Flow Rate = 310 mL/min, Contact Time = 1.6 min, pH = $8.3$
E22.02:UV	2: Flow Rate = $209 \text{ mL/min}$ , Contact Time = $2.3 \text{ min}$ , pH = $8.3 \text{ min}$
E22.03:UV	2: Flow Rate = $104 \text{ mL/min}$ , Contact Time = $4.7 \text{ min}$ , pH = $8.3 \text{ min}$
	2: Flow Rate = $52 \text{ mL/min}$ , Contact Time = $9.3 \text{ min}$ , pH = $8.3 \text{ min}$
E22.05:UV	2: Flow Rate = $26 \text{ mL/min}$ , Contact Time = $18.7 \text{ min}$ , pH = $8.3 \text{ min}$
E22.06:UV	2: Flow Rate = $26 \text{ mL/min}$ , Contact Time = $18.7 \text{ min}$ , pH = $7.3 \text{ min}$
F22 07:ITV	2. Flow Rate = $26 \text{ mL/min}$ . Contact Time = $18.7 \text{ min}$ . pH = $6.3 \text{ min}$

Table K-1. Residual As(III) Conc. for UV Experiments.

	UV Unit 1					
Sample ID	UV Intensity mW-sec/cm <sup>2</sup>	Residual As(III) Concentration  µg/L				
E21.01	11520	35.7				
E21.02	5760	42.2				
E21.03	1920	48.8				
E21.04	1920	13.5				
E21.05	5760	21.2				
E21.06	11520	37.3				
E21.07	23040	43.4				
E21.08	46080	47.7				
E21.09	46080	14.5				
E21.10	46080	17.9				
E21.11	1780	0.1				

	UV Unit 2					
Sample	UV Intensity	Residual As(III)				
ID	mW-sec/cm <sup>2</sup>	Concentration				
		μg/L				
E22.01	3380	28.5				
E22.02	5760	35.8				
E22.03	11520	44.0				
E22.04	23040	47.4				
E22.05	46080	49.2				
E22.06	46080	29.8				
E22.07	46080	36.7				

## Appendix L. As(III) Stock Solution

An As(III) stock solution containing 88.0 mg/L As(III) was prepared in a synthetic water of a composition similar to the synthetic test water shown in Table 2-1 except that no calcium chloride was added to the stock solution. Calcium chloride was not added as the high pH of the As(III) stock solution (due to added bicarbonate and silicate) would have resulted in the precipitation of calcium carbonate.

Approximately 500 mL of reagent grade water was added to a 1-L volumetric flask. All of the ions except calcium chloride were added to the flask.

Finally, the required amount of sodium m-arsenite (Sigma Chemical Co.) was give final As(III) added a concentration of approximately 88 mg/L and the volume of the As(III) stock solution was made up to 1.0 L. The pH of this As(III) stock solution was 9.1. The stock solution was then refrigerated (4 °C). When required, the necessary volume of this As(III) stock solution was added to the synthetic test water to provide a final As(III) concentration of 50 or 1000 μg/L.

## Appendix M. QC Data

The following QC samples were analyzed:

#### (1) QC standards

These were prepared by the QA/QC Officer for this project, Anthony Tripp, and served as "in-house" OC check standards. Four standards were prepared at a time and any one of these standards were analyzed along with the four WAL analysis. standards during The concentrations of these QC standards were within the range of 1.0-11.0 μg/L As. These standards were analyzed without dilution. Results from all the OC samples are shown in Table M-1.

#### (2) WS Standards

Four WS standards were preserved in a 0.2 M nitric acid solution and measured

once during a batch of samples. The concentrations of these standards are shown in Table 2-3. Standards WS 037, WS 038, and WS 041 were always diluted 10-fold before analysis. Standard WS 040 was diluted 10- and 20-fold before analysis. Results from all the WS samples are shown in Table M-2.

#### (3) Spikes

Standards WS 037, WS 038, and WS 041 were always diluted 10-fold and spiked with 2.0  $\mu$ g/L As. Standard WS 041 was diluted 20-fold and then spiked with 2.0  $\mu$ g/L As. Results of arsenic recoveries from all the WS-spiked samples are shown in Table M-3.

Table M-1. Results of QC Analysis

Run#	Date	Dilution	QC Conc	Measured Conc
Kun ii	Duit	Factor	μg/L	μg/L
E19.13-19.16	7/9/1999	1	1.00	0.95
E19.13-19.16	7/9/1999	1	1.00	0.94
E19.13-19.16	7/9/1999	1	1.00	0.99
E19.13-19.16	7/9/1999	1	1.00	0.97
E19.13-19.16	7/9/1999	1	1.00	1.01
E19.13-19.16	7/9/1999	1	1.00	0.97
E20.1-20.4	9/25/1999	1	1.00	0.92
E20.1-20.4	9/25/1999	1	1.00	0.94
E20.1-20.4	9/25/1999	1	1.00	0.94
E20.5-20.8	9/28/1999	1	1.00	0.96
E20.5-20.8	9/28/1999	1	1.00	0.98
E20.5-20.8	9/28/1999	1	1.00	0.96
E20,14-20.22	10/26/1999	1	1.00	0.95
E20.14-20.22	10/26/1999	1	1.00	0.94
E20.14-20.22	10/26/1999	1	1.00	0.95
E20.14-20.22	10/26/1999	1	1.00	0.97
E20.14-20.22	10/26/1999	1	1.00	1.01
E20.14-20.22	10/26/1999	1	1.00	0.99
E20.14-20.22	10/26/1999	1	1.00	1.02
Number = 19	Avg	= 0.97		
1144111001	SD	= 0.03		
	Range	= 0.92 - 1.0	02 (-8 to + 2%	6)
Run#	Date	Dilution	QC Conc	Measured Conc
		Factor	μg/L	μg/L
E16.1-16.6	3/26/1999	1	1.02	0.90
E16.1-16.6	3/26/1999	1	1.02	0.93
E16.1-16.6	3/26/1999	1	1.02	0.84
E16.1-16.6	3/26/1999	1	1.02	0.86
E16.1-16.6	3/26/1999	- 1	1.02	0.86
E17.1-17.6	5/13/1999	1	1.02	0.95
E17.1-17.6	5/13/1999	1	1.02	0.99
E17.1-17.6	5/13/1999	1	1.02	0.97
E17.1-17.6	5/13/1999	1	1.02	0.97
E17.1-17.6	5/13/1999	1	1.02	0.99
E17.1-17.6	5/13/1999	1	1.02	1.02
E17.1-17.6	5/13/1999	1	1.02	1.06
E18.7-18.8	6/15/1999	1	1.02	1.03
E18.7-18.8	6/15/1999	1	1.02	1.07
E18.7-18.8	6/15/1999	. 1	1.02	0.98
E18.7-18.8	6/15/1999	1	1.02	0.96
E18.7-18.8	6/15/1999	1	1.02	0.98
E18.7-18.8	6/15/1999	1	1.02	0.98
E18.7-18.8	6/15/1999	1	1.02	1.00
E18.7-18.8	6/15/1999	1	1.02	0.98
Number $= 20$	Avg	= 0.97	- '	=
	SD	= 0.06		
ł	Range	= 0.84 - 1.	07 (-16 to + 7	7%)

Table M-1. Results of QC Analysis (Contd)

Run#	Date	Dilution	QC Conc	Measured Conc
		Factor	μg/L	μg/L
E16.7-16.12	3/29/1999	1	2.96	2.88
E16.7-16.12	3/29/1999	1	2.96	3.04
E16.7-16.12	3/29/1999	1	2.96	2.92
E16.7-16.12	3/29/1999	1	2.96	3.14
E16.7-16.12	3/29/1999	1	2.96	3.00
E17.7-17.12	5/15/1999	1	2.96	2.89
E17.7-17.12	5/15/1999	1	2.96	2.89
E17.7-17.12	5/15/1999	1	2.96	2.98
E17.7-17.12	5/15/1999	1	2.96	3.01
E17.7-17.12	5/15/1999	1	2.96	2.98
E17.7-17.12	5/15/1999	1	2.96	3.01
E17.25-17.28	6/2/1999	1	2.96	2.97
E17.25-17.28	6/2/1999	1	2.96	2.97
E17.25-17.28	6/2/1999	1	2.96	2.92
E17.25-17.28	6/2/1999	1	2.96	2.94
E17.25-17.28	6/2/1999	1	2.96	3.01
E17.25-17.28	6/2/1999	1	2.96	2.92
E18.1-18.6	6/11/1999	1	2.96	2.92
E18.1-18.6	6/11/1999	1	2.96	2.90
E18.1-18.6	6/11/1999	1	2.96	2.97
E18.1-18.6	6/11/1999	1	2.96	2.95
Number = 21	Avg	= 2.96		
	SD	= 0.06		=
	Range	= 2.88 - 3.1	14 (-3 to + 6%	<b>6</b> )

Table M-1. Results of QC Analysis (Contd)

Run#	Date	Dilution	QC Conc	Measured Conc
		Factor	μg/L	μg/L
E15.17-15.18	9/27/1999	. 1	3.03	2.90
E15.17-15.18	9/27/1999	. 1	3.03	3.03
E15.17-15.18	9/27/1999	1	3.03	3.06
E15.17-15.18	9/27/1999	1	3.03	3.06
E15.17-15.18	9/27/1999	1	3.03	2.97
E15.17-15.18	9/27/1999	1	3.03	2.99
E15.17-15.18	9/27/1999	1	3.03	2.95
E15.17-15.18	9/27/1999	1	3.03	3.06
E15.21-15.22	9/11/1999	1	3.03	2.97
E15.21-15.22	9/11/1999	1	3.03	3.07
E15.21-15.22	9/11/1999	1	3.03	3.09
E15.21-15.22	9/11/1999	1	3.03	2.92
E15.21-15.22	9/11/1999	1	3.03	2.96
E15.21-15.22	9/11/1999	1	3.03	2.94
E20.9	10/7/1999	1	3.03	2.94
E20.9	10/7/1999	1	3.03	3.05
E20.9	10/7/1999	1	3.03	2.90
E20.9	10/7/1999	1	3.03	2.92
E20.9	10/7/1999	1	3.03	2.94
E20.23-20.30	11/15/1999	1	3.03	2.90
E20.23-20.30	11/15/1999	1	3.03	2.92
E20.23-20.30	11/15/1999	1	3.03	2.97
E20.23-20.30	11/15/1999	1	3.03	2.95
E20.23-20.30	11/15/1999	. 1	3.03	3.00
E20.23-20.30	11/15/1999	1	3.03	3.09
Number = 25	Avg	= 2.98		
	SD	= 0.06		
	Range	= 2.90 - 3.0	09 (-2 to + 2%	6)

Table M-1. Results of QC Analysis (Contd)

Run#	Date	Dilution	QC Conc	Measured Conc
		Factor	μg/L	μg/L
E19.19-19.24	9/10/1999	1	5.84	5.83
E19.19-19.24	9/10/1999	1	5.84	5.90
E19.19-19.24	9/10/1999	1	5.84	5.83
E19.19-19.24	9/10/1999	1	5.84	5.78
E19.19-19.24	9/10/1999	1	5.84	5.85
E19.19-19.24	9/10/1999	1	5.84	5.94
E19.19-19.24	9/10/1999	1	5.84	5.99
E19.19-19.24	9/10/1999	1	5.84	5.71
E20.10-20.12	10/13/1999	1	5.84	5.68
E20.10-20.12	10/13/1999	1	5.84	5.77
E20.10-20.12	10/13/1999	1	5.84	5.71
E20.10-20.12	10/13/1999	1	5.84	5.75
E21.4-21.10	1/12/2000	1	5.84	5.49
E21.4-21.10	1/12/2000	1	5.84	5.67
E21.4-21.10	1/12/2000	1	5.84	5.80
E21.4-21.10	1/12/2000	1	5.84	5.73
E22.1-22.7	2/2/2000	1	5.84	5.82
E22.1-22.7	2/2/2000	1	5.84	5.89
E22.1-22.7	2/2/2000	1	5.84	5.82
E22.1-22.7	2/2/2000	1	5.84	5.88
E22.1-22.7	2/2/2000	1	5.84	5.93
Number = 21	Avg	= 5.80		
	SD	=0.11		
	Range	= 5.49 - 5.9	99 (-6 to + 3%	6)

Table M-1. Results of QC Analysis (Contd)

Run#	Date	Dilution	QC Conc	Measured Conc
		Factor	μg/L	μg/L
E16.13-16.16	3/31/1999	1	5.97	5.98
E16.13-16.16	3/31/1999	1	5.97	5.84
E16.13-16.16	3/31/1999	1	5.97	6.06
E16.13-16.16	3/31/1999	1	5.97	6.04
E17.19-17.22	5/26/1999	1	5.97	5.86
E17.19-17.22	5/26/1999	1	5.97	6.00
E17.19-17.22	5/26/1999	1	5.97	6.02
E19.1-19.6	7/1/1999	1	5.97	5.86
E19.1-19.6	7/1/1999	1	5.97	5.84
E19.1-19.6	7/1/1999	1	5.97	5.83
E19.1-19.6	7/1/1999	1	5.97	5.95
E19.1-19.6	7/1/1999	1	5.97	5.95
E19.1-19.6	7/1/1999	1	5.97	5.90
E19.1-19.6	7/1/1999	1	5.97	5.98
E19.1-19.6	7/1/1999	i	5.97	5.95
Number = 15	Avg .	= 5.94	· ·	
	SD	= 0.08		
	Range	= 5.83 - 6.0	)6 (-2 to + 2%	ó)

Run#	Date	Dilution	QC Conc	Measured Conc
		Factor	μg/L	μg/L
E19.24-19.30	9/18/1999	1	9.88	9.26
E19.24-19.30	9/18/1999	1	9.88	9.42
E19.24-19.30	9/18/1999	1	9.88	9.69
E19.24-19.30	9/18/1999	1	9.88	9.66
E19.24-19.30	9/18/1999	1	9.88	9.49
E19.24-19.30	9/18/1999	1	9.88	9.51
E19.24-19.30	9/18/1999	1	9.88	9.53
E19.24-19.30	9/18/1999	1	9.88	9.55
E20.13	10/14/1999	1	9.88	9.36
E20.13	10/14/1999	. 1	9.88	9.57
E20.13	10/14/1999	1	9.88	9.50
E21.1-21.3	12/30/1999	1	9.88	9.55
E21.1-21.3	12/30/1999	1	9.88	9.75
E21.1-21.3	12/30/1999	1	9.88	9.95
E21.1-21.3	12/30/1999	1	9.88	9.75
Number = 15	Avg	= 9.57		
	SD	=0.17		
	Range	= 9.26 - 9.9	95 (-6 to + 1%	6)

Table M-1. Results of QC Analysis (Contd)

Run#	Date	Dilution	QC Conc	Measured Conc
		Factor	μg/L	μg/L
E15.13-15.16	3/20/1999	1	10.29	9.97
E15.13-15.16	3/20/1999	1	10.29	9.85
E15.13-15.16	3/20/1999	1	10.29	9.77
E15.13-15.16	3/20/1999	1	10.29	9.67
E17.23-17.24	6/1/1999	1	10.29	9.78
E17.23-17.24	6/1/1999	1	10.29	9.85
E17.23-17.24	6/1/1999	1	10.29	9.97
E17.23-17.24	6/1/1999	1	10.29	10.11
E19.7-19.12	7/6/1999	1	10.29	10.04
E19.7-19.12	7/6/1999	1	10.29	9.97
E19.7-19.12	7/6/1999	1	10.29	9.96
E19.7-19.12	7/6/1999	1	10.29	9.85
E19.7-19.12	7/6/1999	1	10.29	9.80
E19.7-19.12	7/6/1999	1	10.29	9.76
E19.7-19.12	7/6/1999	1	10.29	9.73
E19.7-19.12	7/6/1999	1	10.29	9.96
Number = 16	Avg	= 9.88		
	SD	= 0.12		
	Range	= 9.67 - 10	.11 (-6 to -2%	<b>6</b> )

Table M-2. Results of WS Standards Analysis (WS 037)

Run#	Date	Dilution	EPA Conc	Measured Conc
1011 11	J0	Factor	μg/L	μg/L
E03-04	11/26/1998	10	49.3	46.31
E05	1/27/1998	10	49.3	46.35
E07-10	12/4/1998	10	49.3	48.56
E07-10	12/4/1998	10	49.3	49.51
E11-12	12/17/1998	10	49.3	49.30
E14	2/22/1999	10	49.3	49.96
E15.1-15.6	3/8/1999	10	49.3	47.80
E15.7-15.12	3/16/1999	10	49.3	47.01
E15.13-15.16	3/20/1999	10	49.3	48.99
E15.17-15.18	9/27/1999	10	49.3	47.21
E15.19-15.20	5/8/1999	10	49.3	47.28
E15.19-15.20 E15.21-15.22	9/11/1999	10	49.3	47.16
E16.1-16.6	3/26/1999	10	49.3	46.23
E16.7-16.12	3/29/1999	10	49.3	47.94
E16.13-16.16	3/31/1999	10	49.3	47.47
E17.1-17.6	5/13/1999	10	49.3	46.80
E17.7-17.12	5/15/1999	10	49.3	48.76
	5/26/1999	10	49.3	47.33
E17.19-17.22		10	49.3	48.08
E17.23-17.24	6/1/1999	10	49.3	46.84
E17.25-17.28	6/2/1999		49.3	46.38
E18.1-18.6	6/11/1999	10		47.98
E18.7-18.8	6/15/1999	10	49.3	
E19.1-19.6	7/1/1999	10	49.3	50.10 46.25
E19.7-19.12	7/6/1999	10	49.3	
E19.13-19.16	7/9/1999	10	49.3	47.27
E19.19-19.24	9/10/1999	10	49.3	48.41
E19.24-19.30	9/18/1999	10	49.3	49.09
E20.1-20.4	9/25/1999	10	49.3	49.19
E20.5-20.8	9/28/1999	10	49.3	49.00
E20.9	10/7/1999	10	49.3	49.25
E20.10-20.12	10/13/1999	10	49.3	48.34
E20.13	10/14/1999	10	49.3	48.83
E20.14-20.22	10/26/1999	10	49.3	45.01
E20.23-20.30	11/15/1999	10	49.3	48.50
E21.1-21.3	12/30/1999	10	49.3	50.13
E21.4-21.10	1/12/2000	10	49.3	48.87
E21.11	2/8/2000	10	49.3	48.94
E22.1-22.7	2/2/2000	10	49.3	50.39
Number = 38	Avg	= 48.1		
	SD	= 1.3		
1	Range	=45.0-50	).4 (-9 to +2%)	

Table M-2. Results of WS Standards Analysis (WS 038)

Run#	Date	Dilution	EPA Conc	Measured Conc
		Factor	μg/L	μg/L
E07-10	12/4/1998	10	83.1	79.44
E07-10	12/4/1998	10	83.1	80.38
E11-12	12/17/1998	10	83.1	73.50
E14	2/22/1998	10	83.1	77.59
E15.1-15.6	3/8/1999	10	83.1	76.67
E15.7-15.12	3/16/1999	10	83.1	72.97
E15.13-15.16	3/20/1999	10	83.1	76.19
E15.17-15.18	9/27/1999	10	83.1	74.29
E15.19-15.20	5/8/1999	10	83.1	76.94
E15.21-15.22	9/11/1999	10	83.1	74.76
E16.1-16.6	3/26/1999	10	83.1	73.80
E16.7-16.12	3/29/1999	10	83.1	75.05
E16.13-16.16	3/31/1999	10	83.1	74.66
E17.1-17.6	5/13/1999	10	83.1	73.77
E17.7-17.12	5/15/1999	10	83.1	75.33
E17.19-17.22	5/26/1999	10	83.1	75.30
E17.23-17.24	6/1/1999	10	83.1	76.70
E17.25-17.28	6/2/1999	10	83.1	73.88
E18.1-18.6	6/11/1999	10	83.1	74.73
E18.7-18.8	6/15/1999	10	83.1	75.67
E19.1-19.6	7/1/1999	10	83.1	77.85
E19.7-19.12	7/6/1999	10	83.1	73.69
E19.13-19.16	7/9/1999	10	83.1	75.70
E19.19-19.24	9/10/1999	10	83.1	77.51
E19.24-19.30	9/18/1999	10	83.1	76.89
E20.1-20.4	9/25/1999	10	83.1	76.48
E20.5-20.8	9/28/1999	10	83.1	77.12
E20.9	10/7/1999	10	83.1	75.95
E20.10-20.12	10/13/1999	10	83.1	78.03
E20.13	10/14/1999	10	83.1	74.66
E20.14-20.22	10/26/1999	10	83.1	74.41
E20.23-20.30	11/15/1999	10	83.1	76.74
E21.1-21.3	12/30/1999	10	83.1	76.32
E21.4-21.10	1/12/2000	10	83.1	75.49
E21.11	2/8/2000	10	83.1	78.29
E22.1-22.7	2/2/2000	10	83.1	77.82
Number = 36	Avg	= 76.0		
1	SD	= 1.7	4 ( 10 ) 200	
	Range	= 73.0 - 80	.4 (-12 to -3%)	

Table M-2. Results of WS Standards Analysis (WS 040)

Run#	Date	Dilution	EPA Conc	Measured Conc
Kuli #	Date	Factor	μg/L	μg/L
E07-10	12/4/1998	10	102	107.48
E07-10	12/4/1998	10	102	108.66
E11-12	12/17/1998	10	102	103.27
E11-12	2/22/1998	10	102	101.13
E15.1-15.6	3/8/1999	10	102	90.99
E15.7-15.12	3/16/1999	10	102	105.36
E15.13-15.16	3/20/1999	10	102	99.44
E15.17-15.18	9/27/1999	10	102	95.47
E15.19-15.20	5/8/1999	10	102	95.71
E15.21-15.22	9/11/1999	10	102	94.56
E16.1-16.6	3/26/1999	10	102	96.34
E16.7-16.12	3/29/1999	10	102	97.35
E16.13-16.16	3/31/1999	10	102	103.58
E17.1-17.6	5/13/1999	10	102	98.84
E17.7-17.12	5/15/1999	10	102	105.19
E17.19-17.22	5/26/1999	10	102	101.27
E17.23-17.24	6/1/1999	10	102	99.13
E17.25-17.28	6/2/1999	10	102	95.51
E18.1-18.6	6/11/1999	10	102	103.07
E18.7-18.8	6/15/1999	10	102	98.44
E19.1-19.6	7/1/1999	10	102	98.80
E19.7-19.12	7/6/1999	10	102	97.09
E19.13-19.16	7/9/1999	10	102	99.13
E19.19-19.24	9/10/1999	10	102	101.21
E19.24-19.30	9/18/1999	10	102	97.30
E20.1-20.4	9/25/1999	10	102	105.25
E20.5-20.8	9/28/1999	10	102	98.60
E20.9	10/7/1999	10	102	97.03
E20.10-20.12	10/13/1999	10	102	100.99
E20.13	10/14/1999	10	102	97.22
E20.14-20.22	10/26/1999	10	102	94.45
E20.23-20.30	11/15/1999	10	102	99.51
E21.1-21.3	12/30/1999	10	102	99.11
E21.4-21.10	1/12/2000	10	102	96.26
E21.11	2/8/2000	10	102	98.74
E22.1-22.7	2/2/2000	10	102	99.01
Number = 36	Avg	= 99.5		-
	SD	= 3.9		
	Range	=91.0 - 10	8.7 (-11 to +7%	ó)

Table M-2. Results of WS Standards Analysis (WS 040) (Contd)

Run#	Date	Dilution	EPA Conc	Measured Conc
		Factor	μg/L	μg/L
E15.17-15.18	9/27/1999	20	102	96.27
E15.21-15.22	9/11/1999	20	102	96.36
E19.7-19.12	7/6/1999	20	102	97.43
E19.13-19.16	7/9/1999	20	102	99.02
E19.19-19.24	9/10/1999	20	102	100.65
E19.24-19.30	9/18/1999	20	102	98.54
E20.1-20.4	9/25/1999	20	102	104.23
E20.5-20.8	9/28/1999	20	102	99.08
E20.9	10/7/1999	20	102	98.84
E20.10-20.12	10/13/1999	20	102	100.82
E20.13	10/14/1999	20	102	95.19
E20.14-20.22	10/26/1999	20	102	95.02
E20.23-20.30	11/15/1999	20	102	100.77
E21.1-21.3	12/30/1999	20	102	100.61
E21.4-21.10	1/12/2000	20	102	96.88
E21.11	2/8/2000	20	102	100.37
E22.1-22.7	2/2/2000	20	102	99.01
Number = 17	Avg	= 98.8		
	SD	= 2.4		
	Range	= 95.0 - 10	4.2 (-7 to +2%)	

Table M-2. Results of WS Standards Analysis (WS 041)

Run #	Date Date	Dilution	EPA Conc	Measured Conc
Kuii #	Date	Factor	EFA Conc μg/L	μg/L
E07-10	12/4/1998	10	μ <u>g</u> /L 65.6	66.24
	12/4/1998	10	65.6	67.18
E07-10	12/17/1998	10	65.6	63.26
E11-12	2/22/1998	10	65.6	63.27
E14 E15.1-15.6	3/8/1999	10	65.6	63.27
			65.6	64.47
E15.7-15.12	3/16/1999	10		
E15.13-15.16	3/20/1999	10	65.6	65.56
E15.17-15.18	9/27/1999	10	65.6	61.58
E15.19-15.20	5/8/1999	10	65.6	61.40
E15.21-15.22	9/11/1999	10	65.6	60.03
E16.1-16.6	3/26/1999	10	65.6	59.58
E16.7-16.12	3/29/1999	10	65.6	64.49
E16.13-16.16	3/31/1999	10	65.6	64.73
E17.1-17.6	5/13/1999	10	65.6	66.73
E17.7-17.12	5/15/1999	10	65.6	64.63
E17.19-17.22	5/26/1999	10	65.6	63.99
E17.23-17.24	6/1/1999	10	65.6	63.94
E17.25-17.28	6/2/1999	10	65.6	59.75
E18.1-18.6	6/11/1999	10	65.6	66.06
E18.7-18.8	6/15/1999	10	65.6	63.75
E19.1-19.6	7/1/1999	10	65.6	63.21
E19.7-19.12	7/6/1999	10	65.6	63.67
E19.13-19.16	7/9/1999	10	65.6	59.68
E19.19-19.24	9/10/1999	10	65.6	63.22
E19.24-19.30	9/18/1999	10	65.6	63.90
E20.1-20.4	9/25/1999	10	65.6	66.96
E20.5-20.8	9/28/1999	10	65.6	61.72
E20.9	10/7/1999	10	65.6	62.17
E20.10-20.12	10/13/1999	10	65.6	62.32
E20.13	10/14/1999	10	65.6	63.38
E20.14-20.22	10/26/1999	10	65.6	60.36
E20.23-20.30	11/15/1999	10	65.6	63.56
E21.1-21.3	12/30/1999	. 10	65.6	63.40
E21.4-21.10	1/12/2000	10	65.6	62.94
E21.11	2/8/2000	10	65.6	64.06
E22.1-22.7	2/2/2000	10	65.6	63.39
Number = 35	Avg	= 63.4	ŧ	
	SD	= 2.0		
	Range	= 59.6 - 67	.2 (-9 to +2%)	

Table M-3. Recoveries of Spiked WS Standards

Table IVI-5. F					Called Carr	%
Run#	Date	Sample ID	Dilution	Unspiked Conc	Spiked Cone	ŧ :
T10.1.10.6	6/11/1000		Factor	μg/L	μg/L	Recovery
E18.1-18.6	6/11/1999	WS 037	10	4.63	6.72	104.2
E18.7-18.8	6/15/1999	WS 037	10	4.79	6.87	103.4
E19.1-19.6	7/1/1999	WS 037	10	5.00	6.95	97.1
E19.7-19.12	7/6/1999	WS 037	10	4.62	6.79	108.2
E19.13-19.16	7/9/1999	WS 037	10	4.72	6.83	105.1
E19.19-19.24	9/10/1999	WS 037	10	4.84	6.91	103.7
E19.24-19.30	9/18/1999	WS 037	10	4.90	6.84	96.6
E20.1-20.4	9/25/1999	WS 037	10	4.91	6.92	99.9
E20.5-20.8	9/28/1999	WS 037	10	4.90	6.83	96.7
E20.9	10/7/1999	WS 037	10	4.92	6.86	96.9
E20.10-20.12	10/13/1999	WS 037	10	4.83	6.78	97.5
E20.13	10/14/1999	WS 037	10	4.82	6.86	101.5
E20.14-20.22	10/26/1999	WS 037	10	4.50	6.57	103.5
E20.23-20.30	11/15/1999	WS 037	10	4.85	6.87	101.0
E21.1-21.3	12/30/1999	WS 037	10	5.01	7.00	99.6
E21.4-21.10	1/12/2000	WS 037	10	4.88	6.79	95.2
E21.11	2/8/2000	WS 037	10	4.89	6.96	103.2
E22.1-22.7	2/2/2000	WS 037	10	5.03	6.78	87.3
E14	2/22/1999	WS 037	10	4.99	6.65	82.9
E15.1-15.6	3/8/1999	WS 037	10	4.93	6.93	100.0
E15.7-15.12	3/16/1999	WS 037	10	4.70	6.86	108.0
E15.13-15.16	3/20/1999	WS 037	10	4.89	7.00	105.1
E15.17-15.18	9/27/1999	WS 037	10	4.72	6.58	93.0
E15.19-15.20	5/8/1999	WS 037	10	4.72	6.87	106.9
E15.21-15.22	9/11/1999	WS 037	10	4.71	6.76	102.4
E16.1-16.6	3/26/1999	WS 037	10	4.62	6.59	98.5
E16.7-16.12	3/29/1999	WS 037	10	4.79	6.71	95.9
E16.13-16.16	3/31/1999	WS 037	10	4.74	6.84	104.7
E17.1-17.6	5/13/1999	WS 037	10	4.69	6.78	103.9
E17.7-17.12	5/15/1999	WS 037	10	4.87	6.86	99.2
E17.19-17.22	5/26/1999	WS 037	10	4.77	6.93	108.1
E17.23-17.24	6/1/1999	WS 037	10	4.80	7.07	113.1
E17.25-17.28	6/2/1999	WS 037	10	4.68	6.92	111.6
						•
E18.1-18.6	6/11/1999	WS 038	10	7.47	9.52	102.5
E18.7-18.8	6/15/1999	WS 038	10	7.56	9.31	87.6
E19.1-19.6	7/1/1999	WS 038	10	7.78	9.69	95.4
E19.7-19.12	7/6/1999	WS 038	10	7.36	9.26	95.0
E19.13-19.16	7/9/1999	WS 038	10	7.57	9.53	98.2
E19.19-19.24	9/10/1999	WS 038	10	7.75	9.75	100.2
E19.24-19.30	9/18/1999	WS 038	10	7.68	9.54	93.0
E20.1-20.4	9/25/1999	WS 038	10	7.64	9.84	109.9
E20.5-20.8	9/28/1999	WS 038	10	7.71	9.71	100.3
E20.9	10/7/1999	WS 038	10	7.59	9.72	106.3
E20.10-20.12	10/13/1999	WS 038	10	7.80	9.70	94.9
E20.10-20.12	10/13/1999	WS 038	10	7.46	9.54	104.1
E20.13 E20.14-20.22	10/26/1999	WS 038	10	7.41	9.30	94.6
E20.14-20.22 E20.23-20.30	11/15/1999	WS 038	10	7.67	9.72	102.7
E20.23-20.30 E21.1-21.3	12/30/1999	WS 038	10	7.63	9.51	94.2
E21.1-21.3 E21.4-21.10	1/12/2000	WS 038	10	7.54	9.58	101.7
	2/8/2000	WS 038	10	7.82	9.89	101.7
E21.11	2/2/2000	WS 038	10	7.78	9.68	95.3
E22.1-22.7	21212000	W 2 020	10	1.10	7.00	93.3

E14	2/22/1998	WS 038	10	7.75	9.47	86.0
E15.1-15.6	3/8/1999.	WS 038	10	7.49	9.49	100.0
E15.7-15.12	3/16/1999	WS 038	10	7.30	9.30	100.0
E15.13-15.16	3/20/1999	WS 038	10	7.61	9.74	106.3
E15.17-15.18	9/27/1999	WS 038	10	7.42	9.28	93.0
E15.19-15.20	5/8/1999	WS 038	10	7.69	9.44	87.8
	9/11/1999	WS 038	10	7.47	9.47	99.9
E15.21-15.22	3/26/1999	WS 038	10	7.38	9.48	105.0
E16.1-16.6		WS 038	10	7.50	9.47	98.3
E16.7-16.12	3/29/1999				9.68	111.1
E16.13-16.16	3/31/1999	WS 038	10	7.46	9.60	111.6
E17.1-17.6	5/13/1999	WS 038	10	7.37		
E17.7-17.12	5/15/1999	WS 038	10	7.53	9.58	102.7
E17.19-17.22	5/26/1999	WS 038	10	7.52	9.75	111.0
E17.23-17.24	6/1/1999	WS 038	10	7.66	9.75	104.4
E17.25-17.28	6/2/1999	WS 038	10	7.38	9.30	95.9
	T - 10 - 11 - 00 0				7.00	100.6
E20.1-20.4	9/25/1999	WS 040	20	5.21	7.26	102.6
E20.5-20.8	9/28/1999	WS 040	20	4.95	7.08	106.5
E20.9	10/7/1999	WS 040	20	4.94	6.99	102.9
E20.10-20.12	10/13/1999	WS 040	20	5.04	7.04	100.1
E20.13	10/14/1999	WS 040	20	4.75	6.78	101.5
E20.14-20.22	10/26/1999	WS 040	20	4.75	6.80	102.6
E20.23-20.30	11/15/1999	WS 040	20	5.03	7.00	98.4
E21.1-21.3	12/30/1999	WS 040	20	5.03	7.11	104.1
E21.4-21.10	1/12/2000	WS 040	20	4.84	6.94	105.0
E21.11	2/8/2000	WS 040	20	5.01	7.11	104.9
E22.1-22.7	2/2/2000	WS 040	20	4.95	7.06	105.9
E18.1-18.6	6/11/1999	WS 041	10	6.60	8.47	93.4
E18.7-18.8	6/15/1999	WS 041	10	6.37	8.46	104.2
E19.1-19.6	7/1/1999	WS 041	10	6.32	8.17	92.8
E19.7-19.12	7/6/1999	WS 041 ·	10	6.36	8.17	90.5
E19.13-19.16	7/9/1999	WS 041	10	5.96	8.05	104.3
E19.19-19.24	9/10/1999	WS 041	10	6.32	8.37	102.8
E19.24-19.30	9/18/1999	WS 041	10	6.38	8.53	107.4
E20.1-20.4	9/25/1999	WS 041	10	6.69	8.83	107.2
E20.5-20.8	9/28/1999	WS 041	10	6.17	8.35	109.2
E20.9	10/7/1999	WS 041	10	6.21	8.22	100.3
E20.10-20.12	10/13/1999	WS 041	10	6.23	8.28	102.7
E20.13	10/14/1999	WS 041	10	6.33	8.36	101.5
E20.14-20.22	10/26/1999	WS 041	10	6.03	7.94	95.5
E20.23-20.30	11/15/1999	WS 041	10	6.35	8.25	95.0
E21.1-21.3	12/30/1999	WS 041	10	6.34	8.27	96.9
E21.4-21.10	1/12/2000	WS 041	10	6.29	8.17	94.1
E21.11	2/8/2000	WS 041	10	6.40	8.39	99.6
E22.1-22.7	2/2/2000	WS 041	10	6.33	8.24	95.3
E14	2/22/1998	WS 041	10	6.32	8.20	94.2
E15.1-15.6	3/8/1999	WS 041	10	6.56	8.56	100.0
E15.7-15.12	3/16/1999	WS 041	10	6.45	8.22	88.5
E15.13-15.16	3/20/1999	WS 041	10	6.55	8.78	111.3
E15.13-15.16 E15.17-15.18	9/27/1999	WS 041	10	6.15	8.03	93.9
E15.17-15.18 E15.19-15.20	5/8/1999	WS 041	10	6.14	8.17	101.9
	9/11/1999	WS 041	10	6.00	8.08	104.1
E15.21-15.22	3/26/1999	WS 041	10	5.96	8.01	102.5
E16.1-16.6	3/20/1999	WS 041	10	6.44	8.53	104.3
E16.7-16.12		1	10	6.47	8.67	110.1
E16.13-16.16	3/31/1999	WS 041	10	0.47	0.07	110.1

	Range	= 82.9 - 113	3.1			
	SD	= 6.1				
Number = 110	Avg	= 100.6				
E17.25-17.28	6/2/1999	WS 041	10	5.97	7.87	95.1
E17.23-17.24	6/1/1999	WS 041	10	6.39	8.48	104.4
E17.19-17.22	5/26/1999	WS 041	10	6.39	8.34	97.2
E17.7-17.12	5/15/1999	WS 041	10	6.46	8.60	107.0
E17.1-17.6	5/13/1999	WS 041	10	6.67	8.57	95.3

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