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IN SITU CATALYTIC GROUNDWATER TREATMENT USING PD-CATALYSTS AND HORIZONTAL FLOW TREATMENT WELLS

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In Situ Catalytic Groundwater Treatment Using Pd-Catalysts and Horizontal Flow Treatment Wells
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List of Acronyms and Abbreviations

AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
AFFTC	Air Force Flight Test Center
AFIT	Air Force Institute of Technology
AFOTEC	Air Force Operational Test and Evaluation Center
AFRPL	Air Force Rocket Propulsion Laboratory
AFRL	Air Force Research Laboratory
BEHIVS	Bioenhanced In-well Vapor Stripping
bgs	below ground surface
DBCP	1,2-dibromo-3-chloropropane
DCE	dichloroethylene
DHS	(California) Department of Health Services
DoD	Department of Defense
EE/CA	engineering evaluation / cost analysis (or cost assessment)
ElCD	electro-conductivity detection
EPA	Environmental Protection Agency
ESTCP	Environmental Security Technology Certification Program
FSP	Field Sampling Plan
GC	gas chromatography
HASP	Health and Safety Plan
HazWOpER	Hazardous Waste Operations and Emergency Response
HFTW	horizontal flow treatment well
ISACB	*In Situ* Aerobic Cometabolic Biodegradation
LLNL	Lawrence Livermore National Laboratory
MCL	maximum contaminant level (established under the Safe Drinking Water Act)
NASA	National Aeronautics and Space Administration
NAVFAC	Naval Facilities Engineering Command
NFESC	Naval Facilities Engineering Service Center
O&M	operations & maintenance
OSHA	Occupational Safety and Health Administration
PCE	perchloroethylene
Pd	palladium
PID	photo-ionization detection
PMC	Precious Metals Corporation, located in Sevierville, TN
POC	point of contact
PRB	permeable reactive barrier
RAB	Restoration Advisory Board
RPM	Remedial Program Manager (also Restoration Program Manager, Remedial Project Manager, and Restoration Project Manager)
QAPP	Quality Assurance Project Plan
SEM	scanning electron microscopy
SERDP	Strategic Environmental Research and Development Program
SPSS	Space Surveillance Squadron
TCE	trichloroethylene
VC	vinyl chloride
VOC	volatile organic compound
XPS	X-ray photo-electron spectroscopy

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Executive Summary

The U.S. Environmental Protection Agency (EPA) estimated in 1996 that approximately 70% of the 8,336 Department of Defense (DoD) sites requiring cleanup had contaminated groundwater, usually from chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE). As a result, there is significant need for efficient treatment methods. Palladium (Pd) catalysis is a rapid destruction method that, in the presence of hydrogen gas, transforms many chlorinated ethylenes into ethane and some other halogenated volatile organic compounds (VOCs) into their respective hydrocarbon compounds. The dechlorination reactions for chlorinated ethylenes are complete and rapid and occur in water under ambient temperature, pH and pressure conditions. Hydrogen gas is used as the reducing agent, with residence times on the order of minutes. Catalytic contaminant destruction in a one-pass process has many potential advantages such as eliminating the secondary waste stream created by other processes that transfer contaminants to another medium (e.g. air or activated carbon). The technology is also effective in areas of high contaminant concentrations making it applicable to source control.

The objective of this project was to demonstrate the feasibility of catalytic destruction of chlorinated VOCs in groundwater using reactors containing palladium-coated beads that were operated in-situ within two previously established horizontal flow treatment wells (HFTWs). Unfortunately, deploying the reactors in situ proved an insurmountable challenge throughout the demonstration period and the reactors were operated above grade. Although installation of the reactors inside the treatment wells could be possible in a full scale application, it is not recommended due to complications associated with installing feed lines for backflushing and regenerating reactors coupled with high costs for removing reactors from the wells for maintenance, leak checks, etc.

The performance objectives of this study were to:

(1) Demonstrate the efficacy of catalytic treatment for the destruction of chlorinated ethylenes in groundwater using palladium catalyst;
(2) Optimize treatment efficiency; and,
(3) Develop cost and performance data for full-scale application of the technology.

Collected data show process efficacy and a protocol for treating TCE contaminated groundwater was developed based on operational experience. On the basis of these developed parameters, the cost and performance for a dual-reactor system that treats a total of 4 gpm (2x 2 gpm) were evaluated. As part of the project, modeling was used to estimate the performance of a treatment system in conjunction with HFTWs. Modeling indicates that a series of HFTWs aligned perpendicular to the direction of groundwater regional flow could serve as an effective barrier to TCE migration.

Demonstration Results: Catalytic destruction of TCE in groundwater was demonstrated at Edwards AFB. The site was contaminated with 800 to 1,200 $\mu g\ L^{-1}$ TCE, which was the sole contaminant. A treatment methodology was developed to maintain catalyst activity and keep

treated water TCE concentrations at or below the maximum contaminant level (MCL) of 5 μg L^{-1} without byproduct formation. The treatment protocol entailed treating 2 gpm in a single catalyst column for 21 h (contact time approximately 1 min) followed by a 3 h bleach cycle to restore and maintain catalyst activity. The maintenance cycle consisted of bleaching of the catalyst for 1 h and flushing with hydrogen-containing groundwater for 2 h. After each maintenance cycle, TCE in the product water was at or below 1 μg L^{-1} corresponding to 99.9% removal. During a 21 h treatment cycle, effluent TCE concentrations increased slowly to approximately 10-15 μg L^{-1}, corresponding to approximately 99% removal.

Daily bleaching maintained catalyst activity by preventing biological fouling with sulfidogenic bacteria (bacteria oxidizing hydrogen and reducing sulfate to hydrogen sulfide). Operational problems led to episodes of biological sulfide formation and severe catalyst poisoning marked by complete activity loss. Laboratory experiments and field observations demonstrated that the activity of the catalyst can be nearly completely recovered by treating the catalyst with bleach.

Based on data obtained in this demonstration, it is estimated that a capital investment of $572,000 and annual O&M costs of $72,000 (including monitoring & analysis) are sufficient to install and operate a treatment system that creates a barrier approximately 20 m wide in a plume of contaminated groundwater. This estimate applies to sites contaminated with chlorinated ethylenes (PCE, TCE, DCE isomers and vinyl chloride) with a relatively permeable aquifer, shallow water table and low gradient, similar to the Edwards AFB field site. This cost estimate is for a two-well system having a total flow of 2 gpm per treatment well or 4 gpm total. The system operates 87.5% of the time in a daily 21h:3h treatment:regeneration cycle and remediates a TCE concentration of 1000 μg L^{-1}. The estimate is directly applicable to a full scale system and scalable to multiple sets of two wells. Sites with lower quality water would require more frequent bleaching whereas sites with cleaner (more aerobic) water are expected to require less frequent bleaching. A modification is proposed for continuous (100%) treatment by using two catalytic columns per well whereby one reactor is bleached and reactivated while the other treats the contaminated groundwater.

1. Introduction

1.1 Background

Groundwater contamination is a significant problem at thousands of Department of Defense (DoD) installations. The U.S. Environmental Protection Agency (EPA) estimated in 1996 that of 8,336 DoD sites needing cleanup, approximately 70% had contaminated groundwater [U.S. EPA, 1997]. The most common type of groundwater contamination is from volatile organic compounds (VOCs), found at approximately 75% of contaminated sites; the most common VOCs are chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (PCE). Based on EPA estimates, TCE and PCE contaminate groundwater at over 2,000 DoD installations. These contaminants are mobile and refractory in aerobic environments. There is significant need for efficient treatment methods because remediation of VOC sites using conventional pump-and-treat technology (i.e. activated carbon adsorption) is expensive and inefficient.

The objective of this project was to demonstrate the feasibility of catalytic destruction of chlorinated VOCs in contaminated groundwater. Catalytically destroying contaminants in a one-pass process has many advantages, chiefly that contaminants are completely destroyed instead of transferred to another medium (e.g. air or activated carbon), thus eliminating any secondary waste stream requiring further remediation. The technology is also applicable to high concentrations for control of contaminant sources where biological processes may be susceptible to toxic effects.

Laboratory and field studies have shown TCE, PCE and other halogenated VOCs can be destroyed in minutes by palladium catalysts contacted with dissolved hydrogen [Schreier and Reinhard, 1995; Siantar et al., 1996; Lowry and Reinhard, 1999; McNab et al., 2000]. In the process, chlorine atoms are replaced with hydrogen atoms forming products that are less toxic or benign in many cases. In the case of TCE, dechlorination is followed by saturation of the double bond, forming ethane and hydrochloric acid – the reaction is complete within minutes at ambient temperature. If hydrogen is present in excess, TCE dechlorination is complete and no chlorinated intermediates are formed. Palladium catalysts are commercially available, making the technology accessible to commercial users.

This report is organized as follows: The body of the report follows the required ESTCP format and describes the basics of the technology and demonstration design, summarizes performance and assessment of the technology, provides a the summary of the cost analysis (detailed in a separate report) and finally discusses implementation issues. APPENDIX A contains analytical methods supporting the experimental design, APPENDIX B is a description of relevant EPA methods, APPENDIX C is the quality assurance project plan, APPENDIX D is the health and safety plan, APPENDIX E is the design package for treatment system and APPENDIX F contains published reports related to the project.

1.2 Objectives of the Demonstration

The principal objectives of this study were to:

(1) Demonstrate the efficacy of catalytic treatment for the destruction of chlorinated ethylenes in groundwater using palladium catalyst;
(2) Optimize treatment efficiency; and,
(3) Develop cost and performance data for full-scale application of the technology.

The study at Edwards AFB was close enough to full-scale that costs were scaled accordingly to represent full-scale application. In the initial proposal, the reactors were expected to be mounted below grade within the horizontal flow treatment wells (HFTWs), thus qualifying as an in situ technology. The test site was installed at the Edwards AFB site where the HFTW technology was tested previously in the context of biological treatment (McCarty et al. 1998). Experience gained during the execution of the project demonstrated that the best application of this technology at the Edwards AFB field site required a dual-column configuration with two reactors operating in tandem for each well, as explained below. Although a dual-column configuration in situ might be possible in principle, its realization was not feasible within the constraints of this pilot-scale demonstration. Once operational issues were resolved and the regeneration protocol was optimized, the catalyst reactor successfully reduced the TCE concentrations in the groundwater by 2-3 orders of magnitude (more than 99%) consistently and without significant loss of catalyst activity.

1.3 Regulatory Drivers

The primary health risk associated with TCE is cancer; the MCL adopted by EPA and the California Department of Health Services (DHS) is 5 $\mu g\ L^{-1}$. California requires sites with contamination exceeding the MCL to provide treatment that lowers TCE concentrations to below 5 $\mu g\ L^{-1}$. At the time that DHS adopted the MCL, it designated both packed tower aeration and granular activated carbon (GAC) as the best available technologies for TCE removal [California DHS, 2001]. As shown in this study, palladium catalyzed destruction is a potential cost effective strategy for meeting the MCL.

The cleanup of groundwater contamination at Site 19 is managed by the Environmental Management Office of Edwards AFB, and is overseen by the following regulatory agencies:

- U.S. Environmental Protection Agency, Region 9;
- California Department of Toxic Substances Control; and,
- Regional Water Quality Control Board, Lahontan Region (part of the California State Water Resources Control Board).

1.4 Stakeholder/End-User Issues

This demonstration evaluated the following potential stakeholder and end-user issues and came to the following conclusions:

- Palladium catalyzed destruction is a technology capable of treating groundwater contaminated with TCE, PCE, dichloroethylene isomers (DCE) and vinyl chloride at a wide range of concentrations;
- The operational conditions (bleaching duration and frequency, bleach concentration, catalyst regeneration) were optimized such that product water met treatment objectives and catalyst activity could be maintained for indefinite periods (years). Bleaching the reactor to prevent biological fouling and maintaining catalyst activity was the most critical operational issue. Catalyst cost and longevity were not important factors;
- Pilot-scale cost data were generated and can be used to estimate the cost of full-scale implementation, as provided in the Cost and Performance report. Full-scale implementation using the same method implemented at Edwards AFB is estimated at:
    - A one-time capital investment of approximately $638,000; and,
    - Annual O&M costs of $70,000.

  The operating parameters at such a site would be close to those of this study: initial TCE concentration around 1000 $\mu g\ L^{-1}$, hydrogen flow rate 250 $mL\ min^{-1}$, two parallel reactors (one reactor per well) with total flow 2 gpm, regeneration for 3 h daily. To cost for 24-hour operation, the cost estimate would need modification to include 2 reactors per well instead of the 1 per well used in this pilot study; and,
- Using the field experience of implementing a new and innovative technology, cost efficient and robust systems can be built and operated.

These conclusions are site specific and depend on water quality, hydrogeological conditions, and treatment and regulatory requirements and can be addressed by appropriate site specific pilot studies and hydrogeological investigations.

From a regulatory point of view, an important consideration was implementing the technology below surface to qualify as an in situ technology (as opposed to a pump-and-treat technology). To meet this objective, the design of the first system built and operated at the Lawrence Livermore National Laboratory (LLNL) [McNab et al., 2000] was followed, where the reactor was mounted below grade within a well. However, operating the reactor below the surface provided no technical benefits and many disadvantages; LLNL designed the second system for both above and below ground operation. For the Edwards AFB demonstration, the plan was to mount the reactors inside the treatment wells, above the sampling and treatment pumps, once testing and optimization was completed above ground. Due to technical challenges, in situ operation was not tested in this study.

2. Technology Description

2.1 Pd-Catalyzed Dehalogenation

Palladium (Pd) catalysts, in the presence of hydrogen gas, transform many chlorinated VOCs into their respective hydrocarbon compounds. To maximize the specific Pd surface area while minimizing the amount of metal used, a thin layer of Pd is supported on a porous support material such as porous gamma-alumina (γ-Al_2O_3). Pd catalyst transforms chlorinated ethylenes to ethane by replacing all chlorine atoms with hydrogen and hydrogenating the double bond. TCE, for example, reacts with 4 moles of hydrogen gas to form ethane and 3 moles of hydrochloric acid, as shown below:

$$CH_2Cl = CHCl + 4H_2 \xrightarrow{Pd-on-Al_2O_3} H_3C - CH_3 + 3HCl$$

This reaction is extremely rapid in water (nearly diffusion limited), even at ambient temperature, and proceeds completely to ethane [Lowry and Reinhard, 1999]. In the presence of excess hydrogen, no significant amounts of intermediates (e.g. vinyl chloride) are formed.

The formation of hydrochloric acid as a reaction product does not generally represent an obstacle for technology application to contaminated groundwater sites because the reactant TCE concentrations are generally low (less than 30 mg L^{-1}) and groundwater usually has some natural buffer capacity. If the contaminated groundwater contains high enough concentrations of chlorinated compounds (e.g. greater than 100 mg L^{-1} TCE) it is possible that enough hydrochloric acid would be formed to significantly alter the pH of the system, but this was not the case for the Edwards AFB groundwater site studied where TCE concentrations ranged from 800-1,200 µg L^{-1}.

The ability of Pd metal to catalyze dehalogenation reactions has been known for decades, but has only recently been applied to treatment of contaminated water. Previously, Pd-catalyzed hydrogenation or dehalogenation reactions were used primarily for synthesis of organic chemicals [Rylander, 1973]. Catalytic dehalogenation was applied to waste treatment in the 1980s, but it was either applied to organic waste streams [Kalnes and James, 1988] or required high temperatures or pressures to treat aqueous waste streams [Baker et al., 1989]. It was about a decade ago that Kovenklioglu et al. [1992] suggested Pd catalyst for ambient condition treatment of waste or groundwater contaminated by chlorinated hydrocarbons. Since that time, Reinhard and co-workers have investigated which contaminants are amenable to dechlorination or reduction via Pd catalysis, how fast the reactions occur and how to maintain catalyst activity over time [Schreier and Reinhard, 1995; Siantar et al., 1996; Lowry and Reinhard, 1999, 2000; Munakata, 2005; Davie and Reinhard, 2006].

A column reactor was designed for this demonstration in conjunction with HFTWs. The treatment system design was based on the subsurface reactor system that has been operated since 1999 at the LLNL [McNab et al., 2000]. That system relies on daily venting with air for

approximately 12 h to prevent growth of sulfidogenic bacteria and fouling – these operating conditions limit the overall efficiency of the system to about 50% [McNab et al., 2000]. To increase the operating time,, the Edwards AFB system was equipped with an automatic bleaching system to allow for more aggressive regeneration and fouling prevention protocols, relying on bleach or hydrogen peroxide as oxidants [Lowry and Reinhard, 2000].

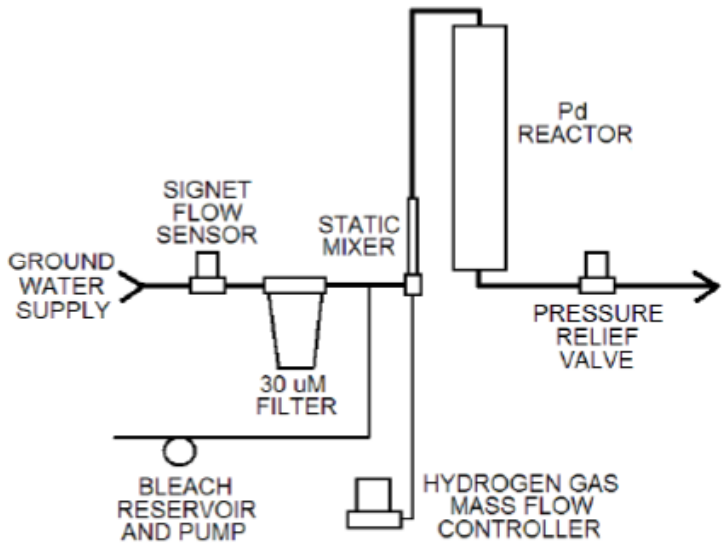

Figure 2-1: Simplified Schematic of Treatment System.

The system was built by a commercial vendor (Bigler and Associates, Lakewood, NJ) and delivered directly to the site. During the start-up phase, numerous components of the system had to be modified to meet the needs and conditions of the Edwards AFB site, significantly delaying operation and augmenting expenses, as discussed below.

2.1.1 Reactor Development

The treatment system was developed based on the designs of two previous systems and Stanford laboratory studies [Munakata, 2005]. The design packet developed by the LLNL team is provided in APPENDIX E. A reactor schematic and symbols legend are given in Figures 2-2 and 2-3, respectively. Five major considerations influenced the design:

(1) The requirement to mount the reactors inside the existing treatment wells;
(2) The need to operate the system at a remote location;
(3) Budget and time constrains;
(4) TCE effluent concentrations below the MCL (5 $\mu g\ L^{-1}$); and,
(5) hydrogen safety concerns.

Requirement 1 was driven by regulatory standards (which have since been relaxed). To operate the reactor remotely, an internet-based system control was installed which added significant cost and was eventually deemed nonfunctional for this study. Financial and time constraints resulted in selecting the lowest bidder for construction and using limited factory support and testing onsite. Residence times and catalyst amounts per column were driven by meeting the MCL for TCE. Figure 2-1 is the simplified schematic of the final configuration used for the demonstration. Because of hydrogen safety concerns, a number of hydrogen sensors and safety features were installed, further augmenting total system cost and adding complexity. Figures 2-2 and 2-3 show the design schematic; details are given in APPENDIX E. Below, the major system elements and the associated control requirements are listed. The most important control requirements were:

(1) Automatic system shutoff in the event of malfunctioning major system components, deviation from normal operating conditions, low bleach levels and dangerous levels of hydrogen gas;
(2) In the event of system shut down, hydrogen flow to the reactors is discontinued and replaced with nitrogen gas (to prevent catalyst fouling); and,
(3) Hydrogen is replaced with nitrogen during regeneration cycles. Safety interlocks could not be bypassed.

The major electronics requirements for the system were:

(1) Groundwater pump (one for each treatment well)
    a. 0-6.5 gpm flow rate
        - System shutdown on pump fault
        - Shutdown pumps on interlock trip (via relay contacts)
        - Operate flow rate via pump speed control
        - Manual on/off
        - Display on/off status
        - Set system pressure via pressure regulating valve
(2) Flow meter (one per reactor)
    a. 0-10 gpm Flow Rate Range; 4-20 mA Transmitter
        - Monitor / display flow rate at extraction
        - Monitor / display flow total (digital pulse count per gallon)
        - Interlock on flow rate high / low
(3) Hollow fiber hydrogen contactor (one for each reactor)
    a. Differential Pressure Transducer (2ea.)
        - -36.1 psi to 36.1 psi (4-20 mA)
        - Interlock on high / low DP
    b. Hydrogen Flow Rate
        - Measure flow rate only (0-1000 sccm)
        - Interlock on high and low flow rates
    c. 3-way valve (2 ea.)
        - Hydrogen approved solenoid valves
        - Automatic control
        - Switch to nitrogen on interlock trip

(4) Switch to nitrogen during regeneration cycle
    a. Hydrogen flow bypass switch
        - Switch nitrogen to contactor
(5) Personnel and hydrogen safety
    a. Gas (H2) LEL (Lowest Explosive Limit) monitor / transmitter (1 ea.)
    b. Hydrogen detectors (3 ea.)
        - Monitor LEL level (0-100%; 4-20 mA) at well heads (2 detectors)
        - Monitor LEL level (0-100%; 4-20 mA) at hydrogen manifold (1 detector)
        - Interlock on 10% LEL at well heads and hydrogen manifold
        - Interlock on detector *I* monitor fail
    c. System shutdown button
        - Interlock input
(6) Miscellaneous interlocks
    a. Gas pressure switches
        - Hydrogen supply (2 ea.) - interlock on low pressure
        - Nitrogen supply (2 ea.) - interlock on low pressure
        - Air supply (2 ea.) - interlock on low pressure
(7) Regeneration and fouling control system
    a. Bleach metering pump (2 ea.)
        - Automatic on/off control
        - Manual preset pumping volume
    b. Bleach tank level switch
        - System shutdown on low level
(8) System pressure (2 ea.)
    a. Pressure transducer
        - Monitor (0-100 psi; 4-20 mA)
        - Interlock on high and low pressure setpoints
(9) Control and remote operating system
    a. PLC (programmable logic controller)
        - Digital / analog I/O
        - Remote communications link (modem)
        - Data processing
        - Control logic
    b. Display panel
        - Operating parameters
        - Fault indicators
    c. Interlocks control cystem
        - Any interlock fault shuts down entire system
            - Turn pumps off
            - Switch 3-way hydrogen valve to nitrogen supply

    - Stop regeneration cycle
    - Display first interlock fault input
    - Display all subsequent interlock faults
- All interlock faults latch
- Manual reset pushbutton to clear interlock faults
- Interlocks bypass switch
    - Bypass process interlocks for start up
    - Safety interlocks never bypassed
    - One hour timeout enables all interlocks

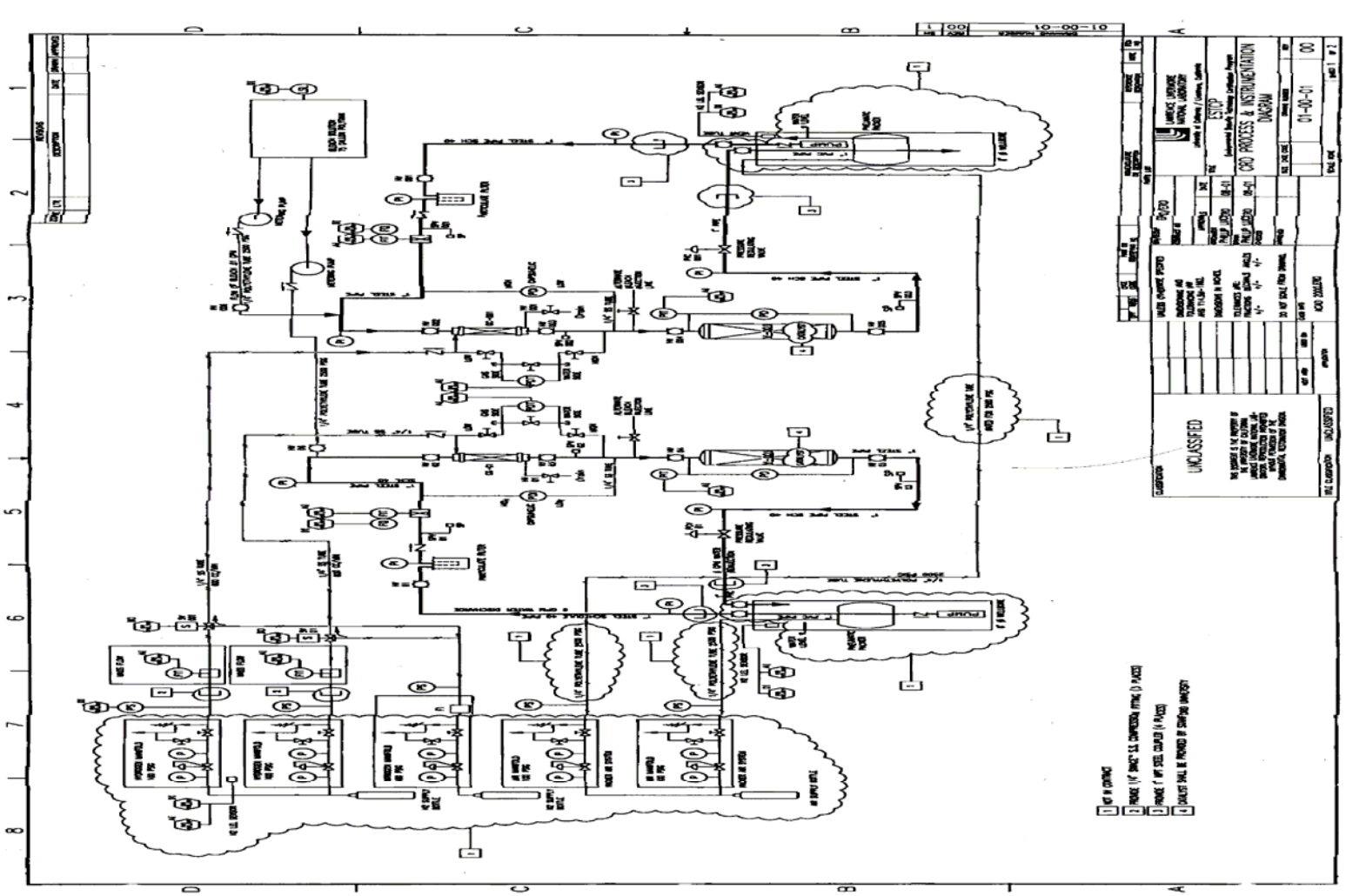

Figure 2-2: Reactor Schematic.

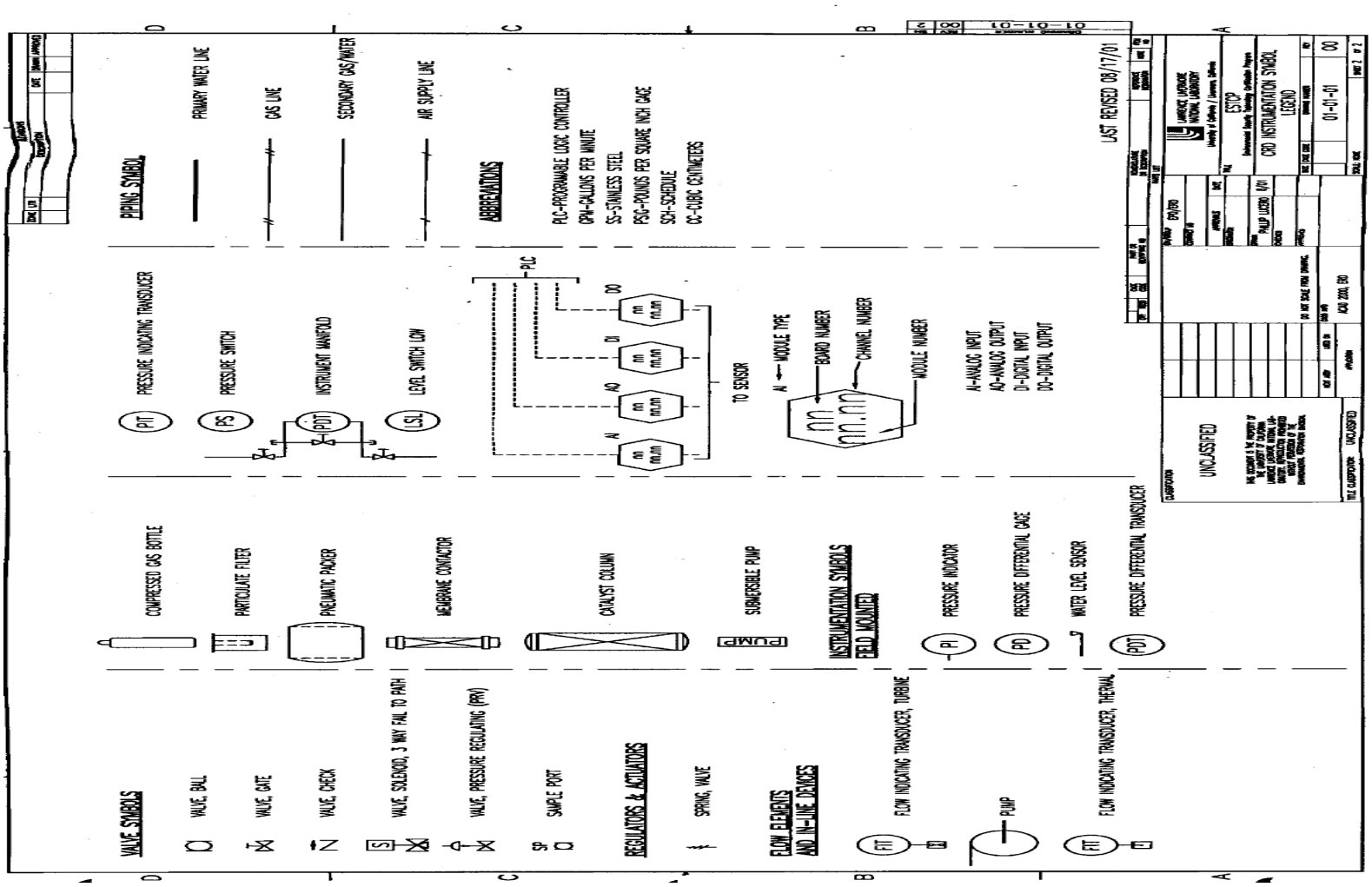

Figure 2-3: Reactor Schematic Symbols Legend.

The final design parameters selected are summarized in Table 2-1 for 1% Pd-on-Al_2O_3 catalyst. The efficiency of the catalyst expressed as percent conversion was calculated based on a first order rate constant of 4.2 min^{-1} derived from existing reactors. The system was designed to produce water to meet the MCL of 5 µg L^{-1} for TCE in two passes at a design flow of 3 gpm. At this flow rate, the predicted removal efficiencies were 94.7% and 99.5% for one and two passes, respectively. At an influent concentration of 1,000 µg L^{-1}, the predicted concentrations in the reactor effluent were 53 µg L^{-1} and 5 µg L^{-1}, respectively. Because the reactors were to be mounted inside the existing 8 in treatment wells, the outside diameter of the reactors was set to 6 in resulting in a length of 4.5 ft. To increase the space between reactor column and well, the outer diameter of the reactor was reduced to 5.5 in so that sampling tubes and cables could be accommodated even if the well was not perfectly straight.

Table 2-1: Original Design Parameters for Pack Bed Reactor.

Design Parameter	Value	Value (metric)
Diameter	6 in	15.24 cm
Length	4.5 ft	1.37 m
Column gross volume	1526 cu-in	25 L
Net mass of catalyst	44.09 lb	20 kg
Void volume	488 in^3	8.0 L
Catalyst cost (2 Reactors)	$10,810	
Flow rate	3 gpm	11.36 L min^{-1}
Residence time	0.71 min	0.71 min
Influent	1000 µg L^{-1}	
Efficiency one pass	94.7 %	
Effluent	53 µg L^{-1}	
Efficiency two passes	99.5 %	
Effluent after 2nd pass	5 µg L^{-1}	

The design catalyst, 1% Pd-on-Al_2O_3 beads, was changed to 2% Pd loading to increase removal efficiencies. Catalyst was supplied by Johnson Matthey (and Precious Metals Corporation, which it acquired). The alumina support is used because its high surface area (~140 m^2 g^{-1}) allows for high surface availability per mass Pd. Additionally, the alumina support is robust in field applications; minimal loss of catalyst was observed during the project duration.

Although the Edwards AFB system was designed for subsurface operation, reactors were tested above grade to allow easy access to all system components. The HFTW components (pumps, packers, and sampling pumps) were installed subsurface and required heavy-duty cranes for maintenance. Before the Edwards AFB reactor system was completely connected, the reactors were operated under manual control to test the system at an extraction flow rate of 2 gpm and a hydrogen flow rate of 250 mL min^{-1}. During testing and debugging of the electrical control system, the steel pipes formed rust flakes which inhibited the magnetic flow sensors. The unanticipated corrosiveness of the site water, extreme variations in the temperature, and the

unreliability of major system components (in particular the bleach and the hydrogen feed system, which is vulnerable to bleach system failures) required us to rebuild the most of the original system on site. For rebuilding, PVC was used and the hollow fiber membrane hydrogen feed modules were replaced with system described in Section 2.1.2. The cost estimates given in this report are modified based on lessons learned in this project; they incorporate all modifications either made or proposed in the demonstration.

The major design specifications, encountered problems, and subsequent system modifications are given in Table 2-2.

Table 2-2: Design Specifications, Problems and Modifications.

Design Specification	Problem	Modification
Upstream 10 micron particulate filters to remove particulate matter and prevent reactor clogging.	Filtration unit was necessary but the provided one was bulky, rusted, and did not fit into the well.	Replaced particulate filter with 10 in plastic filter; bleaching and periodic back flushing required to prevent filter clogging.
Hollow fiber gas diffusion units to supply bubble-less hydrogen feed (Celgard Liqui-Cell).	Bleaching system malfunction allowed bacterial growth and scaling which clogged the units; impossible to restore and was discarded; expensive.	Redesigned hydrogen supply system: flow controlled hydrogen feed to low pressure solvent frit producing fine bubbles followed by a static mixing for complete dissolution.
Hydrogen mass flow meters for adjusting hydrogen feed to hollow fiber gas diffusion units.	Poor control of hydrogen flow rate.	Installed hydrogen mass flow controllers that automatically adjust hydrogen gas flow for changes in reactor pressure and operation range of the meter into a range closer to operation conditions.
Hydrogen safety interlocks shut off system if hydrogen is detected by hydrogen sensors.	Spurious signals shut down system or prevent start up, programming errors make system inoperable.	Elimination of outdoor hydrogen sensors; hydrogen flow lowered closer to level required.
Bleach flushing system, polyethylene tank.	Decomposition of bleach in sunlight, unreliable bleach delivery, gas bubbles formed in metering pumps block valves and flow.	Redesigned bleach flushing system: replaced valves and lines necessary to provide hypochlorite, tank coated with aluminum foil to eliminate sunlight exposure; reservoir with bottom discharge moved to a location above the delivery pump.
Automated system control for remote operation.	System control and catalyst maintenance required frequent manual intervention for process optimization; programming	System control switched to manual (on-site) operation with limited computer control, remote control was eliminated.

	errors.	
Pressure regulating valve.	Difficult to maintain stable flow/pressure with on/off valve.	Installed pressure relief valve to stabilize system backpressure.
Primary water piping steel.	2 gpm flow is near the stalling speed of the magnetic flow sensor in a 1¼ in pipe; rust flakes stick to the magnet of the flow sensor causing the flow meter to fail.	The 1¼ inch steel pipe was replaced with either ½ in PVC or ⅜ in stainless steel tubing.
Pressure gauges and differential sensors	Destroyed by freezing.	Removed and operated reactors without differential pressure data.

A major consideration in reconfiguring the reactor system was how to fit the components into the HFTW. Although technically feasible, mounting reactors inside well bores was not attempted due to technical challenges and time constraints. The predicted residence times for 99% and 99.7% conversion using 1% Pd catalyst were 9.8 min and 12 min, respectively. To reduce residence times, the Pd loading of the catalyst was increased to 2%. Laboratory studies also indicated the need for repeated bleaching due to sulfide production. It was impossible, however, to predict the necessary bleaching regime from laboratory data; as described in Section 2.1.4, this information was determined by trial and error on site.

2.1.2 Development of the Hydrogen Feed System

According to the original design, the hydrogen feed system consisted of a hollow fiber diffusion modules, a 5 L min^{-1} mass flow meter for hydrogen feed and controlled by a hydrogen pressure regulator. Hydrogen was then dissolved into the groundwater via fiber-diffusion modules. This combination functioned poorly considering the stoichiometric hydrogen demand of approximately 10 mL min^{-1}, a value on the border of the mass flow meter's sensitivity range; pressures within the reactor system varied over time. In addition, diffusion modules were expensive and frequently clogged due to scaling after very short periods of operation.

To achieve reliable hydrogen feed, mass flow meters were replaced with mass flow controllers; to make the system resistant against biological fouling, gas diffusion modules were replaced with a low-pressure solvent frit and static mixer. The frit produced fine hydrogen bubbles that were dissolved in the static mixer (Figure 2-4).

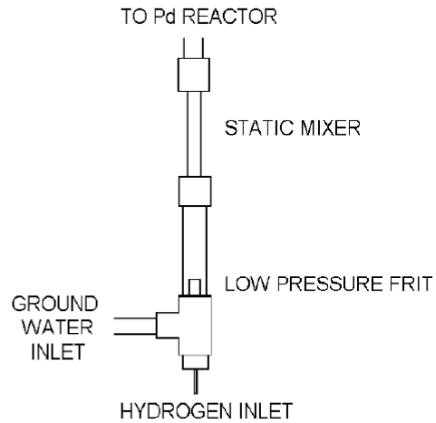

Figure 2-4: Schematic of Hydrogen Feed System.

2.1.3 Hydrogen Safety

The flammability of hydrogen is a well known risk and prompted health and safety precautions at the Edwards AFB site. For hydrogen/air mixtures, the flammability at standard temperature and pressure is 6.2 to 71.1% by volume [Lange's Handbook of Chemistry] (62 to 711 mL L^{-1} in air). The average concentration of TCE in the influent groundwater was approximately 15 µM. The stoichiometric hydrogen demand for TCE reduction to ethane is 4:1, thus a hydrogen flow of approximately 10 mL min^{-1} was required to remediate the site contaminated groundwater. Pd column operational conditions included using 30 mL min^{-1} hydrogen gas dissolved in 2 gpm (7.69 L min^{-1}) groundwater, resulting in a hydrogen application rate of 0.35 mg L^{-1}. Hydrogen solubility is low (1.7 mg L^{-1} at 25ºC and 1 atm). Considering the low surface area of exposed discharge within the well, the cross sectional area of the well casing and the hydrogen concentration being less than about 20% its solubility, very little hydrogen was expected to volatilize within the well – most would transport into the aquifer as dissolved hydrogen or would rapidly be consumed by sulfate-reducing bacteria.

Furthermore, any hydrogen volatilizing up the well can easily be reduced in concentration to well below the lower explosive level (LEL) by inserting a medium diameter pipe and adding a small blower to pump air into the well, a simple engineering design. For example, at the hydrogen flow rate used for most of this demonstration, 30 mL min^{-1}, the addition of blower air at a flow rate of 5 L min^{-1} would have reduced the hydrogen concentration to 10% of the LEL assuming no hydrogen was consumed in the Pd reactor (i.e. no reaction at Pd surface, no sulfate-reducing bacteria).

2.1.4 Optimization of Treatment Conditions, Catalyst Maintenance and Regeneration

Bleaching the Pd catalyst with a dilute solution serves three purposes; it:

(1) Prevents growth of sulfidogenic bacteria;
(2) Can be used to restore catalyst activity after sulfide poisoning; and,
(3) Regenerates activity lost by accumulation of inhibitory materials on the catalyst surface.

Preventing growth of sulfidogenic bacteria is imperative because once sulfide production starts the catalyst is poisoned, TCE removal decreases rapidly and breakthrough occurs. Prolonged oxidation (by bleaching) is then required to restore catalyst activity. Also, accumulation of inhibitory materials at the surface of the catalyst can lead to slow activity degradation. Loss of activity can be tolerated up to the point where effluent specifications (MCLs) are exceeded, but preventive regeneration with bleach oxidation curtails these operational issues.

Bleaching the catalyst temporarily suspends its activity for TCE reduction because the palladium surface is oxidized in the process. Reactivation of the catalyst is accomplished by contacting the catalyst with hydrogen-saturated water, reducing the oxidized active sites on the Pd surface. Recovery of catalytic activity is shown in Figure 2-5: catalyst that was severely poisoned and subsequently oxidized by bleaching regained activity for TCE reduction as hydrogen-saturated groundwater was passed through the column. Effluent TCE concentrations gradually decreased to nearly zero over a period of approximately one day as the catalyst surface was reduced by hydrogen to metallic palladium, and thus became available for TCE dehalogenation. As sulfide poisoning becomes more severe, i.e. exposure of the catalyst to higher sulfide concentrations for longer times, higher bleach concentrations must be applied for longer periods of time (up to one week) to regain activity.

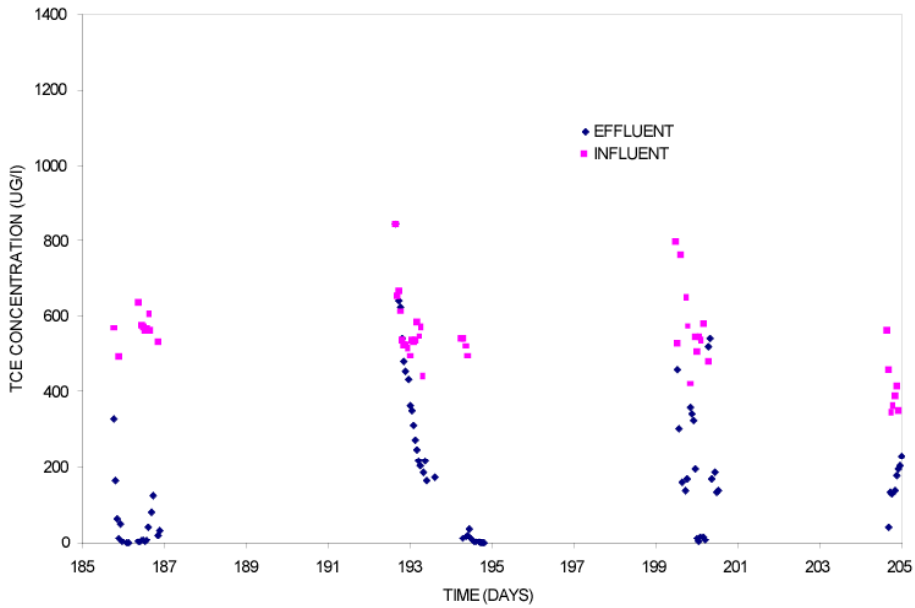

Figure 2-5: Regeneration After Severe Episodes of Reactor Poisoning During 2004.

Establishing operational protocols required several iterations to adapt to the corrosive water quality at the site. The anticipated bleach pulsing frequency was once in four days for 18 min at a bleach concentration of 75 mg L^{-1} based earlier laboratory experience. This bleaching regime was expected to both disinfect the system to prevent biological growth and maintain catalyst activity by regenerating sulfate-poisoned Pd surfaces. However, with Edwards AFB

groundwater being borderline sulfidogenic, this bleaching regime was insufficient; reactors were poisoned repeatedly with sulfide to nearly complete loss of TCE removal efficiency. Fouling was especially severe after bleach system malfunction events.

Figure 2-5 represents data where the system was left in unattended operation for several weeks and was later found to have shut down due to power failures and/or system malfunctions. The most significant setback associated with such instances was severe sulfide poisoning of the Pd catalyst. These problems were frequently encountered during the initial start-up as groundwater stagnated in the reactor and sulfidogenic bacteria quickly reduced sulfate to sulfide. Manual bleach cycles, sometimes multiple times in succession, were used to recover catalytic activity. After severe poisoning events, reactivating the catalyst took weeks instead of minutes. A severe poisoning event was caused by site flooding and power failure during Winter 2004/2005, which left the catalyst in sulfide-containing water for several weeks. This is consistent with laboratory experiments, which suggested that sulfide or elemental sulfur slowly incorporated into the palladium metal, and the reverse diffusion out of bulk Pd and alumina support requires weeks [Munakata, 2005]. Short bleach cycles were less effective at reactivating the poisoned Pd catalyst but were sufficient to control fouling. In order to re-reduce the catalyst, the normally applicable hydrogen flow rate (20 mL min^{-1}, roughly twice the stoichiometric demand) was used. Higher hydrogen flow rates would have sped recovery of the active Pd catalyst surface (after oxidation by bleaching); this process was not optimized.

A sequence of several maintenance bleaching cycles is shown in Figure 2-6. Bleach affects the catalyst surface by creating oxidative conditions within the reactor – eliminating hydrogen from the water oxidizes Pd active sites. When groundwater containing sulfide species is treated in a reductive catalytic reactor, hydrogen sulfide strongly binds to active Pd sites and poisons the catalyst. However, catalyst activity and capacity for TCE reduction may remain high for several days, keeping the effects of sulfide poisoning undetected. After 3-4 days and treatment of approximately 10,000 gal water (at 2 gpm), the number of active Pd sites poisoned by hydrogen sulfide becomes significant and overall TCE removal efficiency decreases. Effluent TCE concentrations eventually exceed the MCL (5 $\mu g\ L^{-1}$) and another oxidative treatment (bleach) must be applied to regain catalyst activity.

The maintenance bleach cycle shown in Figure 2-6 includes a daily bleach pulse (t = 0 is midnight). Initial TCE reduction is high with >99% removal; efficiency slowly decreases over the subsequent 50 hours to ~94%. The sharp pulse in TCE concentration at Day 2.5 (two data points in Figure 2-6) was caused by a bleach cycle. When the Pd active sites were oxidized by bleach application, TCE was not reduced effectively. As the hydrogen-saturated water was passed over the oxidized catalyst, Pd surfaces were re-reduced and TCE removal efficiency increased. Similar pulses in effluent TCE concentration should be present for Days 1.5 and 3.5 but for unknown reasons the data system did not operate during these bleach pulses, possibly because the GC oven did not cool sufficiently during the hot daytime temperatures, triggering a shutdown of the data acquisition system. Immediately after all effluent TCE spikes prompted by bleach pulses, TCE reduction efficiency returned to >99%.

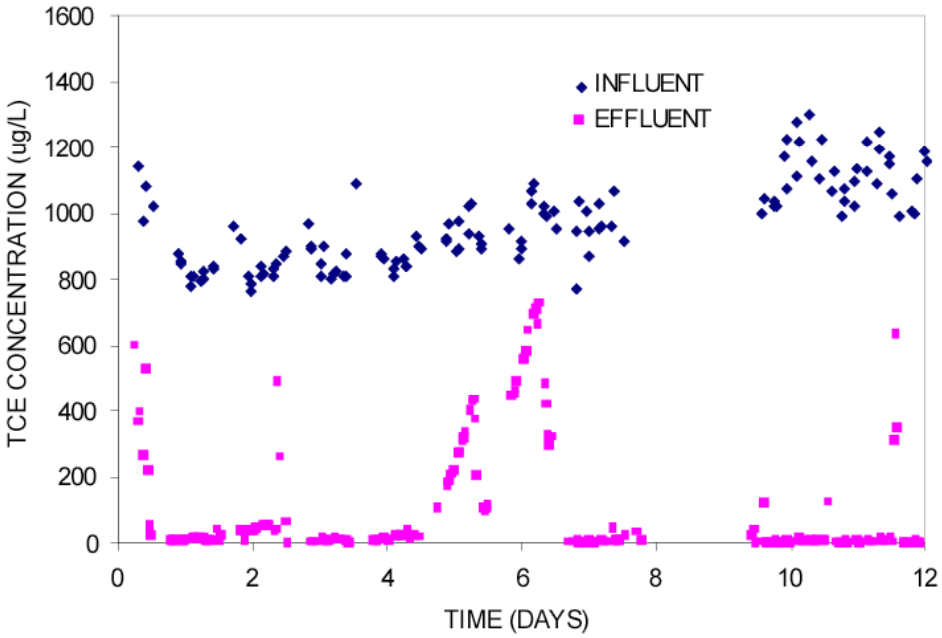

Figure 2-6: Regeneration and Reactivation of Reactor After Poisoning Events Due to Insufficient Maintenance Bleaching.

The effect of omitted daily bleach cycles on reactor performance is also evident from the data shown in Figure 2-6. The expected TCE pulse on Day 4 was not detected. On Day 5, TCE concentrations began to rise rapidly, likely due to a malfunctioning bleach system. After two missed bleach cycles, TCE started to break through because biologically-formed sulfide poisoned Pd active sites. As a consequence, the bleach cycle of Day 5 (indicated by the sharp drop in TCE concentration) was not sufficient to regenerate catalyst activity. Catalyst poisoning increased until two manual bleach cycles were applied on Day 6.

The data show that long-term maintenance of catalyst activity required daily bleach treatment to oxidize Pd surfaces and remove sulfide from the bulk and surface Pd. Also, system performance was recoverable by multiple bleach pulses if mild catalyst poisoning occurred due to missed bleach cycles. The regenerant solution contained 500 $\mu g\ L^{-1}$ TCE, nearly the same as that found in the groundwater influent. Since this solution was not collected and re-treated or treated separately, the average effluent TCE concentrations shown in Figure 2-6 seem artificially high when compared with optimal system performance. The experiences at Edwards AFB show that catalyst maintenance and regeneration treatment should be adjusted to daily pulses, as detailed in Section 6.4.

2.2 Previous Testing of the Technology

McNab et al. (2000) describe the design and performance of the first LLNL system, which has been operated since 1999 in situ with reactor columns mounted in the well bore. The second LLNL system is an above grade system operated since 2002. Both systems are regenerated through a combination of draining and exposing the catalyst to air and biweekly oxidative

bleaching. The first LLNL system operates for 12 h followed by regeneration in air for 12 h. The second system is limited by the yield of the wells and operates only 6 h daily. During the remaining 18 h, the system is drained and catalyst is exposed to air to prevent growth of anaerobic bacteria. Preventing bacterial fouling of the hydrogen feed module is the most critical maintenance issue for both LLNL systems because such fouling can irreversibly clog the $5,000 unit (Roberto Ruiz, LLNL, personal communication). Every two weeks, the systems are bleached to prevent microbial fouling of the hydrogen feed module and to clean the catalyst surface of sulfide and other matrix species. With this mode of operation, catalyst activity has been sustained for many years (same catalyst since 1999 in the first LLNL system).

Reactor design for this demonstration was based on the experiences gained through operation of the LLNL systems and laboratory research at Stanford on catalyst fouling. Compared with the LLNL systems, the Edwards AFB project incorporated three major modifications to improve overall efficiency:

(1) Catalyst regeneration with bleach instead of air venting;
(2) Treatment of groundwater streams with two catalytic reactors simultaneously in conjunction with HFTWs; and,
(3) Internet based remote control.

Although these modifications were previously tested separately, the Edwards AFB site was the first combination of the three. Regeneration with bleach was tested at the laboratory scale (Lowry and Reinhard, 2000) and groundwater remediation using HFTWs was tested previously at the Edwards AFB site in conjunction with biological remediation technologies (McCarty et al., 1998). Remote control of treatment systems was accomplished via off-the-shelf components.

2.3 Factors Affecting Cost and Performance

Two major cost factors were considered: (1) capital investment in the reactor system including Pd catalyst and (2) personnel costs associated with maintenance of the reactor, sampling, and analysis. Both capital and personnel costs can be substantially lower than shown in this pilot-scale study based on lessons learned in operating the reactor at Edwards.

The overall estimated operating costs are $8.48 per 1,000 gal, with labor costs contributing $4.62 per 1,000 gal (at $100 h^{-1} for 4 h wk^{-1}). This calculation assumes no travel and a high degree of automation. Costs of lesser importance are catalyst costs and expendable materials. The cost of Pd catalyst depends on the current market for Pd and can vary greatly, but is a one-time expense assuming activity can be maintained over long time scales as shown in the LLNL studies. Two catalyst purchases were made for this project with costs per pound of $251.94 and $157.46 per lb, respectively; these costs contributed $3.04 and $1.90 per 1,000 gal treated, respectively, assuming the Pd catalyst lasts 5 years. Recycling of the catalyst and longer assumed and actual catalyst useful lives would lower these costs substantially. The cost for consumables (hydrogen, bleach, electricity, and filters) for reactor operation, excluding labor, is relatively small – $0.81 per 1,000 gal. This cost analysis shows that system automation and remote control are necessary to make this technology economically attractive for ground water remediation.

The principal drivers for performance of reductive catalytic reactors are the required residence times to meet MCLs and water quality characteristics that affect the efficacy of the catalyst and determine the catalyst regeneration requirements. The residence time depends on the initial contaminant concentration and the MCL value (5 μg L^{-1}). Reactors should be designed to meet the optimum safety margin; we recommend a safety factor of 5-10 such that MCL requirements of 5 μg L^{-1} would mean target effluent concentrations of 0.5-1 μg L^{-1}. The safety factor allows for flexibility in adjusting the hydraulic loading rates and scheduling of regeneration and maintenance. The most significant site water quality characteristic that needs to be considered is the redox status of the groundwater: sulfate reducing conditions and the presence of reduced sulfur species rapidly poison the Pd catalyst and prevent continuous operation. In laboratory studies, adding 450 μM oxygen reduced TCE conversion from 46.0% to 13.4% (oxygen was converted by 67%) [Lowry and Reinhard, 2001].

For the Edwards AFB reactor, the residence time was approximately 2.3 minutes for 1 mg L^{-1} TCE to meet on average the MCL at the Edwards AFB site. The hydraulic loading rate of the system was 1.23 m min^{-1} (5.5 in diameter, 4.5 ft length, 2 gpm flowrate), providing a safety factor of 5 at the Edwards AFB site under optimal operating conditions. Residence times for other chlorinated ethylenes would be expected of similar magnitudes. The principal water quality characteristic affecting the costs is the tendency of the groundwater to turn sulfidogenic in the reactor after the addition of hydrogen gas, requiring periodic bleach treatment. Although bleach treatment is not by itself expensive, it reduces the operational availability of the system.

2.4. Advantages and Limitations of the Technology

For remediation of groundwater contaminated by chlorinated solvents, the most likely alternative technologies are:

(1) Pump-and-treat;
(2) Biological reductive dechlorination; and,
(3) Permeable reactive iron barrier.

Reductive catalysis, as tested at Edwards AFB, is well suited for sites where chlorinated ethylenes (PCE, TCE, DCE isomers, and vinyl chloride) are the major contaminants. The Edwards AFB site had a minor concentration of cis-DCE (<20 μg L^{-1}), which was dechlorinated during this demonstration. For vinyl chloride, the technology may be most competitive because there are few alternatives. Table 2-2 presents the advantages of the Pd/HFTW technology relative to each of these three alternatives.

Table 2-3: Advantages of Pd/HFTW Technology Relative to Competing Technologies.

Competing Technology	Advantages of Pd/HFTW Technology
Pump-and-Treat	(1) Pd/HFTW technology generates no secondary waste stream except spent regenerant solution (dilute bleach). (2) Pd/HFTW technology destroys TCE, PCE, 1,1-DCE, cis-DCE, trans-

	DCE, carbon tetrachloride, chloroform and other chlorinated compounds, rather than merely transferring them from the groundwater to another medium (e.g., activated carbon) [Lowry and Reinhard, 1999]. (3) Pd/HFTW technology transforms chlorinated ethylenes compounds very rapidly, leading to shorter remediation times and minimal intermediates.
Biological Reductive Dechlorination	(1) Pd/HFTW technology is applicable at high contaminant concentrations. (2) The technology generates little or no hazardous by-products, such as dichloroethylene (DCE) or vinyl chloride (VC), when applied properly. (3) Pd/HFTW technology can be deployed in groundwater where dissolved oxygen is present (e.g. LLNL site). (4) Pd/HFTW technology transforms most target compounds very rapidly, so that the Pd/HFTW technology will be less expensive in many cases; cleanup times are shorter. (5) Pd/HFTW technology used hydrogen gas as an electron donor, which is cheap, easy to apply and does not depend upon biological processes.
Permeable Reactive Barrier (PBR)	(1) Pd/HFTW technology is much less expensive to install, especially at sites where the water table is deep below the ground surface. (2) Pd/HFTW technology provides much faster transformation of contaminants than zero-valent iron, the metal typically used in PRBs.

Limitations to the Pd/HFTW technology include the following:

- The presence of high hydrogen sulfide concentrations: the technology can be more easily implemented where the water is aerobic and relatively free of sulfide or other inhibitory matrix species. This has been one of the major difficulties in demonstrating the technology at Edwards AFB. Anoxic conditions and the tendency for sulfidogenic conditions made it necessary to bleach the reactor daily rather than weekly; and,
- At sites where halogenated contaminants other than ethylenes are present (1,1-dichloroethane, 1,2-dichloroethane, and methylene chloride), the technology is not effective as a remediation strategy because these compounds are not destroyed with the same efficacy as TCE and other chlorinated ethylenes listed above.

The presence of high sulfate at a demonstration site is not necessarily problematic because sulfate itself does not adversely affect Pd catalysts. However, in the presence of hydrogen, sulfate-reducing bacteria will likely grow and reduce sulfate to sulfide, which will cause catalyst poisoning after incubation times of days to weeks. To control growth of hydrogen-oxidizing sulfate-reducing bacteria, application of disinfectant (bleach or hydrogen peroxide) is recommended. At Edwards AFB, the frequency of these applications was 3 h every day, but is likely to vary from site to site with aerobic water requiring less frequent disinfection.

3. Demonstration Design

3.1 Performance Objectives

Table 3-1 summarizes the primary performance criteria of this field demonstration, the expected performance metrics and comments on field results and observations. Performance was assessed based on data collected mid July 2005 through mid November 2005 when the system was fully functioning; operating parameters were established during this period. The system operated reliably once the driving operating parameters were controlled. Routine maintenance required two visits each week, which could be reduced to one per week (ore even bi-weekly) with more sophisticated (remote) system control. Maintenance protocol included daily bleaching and catalyst regeneration using hydrogen-saturated water, both of which can be accomplished via automated system control. Troubleshooting the automated control system requires a high level of expertise and thus requires a trained and/or experienced operator. TCE reduction >99% is possible with a properly operating system, even at influent concentrations in excess of 1 mg L^{-1}. The treatment system was designed for in situ operation with the reactors mounted inside the HFTW wells; technical challenges encountered in the field prevented such operation.

Since the system was operated above ground and the treated water was returned to the aquifer, meeting the regulatory MCL 5 µg L^{-1} was necessary. The technology was evaluated in terms of overall catalyst activity, shown using 21 h operation and 3 h regeneration daily. TCE effluent concentration remained approximately 5 µg L^{-1} during this operational protocol. Because catalyst activity was recoverable even after severe (and repeated) sulfide poisoning events, the process is quite robust under the conditions observed at Edwards AFB. Byproducts were not formed during TCE dechlorination, as expected.

Table 3-1: Primary Performance Criteria.

Performance Objective	Primary Performance Criteria	Expected Performance (Metric)	Actual Performance Objective Met?
Qualitative	Safety and Reliability	Operation of the technology, including hydrogen addition, can be performed without creating any unacceptable safety hazards. Technology gains regulatory acceptance	Yes, with proper routine maintenance, an appropriate treatment and regeneration cycles the system is reliable. Technology is accepted by regulators.

	Maintenance	Requires routine maintenance (e.g., changing hydrogen cylinders and preparing bleach solution) for duration of demonstration	Yes, after developing SOP and modifying reactor, two weekly visits were sufficient. With remote control, this might be reduced to one visit in a week or two depending on conditions. Implementation of a regular oxidative regeneration and cleaning schedule was required for biological fouling control and catalyst regeneration to maintain reactor performance
	Ease of Use	Routine operation does not require a permanent operator	No, on-site maintenance required biweekly operator visits, in situ treatment was not feasible due to install/remove logistics.
Quantitative	Contaminant Reduction	At least 99% destruction of TCE and other applicable contaminants	Yes, destruction was greater than 99% under normal operating conditions.
	Ability to Meet Regulatory Standards	Final concentration of TCE is below MCL (5 µg L^{-1}).	Yes, on average concentrations were below MCL (5 µg L^{-1}) during a 21 h operating cycle.
	In situ operation	System is operated in sutu in conjunction with HFTW wells	Was not accomplished due to technical challenges
	Robustness	Achieves contaminant reduction goals when TCE concentration is > 1 mg L^{-1}	Influent concentrations ranged from 0.8 to 1.2 mg L^{-1} and system was still able to reduce concentrations to below MCL. Treatment efficiency is sensitive to certain chemical characteristics in the influent groundwater. Laboratory experiments have shown the technology is sensitive to reduced sulfur species, especially sulfide. High oxygen content in the groundwater increases the hydrogen consumption but assures the absence of sulfide. Other common water quality parameters, including total dissolved solids and high sulfate do not seem to interact with the Pd catalyst [Lowry and Reinhard, 2000].

	By-Product Formation	MCLs are met for cis-DCE (6 µg L^{-1}) and vinyl chloride (0.5 µg L^{-1})	Yes, ethylene was the only end product.

3.2 Selecting Test Site

Edwards AFB is located in the Mojave Desert of Southern California, approximately 60 miles north-northeast of Los Angeles, as shown in Figure 3-1. The base is divided into different Operable Units, which are further sub-divided into Sites. The location for this demonstration project was Site 19, which is part of Operable Unit 1. A major reason for selecting this test site was Stanford's previous experience operating HFTW wells at the site (McCarty et al., 1998).

3.3 Test Site Description

Edwards Air Force Base occupies about 470 square miles of high desert area, including all of Rogers and Rosamond Dry Lakes. The primary mission of the base has been aviation development through experimental and test flight activities. The base presently is operated by the U.S. Air Force Flight Test Center (AFFTC).

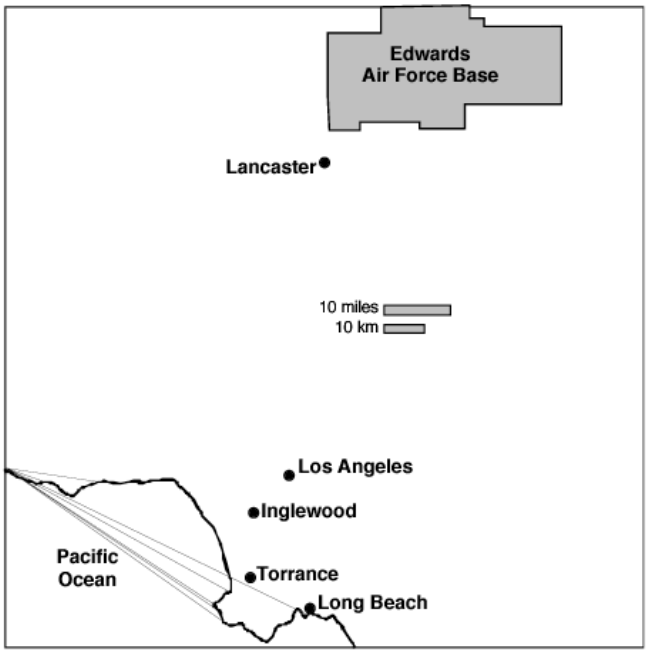

Figure 3-1: Location of Edwards Air Force Base.

Site 19 is an open tract of approximately 100 acres situated east of Taxiway E and south of Taxiway D, as shown in Figure 3-2. The site includes buildings 1928, 1931 and adjoining parking areas, which were constructed in 1958 to house maintenance equipment and test racks for engines used in the X-15 rocket plane.

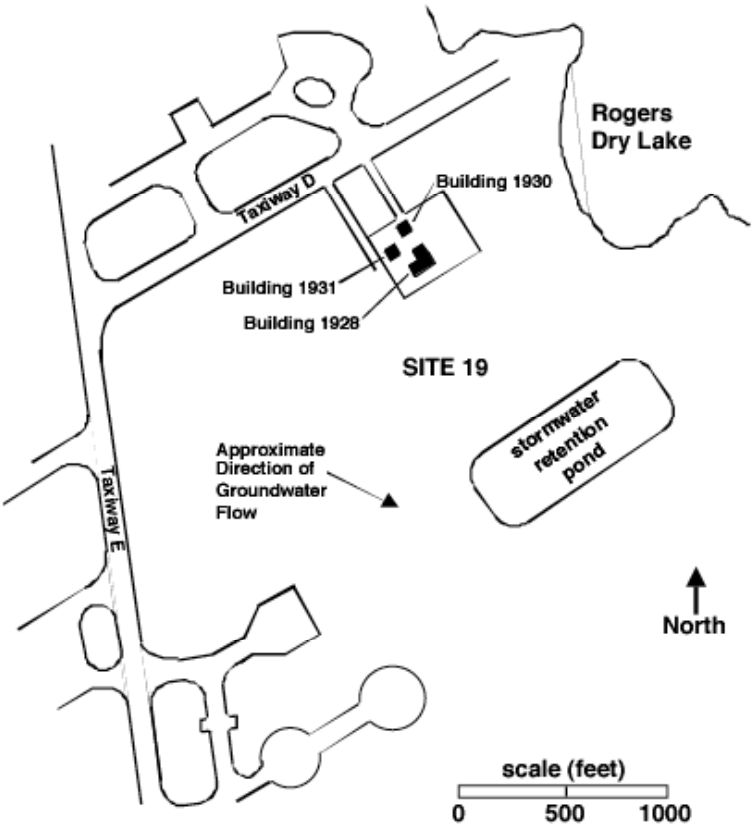

Figure 3-2: Site 19 at Edwards Air Force Base.

During 1958-1967, approximately one 55 gal drum of TCE per month was used to clean X-15 rocket engine parts. After 1967, the facility was used for much smaller engines and the TCE use dropped substantially; testing at the site ceased in 1975. During testing, standard practice was to rinse spent solvent from the test stands into maintenance shop drains that fed a concrete holding pond. Wastewater which did not evaporate from the holding pond was periodically pumped and discharged into the desert south of Building 1931. The majority of the wastewater was discharged through a steel pipe leading from the holding pond and terminating approximately 300 feet to the south. Additional site contamination may stem from a septic tank and leach field servicing Building 1931; the tank was removed in 1984 but the drain field was left intact. The exact location of this leach field is undetermined.

Two other potential sources for contamination include the original storm water retention pond and the Drainage Area B channel. The original retention pond was located to the west of the current storm water retention pond, covering an area approximately 350 ft by 180 ft. Surface runoff from Drainage Area A, which feeds the existing pond, previously flowed into the original pond. The unlined drainage channel in the northern portion of the site (discharging onto Rogers Dry Lake) is the terminus for surface runoff from Drainage Area B. Contaminated surface

runoff from Drainage Area B may have entered the soil, and subsequently the groundwater along any portion of this unlined channel.

The area south of the buildings has not been developed; the current storm water retention pond was constructed in the 1960s to prevent drainage from the paved areas west of Site 19 from reaching Rogers Dry Lake. The pond is approximately 1,000 ft long, 400 ft wide, and less than 10 ft deep. Historical photographs from Base History Office (Edwards AFB) indicate that parts of Site 19 and parts of Rogers Dry Lake east of Site 19 were periodically flooded prior to construction of the current pond. During wet seasons, excess water from the retention pond periodically overflowed into low-lying areas to the north.

The first evidence of TCE contamination at Site 19 was the detection in a water sample from a well upgradient of the storm water retention pond. The aquifer contaminated with TCE is not used as a potable or agricultural water supply near the site, but Edwards AFB supply wells are withdrawing from similar alluvial materials approximately 3 miles to the south. The plume has moved approximately 700 m (2,300 ft) since TCE introduction to the aquifer more than 4 decades ago. Figure 3-3 shows the approximate shape of the TCE plume [after McCarty et al., 1998]. PCE has not been detected at Site 19 and was not evaluated.

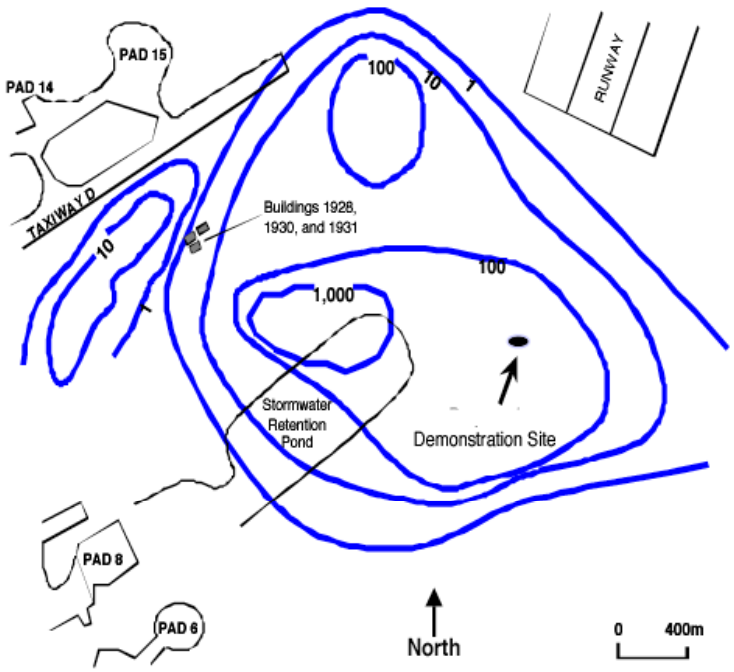

Figure 3-3: TCE Concentration Contours (µg L^{-1}) at Edwards AFB, Site 19.

Figure 3-3 also shows the location for this demonstration project. McCarty et al. [1998] and Gandhi et al. [2001] reported TCE concentrations of 1.1-1.4 mg L^{-1} in the groundwater entering the demonstration site in the upper aquifer zone. Recent measurements elsewhere at Site 19 have

shown TCE concentrations of 2.3 mg L^{-1} in shallow wells and 4.5 mg L^{-1} in deep wells [internal communication between Stanford University and Edwards AFB personnel].

Site 19 also contains parts of the main fuel transfer (pipeline) system that extends along Taxiway E. Fuel leakage from the pipeline occurred in the 1960s in the northwestern corner of Site 19 when an estimated 250,000 gallons of JP-4 jet fuel were released. Soil was excavated and approximately 100,000 gallons of fuel were recovered during remediation efforts. JP-4 jet fuel was last detected in 1992 and benzene was last detected in 1993.

3.4 Pre-Demonstration Testing and Analysis

Water quality data from McCarty et al. (1998) indicated nitrate reducing conditions at the Edwards AFB site. Oxygen was not present and sulfate was measured at 710 mg L^{-1}.

Table 3-2: Groundwater Chemistry at the Treatment Evaluation Site. [a]

Parameter	Value
Total organic carbon (mg L^{-1})	6.7
Boron (mg L^{-1})	3.4
Calcium (mg L^{-1})	180
Chemical oxygen demand (mg L^{-1})	60
Chloride [b] (mg L^{-1})	720
Iron (mg L^{-1})	<0.1
Manganese (mg L^{-1})	0.02
Nitrate [b] (mg L^{-1})	26
Dissolved oxygen (mg L^{-1})	<0.5
Potassium (mg L^{-1})	1.7
Sodium (mg L^{-1})	560
Total dissolved solids (mg L^{-1})	2500
Sulfate [b] (mg L^{-1})	710
Total phosphates (as P) (mg L^{-1})	<0.05
pH	7.36
total alkalinity (as CaCO3) (mg L^{-1})	340

[a] Data from McCarty et al. (1998). Measurements, except as indicated, from PACE Environmental Laboratories (Novato, CA), report dated November 30, 1994.
[b] Measurements from on-site ion chromatography analysis using automated sampling and analysis platform (ASAP).

The average nitrate concentration decreased considerably after the data in Table 3-2 was obtained during background sampling(from approximately 26 mg L^{-1} to 3.2 mg L^{-1} (± 3.8 mg L^{-1})). The average sulfate concentration remained constant at about 813 mg L^{-1} (± 45 mg L^{-1}). Attempts to measure sulfide via ion-specific probe failed during background sampling due to nonlinear analog response of the probe at very low concentrations. Manual measurements of sulfide using a Hach kit failed to detect sulfide in the influent samples with a detection limit of

0.1 mg L^{-1}. The continuing depletion of nitrate indicated that conditions favored sulfide reduction even though sulfide was not detected. Microbial dechlorination of TCE was not observed since only very small amounts of DCE (reaction intermediate) were detected.

Laboratory studies were performed (with support from this and other projects) prior to and during the demonstration. The practical objectives of these studies were to:

(1) Predict catalyst activity under field conditions (in Edwards groundwater);
(2) Evaluate the potential for catalyst poisoning by biogenically produced sulfide in Edwards groundwater augmented with hydrogen; and,
(3) Develop protocols for regenerating poisoned catalyst and controlling growth of sulfidogenic bacteria and sulfide formation.

Other studies aimed to elucidate the mechanism of dehalogenation and specifically the interaction of TCE and the Pd surface. Findings are detailed in the collected reports of APPENDIX F. Catalyst activity under field conditions and was investigated by Munakata et al. (2002), revealing that Edwards AFB groundwater was amenable to catalytic treatment as long as biogenic sulfide production was controlled. The data indicated an apparent first-order reaction rate in the laboratory columns for TCE of 0.43 min^{-1}, corresponding to a half-life of 1.6 min.

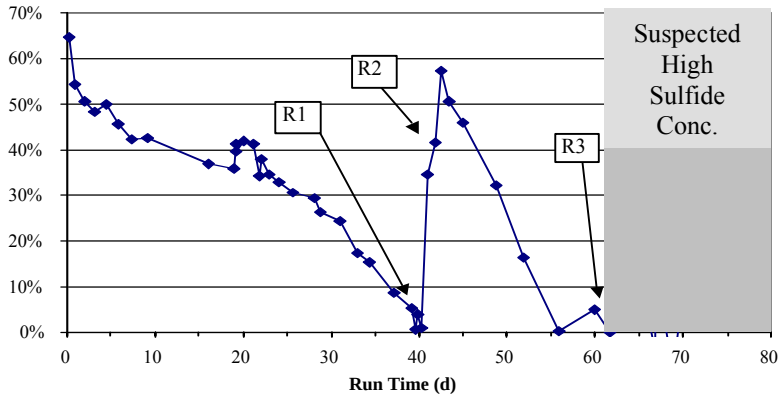

Figure 3-4: Loss of Activity in the Absence of Maintenance Bleaching, Regeneration With Bleach, and Poisoning With High Sulfide

The regeneration cycles shown in Figure 3-4 correspond to:

R1: Regeneration with 150 mg L^{-1} as free chlorine for 1000 min;
R2: 1500 mg L^{-1} for 240 min; and,
R3: 1500 mg L^{-1} for 1200 min.

The data in Figure 3-4 indicate that after initial rapid loss of catalyst activity, efficacy continuously decreased until the catalyst was completely deactivated after 40 d. Bleach is shown

as an effective regenerant by recovery of Pd activity after each regeneration cycle. After R2, the rate of deactivation increased compared to the initial deactivation rate, indicating that sulfidogenic bacteria were present in the system; operating columns for several weeks and bleaching did not prevent sulfide production. This was attributed to regrowth because some parts of the system may have eluded bleach contact. Based on this experiment, catalyst activity in the field was anticipated to be maintained by periodic bleaching pulses (e.g. 3 h daily). The experiment illustrates (1) need for harsher bleaching conditions to remedy severe poisoning events and (2) the necessary protocol of removing hydrogen from the reactor column when not operating to minimize microbial growth.

To investigate requirements for regeneration of palladium catalysts poisoned by sulfide poisoning, a detailed laboratory study was completed at Stanford. A quantitative model for deactivation kinetics with sulfide was developed and regenerations with acid, base and oxidizing agents were investigated. Findings are summarized in a report by Munakata and Reinhard entitled *Palladium-Catalyzed Aqueous Hydrodehalogenation in Column Reactors: Modeling of Deactivation Kinetics with Sulfide and Comparison of Regenerants*. Deactivation increased with sulfide concentration and exposure time and was independent of sulfide speciation. Results also suggest that sulfide diffuses into the Pd bulk during deactivation if exposure occurs over extended periods (weeks to months) without regeneration. Slow poisoning of the catalyst, even after removing sulfide from the catalyst surface, was inferred as mass transport of sulfide from within the bulk Pd to the surface. As a result, the time required for regeneration increased with increasing sulfide concentration and exposure time. Deactivation was slowly reversible by flushing the catalyst with deionized water at pH 10.4. Treatment with 20 mM sodium hypochlorite quickly and completely regenerated the catalyst, and was significantly more effective than hydroxide, hydrochloric acid, hydrogen peroxide and air-saturated water. These results are consistent with field observations: after prolonged exposure to high sulfide concentration (weeks) bleach treatment for several weeks was necessary to recover activity.

Another related laboratory study Sriwatanapongse et al. (2006) investigated the mechanism of TCE dechlorination using Pd catalyst using solid-state NMR. Carbon-13 NMR spectra indicated that at low coverage strongly adsorbed species are formed while at high coverage additional physisorbed species are present. Chemisorption of carbon species and subsequent carbon-carbon bond scission leads to the formation of single-carbon fragments. Catalysis is attributed to surface species with elongated double bonds (1.46±0.03 Å) suspected to be chemically-bonded ethynyl. These results explain the high selectivity of Pd catalyst for reduction of chlorinated ethylenes.

3.5 Testing and Evaluation Plan

3.5.1 Demonstration Installation and Start-Up

The demonstration site was equipped with two treatment wells and 20 monitoring wells from previous demonstrations, as indicated in Figure 3-5 [Gandhi et al. 2001]. For this demonstration,

the skid and the trailer housed the automated analytical laboratory; control equipment, tools and supplies were placed near the treatment wells.

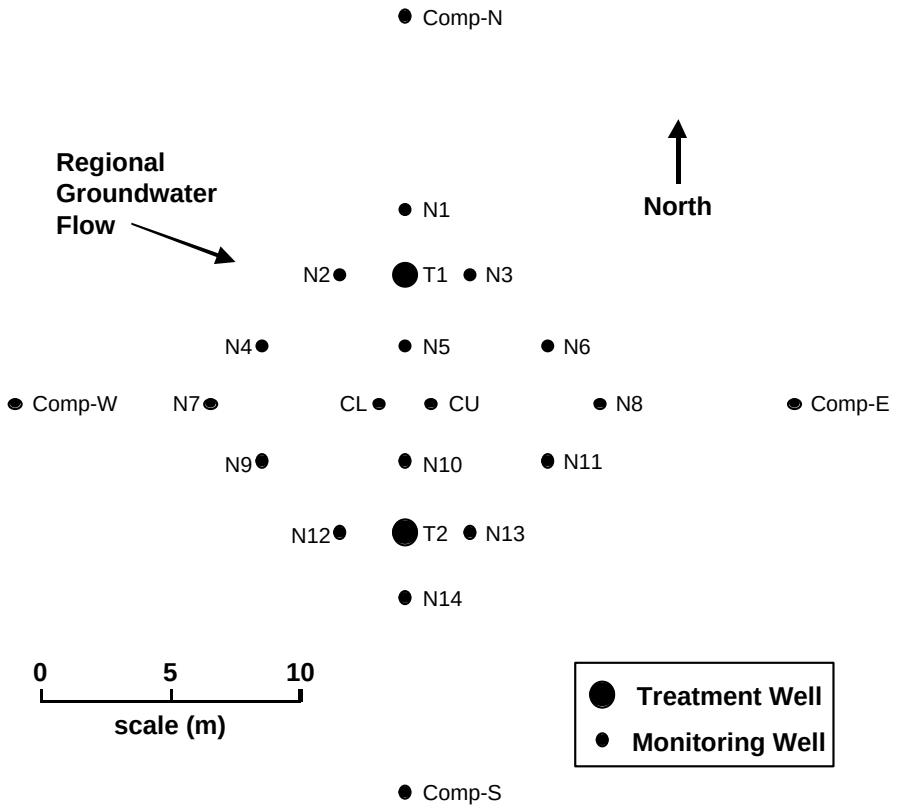

Figure 3-5: Relative Treatment and Monitoring Well Locations at ISACB Demonstration Site.

T1 and T2 are treatment wells; Comp-N, -E, -W and -S are compass point wells to monitor the perimeter of the demonstration area; CL and CU are 4-inch monitoring wells, screened in the lower and upper aquifers, respectively; N1–N14 are 2-inch monitoring wells.

Using the developed Edwards AFB site provided significant cost savings because it had been used for similar demonstrations and had existing wells and infrastructure. Existing equipment, such as ground water and sampling pumps, packers for the HFTWs, were available, but had to be refurbished. The reactor columns were designed to fit within the existing wells, but required non-standard dimensions (diameter 5.5 in). The analytical equipment was on site and needed only to be moved to this location. Good working relations existed between Stanford and base personnel. The cost saving gained from using the existing site were quickly consumed by added travel expenses, especially during the labor intensive testing and rebuilding period which lasted much longer than anticipated. The workplan allotted for start up and optimization of operating conditions (pumping rate, hydrogen addition rate, regenerant dose, etc.) four months. Technical challenges stemming from design problems, floods, (Section 3.5.2) and the corrosivness of the groundwater extended the shakedown period. Edwards AFB site water was essentially anaerobic

(borderline sulfidogenic) and required an aggressive regeneration schedule. Although this demonstration would probably have been easier in aerobic water, one of the significant findings of this study is that anoxic water (nitrate reducing) is amenable to treatment if bleaching protocols are adapted accordingly.

3.5.2 Period of Operation

The period of operation under optimized conditions was from mid-July through mid-November 2005. The period preceding this time was spent debugging and rebuilding the system, optimizing the bleaching frequency to site conditions and testing procedures to recover severely poisoned catalyst. Major operational milestones are summarized in Table 3-3.

Table 3-3: Project Development Phases.

Reactor delivery at the site	May 2002
Unpacking, manual testing; damage due to corrosion noted	June – July 2002
Repair and installation of monitoring well sampling pumps (Groundfos Rediflo-2); Automated Sampler and Analysis Platform (ASAP) installation	Fall 2002 - Spring 2003
Installing and debugging electrical connections between computer, reactor, and gas supply system	Summer 2003
Start background sampling; continuing problems with reactor software and connections; re-plumbing the system	Fall 2003
Start reactors; noted severe catalyst poisoning due to bleach system malfunctioning; noted damage to hollow fiber hydrogen feed module; development and testing of new hydrogen feed module	Winter 2004
Testing bleach feeding system, optimization of bleach cycles	Spring/Summer 2004
Shut down due to heavy rains	Fall 2004
Field site flooded and inaccessible	Nov. 2004 – Mar. 2005
Repair of flood damage; optimization of regeneration cycle	April 2005
Data collection of system in 24hr/3hr regeneration cycle reactor #2	mid April – mid July 2005
Data collection of system in 24hr/3hr regeneration cycle reactor #2	mid July – mid Nov. 2005
Data evaluation and reporting	Winter – Summer 2006

3.5.3 Groundwater Treatment Rate

During operation from mid-July through mid-November 2005, the standard operating condition was 2 gpm. Flowrates during non-optimized periods of operation were not evaluated.

3.5.4 Residuals Handling

The only residual from this process was dilute bleach solution used for daily catalyst regeneration. In the proposed system design, 30 gal chlorinated water (dilute hypochlorite solution) would be reused for daily bleaching and spent to waste once strength decreases below effective levels (estimated 1 week).

3.5.5 Operating Parameters

The standard operating conditions were groundwater flowrate of 2 gpm, hydrogen flowrate of 30 mL min^{-1} and bleach cycle frequency of once daily. The bleach cycle consisted of groundwater flow at 0.5 gpm spiked at approximately 500 mg L^{-1} (based upon bleach volume consumed) for 30 to 40 min followed by a 20 to 30 min soaking (1 hr total). In order to maintain sufficient oxidation during these bleach cycles, the duration of the bleach spiking was determined by measuring bleach concentration in the effluent of the reactor using a standard pool chlorine test kit. The measurement should yield at least 50 mg L^{-1} hypochlorite.

3.5.6 Experimental Design

Experiments focused on variations of intervals between bleaching and regeneration, duration of bleach treatments and bleach concentrations. After initially varying the flow rates between 1 and 3 gpm, the flow rate was kept constant at 2 gpm. The influent TCE concentration was relatively constant (800-1,200 mg L^{-1}. Experiments were conducted to recover catalyst activity after major fouling events with sulfide by varying the bleach concentration and duration of bleach treatment from days to weeks; such trials found effective methods for each poisoning event.

3.5.7 Sampling Plan

The sampling approach was taken from similar investigations executed at this site [Gandhi et al. 2001] and an automated off-site analytical laboratory was used. All observation and treatment wells (which fed the reactors) were equipped with sampling pumps and connected with stainless steel tubing to the Automated Sampling and Analysis Platform (ASAP) and set up for automated sampling, as described in APPENDIX A. Reactor effluent was also connected directly to the ASAP system. Samples were analyzed for TCE and potential by-products (always) and the final product ethane (periodically) using an automated purge-and-trap procedure similar to that described in APPENDIX B. Contaminants other than TCE were not present at the site in significant concentrations but cis-DCE was monitored. Calibration procedures were pre-programmed in the ASAP; standards were run periodically according to the operational schedule. Quality control checks were manual and involved inspecting the printed chromatograms, comparing sample with calibration data and checking for consistency of time series data. Corrective actions were taken during biweekly site visits. Experiments with insufficient data collection (due to freezing, leaks, out gassing, instrument malfunction, power failure, etc.) were not analyzed. The reporting limits of TCE and cis-DCE were 0.5 μg L^{-1}. The system was operated and maintained by Gary Hopkins of Stanford University.

Reactor influent and effluent samples were automatically collected and fed to the ASAP system. All samples were analyzed for TCE and potential byproducts; ethane was analyzed periodically. Effluent concentrations directly downstream of the reactor were compared with those immediately upstream. Data quality were assured by frequent calibration. Samples from other locations throughout the field were collected as background data before the Pd reactors were installed; during site demonstration, field samples were not collected. The design and scale of the field site for use with HFTW was based upon a 5 gpm flow in each treatment well, but the demonstration operated at 2 gpm due to above grade reactor mounting and system backpressure

constraints. Loss of a sampling pump or main pump required removal of in situ components but flooding prevented access with a crane during the winter/spring of 2004/05 so only one reactor system was operational during much of the data collection period.

Ion Chromatography (IC) was used to measure anions (chloride, nitrate and sulfate). The IC was composed of a standard Wescan standard anion column (with guard column) and detected by a Wescan conductivity detector using 4 μM KHP with 100 mL hydrogen peroxide added per 10 L to prevent microbial growth. Peaks were integrated with a Chromjet integrator (LabAlliance, State College, PA) with automatic data transfer to a PC via ASAP.

Higher sulfide concentrations will poison the catalyst more rapidly and require stronger and more frequent oxidative regeneration cycles [Munakata, 2005]. Furthermore, the presence of sulfide in the groundwater would poison the catalyst at any concentration. Fortunately, sulfide concentrations remained consistently below the detection limit in the groundwater from the Edwards site. We initially used a probe (Orion, combined reference) attached to an Orion digital mV meter to measure sulfide. The samples supplied and analyzed via the Automated Sampler and Analysis Platform system were consistently under detection limit. Subsequently, manual grab samples were analyzed using a Hach sulfide test kit with a 0.1 mg L^{-1} detection limit. Sulfide was not detected by odor in the extracted groundwater either (on occasion, sulfide was detected by odor in the reactor effluent but only after fouling events). No sulfide in the groundwater is to be expected at this site because the groundwater contains nitrate, which would prevent biological sulfide production. Unfortunately, slip samples were not taken to an outside laboratory for confirmation. Even then, we believe that in most instances, palladium deactivation was attributable to biogenic sulfide production inside the reactor, for instance if the bleach system malfunctioned or the power failed. Sulfide was detected by odor (threshold 29 ng L^{-1}) only on effluent samples and only after malfunction of the bleaching system, leading to the conclusion that biogenically-produced sulfide had deactivated the catalyst.

To evaluate TCE removal efficiency, effluent concentrations were compared against reactor influent concentrations. Quality control was verified by frequent calibration.

Bleach concentration was calculated by dilution from known concentrated solutions; the concentration inside the reactors during regeneration cycles was 500 mg L^{-1}.

3.5.8 Demobilization

Demobilization includes the removal of any in situ components in the HFTW and any permanently installed sampling instrumentation in the monitoring wells. Well decommissioning (destruction) with appropriate permits would be required at most sites. HFTWs and monitoring wells at Edwards AFB had been installed during a prior demonstration (Perry McCarty, BEHIVS project) and as such well decommissioning was not required. The reactor catalyst can be retuned to manufacturer for Pd recovery. Other required activities include disconnection of power and utilities and removal of temporary structures and reactors; some locations may require revegetation as needed.

3.6 Selection of Analytical Method

The compounds of interest in this demonstration were TCE and potential byproducts (DCE and vinyl chloride). Frequent automated sampling analysis (hourly) was required due to remote reactor operation – diagnosis of performance required a dense data set. An automated gas chromatography system operated by the ASAP was selected, as detailed in APPENDIX A.

4. Performance and Assessment

4.1 Performance Criteria

The primary performance criterion for this demonstration project was catalytic TCE removal. Figure 4-1 represents the data collected from mid-July through the end of November 2005, the period of optimal system performance. Data gaps indicate interruption in analytical data collection, reactor down time and/or power failure at the site. TCE removals exceeded 99% during normal operating conditions (outside catalyst regeneration) and 99.5% immediately after regeneration cycles. Data showing TCE spikes from bleach cycles have been removed.

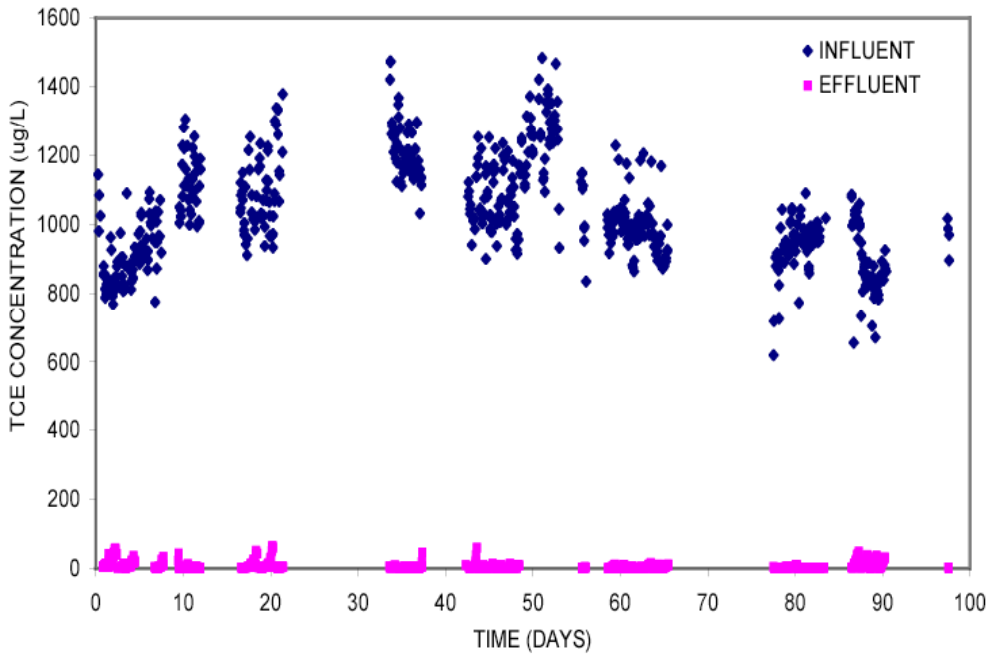

Figure 4-1: Performance of T1 Pd Catalyst Reactor.

Figure 4-2 shows the removal efficiency under normal operating conditions with influent concentrations ranging from 863 to 1,230 µg L^{-1} with effluent concentrations ranging from 0 to ~10-20 µg L^{-1}. During regeneration, catalytic activity decreased and effluent TCE concentrations approached influent concentrations. Long-term average removals during treatment were 99.6%; on average the MCL of 5 µg L^{-1} was met. Including the regenerant water (dilute hypochlorite mixed with groundwater) decreased average removal to 95.5%. A full scale system would include a recycle loop for regenerant solution and eliminate such discharge, maintaining removal efficiency >99%.

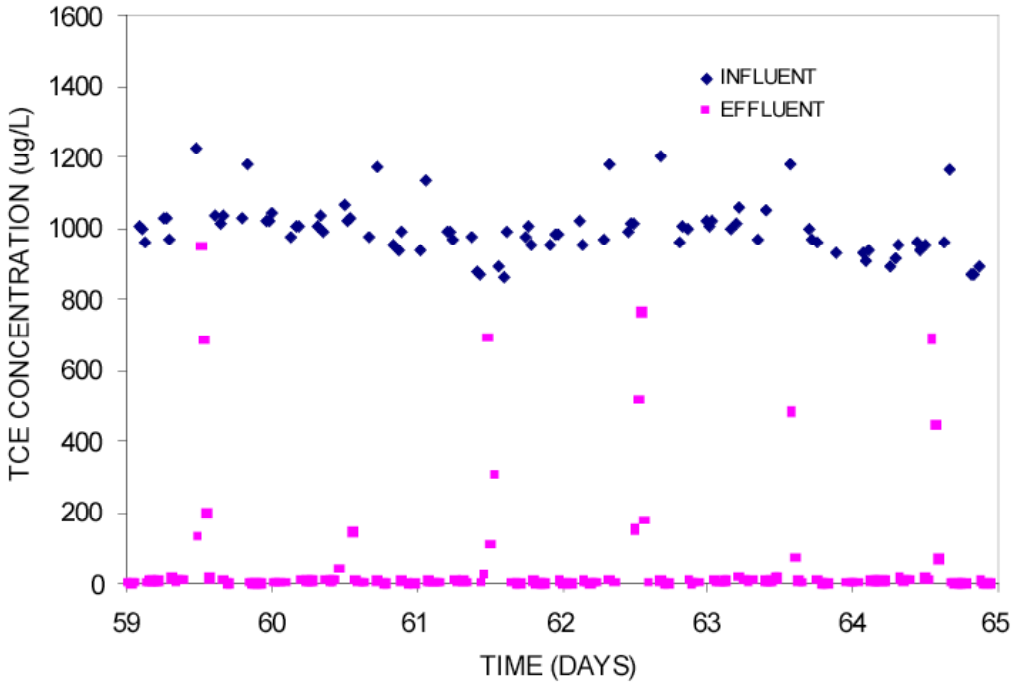

Figure 4-2: TCE Removal During One-Day Bleaching Regime.

After the daily bleaching, effluent concentrations decreased to below or nearly below the detection limit and then gradually increased during the subsequent 21 h operating cycle, as shown Figure 4-3. At approximately the midpoint of each treatment cycle, concentrations exceeded the MCL of 5 µg L^{-1}; the next regeneration cycle was initiated after 21 h of operation. The average effluent TCE concentration during a treatment cycle was approximately 5 µg L^{-1} excluding discharge associated with catalyst regeneration.

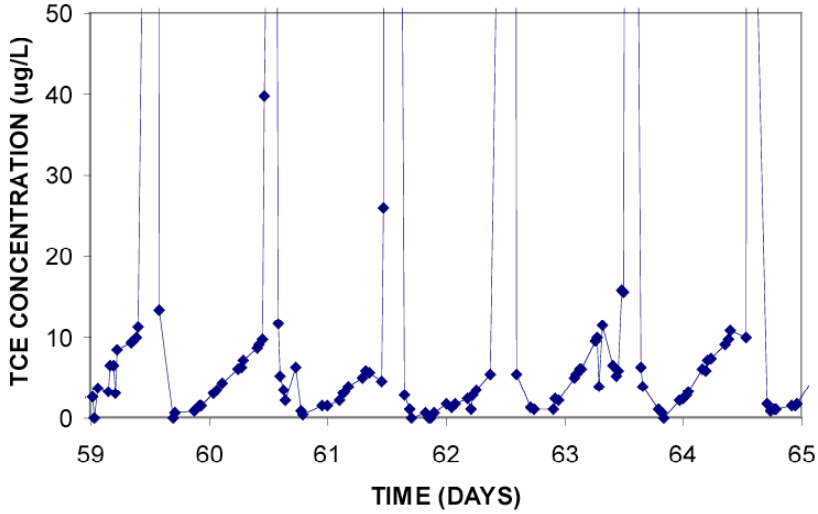

Figure 4-3: TCE Residual Concentration Detail Under One-Day Bleaching Regime.

Table 4-1 summaries the conditions for the treatment cycles. The water used to regenerate the reactor was not recycled in this demonstration (but would be in a full scale implementation). The need for recycling the regenerant solution is illustrated in Table 4-1, which indicates the TCE mass release through the effluent for the various steps of a one-day cycle. This estimate produces a TCE time-averaged concentration (TCE_{TA}) of 22 μg L^{-1} (via totaling mass and calculation total treated volume). The TCE released in the catalyst reduction step is the major component the TCE_{TA}; reducing this mass would have the greatest impact on TCE_{TA}. For example, reducing the flow rate from 2 gpm to 0.5 gpm would reduce the TCE_{TA} to 9 μg L^{-1}.

Table 4-1: Estimating Time Averaged TCE of Effluent.

Process Step	Duration (h)	Flow Rate (gpm)	Augmentation	TCE Conc. (μg L^{-1})	TCE discharge (mg)	Vol. (L)
Bleach Flushing	0.5	0.5	0.5g L^{-1} bleach	50	2.84	56.8
Bleach Soaking	0.5	0.0	nothing	0	0	0
Catalyst	2	2	30 mL min^{-1} H_2	200	181	908
Reduction Treatment	21	2	30 mL min^{-1} H_2	5	47.7	9697

More frequent bleach cycles were tested with shorter pulse durations of higher bleach concentration in order to minimize system downtime. These cycles resulted in lower TCE reduction efficacy and did not reduce the TCE spike post-regeneration. Table 4-2 lists other performance criteria used to evaluate catalytic Pd treatment technology; a method to eliminate TCE spikes during and after regeneration is described in section 6.4

We tried increasing the frequency of bleach cycles with shorter pulse durations of higher bleach concentrations to minimize system downtime for regeneration. Unfortunately, this resulted in lower TCE reduction efficiencies, presumably from the shorter pulse durations, but did not decrease the concentrations of the resulting spike in TCE concentrations. Other performance criteria used to evaluate Pd treatment technology are listed in Table 4-2. A possible solution to avoid TCE spiking during regeneration is described in Section 6.4.

Table 4-2: Performance Criteria.

Performance Criteria	Description	Importance
Contaminant Reduction	The technology demonstrated to remediate TCE in groundwater. With the exception of spikes associated with bleach pulses, TCE was reduced by 99.6%. Data including bleaching pulses produced 95.5% reduction of TCE. Small concentrations of cis-DCE were also removed significantly and vinyl chloride was not produced.	Primary
Meeting Regulatory Standards	The MCL for TCE (5 μg L^{-1}) was met under normal operating conditions (excluding regeneration). Influent TCE concentrations ranging from 800 to 1,200 μg L^{-1} were removed	Primary

Performance Criteria	Description	Importance
	to below 5 μg L^{-1}.	
By-Product Formation	Lab studies indicate no significant byproduct (lesser-chlorinated alkene) formation during TCE reduction. In the field, no byproducts were observed.	Primary
Reliability	(1) Technology can achieve contaminant reduction goals for groundwater with TCE concentration exceeding 1 mg L^{-1} (2) Technology can operate under anoxic (nitrate reducing) conditions. (3) Variations in influent concentration were not evaluated.	Primary
Safety	(1) Operation of the technology, including hydrogen addition, can be performed without creating any unacceptable safety hazards	Primary
Catalyst Activity	(1) Pd catalyst is robust and survived multiple severe poisoning and regeneration events. (2) Pd catalyst activity can be maintained by regular bleaching.	Primary
Maintenance	(1) General maintenance involves replacement of the hydrogen cylinder every 6 months. (2) Daily bleaching (1 hour duration) and reactivation of catalyst for biofouling control (3) Emergency shut down requires draining and aeration of reactor column. (4) Removal of scaling with dilute acid (1L 10% HCl), as needed (5) .Back flushing to remove any particulate matter, as needed.	Primary
Ease of Use	System maintenance consisted of short visits twice a week to fill the bleach reservoir and restart system after power failures or program crashes. With further optimization and improved process control, the frequency of these visits could probably be reduced to one visit every two weeks for sampling and maintenance.	Primary
Versatility	The technology as tested is limited to chlorinated ethylenes.	Secondary
Process Waste	No waste stream generated as practiced. A modified system could recover the regenerant (bleach) and re-use or re-process.	Secondary
Factors Affecting Technology Performance	Water quality, in particular the presence of hydrogen sulfide and sulfidogenic bacteria lead to catalyst fouling and necessitate frequent catalyst regeneration.	Primary
Scale-up Constraints	The demonstration was operated at 2 gpm. Scaling up to larger flows is possible but should be tested.	Secondary

4.2 Performance Confirmation Methods

The most important performance metrics for the reactor were removal efficiency, effluent TCE concentration and operating period between regeneration cycles. System TCE removal efficiency was evaluated by measuring influent and effluent concentrations over time. Accuracy of the data was ascertained by frequent calibration. Data completeness for reactor performance evaluation required frequent and automated sampling. Because effluent concentrations increased with time after regeneration it was critical during treatment optimization to develop data at least at an hourly rate. It took the ASAP approximately 30 min to process one sample, so monitoring influent and effluent occurred hourly. The need for such a high data density was not anticipated because the system was originally expected to operate for 4 d between regenerations. The ASAP was essential to diagnose problems and optimize treatment. Once optimized, weekly or bi-weekly sampling was sufficient to monitor the process.

Evaluation of the technology is based on the factors summarized in Table 4-3. A summary of the cost evaluation is given in Section 5, details are provided in the Cost & Performance Report.

Table 4-3: Expected Performance and Performance Confirmation Results.

Performance Criteria	Expected Performance Metric (pre demo)	Performance Confirmation Method	Actual (post demo)
Primary Criteria (Performance Objectives) – Qualitative			
Maintenance	Requires only routine maintenance (e.g., changing hydrogen cylinders) for duration of demonstration	- Observations during technology demonstration - Review of maintenance records	Operation with low maintenance level was possible after system design was improved
Ease of Use	- Routine operation does not require an operator - Sample collection and changing hydrogen tanks can be performed by personnel with minimum training - System can be operated by personnel with OSHA 24-hour or 40-hour HazWOpER training	- Observations during technology demonstration - Review of maintenance records.	Use was straight forward once standard operating procedures were in place.
Primary Criteria (Performance Objectives) – Quantitative			
Contaminant Reduction	At least 99% destruction of TCE and other applicable contaminants	Compare influent, effluent concentrations of Pd reactors	>99% removal; better than expected performance
Meeting Regulatory Standards	Final concentration of TCE is below MCL (5 µg L^{-1})	Effluent concentration analysis	Effluent concentration below MCL when calculated as daily average (see comments).
By-Product Formation	MCLs are met for cis-DCE (6 µg L^{-1}) and vinyl	Effluent concentration analysis	No by-products were formed. By-products below MCL

	chloride (0.5 µg L^{-1})		
Robustness/ Flexibility		Effluent concentration histories	System failures result in hydrogen sulfide production
Catalyst Activity	Pd catalyst does not need replacement for at least 12 months	Catalyst was used for the entire project period (2 years) even though is was repeatedly poisoned	Catalyst remained active for longer than 12 months are could be regenerated after prolonged sulfide poisoning.

Secondary Performance Criteria			
Performance Criteria	**Expected Performance Metric (pre demo)**	**Performance Confirmation Method**	**Actual (post demo)**
Operational Safety	Hydrogen addition can be performed without acceptable safety hazard.	Hydrogen was handled within safety margins	Hydrogen safety concerns need to be appropriately incorporated into the design of the system
Versatility	Technology has been tested at lab-scale for multiple chlorinated ethylenes with relative success	Laboratory studies testing other contaminants.	Technology was demonstrated for TCE only but is applicable for other chlorinated ethylenes.
Process Waste	System operates *in situ* without generation of any secondary waste stream	Experience and observations during technology demonstration	The regenerant bleach solution was discharged to the treatment well. Future designs could easily incorporate a neutralization step for bleach.
Factors Affecting Technology Performance	Water quality, especially the presence of sulfide compounds, is the most important determinant affecting technology performance	Experience from this and other sites and laboratory experiments.	The original single column design requires modification to include regenerant recycling and treatment.
Scale-up Constraints	System was expected to treat up to six gpm.	Pumps delivered 3 to 4 gpm, well yield was slightly higher.	Tests were conducted at 2 gpm to achieve treatment objective.

4.3 Data Analysis and Evaluation

Under normal operating conditions (2 gpm, TCE influent 800-1,200 µg L^{-1}) the MCL for TCE (5 µg L^{-1}, time-averaged) was met on average for a 21 h operation cycle. Immediately after regeneration, TCE concentrations were typically below 1 µg L^{-1} and increased steadily to approximately 10 µg L^{-1} over 21 h of operation (Figure 4-3). This increase is attributed to catalyst deactivation by traces of sulfide (below detection limit) present in the anaerobic groundwater and/or to hydrogen sulfide formed by sulfidogenic bacteria inside the reactor. In aerobic groundwater free of sulfide catalyst activity would presumably decrease less quickly. In the absence of a bleach pulse after 21 h (for instance due to equipment failure), activity loss increased rapidly, leading to more severe sulfide poisoning and ultimately to TCE breakthrough.

When that happened, recovering catalyst activity required more aggressive bleaching, as discussed in Section 4-1. Factors impacting operation and performance of the technology are listed in Table 4-4. Generally lower flow rates produced lower effluent concentrations, but the relationship between effluent concentration, the optimal regeneration frequency and time, was not evaluated. Optimal operating parameters are expected to vary from site to site and over time.

Table 4-4: Factors Affecting Technology Performance.

Effects of Operating Conditions	
Operating Parameter	**Anticipated Effect on Technology Performance**
Hydrogen addition rate	Sufficient hydrogen gas must be added to completely reduce contaminants of concern. Lower hydrogen addition rates can lead to by-product formation.
Catalyst regeneration: Type of regenerant	Some regenerants (e.g., hypochlorite, peroxide) might be more effective than others at restoring catalyst activity. Lab studies confirmed that hypochlorite is the most effective regenerant for sulfide-poisoned Pd catalyst; peroxide was also effective but required much longer contact.
Catalyst regeneration: Concentration of regenerant solution	Regenerant solution might be ineffective if the concentration is too low.
Catalyst regeneration: Frequency of regenerant pulses	Catalyst must be regenerated often enough that the overall contaminant destruction efficiency meets clean-up goals.
Catalyst regeneration: Duration of regenerant pulses	Regenerant pulses must be of sufficient duration to restore catalyst activity.
Matrix Effects	
Matrix Parameter	**Anticipated Effect on Technology Performance**
Dissolved oxygen in groundwater	No anticipated effect as long as hydrogen addition rate is sufficiently high.
Sulfide ion in groundwater	Sulfide ion concentrations even at concentrations below the detection limit of common test kits (.01 mg L^{-1}) can poison Pd catalyst. It is unknown whether catalyst regeneration can control this problem adequately.
Soil microbial population	Sulfate-reducing bacteria, and perhaps other hydrogen-utilizing bacteria, might form biofilms on Pd catalyst beads, reducing catalyst activity. This can be controlled via catalyst reactivation with hypochlorite.
Groundwater buffer capacity	Groundwater must be sufficiently buffered that formation of hydrochloric acid (see Section 2.1.1) does not significantly reduce the groundwater pH. It is expected that all natural waters will have sufficient buffer capacity to avoid this problem.
Aquifer hydraulic conductivity	Aquifer must have zones of sufficiently high hydraulic conductivity that the HFTWs can extract and inject water to establish groundwater recirculation.
Aquifer anisotropy	Aquifer must be sufficiently anisotropic that groundwater recirculation between HFTWs is established. A hydraulic conductivity ratio of 10:1 (horizontal:vertical) is sufficient. Most aquifers are sufficiently anisotropic to avoid short-circuiting of the groundwater flow paths.

Although the factors listed impacted the Pd reduction process they resulted from hydrogeological conditions at the site and by water quality factors that are not considered here.

The technology has been demonstrated at a site where TCE was the only contaminant. From laboratory studies, we know that all chlorinated ethylenes react at rate that is approximately equal to that of TCE. Regeneration and fouling issues are the primary concern – lab studies showed that sulfide is the major poison to Pd catalyst activity, so sites with minimal sulfide concentrations will require the least amount of maintenance to keep the reactor bed active for TCE dechlorination. Sites with high sulfide concentrations are not eliminated from remediation efforts, but will require additional regenerations in order to maintain activity.

4.4 Modeling Groundwater Concentrations

Based upon reactor performance, a site model was constructed to simulate operation of an HFTW system at Site 19 Edwards AFB. The HFTW system consists of upflow and downflow treatment wells, with Pd reactors installed in each well. The site model was based on the hydrogeological conditions and engineering design for the HFTW system installed at Site 19 for the evaluation of in situ bioremediation presented in McCarty et al. (1998) and shown in Figure 4-4. Engineering and hydrogeological parameters used in the model are listed in Table 4-5. For the sake of the modeling exercise, the Pd reactors are assumed to be sized so that TCE concentration in the reactor effluent is 0.5% of the influent concentration.

Table 4-5: Model Parameter Values.

Parameter	Value
Distance between treatment wells	10 m
Treatment well pumping rate	2 gpm
Hydraulic conductivity (horizontal, vertical)	2.95 m d^{-1}, 0.295 m d^{-1}
Regional hydraulic gradient	0.007 m m^{-1}
Dispersivities (longitudinal, transverse, vertical)	1.0 m, 0.1 m, 0.1 m
Porosity	0.3

Figure 4-5 depicts model-simulated TCE concentrations injected into the aquifer through the two treatment well injection screens (the upper screen of the upflow well and the lower screen of the downflow well). The modeling assumed a continuous upgradient source of TCE at 1 mg L^{-1}, and that each of the two HFTW treatment wells pump at 2 gpm. As shown in the figure, the model predicts that at steady-state, approximately 3 µg L^{-1} TCE is injected into the aquifer from the upflow and downflow wells, respectively. Figure 4-6 depicts TCE concentration contours in the upper aquifer resulting from operation of the HFTW system at 2 gpm for 180 days (lower aquifer contours are similar). Increasing the pumping rate to a more realistic 20 gpm increases the size of the TCE concentration "hole" in the aquifer. Modeling indicates that a series of HFTWs

aligned perpendicular to the direction of groundwater regional flow could serve as a barrier to TCE migration [Christ et al., 1999].

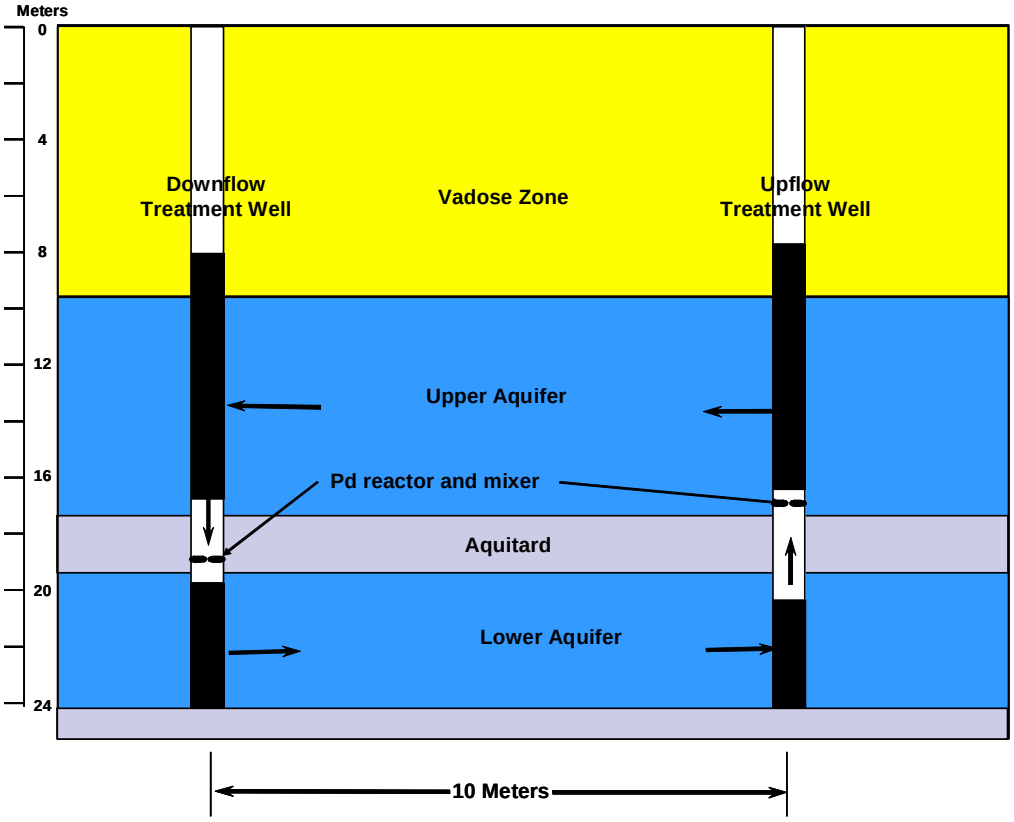

Figure 4-4: HFTW System at Site 19 Edwards AFB (After McCarty et al., 1998).

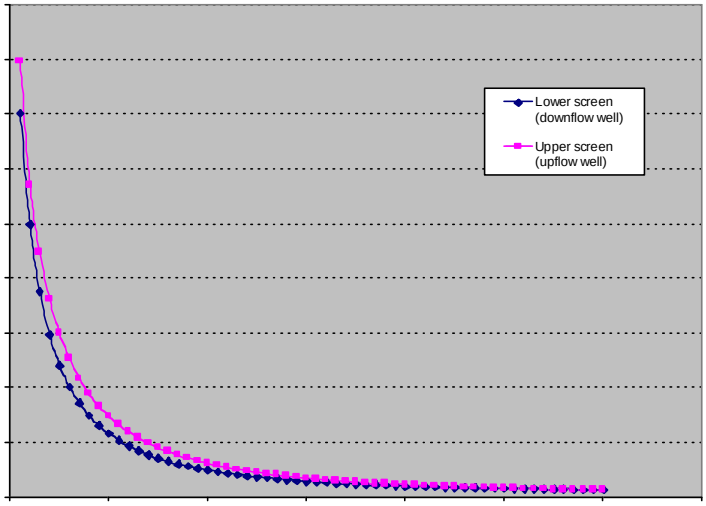

Figure 4-5: Simulated TCE Concentrations Versus Time at the Injection Screens of the Treatment Wells.

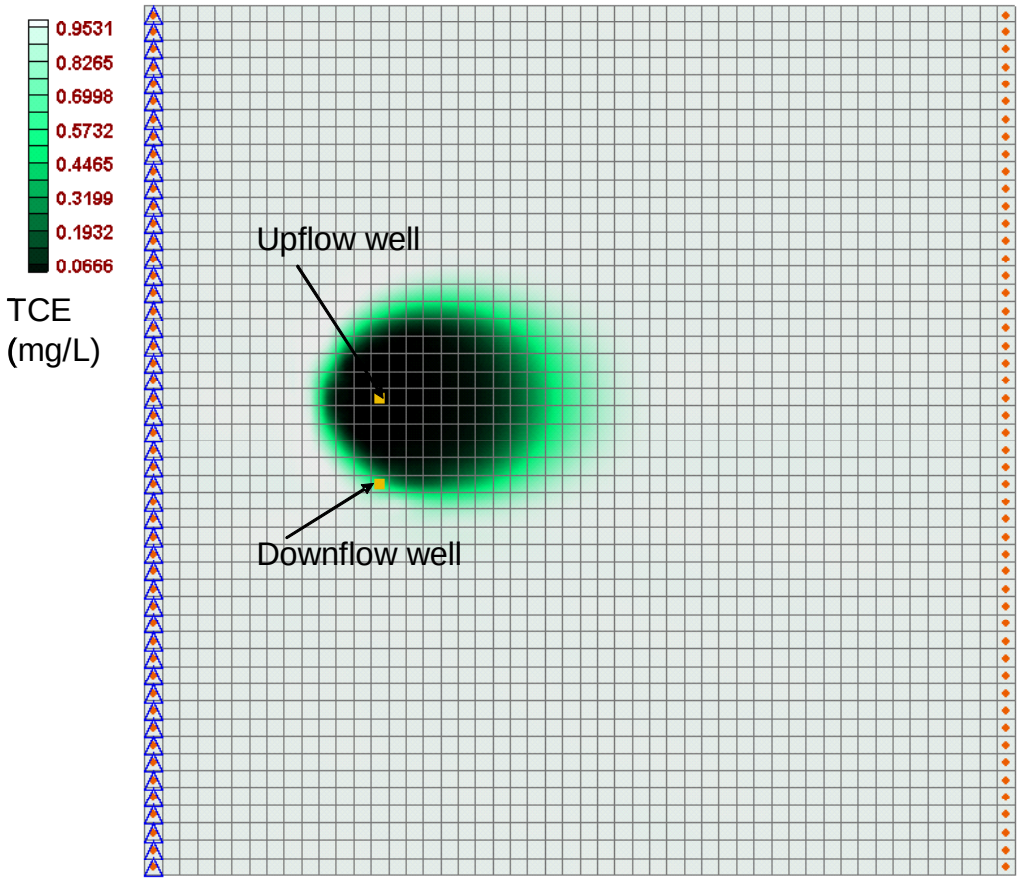

Figure 4-6: Simulated TCE Concentrations in the Upper Aquifer After 180 Days of Operation of Treatment Wells at 2 gpm.
The Distance Between the Wells is 10 m.

5. Cost Assessment

5.1 Cost Reporting

Table 5-1 summarizes the capital costs for the Edwards AFB demonstration. The calculations are for a full-scale system designed to treat a TCE contaminated site of similar size and characteristic to the Edwards AFB demonstration. The design setup consisted of two catalytic reactors treating 2 gpm each in tandem with two HFTW 10 m apart, creating a treatment zone of approximately 20 m width. Maintenance of the HFTWs is assumed negligible.

Table 5-1: Capital Cost Tracking.

Capital Cost Element	Cost	Sub-cost
Site Characterization	$118,000	
Hydrogeological characterization	$118,000	
Wells for estimating hydraulic head and gradient (7 wells, $10,000 per well)		$70,000
Pump tests to estimate hydraulic conductivity		$24,000
Cores and analysis to estimate hydraulic conductivity		$24,000
Technology Mobilization, Set-up, and Demobilization	$59,000	
Transportation/delivery of equipments, facilities, and personnel		$24,000
Set-up of temporary facilities (e.g. trailer) and utilities		$24,000
Demobilization		$11,000
Planning and Preparation	$155,000	
Engineering design and modeling		$85,000
Permits and licenses, including water discharge		$24,000
License fees associated with use of a technology		$0
Regulatory interaction		$6,000
Written plans		$40,000
Work plans		$12,000
Sampling and analysis plans		$12,000
Health and safety plans		$6,000
Community relations plans		$5,000
Site management plans		$5,000
Site Work	$70,500	
Establish physical infrastructure for technology application		$17,500
Activities to restore site to pre-remediation conditions		$17,500
Activities to meet specifications if site restoration plan		$17,500
Preparing specific site of the technology		$18,000
Clearing and grubbing		$6,000
Earthwork		$6,000
Construction of utilities, etc.		$6,000
Installation of the Treatment System	$133,810	

Treatment wells (2 wells, $20,000 per well)		$40,000
Pumps (2 pumps, 2 gpm flowrate, $5,000 per pump)		$10,000
Packet		$5,000
Assembly		$2,000
Monitoring wells (4 wells, $4,000 per well)		$16,000
Palladium catalyst treatment system		$60,810
Palladium catalyst with eggshell coating (20 kg catalyst, $245 per lb catalyst)		$10,810
Skid-mounted reactor system and gas skid		$50,000
Start-up and Testing	$18,000	
Establishment of operation conditions		$6,000
Shakedown		$6,000
Training of O&M personal		$6,000
Other Capital Cost	$18,000	
Data processing and computer equipment		$6,000
Safety equipment		$6,000
Vehicles		$6,000
Miscellaneous		$0
TOTAL CAPITAL COST	$572,310	

Table 5-2 summarizes the annual O&M costs for the Edwards AFB demonstration. As discussed in that report, these expenses depend on site location, the number of sampling and analysis wells and other factors that can be site-dependent.

Table 5-2: Annual O&M Cost Tracking.

Operation and Maintenance Cost Element	Cost	Sub-cost
Labor	$35,000	
Maintenance of technology and associated equipment		$25,000
Labor supervision (100 h, $50 per h)		$5,000
Payroll expense (100 h, $50 per h)		$5,000
Materials	$1,350	
Pd Catalyst		$0
Chemicals		$1,350
Hydrogen gas (6 cylinders, $50 per cylinder + $10 per month rental fee)		$720
Bleach (2 gal per column per week, 2 columns, $3 per gal)		$630
Utilities and Fuel	$2,000	
Fuel		$500
Electricity		$1,000
Water		$500
Equipment ownership, Rental or Lease	$0	
Equipment ownership		$0
Rental		$0

Lease		$0
Other Operation and Maintenance Cost	$10,000	
Repair/maintenance of office/addmistrative equipments		$5,000
Health and safety cost		$5,000
Personal protective Equipments		$2,000
Monitoring of personnel health and safety		$3,000
TOTAL OPERATION & MAINTENANCE COST	$48,350 per year	

5.2 Cost Analysis

Costs for the Pd/HFTW technology are being compared with two baseline alternative technologies. The two baseline alternative technologies chosen for this comparison are the pump-and-treat (P&T) technology and the permeable reactive barrier (PRB) technology. P&T is the most commonly applied groundwater remediation method. PRB is also referred to as "iron wall" or "iron curtain," because iron is almost always the catalytic material used in the PRB. PRBs are often used for remediation of groundwater contaminated by chlorinated solvents.

In order to compare the costs for these three technologies, it is necessary to specify the operational conditions, such as the scale of the operation, the hydrogeologic setting, the contaminant concentrations, and any other relevant factors. Values for these factors are specified in Table 5-2, and represent optimized full scale conditions.

For the Pd/HFTW technology, the factors which are expected to most significantly affect the cost of the technology are:

(1) Cost of Pd catalyst;
(2) Frequency of Pd catalyst replacement;
(3) Cost of reactor fabrication and installation; and,
(4) Cost of well installation.

In recent years, Pd metal has fluctuated between $120 and $1050 per ounce, with a current price of about $750/ounce. If the price of Pd catalyst increases significantly, or if the Pd catalyst needs to be replaced frequently, then the Pd/HFTW technology might not be economically advantageous. However, if the activity of the Pd catalyst can be effectively maintained in the field as shown in this demonstration, the Pd/HFTW technology is a likely cost-effective alternative. The cost of installing treatment wells depends strongly on the depth of the groundwater table and the extent of TCE contamination. Installing shallow wells is relatively inexpensive; installing deep wells can be very expensive. The depth of the groundwater table and the contamination also strongly affect the cost of installing a trench for the PRB technology, such that the Pd/HFTW technology is competitive even at sites where the contamination is deep. The cost of hydrogen gas is not likely to significantly impact the cost of the Pd/HFTW technology, because hydrogen gas is inexpensive and is consumed slowly if an appropriate technology is used for delivering hydrogen to the contaminated groundwater.

The costs of the three technologies must be compared over their entire life cycles. This analysis will be based upon a net-present-value approach, assuming a 5% annual inflation rate and an 8% interest rate. The costs considered will be start-up costs, capital costs, operations and maintenance (O&M) costs, and recurring regulatory or institutional oversight costs. Future liability will not be considered for the PRB and the Pd/HFTW technologies, because these destroy TCE rather than transferring it to a different medium. Future liability must be considered for evaluation of the P&T technology. The life cycle period will be whatever time period is required for each technology to treat the entire contaminant plume.

Table 5-3 shows the calculated costs of alternative technologies based on other field demonstration sites:

Table 5-3: Cost comparison of alternative technologies.

Technology	TCE	Removal	Cost per 1,000 gal treated
Air Stripping			
Des Moines, IA	0.045 mg L^{-1}	96%	$1
Gold Coast, FL	0.45 mg L^{-1}	99%	$10
Granular Activated Carbon (GAC)			
Old Mill, OH	6.1 mg L^{-1}	75%	$375
La Salle, IL (Superfund site)	13.3 mg L^{-1}	96%	$485
Permeable Reactive Barrier (PRB)			
Lawrence Livermore National Lab, CA	240 mg L^{-1}	99%	$99
Commencement Bay, WA	0.13 mg L^{-1}	98%	$10
Palladium Reductive Catalysis			
Edwards AFB, CA	1 mg L-1	99.5%	$8

At $8 per 1,000 gal, catalytic technology is expected to be competitive with activated carbon P&T when compounds are not easily amenable by other technologies, i.e., for compounds that adsorb only weakly onto carbon, such as vinyl chloride and dichloroethylenes, and TCE at high concentrations. Catalytic technology should be competitive with PRB technologies where the contamination is deep, i.e., where building trenches to capture the plume is prohibitively expensive.

6. Implementation Issues

6.1 Lessons Learned

Overall, the Edwards Air Force Base (AFB) demonstration project showed that reductive catalytic destruction of TCE is an efficient technology ready for field implementation, provided the lessons learned from this project are applied to future sites. The capability of the technology to handle high TCE concentrations makes it very attractive for source control at many Department of Defense (DoD) and commercial contaminated groundwater sites. This memorandum identifies and explains the major technical, regulatory and management aspects that must be considered in applying catalytic groundwater treatment at other field sites.

6.1.1 In Situ Versus Ex Situ

The Edwards AFB demonstration project was planned and designed to operate in situ by installing the reactors inside 6-inch diameter treatment wells, but was only tested ex situ, i.e., with the reactors and the associated plumbing and instrumentation mounted above grade on a rig accessible for maintenance. Mounting the reactor column inside the treatment wells (i.e., operating in situ) would result n higher maintenance costs since lifting the reactors from the wells would require a crane. The reasons to operate this technology in situ are:

(1) Regulatory compliance
(2) Site footprint requirements

For the Edwards AFB demonstration project, the regulatory requirement that the treated water was not to be reinjected into the subsurface was waived, allowing evaluation of the technology above in ex situ mode. Considering the technology is still relatively immature, it is recommended that the technology be operated ex situ until all reliability issues are resolved, which will require regulatory approval.

At military and industrial sites, it is not expected that the footprint will be of concern as open space is ample and the footprint of an ex situ system is still relatively small. In urban settings or locations where an extremely small footprint is required, operating in situ will reduce the visible footprint of the site.

6.1.2 Site Selection

Applicability of catalytic technology is determined by two criteria:

(1) Target contaminant reactivity and site water concentration
(2) Site water quality

While this demonstration examined groundwater contaminated with TCE, the technology is also applicable to other contaminated aqueous streams such as wastewater, industrial effluent and drinking water as long as water quality does not significantly hinder the catalytic process. For contaminants that are less reactive than TCE and other chlorinated ethylenes, reactors would

need to be larger than that used at Edwards AFB. Table 1 provides a preliminary list of contaminants that are potentially amenable to catalytic reduction using Pd and hydrogen gas and their corresponding reactivities (normalized to TCE).

Table 6-1: Compounds Amenable to Catalytic Destruction Using Pd and Hydrogen Gas.

Contaminant	By-products	Relative Reactivity
Trichloroethylene (TCE)		1.00
Dichloroethylene isomers (DCE)		
c-DCE		1.30
t-DCE		1.22
1,1-DCE		1.09
1,2-dibromo-3-chloropropae (DBCP)		0.97
Carbon tetrachloride (CT)	Chloroform	0.91
Vinyl chloride (VC)		0.90
Tetrachloroethylene (PCE)		0.83
1,1,2-trichlorotriflouroethane (Freon-113)		0.23
Nitrite		0.10
Chloroform (CF)		0.06
N-Nitrosodimethylamine (NDMA)		0.01

Site water quality can significantly impact the efficacy of Pd-catalyzed contaminant reactivity. The most significant groundwater matrix species is sulfide, which is believed to poison Pd catalyst at any concentration, even at or below the odor threshold of ~ 29 ng L^{-1}. From a practical standpoint, the technology should not be implemented where sulfide is detectable by odor or any other method. Similarly, if sulfide odor is noticed in the reactor effluent but not in the influent, sulfide is biogenically produced within the reactor, indicating the need for bleaching.

There was no oxygen in the Edwards AFB groundwater. In laboratory experiments it was shown that dissolved oxygen impacts the process by consuming hydrogen; TCE conversion was reduced from 46.0% to 13.4% by adding 450 μM oxygen to the influent water (oxygen was 67% converted) [Lowry and Reinhard, 2001]. However, these impacts are relatively insignificant and can be overcome increasing the reactor size and adding excess hydrogen. Overall, the presence of oxygen is beneficial because is inhibits sulfide formation.

Table 2 lists these and other groundwater quality parameters, showing their effect on Pd catalyst performance.

Table 6-2: Site Characteristics Affecting CRD Technology Performance.

Site Characteristic	Anticipated Effect on Technology Performance
Dissolved oxygen	No anticipated effect given sufficient hydrogen addition.

Sulfide	Can poison Pd catalyst, even below detection limit of common test kits (0.01 mg L^{-1}). Requires oxidative regeneration (hypochlorite).
Soil microbial population	Possible reduction in activity if sulfate-reducing bacteria form biofilms on Pd catalyst surface and/or generate sulfide. Can be controlled via hypochlorite treatment.
Groundwater buffer capacity	Groundwater must be sufficiently buffered that formation of hydrochloric acid during contaminant dechlorination (if applicable) does not significantly alter groundwater pH. It is expected that most natural waters will have this capacity.

Sulfate itself does not affect catalyst performance because it is not reduced by Pd and hydrogen, but in the presence of hydrogen and sulfate-reducing bacteria it is readily converted to sulfide which poisons the catalyst. The ideal site for Pd-catalyzed reduction of a target contaminant would have a very reactive contaminant (e.g., TCE) and a low concentration of oxygen to inhibit sulfide formation. Overall, anoxic sites such as the Edwards AFB site with no oxygen but some nitrate are suited for the application Pd catalysis.

6.1.3 System Design, Fabrication and Procurement

As each field site has different groundwater contaminant and matrix conditions, sites must be evaluated on a case-by-case basis. Once groundwater hydrogeology is understood and contaminant removal levels are established, system sizing and detailed design can follow simple guidelines.

(1) Systems should be sized based on the optimal design of horizontal flow treatment wells and the hydrogeological conditions
(2) Components should be extensively tested at the factory under realistic treatment conditions
(3) Delivery should only be considered complete after <u>on-site</u> testing
(4) Systems should be equipped for remote control
(5) For remote systems, local maintenance support should be available on an as needed basis.

Sizing of the system depends on the overall treatment needs and the design of the water extraction and re-injection system. Hydraulic loading several times of what has been tested at the Edwards AFB site should be possible. Scaling to lower flows is also possible.

Component testing requires operating the system with similar groundwater (i.e., similar pH and matrix species). The desired flowrate should be verified and tested for pump and pipe sizing verification. Extreme temperatures should be considered if they will be encountered on-site.

Requiring <u>on-site</u> testing of the system is essential to ensure hydraulic performance on-site is commensurate with that in the lab. Flow control and valve systems must be checked with the integration of automated sampling and analysis mechanical equipment. Also, training of on-site personnel is essential to minimize operation and maintenance costs. Remote control of the system should be tested to ensure technical feasibility of remote operation.

Finally, post-delivery support must be local. System downtime increases significantly when support is distant and/or non-responsive.

6.1.4 Project Management

Managing a demonstration or full-scale field site using catalytic reductive technology requires trained management and operations personnel and well-designed operational and safety plans. The recommended approach is to develop a project management structure as follows:

(1) Implement a phased approach to all tasks with discrete goals for each phase; and,
(2) Scrutinize the interdependencies of each task and allow slack for adjustments.

The phased approach creates a much longer anticipated timeline, but better addresses the needs encountered in the field. Having discrete goals focuses efforts on the task at hand and results in achievable deliverables. Scrutiny of the interdependencies of each task is important because delays in one task will inevitably impact all related tasks. For example, the technology should be contemplated for use only at well-characterized sites.

If the system is to be operated remotely, it is important to have an operational plan that details the interaction between remote operators and site personnel – especially during periods of system malfunction or maintenance.

6.2 Environmental Checklist

Although it is possible, in principle, to mount the reactor columns inside treatment wells and to operate the systems as true "in situ", the technology was tested above ground during this demonstration. Permits required for implementation of this technology pertain to:

(1) Re-injection or disposal of the treated water; and,
(2) Safe storage of hydrogen at the site.

6.3 Other Regulatory Issues

In Reinhard's experience, catalytic destruction technology is perceived by the public and regulators as a green technology because the only chemicals used are hydrogen and noble metal (Pd) as the catalyst; the only products formed are water, ethane and dilute hydrochloric acid. In the case of the LLNL reactors, California regulators accepted the technology even though it is not an in situ technology, setting a positive precedent for future development of the technology. For the Edwards AFB or other sites, regulatory implications have not been evaluated in depth. Additional funding will be required to continue demonstration and technology improvement.

6.4 End-User Issues

Potential end users for this technology include:

- Department of Defense (DoD);
- Other government or private organizations which own sites contaminated by chlorinated organic compounds; and,
- Environmental/engineering consulting firms that are hired to remediate contaminated sites.

Because of the very large number of sites contaminated by TCE and other chlorinated solvents, the potential interest in this technology is very high. End users' issues that need to be addressed before the technology can be implemented are based on experience from this demonstration. They include:

- Whether the technology is able to destroy the chlorinated compounds at a particular site.
  The technology is dependent on water quality and readily applicable in clean (minimal matrix species, e.g. sulfide), aerobic groundwater.

- Whether the technology can produce an environmentally acceptable endpoint (e.g., reduce contaminant concentrations to below the applicable MCLs).
  For TCE and other chlorinated ethylenes, acceptable endpoints can be achieved, even at contaminant concentrations initially exceeding 1,000 $\mu g\ L^{-1}$.

- Whether the technology is acceptable to the applicable regulatory agencies.
  The technology was acceptable to regulatory agencies involved with the EAFB site.

- Whether the equipment required for implementation is commercially available off the shelf, or must be custom built.
  Components to build the equipment are commercially available.

- Whether the technology can be easily applied by a user not previously familiar with the technology.
  The technology requires appropriate training of reactor operator.

- What size/scale site can be effectively treated by this technology.
  At present, experience has been gained for the treatment of 2 gpm but scaling up is possible.

- Whether the technology must be customized for each site, or if a generic conformation is applicable at most sites.
  Some customization is required at this time to account for local water quality and site conditions.

- Whether the technology is cost-effective compared to other competing technologies.
  The technology is most likely going to be applied where a small foot print is required, the contaminant needs to be destructed, and conventional approaches (e.g., activated carbon adsorption and air stripping) are unsuitable. This may be the case for treating

mixed waste or when the formation of secondary waste streams is not an option. Although in the case of mixed waste, the technology may not remediate other contaminants, we have demonstrated that it is effective for TCE.

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8. Points of Contact

Table 8-1: Points of Contact.

POINT OF CONTACT Name	ORGANIZATION Address	Phone/Fax/email	Role in Project
Carmen LeBrón	Naval Facilities Engineering Service Center Restoration Development Branch 1100 23rd Ave., ESC-411 Port Hueneme, CA 93043	Phone: 805-982-1616 FAX: 805-982-4304 carmen.lebron@navy.mil	Project Manager
Dr. Martin Reinhard	Stanford University Dept. of Civil & Environmental Engnrng. Stanford, CA 94305-4020	Phone: 650-723-0308 FAX: 650-723-7058 reinhard@cive.stanford.edu	Principal Investigator
Mary Spencer	Edwards Air Force Base Chief, Envrnmtl. Mgmt. Restoration Branch AFFTC/EMR 5 East Popson Ave, Bldg 2650A Edwards AFB, CA 93524	Phone: 661-277-1466 FAX: 661-277-6145 mary.spencer@edwards.af.mil	Site Host
Richard Russell	U.S. Environmental Protection Agency Region 9, SFD-8-1 75 Hawthorne Street San Francisco, CA 94105	Phone: 415-744-2406 russell.richard@epa.gov	Remedial Program Manager (RPM)
Elizabeth Lafferty	Regional Water Quality Control Board Lahontan Region 6V, Victorville Office 15428 Civic Center Dr., Suite 100 Victorville, CA 92392	Phone: 760-241-6583	Remedial Program Manager (RPM)
John O'Kane	Department of Toxic Substances Control 8800 Cal Center Drive Sacramento, CA 95826		Remedial Program Manager (RPM)
Bob Wood	Edwards Air Force Base Chief, Environmental Restoration Division AFFTC/EMR 5 East Popson Ave., Bldg. 2650A Edwards AFB, CA 93524-1130	Phone: 661-277-1407 FAX: 661-277-6145 robert.wood@edwards.af.mil	Remedial Program Manager (RPM)
Dorothy Coughlin	Computer Sciences Corporation Flight Test Support Center P.O. Box 446 Edwards AFB, CA 93523-0446	Phone: 661-277-9203 FAX: 661-277-1527 dorothy.coughlin@edwards.af.mil	Community Relations
Roberto Ruiz	Lawrence Livermore National Laboratory 7000 East Avenue, L-530 Livermore, CA 94550	Phone: 925-422-0061 FAX: 925-422-9203 mcnab1@llnl.gov	Reactor design
Dr. Mark Goltz	Air Force Institute of Technology Dept. of Engineering & Environmental Mgmt. 2950 P Street, Building 640 Wright-Patterson AFB, OH 45433-7765	Phone: 937-255-6565 FAX: 937-656-4699 mgoltz@afit.af.mil	Model development
Dr. Jeffrey Cunningham	Dept. of Civil & Environmental Engineering University of South Florida 4202 E. Fowler Ave., ENB 118 Tampa, FL 33620	e-mail: cunning@eng.usf.edu phone: 813-974-9540 fax: 813-974-2957 web: http://www.eng.usf.edu/~cunning	Workplan Development
Gary Hopkins	Stanford University Dept. of Civil & Environmental Engnrng. Stanford, CA 94305-4020	Phone: 408-262-2070 FAX: 408-263-8931 hopkins@cive.stanford.edu	Site construction; Site management; Safety Officer

APPENDICES

APPENDIX A

Analytical Methods Supporting the Experimental Design

An ASAP system was used to collect and process ground water samples for this demonstration. The ASAP system was used previous for two other demonstrations on Edwards AFB. The sampling manifolds for the ASAP were connected to Grundfos Rediflo-2 pumps in selected monitoring wells in addition to upper and lower zones of the HFT wells. During the demonstration, only the upper and lower zones of the HFT wells were analyzed thus the influent and effluent of the reactors.

Samples processed by the ASAP were analyzed for VOCs by GC and anions by direct reading ion chromatograph (IC). In addition, during background sampling, samples were processed by specific ion probe for sulfide.

For the VOCs, the ASAP collected the VOCs via an automated, modified "purge-and-trap" type system using a standard 502 trap and a 5ml sample. During the latter period of the demonstration, a second trap of Carbosieve G was added in series in an attempt to trap ethane. This was only partially successful since the trap life was unusually short and no calibration gas was available at the time. The VOC trap was thermally desorbed into the GC carrier gas and VOC resolved using a J&W Scientific 30m mega bore thick film DB5 column in series with 15m of J&W Scientific mega bore thick film XXXX column. VOCs were detected by a flame ionization detector, integrated with a Chromjet integrator with the data automatically transferred to a PC via ASAP software.

The IC used to measure anions (chloride, nitrate and sulfate) was composed of a standard Wescan standard anion column (with a guard column) and detected by a Wescan conductivity detector using 4uM KHP eluant with 100 ml hydrogen peroxide per 10 liter added to prevent microbial growth in the eluant. Peaks were integrated with a Chromjet integrator with data automatically transferred to a PC via ASAP software.

The sulfide probe (Orion, combined reference) was attached to an Orion digital mV meter. The samples were again supplied via the ASAP system, but this measurement failed to produce results because the sulfide concentrations were sufficiently low as to be in the nonlinear range of the probe. Later, manual grab samples were analyzed using a Hach sulfide test kit and this also failed to produce usable results due to the 0.1 mg/L detection limit.

Since the ASAP system was used for two previous projects and process many thousands of sample, we lost significant amounts of data due to worn valves leaking and failing. Many of the gaps in the data were due to ASAP system failure rather than Pd reactor failure.

APPENDIX B

METHOD 300.1

DETERMINATION OF INORGANIC ANIONS IN DRINKING WATER BY ION CHROMATOGRAPHY

Revision 1.0

John D. Pfaff (USEPA, ORD, NERL) - Method 300.0, (1993)

Daniel P. Hautman (USEPA, Office of Water) and David J. Munch (USEPA, Office of Water) - Method 300.1, (1997)

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ERRATA COVER SHEET TO U.S.EPA METHOD 300.1
April 27, 1999

The following were editorial changes which have been incorporated into U.S.EPA Method 300.1. These minor clarifications are incorporated into the body of this text as follows:

ERRATA #1 -
An additional sentence was added to Section 4.1.1 reiterating the analyst's responsibilities when incorporating any method change, including modifying eluent strength, or any other method parameter. The additional sentence states,

> "*...The analyst must verify that these changes do not negatively affect performance by repeating and passing all the QC criteria in Section 9.*"

On this same theme, section 11.9, was also further clarified and specific precautions were added as follows,

> "*...The analysts must verify that this dilution does not negatively affect performance by repeating and passing all the QC criteria in Section 9. As a specific precaution, upon dilution of the carbonate eluent, a peak for bicarbonate may be observed within the retention time window for bromate which will negatively impact the analysis.*"

ERRATA #2 -
An acronym in Section 9.3.2.2 for Laboratory Fortified Blank (LFB) was incorrectly identified as LRB. This typographical error was corrected.

ERRATA #3 -
Clarifications and corrections were made to Section 9.4.1.5, 9.4.3.2 and 9.4.3.3. These clarifications pertain to data reportability for Laboratory Fortified Sample Matrices (LFM) as well as to analysis continuation when Duplicate Sample QC acceptance criteria are not met.

Section 9.4.1.5 clarifies and now specifies how to report data when the LFM recovery falls outside the established control criteria by stating,

> "*...the recovery problem encountered with the LFM is judged to be matrix induced and the results for that sample and the LFM are reported with a "matrix induced bias" qualifier.*"

Section 9.4.3.2 required the correction of a typographical reference by removing "%Diff" in the duplicate sample acceptance criteria and replacing it with the defined RPD, indicating "relative percent difference".

Section 9.4.3.3, also had a "%Diff" reference corrected with RPD and included clarification regarding continuation of an analysis set when a duplicate analysis fails to meet the acceptance criteria. This section now reads,

> "*If the RPD fails to meet these criteria, the samples must be reported with a qualifier identifying the sample analysis result as yielding a poor duplicate analysis RPD. This should not be a chronic problem and if it frequently recurs, (>20% of duplicate analysis) it indicates a problem with the instrument or individual technique.*"

METHOD 300.1

DETERMINATION OF INORGANIC ANIONS IN DRINKING WATER BY ION CHROMATOGRAPHY

1. SCOPE AND APPLICATION

1.1 This method covers the determination of the following inorganic anions in reagent water, surface water, ground water, and finished drinking water. As a result of different specified injection volumes (See conditions in Tables 1A and 1B), these anions are divided between the common anions listed in Part A and the inorganic disinfection by-products listed in Part B. These different injection volumes are required in order to compensate for the relative concentrations of these anions in drinking water and maintain good chromatographic peak shape throughout the expected dynamic range of the detector. Bromide is included in both Part A, due to its importance as a common anion, as well as Part B due to its critical role as a disinfection by-product precursor.

PART A.-- Common Anions

Bromide	Nitrite
Chloride	ortho-Phosphate-P
Fluoride	Sulfate
Nitrate	

PART B.-- Inorganic Disinfection By-products

Bromate	Chlorite
Bromide	Chlorate

1.2 The single laboratory Method Detection Limits (MDL, defined in Sect. 3.11) for the above analytes are listed in Tables 1A, 1B and 1C. The MDL for a specific matrix may differ from those listed, depending upon the nature of the sample and the specific instrumentation employed.

1.2.1 In order to achieve comparable detection limits, an ion chromatographic system must utilize suppressed conductivity detection, be properly maintained and must be capable of yielding a baseline with no more than 5 nS noise/drift per minute of monitored response over the background conductivity.

1.3 This method is recommended for use only by or under the supervision of analysts experienced in the use of ion chromatography and in the interpretation of the resulting ion chromatograms.

1.4 When this method is used to analyze unfamiliar samples for any of the above anions, anion identification should be supported by the use of a fortified sample matrix covering the anions of interest. The fortification procedure is described in Sect. 9.4.1.

1.5 Users of the method data should state the data-quality objectives prior to analysis. Users of the method must demonstrate the ability to generate acceptable results with this method, using the procedures described in Sect. 9.0.

1.6 Bromide and nitrite react with most oxidants employed as disinfectants. The utility of measuring these anions in treated water should be considered prior to conducting the analysis.

2. SUMMARY OF METHOD

2.1 A small volume of sample, 10 uL for Part A and 50 uL for Part B, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, analytical column, suppressor device, and conductivity detector.

2.2 The ONLY difference between Parts A and B is the volume of sample analyzed by the ion chromatographic system. The separator columns and guard columns as well as eluent conditions are identical.

3. DEFINITIONS

3.1 ANALYSIS BATCH -- A group of no more than 20 field samples (Field sample analyses include only those samples derived from a field sample matrix. These include the initial and duplicate field samples as well as all Laboratory Fortified Sample Matrices). The analysis batch must include an Initial Calibration Check Standard, an End Calibration Check Standard, Laboratory Reagent Blank, and a Laboratory Fortified Blank. Within an ANALYSIS BATCH, for every group of ten field samples, at least one Laboratory Fortified Matrix (LFM) and either a Field Duplicate, a Laboratory Duplicate or a duplicate of the LFM must be analyzed. When more than 10 field samples are analyzed, a Continuing Calibration Check Standard must be analyzed after the tenth field sample analysis.

3.2 CALIBRATION STANDARD (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the surrogate analyte. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.2.1 INITIAL CALIBRATION STANDARDS -- A series of CAL solutions used to initially establish instrument calibration and develop calibration curves for individual target anions.

3.2.2 INITIAL CALIBRATION CHECK STANDARD -- An individual CAL solution, analyzed initially, prior to any sample analysis, which verifies previously established calibration curves.

3.2.3 CONTINUING CALIBRATION CHECK STANDARD -- An individual CAL solution which is analyzed after every tenth field sample analyses

which verifies the previously established calibration curves and confirms accurate analyte quantitation for the previous ten field samples analyzed.

3.2.4 END CALIBRATION CHECK STANDARD -- An individual CAL solution which is analyzed after the last field sample analyses which verifies the previously established calibration curves and confirms accurate analyte quantitation for all field samples analyzed since the last continuing calibration check.

3.3 FIELD DUPLICATES -- Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of field duplicates indicate the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.

3.4 INSTRUMENT PERFORMANCE CHECK SOLUTION (IPC) -- A solution of one or more method analytes, surrogates, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of criteria.

3.5 LABORATORY DUPLICATE -- Two sample aliquots, taken in the laboratory from a single sample bottle, and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated specifically with the laboratory procedures, removing any associated variables attributed by sample collection, preservation, or storage procedures.

3.6 LABORATORY FORTIFIED BLANK (LFB) -- An aliquot of reagent water or other blank matrices to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.7 LABORATORY FORTIFIED SAMPLE MATRIX (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.8 LABORATORY REAGENT BLANK (LRB) -- An aliquot of reagent water or other blank matrices that are treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.9 LINEAR CALIBRATION RANGE (LCR) -- The concentration range over which the instrument response is linear.

3.10 MATERIAL SAFETY DATA SHEET (MSDS) -- Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.

3.11 METHOD DETECTION LIMIT (MDL) -- The minimum concentration of an analyte that can be identified, measured and reported with 99% confidence that the analyte concentration is greater than zero.

3.12 MINIMUM REPORTING LEVEL (MRL) -- The minimum concentration that can be reported for an anion in a sample following analysis. This defined concentration can be no lower than the concentration of the lowest calibration standard and can only be used if acceptable quality control criteria for this standard are met.

3.13 PERFORMANCE EVALUATION SAMPLE (PE) -- A certified solution of method analytes whose concentration is unknown to the analyst. Often, an aliquot of this solution is added to a known volume of reagent water and analyzed with procedures used for samples. Results of analyses are used to determine statistically the accuracy and precision that can be expected when a method is performed by a competent analyst.

3.14 QUALITY CONTROL SAMPLE (QCS) -- A solution of method analytes of known concentrations that is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

3.15 SURROGATE ANALYTE -- An analyte added to a sample, which is unlikely to be found in any sample at significant concentration, and which is added directly to a sample aliquot in known amounts before any sample processing procedures are conducted. It is measured with the same procedures used to measure other sample components. The purpose of the surrogate analyte is to monitor method performance with each sample.

3.16 STOCK STANDARD SOLUTION (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

4. INTERFERENCES

4.1 Interferences can be divided into three different categories: direct chromatographic coelution, where an analyte response is observed at very nearly the same retention time as the target anion; concentration dependant coelution, which is observed when the response of higher than typical concentrations of the

neighboring peak overlap into the retention window of the target anion; and, ionic character displacement, where retention times may significantly shift due to the influence of high ionic strength matrices (high mineral content or hardness) overloading the exchange sites in the column and significantly shortening target analyte's retention times.

4.1.1 A direct chromatographic coelution may be solved by changing columns, eluent strength, modifying the eluent with organic solvents (if compatible with IC columns), changing the detection systems, or selective removal of the interference with pretreatment. Sample dilution will have little to no effect. The analyst must verify that these changes do not negatively affect performance by repeating and passing all the QC criteria in Section 9.

4.1.2 Sample dilution may resolve some of the difficulties if the interference is the result of either concentration dependant coelution or ionic character displacement, but it must be clarified that **sample dilution will alter your Minimum Reporting Limit (MRL)** by a proportion equivalent to that of the dilution. Therefore, careful consideration of project objectives should be given prior to performing such a dilution. An alternative to sample dilution, may be dilution of the eluent as outlined in 11.9.

4.1.3 Pretreatment cartridges can be effective as a means to eliminate certain matrix interferences. Prior to using any pretreatment, the analyst should be aware that all instrument calibration standards must be pretreated in exactly the same manner as the pretreated unknown field samples. The need for these cartridges have been greatly reduced with recent advances in high capacity anion exchange columns.

4.1.3.1 Extreme caution should be exercised in using these pretreatment cartridges. Artifacts are known to leach from certain cartridges which can foul the guard and analytical columns causing loss of column capacity indicated by shortened retention times and irreproducible results. Frequently compare your calibration standard chromatograms to those of the column test chromatogram (received when the column was purchased) to insure proper separation and similar response ratios between the target analytes is observed.

4.2 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baselines in an ion chromatogram. These interferences can lead to false positive results for target analytes as well as reduced detection limits as a consequence of elevated baseline noise.

4.3 Samples that contain particles larger than 0.45 microns and reagent solutions that contain particles larger than 0.20 microns require filtration to prevent damage to instrument columns and flow systems.

4.4 Any anion that is only weakly retained by the column may elute in the retention time window of fluoride and potentially interfere. At concentrations of fluoride above 1.5 mg/L, this interference may not be significant, however, it is the responsibility of the user to generate precision and accuracy information in each sample matrix.

4.5 Close attention should be given to the potential for carry over peaks from one analysis which will effect the proper detection of analytes of interest in a second, subsequent analysis. Normally, the elution of sulfate (retention time of 13.8 min.) indicates the end of a chromatographic run, but, in the ozonated and chlorine dioxide matrices, which were included as part of the single operator accuracy and bias study (See Table 2B), a small response (200 nS baseline rise) was observed for a very late eluting unknown peak at approximately 23 minutes. Consequently, a run time of 25 minutes is recommended to allow for the proper elution of any potentially interferant late peaks. It is the responsibility of the user to confirm that no late eluting peaks have carried over into a subsequent analysis thereby compromising the integrity of the analytical results.

4.6 Any residual chlorine dioxide present in the sample will result in the formation of additional chlorite prior to analysis. If any concentration of chlorine dioxide is suspected in the sample, the sample must be purged with an inert gas (helium, argon or nitrogen) for approximately five minutes or until no chlorine dioxide remains. This sparging must be conducted prior to ethylenediamine preservation and at time of sample collection.

5. SAFETY

5.1 The toxicity or carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable. Cautions are included for known extremely hazardous materials or procedures.

5.2 Each laboratory is responsible for maintaining a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of Material Safety Data Sheets (MSDS) should be made available to all personnel involved in the chemical analysis. The preparation of a formal safety plan is also advisable.

5.3 The following chemicals have the potential to be highly toxic or hazardous, consult MSDS.

5.3.1 Sulfuric acid -- When used to prepared a 25 mN sulfuric acid regenerant solution for chemical suppression using a Dionex Anion Micro Membrane Suppressor (AMMS).

6. EQUIPMENT AND SUPPLIES

6.1 Ion chromatograph -- Analytical system complete with ion chromatograph and all required accessories including syringes, analytical columns, compressed gasses and a conductivity detector.

6.1.1 Anion guard column: Dionex AG9-HC, 2 mm (P/N 52248), or equivalent. This column functions as a protector of the separator column. If omitted from the system the retention times will be shorter.

6.1.2 Anion separator column: Dionex AS9-HC column, 2 mm (P/N 52244), or equivalent. The microbore (2 mm) was selected in the development of this method as a means to tighten the bromate elution band and thus reduce the detection limit. An optional column (2 mm or 4 mm) may be used if comparable resolution of peaks is obtained, and the requirements of Sect. 9.0 can be met. The AS9-HC, 2 mm column using the conditions outlined in Table 1A and 1B produced the separation shown in Figures 1 through 4.

6.1.2.1 If a 4 mm column is employed, the injection volume should be raised by a factor of four to 40 uL for Part A anions and 200 uL for Part B anions in order to attain comparable detection limits. A four fold increase in injection volume compensates for the four fold increase in cross sectional surface area of the 4 mm standard bore column over the 2 mm microbore column.

6.1.2.2 Comparable results can be attained using the Dionex, AS9-HC, 4 mm column. MDLs for the part B, inorganic disinfection by-products using this 4 mm column are displayed along with analysis conditions in Table 1C.

6.1.3 Anion suppressor device: The data presented in this method were generated using a Dionex Anion Self Regenerating Suppressor (ASRS, P/N 43187). An equivalent suppressor device may be utilized provided comparable detection limits are achieved and adequate baseline stability is attained as measured by a combined baseline drift/noise of no more than 5 nS per minute over the background conductivity.

6.1.3.1 The ASRS was set to perform electrolytic suppression at a current setting of 100 mA using an external source DI water mode. Insufficient baseline stability was observed using the ASRS in recycle mode.

6.1.4 Detector -- Conductivity cell (Dionex CD20, or equivalent) capable of providing data as required in Sect. 9.2.

6.2 The Dionex Peaknet Data Chromatography Software was used to generate all the data in the attached tables. Systems using a strip chart recorder and integrator or other computer based data system may achieve approximately the same MDL's but the user should demonstrate this by the procedure outlined in Sect. 9.2.

6.3 Analytical balance, ±0.1 mg sensitivity. Used to accurately weigh target analyte salts for stock standard preparation.

6.4 Top loading balance, ±10 mg sensitivity. Used to accurately weigh reagents to prepare eluents.

6.5 Weigh boats, plastic, disposable - for weighing eluent reagents.

6.6 Syringes, plastic, disposable, 10 mL - used during sample preparation.

6.7 Pipets, Pasteur, plastic or glass, disposable, graduated, 5 mL and 10 mL.

6.8 Bottles, high density polyethylene (HDPE), opaque or glass, amber, 30 mL, 125 mL, 250 mL. For sampling and storage of calibration solutions. Opaque or amber due to the photoreactivity of chlorite anion.

6.9 Micro beakers, plastic, disposable - used during sample preparation.

7. REAGENTS AND STANDARDS

7.1 Reagent water: Distilled or deionized water, free of the anions of interest. Water should contain particles no larger than 0.20 microns.

7.2 Eluent solution : Sodium carbonate (CASRN 497-19-8) 9.0 mM. Dissolve 1.91 g sodium carbonate (Na_2CO_3) in reagent water and dilute to 2 L.

7.2.1 This eluent solution must be purged for 10 minutes with helium prior to use to remove dissolved gases which may form micro bubbles in the IC compromising system performance and adversely effecting the integrity of the data.

7.3 Stock standard solutions, 1000 mg/L (1 mg/mL): Stock standard solutions may be purchased as certified solutions or prepared from ACS reagent grade, potassium or sodium salts as listed below, for most analytes. Chlorite requires careful consideration as outline below in 7.3.5.1.

7.3.1 Bromide (Br^-) 1000 mg/L: Dissolve 0.1288 g sodium bromide (NaBr, CASRN 7647-15-6) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.2 Bromate (BrO_3^-) 1000 mg/L: Dissolve 0.1180 g of sodium bromate ($NaBrO_3$, CASRN 7789-38-0) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.3 Chlorate ($C10_3^-$) 1000 mg/L: Dissolve 0.1275 g of sodium chlorate ($NaC10_3$, CASRN 7775-09-9) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.4 Chloride (Cl^-) 1000 mg/L: Dissolve 0.1649 g sodium chloride (NaCl, CASRN 7647-14-5) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.5 Chlorite ($C10_2^-$) 1000 mg/L: Assuming an exact 80.0 % $NaC10_2$ is amperometrically titrated from technical grade $NaC10_2$ (See Sect. 7.3.5.1). Dissolve 0.1676 g of sodium chlorite ($NaC10_2$, CASRN 7758-19-2) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.5.1 High purity sodium chlorite ($NaClO_2$) is not currently commercially available due to potential explosive instability. Recrystallization of the technical grade (approx. 80%) can be performed but it is labor intensive and time consuming. The simplest approach is to determine the exact % $NaClO_2$ using the iodometric titration procedure (Standard Methods, 19th Ed., 4500-ClO_2.C). Following titration, an individual component standard of chlorite must be analyzed to determine if there is any significant contamination (greater than 1% of the chlorite weight) in the technical grade chlorite standard from any of the Part B components. These contaminants will place a high bias on the calibration of the other anions if all four Part B components are mixed in an combined calibration solution. If these other anions are present as contaminants, a separate chlorite calibration needs to be performed.

7.3.6 Fluoride (F^-) 1000 mg/L: Dissolve 0.2210 g sodium fluoride (NaF, CASRN 7681-49-4) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.7 Nitrate (NO_3^--N) 1000 mg/L: Dissolve 0.6068 g sodium nitrate ($NaNO_3$, CASRN 7631-99-4) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.8 Nitrite (NO_2^--N) 1000 mg/L: Dissolve 0.4926 g sodium nitrite ($NaNO_2$, CASRN 7632-00-0) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.9 Phosphate (PO_4^{3-}-P) 1000 mg/L: Dissolve 0.4394 g potassium dihydrogenphosphate (KH_2PO_4, CASRN 7778-77-0) in reagent water and dilute to 100 mL in a volumetric flask.

7.3.10 Sulfate (SO_4^{2-}) 1000 mg/L: Dissolve 0.1814 g potassium sulfate (K_2SO_4, CASRN 7778-80-5) in reagent water and dilute to 100 mL in a volumetric flask.

NOTE: Stability of standards: Stock standards (7.3) for most anions are stable for at least 6 months when stored at 4°C. Except for the chlorite standard which is only stable for two weeks when stored protected from light at 4°C, and nitrite and phosphate which are only stable for 1 month when stored at 4°C. Dilute working standards should be prepared monthly, except those that contain chlorite, or nitrite and phosphate which should be prepared fresh daily.

7.4 Ethylenediamine (EDA) preservation solution, 100 mg/mL: Dilute 2.8 mL of ethylenediamine (99%) (CASRN 107-15-3) to 25 mL with reagent water. Prepare fresh monthly.

7.5 Surrogate Solution: 0.50 mg/mL dichloroacetate (DCA) prepared by dissolving 0.065 g dichloroacetic acid, potassium salt (Cl_2CHCO_2K, CASRN 19559-59-2) in reagent water and dilute to 100 mL in a volumetric flask.

7.5.1 Dichloroacetate is potentially present in treated drinking waters as the acetate of the organic disinfection by product, dichloroacetic acid (DCAA). Typical concentrations of DCAA rarely exceed 50 ug/L, which, for this worst case example, would represent only a five percent increase in the observed response over the fortified concentration of 1.00 mg/L. Consequently, the criteria for acceptable recovery (90% to 115%) for the surrogate is weighted to 115% to allow for this potential background.

7.5.2 Prepare this solution fresh every 3 months or sooner if signs of degradation are present.

8. SAMPLE COLLECTION, PRESERVATION AND STORAGE

8.1 Samples should be collected in plastic or glass bottles. All bottles must be thoroughly cleaned and rinsed with reagent water. Volume collected should be sufficient to insure a representative sample, allow for replicate analysis, if required, and minimize waste disposal.

8.2 Special sampling requirements and precautions for chlorite.

8.2.1 Sample bottles used for chlorite analysis must be opaque to protect the sample from light.

8.2.2 When preparing the LFM, be aware that chlorite is an oxidant and may react with the natural organic matter in an untreated drinking water matrix as a result of oxidative demand. If untreated water is collected for chlorite analysis, and subsequently used for the LFM, EDA preservation will not control this demand and reduced chlorite recoveries may be observed.

8.3 Sample preservation and holding times for the anions that can be determined by this method are as follows:

PART A : Common Anions

Analyte	Preservation	Holding Time
Bromide	None required	28 days
Chloride	None required	28 days
Fluoride	None required	28 days
Nitrate-N	Cool to 4°C	48 hours
Nitrite-N	Cool to 4°C	48 hours
ortho-Phosphate-P	Cool to 4°C	48 hours
Sulfate	Cool to 4°C	28 days

PART B : Inorganic Disinfection By-products

Analyte	Preservation	Holding Time
Bromate	50 mg/L EDA	28 days
Bromide	None required	28 days
Chlorate	50 mg/L EDA	28 days
Chlorite	50 mg/L EDA, Cool to 4°C	14 days

8.4 When collecting a sample from a treatment plant employing chlorine dioxide, the sample must be sparged with an inert gas (helium, argon, nitrogen) prior to addition of the EDA preservative at time of sample collection.

8.5 All four anions, in Part B, can be analyzed in a sample matrix which has been preserved with EDA. Add a sufficient volume of the EDA preservation solution (Sect. 7.4) such that the final concentration is 50 mg/L in the sample. This would be equivalent to adding 0.5 mL of the EDA preservation solution to 1 L of sample.

8.6 EDA is primarily used as a preservative for chlorite. Chlorite is susceptible to degradation both through catalytic reactions with dissolved iron salts and reactivity towards free chlorine which exists as hypochlorous acid/hypochlorite ion in most drinking water as a residual disinfectant. EDA serves a dual purpose as a preservative for chlorite by chelating iron as well as any other catalytically destructive metal cations and removing hypochlorous acid/hypochlorite ion by forming an organochloroamine. EDA preservation of chlorite also preserves the integrity of chlorate which can increase in unpreserved samples as a result of chlorite degradation. EDA also preserves the integrity of bromate concentrations by binding with hypobromous acid/hypobromite which is an intermediate formed

as by-product of the reaction of either ozone or hypochlorous acid/hypochlorite with bromide ion. If hypobromous acid/hypobromite is not removed from the matrix further reactions may form bromate ion.

8.7 Degradation of ortho-phosphate has been observed in samples held at room temperature for over 16 hrs (see table 3A). Therefore, samples to be analyzed for ortho-phosphate must not be held at room temperature for more than 12 cumulative hours.

9. QUALITY CONTROL

9.1 Each laboratory using this method is required to operate a formal quality control (QC) program. The requirements of this program consist of an initial demonstration of laboratory performance, and subsequent analysis in each analysis batch (Sect. 3.1) of a Laboratory Reagent Blank, Laboratory Fortified Blank, Instrument Performance Check Standard, calibration check standards, Laboratory Fortified Sample Matrices (LFM) and either Field, Laboratory or LFM duplicate sample analyses. This section details the specific requirements for each of these QC parameters. The laboratory is required to maintain performance records that define the quality of the data that are generated.

9.2 INITIAL DEMONSTRATION OF PERFORMANCE

9.2.1 The initial demonstration of performance is used to characterize instrument performance (determination of accuracy through the analysis of the QCS) and laboratory performance (determination of MDLs) prior to performing analyses by this method.

9.2.2 Quality Control Sample (QCS) -- When beginning the use of this method, on a quarterly basis or as required to meet data-quality needs, verify the calibration standards and acceptable instrument performance with the preparation and analyses of a QCS. If the determined concentrations are not within ± 15% of the stated values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with on-going analyses.

9.2.3 Method Detection Limit (MDL) -- MDLs must be established for all analytes, using reagent water (blank) fortified at a concentration of three to five times the estimated instrument detection limit.[6] To determine MDL values, take seven replicate aliquots of the fortified reagent water and process through the entire analytical method over at least three separate days. Perform all calculations defined in the method and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$MDL = (t) \times (S)$$

where, t = Student's t value for a 99% confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for seven replicates].

S = standard deviation of the replicate analyses.

9.2.3.1 MDLs should be determined every 6 months, when a new operator begins work or whenever there is a significant change in the background, or instrument response.

9.3 ASSESSING LABORATORY PERFORMANCE

9.3.1 Laboratory Reagent Blank (LRB) -- The laboratory must analyze at least one LRB with each analysis batch (defined Sect 3.1). Data produced are used to assess contamination from the laboratory environment. Values that exceed the MDL indicate laboratory or reagent contamination should be suspected and corrective actions must be taken before continuing the analysis.

9.3.1.1 If conducting analysis for the Part B anions, EDA must be added to the LRB at 50 mg/L. By including EDA in the LRB, any bias as a consequence of the EDA which may be observed in the field samples, particularly in terms of background contamination, will be identified.

9.3.2 Laboratory Fortified Blank (LFB) -- The LFB should be prepared at concentrations similar to those expected in the field samples and ideally at the same concentration used to prepare the LFM. Calculate accuracy as percent recovery (Sect. 9.4.1.3). If the recovery of any analyte falls outside the required concentration dependant control limits (Sect. 9.3.2.2), that analyte is judged out of control, and the source of the problem should be identified and resolved before continuing analyses.

9.3.2.1 If conducting analysis for the Part B anions, EDA must be added to the LFB at 50 mg/L. The addition of EDA to all reagent water prepared calibration and quality control samples is required not as a preservative but rather as a means to normalize any bias attributed by the presence of EDA in the field samples.

9.3.2.2 Control Limits for the LFB

Concentration range	Percent Recovery Limits
MRL to 10xMRL	75 - 125 %
10xMRL to highest calibration level	85 - 115 %

9.3.2.2.1 These control limits only apply if the MRL is established within a factor of 10 times the MDL. Otherwise, the limits are set at 85% to 115%.

9.3.2.3 The laboratory must use the LFB to assess laboratory performance against the required control limits listed in 9.3.2.2. When sufficient internal performance data become available (usually a minimum of 20-30 analyses), optional control limits can be developed from the percent mean recovery (x) and the standard deviation (S) of the mean recovery. These data can be used to establish the upper and lower control limits as follows:

UPPER CONTROL LIMIT = x + 3S
LOWER CONTROL LIMIT = x - 3S

The optional control limits must be equal to or better than those listed in 9.3.2.2. After each five to ten new recovery measurements, new control limits can be calculated using only the most recent 20-30 data points. Also, the standard deviation (S) data should be used to establish an on-going precision statement for the level of concentrations monitored. These data must be kept on file and be available for review.

9.3.3 Instrument Performance Check Solution (IPC) -- The Initial Calibration Check Standard is to be evaluated as the instrument performance check solution in order to confirm proper instrument performance. Proper chromatographic performance must be demonstrated by calculating the Peak Gaussian Factor (PGF), which is a means to measure peak symmetry and monitoring retention time drift in the surrogate peak over time. Critically evaluate the surrogate peak in the initial calibration check standard, and calculate the PGF as follows,

$$PGF = \frac{1.83 \times W(1/2)}{W(1/10)}$$

where: W(1/2) is the peak width at half height
W(1/10) is the peak width at tenth height

9.3.3.1 The PGF must fall between 0.80 and 1.15 in order to demonstrate proper instrument performance.

9.3.3.2 The retention time for the surrogate in the IPC must be closely monitored on each day of analysis and throughout the lifetime of the analytical column. Small variations in retention time can be anticipated when a new solution of eluent is prepared but if shifts of more than 2% are observed in the surrogate retention time, some type of instrument problem is present. Potential

problems include improperly prepared eluent, erroneous method parameters programmed such as flow rate or some other system problem. The chromatographic profile (elution order) of the target anions following an ion chromatographic analysis should closely replicate the profile displayed in the test chromatogram that was shipped when the column was purchased. As a column ages, it is normal to see a gradual shift and shortening of retention times, but if after several years of use, extensive use over less than a year, or use with harsh samples, this retention time has noticeably shifted to any less than 80% of the original recorded value, the column may require cleaning or replacement. Particularly if resolution problems are beginning to become common between previously resolved peaks. A laboratory must retain a historic record of retention times for the surrogate and all the target anions to provide evidence of an analytical columns vitality.

9.4 ASSESSING ANALYTE RECOVERY AND DATA QUALITY

9.4.1 Laboratory Fortified Sample Matrix (LFM) -- The laboratory must add a known amount of analyte to a minimum of 10% of the field samples within an analysis batch. The LFM sample must be prepared from a sample matrix which has been analyzed prior to fortification. The analyte concentration must be high enough to be detected above the original sample and should adhere to the requirement of 9.4.1.2. It is recommended that the solutions used to fortify the LFM be prepared from the same stocks used to prepare the calibration standards and not from external source stocks. This will remove the bias contributed by an externally prepared stock and focus on any potential bias introduced by the field sample matrix.

9.4.1.1 If the fortified concentration is less than the observed background concentration of the unfortified matrix, the recovery should not be calculated. This is due to the difficulty in calculating accurate recoveries of the fortified concentration when the native sample concentration is so high.

9.4.1.2 The LFM should be prepared at concentrations no greater than five times the highest concentration observed in any field sample. If no analyte is observed in any field sample, the LFM must be fortified no greater than five times the lowest calibration level which as outlined in 12.2 is the minimum reported level (MRL). For example, if bromate is not detected in any field samples above the lowest calibrations standard concentration of 5.00 ug/L, the highest LFM fortified concentration allowed is 25.0 ug/L.

9.4.1.3 Calculate the percent recovery for each analyte, corrected for concentrations measured in the unfortified sample. Percent recovery should be calculated using the following equation:

$$R = \frac{C_s - C}{s} \times 100$$

where, R = percent recovery.
C_s = fortified sample concentration
C = sample background concentration
s = concentration equivalent of analyte added to sample.

9.4.1.4 Until sufficient data becomes available (usually a minimum of 20 to 30 analysis), assess laboratory performance against recovery limits of 75 to 125%. When sufficient internal performance data becomes available develop control limits from percent mean recovery and the standard deviation of the mean recovery. The optional control limits must be equal to or better than the required control limits of 75-125%.

9.4.1.5 If the recovery of any analyte falls outside the designated LFM recovery range and the laboratory performance for that analyte is shown to be in control (Sect. 9.3), the recovery problem encountered with the LFM is judged to be matrix induced and the results for that sample and the LFM are reported with a "matrix induced bias" qualifier.

9.4.2 SURROGATE RECOVERY -- Calculate the surrogate recovery from all analyses using the following formula

$$R = \frac{SRC}{SFC} \times 100$$

where, R = percent recovery.
SRC = Surrogate Recovered Concentration
SFC = Surrogate Fortified Concentration

9.4.2.1 Surrogate recoveries must fall between 90-115% for proper instrument performance and analyst technique to be verified. The recovery of the surrogate is slightly bias to 115% to allow for the potential contribution of trace levels of dichloroacetate as the halogenated organic disinfection by-product (DBP) dichloroacetic acid (DCAA) Background levels of this organic DBP are rarely observed above 50 ug/L (0.05 mg/L) which constitutes only 5% of the 1.00 mg/L recommended fortified concentration.

9.4.2.2 If the surrogate recovery falls outside the 90-115% recovery window, a analysis error is evident and sample reanalysis is

required. Poor recoveries could be the result of imprecise sample injection or analyst fortification errors.

9.4.3 FIELD OR LABORATORY DUPLICATES -- The laboratory must analyze either a field or a laboratory duplicate for a minimum of 10% of the collected field samples or at least one with every analysis batch, whichever is greater. The sample matrix selected for this duplicate analysis must contain measurable concentrations of the target anions in order to establish the precision of the analysis set and insure the quality of the data. If none of the samples within an analysis batch have measurable concentrations, the LFM should be employed as a laboratory duplicate.

9.4.3.1 Calculate the relative percent difference (RPD) of the initial quantitated concentration (I_C) and duplicate quantitated concentration (D_c) using the following formula,

$$RPD = \frac{(I_C - D_c)}{([I_C + D_c]/2)} \times 100$$

9.4.3.2 Duplicate analysis acceptance criteria

Concentration range	RPD Limits
MRL to 10xMRL	+/- 20 %
10xMRL to highest calibration level	+/- 10 %

9.4.3.3 If the RPD fails to meet these criteria, the samples must be reported with a qualifier identifying the sample analysis result as yielding a poor duplicate analysis RPD. This should not be a chronic problem and if it frequently recurs (>20% of duplicate analyses) it indicates a problem with the instrument or individual technique.

9.4.4 Where reference materials are available, they should be analyzed to provide additional performance data. The analysis of reference samples is a valuable tool for demonstrating the ability to perform the method acceptably.

9.4.5 In recognition of the rapid advances occurring in chromatography, the analyst is permitted certain options, such as the use of different columns, injection volumes, and/or eluents, to improve the separations or lower the cost of measurements. Each time such modifications to the method are made, the analyst is required to repeat the procedure in Sect. 9.2 and adhere to the condition of baseline stability found in Sect. 1.2.1.

9.4.6 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most

productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should perform analysis of quality control check samples and participate in relevant performance evaluation sample studies.

10. CALIBRATION AND STANDARDIZATION

10.1 Establish ion chromatographic operating parameters equivalent to those indicated in Tables 1A or 1B if employing a 2 mm column, Table 1C if employing a 4 mm column.

10.2 Estimate the Linear Calibration Range (LCR) -- The LCR should cover the expected concentration range of the field samples and should not extend over more than 2 orders of magnitude in concentration (For example, if quantitating nitrate in the expected range of 1.0 mg/L to 10 mg/L, 2 orders of magnitude would permit the minimum and maximum calibration standards of 0.20 mg/L and 20 mg/L, respectively.) The restriction of 2 orders of magnitude is prescribed since beyond this it is difficult to maintain linearity throughout the entire calibration range.

10.2.1 If quantification is desired over a larger range, then two separate calibration curves should be prepared.

10.2.2 For an individual calibration curve, a minimum of three calibration standards are required for a curve that extends over a single order of magnitude and a minimum of five calibration standards are required if the curve covers two orders of magnitude. (For example, using the nitrate example cited above in section 10.2, but in this case limit the curve to extend only from 1.0 mg/L to 10 mg/L or a single order of magnitude. A third standard is required somewhere in the middle of the range. For the calibration range of 0.20 mg/L to 20 mg/L, over two orders of magnitude, five calibrations standards should be employed, one each at the lower and upper concentration ranges and the other three proportionally divided throughout the middle of the curve.)

10.3 Prepare the calibration standards by carefully adding measured volumes of one or more stock standards (7.3) to a volumetric flask and diluting to volume with reagent water.

10.3.1 For the Part B anions, EDA must be added to the calibration standards at 50 mg/L. The addition of EDA to all reagent water prepared calibration and quality control samples is required not as a preservative but rather as a means to normalize any bias attributed by the presence of EDA in the field samples.

10.3.2 Prepare a 10.0 mL aliquot of surrogate fortified calibration solution which can be held for direct manual injection or used to fill an autosampler vial. Add 20 uL of the surrogate solution (7.5) to a 20 mL disposable plastic micro beaker. Using a 10.0 mL disposable pipet, place

exactly 10.0 mL of calibration standard into the micro beaker and mix. The calibration standard is now ready for analysis. The same surrogate solution that has been employed for the standards should also be used in the section 11.3.2 for the field samples.

10.4 Using a 2 mm column, inject 10 uL (Part A) or 50 uL (Part B) of each calibration standard. Using a 4 mm column, inject 50 uL (Part A) or 200 uL (Part B) of each calibration standard. Tabulate peak area responses against the concentration. The results are used to prepare calibration curves using a linear least squares fit for each analyte. Acceptable calibration curves are confirmed after reviewing the curves for linearity and passing the criteria for the initial calibration check standard in section 10.5.1. Alternately, if the ratio of response to concentration (response factor) is constant over the LCR (indicated by < 15% relative standard deviation (RSD), linearity through the origin can be assumed and the average ratio or calibration factor can be used in place of a calibration curve,

10.4.1 Peak areas are strongly recommended since they have been found to be more consistent, in terms of quantitation, than peak heights. Peak height can tend to be suppressed as a result of high levels of common anions in a given matrix which can compete for exchange sites. Using peak areas, it is the analyst responsibility to review all chromatograms to insure accurate baseline integration of target analyte peaks since poorly drawn baselines will more significantly influence peak areas than peak heights.

10.5 Once the calibration curves have been established they must be verified prior to conducting any sample analysis using an initial calibration check standard (3.2.2). This verification must be performed on each analysis day or whenever fresh eluent has been prepared. A continuing calibration check standard (3.2.3) must be analyzed after every tenth sample and at the end of the analysis set as an end calibration check standard (3.2.4). The response for the initial, continuing and end calibration check must satisfy the criteria listed in 10.5.1. If during the analysis set, the response differs by more than the calibration verification criteria shown in 10.5.1., or the retention times shift more than ± 5% from the expected values for any analyte, the test must be repeated, using fresh calibration standards. If the results are still outside these criteria, sample analysis must be discontinued, the cause determined and/or in the case of drift, the instrument recalibrated. All samples following the last acceptable calibration check standard must be reanalyzed.

10.5.1 Control limits for calibration verification

Concentration range	Percent Recovery Limits
MRL to 10xMRL	75 - 125 %
10xMRL to highest calibration level	85 - 115 %

10.5.1.1 These control limits only apply if the MRL is established within a factor of 10 times the MDL. Otherwise, the limits are set at 85% to 115%.

10.5.2 CALIBRATION VERIFICATION REQUIREMENT FOR PART B
As a mandatory requirement of calibration verification, the laboratory MUST verify calibration using the lowest calibration standard as the initial calibration check standard.

10.5.3 After satisfying the requirement of 10.5.2, the levels selected for the other calibration check standards should be varied between a middle calibration level and the highest calibration level.

11. PROCEDURE

11.1 Tables 1A and 1B summarize the recommended operating conditions for the ion chromatograph. Included in these tables are estimated retention times that can be achieved by this method. Other columns, chromatographic conditions, or detectors may be used if the requirements of Sect. 9.2 are met.

11.2 Check system calibration daily and, if required, recalibrate as described in Sect. 10.

11.3 Sample Preparation

11.3.1 For refrigerated or samples arriving to the laboratory cold, ensure the samples have come to room temperature prior to conducting sample analysis by allowing the samples to warm on the bench for at least 1 hour.

11.3.2 Prepare a 10.0 mL aliquot of surrogate fortified sample which can be held for direct manual injection or used to fill an autosampler vial. Add 20 uL of the surrogate solution (7.5) to a 20 mL disposable plastic micro beaker. Using a 10.0 mL disposable pipet, place exactly 10.0 mL of sample into the micro beaker and mix. Sample is now ready for analysis.

11.3.2.1 The less than 1% dilution error introduced by the addition of the surrogate is considered insignificant.

11.4 Using a Luer lock, plastic 10 mL syringe, withdraw the sample from the micro beaker and attach a 0.45 um particulate filter (demonstrated to be free of ionic contaminants) directly to the syringe. Filter the sample into an autosampler vial (If vial is not designed to automatically filter) or manually load the injection loop injecting a fixed amount of well mixed sample. If using a manually loaded injection loop, flush the loop thoroughly between sample analysis using sufficient volumes of each new sample matrix.

11.5 Using a 2 mm column, inject 10 uL (Part A) or 50 uL (Part B) of each sample. Using a 4 mm column, inject 40 uL (Part A) or 200 uL (Part B) of each sample. Tabulate peak area responses against the concentration. During this procedure, retention times must be recorded. Use the same size loop for standards and

samples. Record the resulting peak size in area units. An automated constant volume injection system may also be used.

11.6 The width of the retention time window used to make identifications should be based upon measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for each analyte. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

11.7 If the response of a sample analyte exceeds the calibration range, the sample may be diluted with an appropriate amount of reagent water and reanalyzed. If this is not possible then three new calibration concentrations must be employed to create a separate high concentration curve, one standard near the estimated concentration and the other two bracketing around an interval equivalent to ± 25% the estimated concentration. The latter procedure involves significantly more time than a simple sample dilution therefore, it is advisable to collect sufficient sample to allow for sample dilution or sample reanalysis, if required.

11.8 Shifts in retention time are inversely proportional to concentration. Nitrate, phosphate and sulfate will exhibit the greatest degree of change, although all anions can be affected. In some cases this peak migration may produce poor resolution or make peak identification difficult.

11.9 Should more complete resolution be needed between any two coeluting peaks, the eluent (7.2) can be diluted. This will spread out the run, however, and will cause late eluting anions to be retained even longer. The analysts must verify that this dilution does not negatively affect performance by repeating and passing all the QC criteria in Section 9. As a specific precaution, upon dilution of the carbonate eluent, a peak for bicarbonate may be observed within the retention time window for bromate which will negatively impact the analysis.

11.9.1 Eluent dilution will reduce the overall response of an anion due to chromatographic band broadening which will be evident by shortened and broadened peaks. This will adversely effect the MDLs for each analyte.

12. DATA ANALYSIS AND CALCULATIONS

12.1 Prepare a calibration curve for each analyte by plotting instrument response, as peak area, against standard concentration. Compute sample concentration by comparing sample response with the standard curve. If a sample has been diluted, multiply the response by the appropriate dilution factor.

12.2 Report ONLY those values that fall between the lowest and the highest calibration standards. Samples with target analyte responses exceeding the highest standard should be diluted and reanalyzed. Samples with target analytes identified but quantitated below the concentration established by the lowest

calibration standard should be reported as below the minimum reporting limit (MRL).

12.3 Report results for Part A anions in mg/L and for Part B anions in ug/L.

12.4 Report NO_2^- as N
NO_3^- as N
$HPO_4^=$ as P
Br^- in mg/L when reported with Part A
Br^- in ug/L when reported with Part B

13. METHODS PERFORMANCE

13.1 Tables 1A, 1B, and 1C give the single laboratory (OW OGWDW TSC-Cincinnati) retention times, standard conditions and MDL determined for each anion included in the method. MDLs for the Part A anions were determined in reagent water on the 2 mm column (Table 1A). MDLs for the Part B anions were conducted not only in reagent water but also a simulated high ionic strength water (HIW) on the 2 mm column (Table 1B) and in reagent water on the 4 mm column (Table 1C). HIW is designed to simulate a high ionic strength field sample. It was prepared from reagent water which was fortified with the common anions of chloride at 100 mg/L, carbonate at 100 mg/L, nitrate at 10.0 mg/L as nitrogen, phosphate at 10.0 mg/L as phosphorous, and sulfate at 100 mg/L.

13.2 Tables 2A and 2B give the single laboratory (OW OGWDW TSC-Cincinnati) standard deviation for each anion included in the method in a variety of waters for the standard conditions identified in Table 1A and 1B, respectively.

13.3 Tables 3A and 3B shown stability data for the Part A and B anions, respectively. Each data point in these tables represent the mean percent recovery following triplicate analysis. These data were used to formulate the holding times shown in Sect. 8.3.

14. POLLUTION PREVENTION

14.1 Pollution prevention encompasses any technique that reduces or eliminates the quantity or toxicity of waste at the point of generation. Numerous opportunities for pollution prevention exist in laboratory operation. The EPA has established a preferred hierarchy of environmental management techniques that places pollution prevention as the management option of first choice. Whenever feasible, laboratory personnel should use pollution prevention techniques to address their waste generation. When wastes cannot be feasibly reduced at the source, the Agency recommends recycling as the next best option.

14.2 Quantity of the chemicals purchased should be based on expected usage during its shelf life and disposal cost of unused material. Actual reagent preparation volumes should reflect anticipated usage and reagent stability.

14.3 For information about pollution prevention that may be applicable to laboratories and research institutions, consult "Less is Better: Laboratory Chemical Management for Waste Reduction," available from the American Chemical Society's Department of Government Regulations and Science Policy, 1155 16th Street N.W., Washington D.C. 20036, (202) 872-4477.

15. WASTE MANAGEMENT

15.1 The Environmental Protection Agency requires that laboratory waste management practices be conducted consistent with all applicable rules and regulations. Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The Agency urges laboratories to protect the air, water, and land by minimizing and controlling all releases from hoods and bench operations, complying with the letter and spirit of any waste discharge permit and regulations, and by complying with all solid and hazardous waste regulations, particularly the hazardous waste identification rules and land disposal restrictions. For further information on waste management consult the "Waste Management Manual for Laboratory Personnel," available from the American Chemical Society at the address listed in Sect. 14.3.

16. REFERENCES

1. "Determination of Inorganic Disinfection By-Products by Ion Chromatography", J. Pfaff, C. Brockhoff. J. Am. Water Works Assoc., Vol 82, No. 4, pg 192.

2. Standard Methods for the Examination of Water and Wastewater, Method 4110B, "Anions by Ion Chromatography", 18th Edition of Standard Methods (1992).

3. Dionex, System DX500 Operation and Maintenance Manual, Dionex Corp., Sunnyvale, California 94086, 1996.

4. Method Detection Limit (MDL) as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, page 1426, December, 1981.

5. American Society for Testing and Materials. Test Method for Anions in Water by Chemically-Suppressed Ion Chromatography D4327-91. Annual Book of Standards, Vol 11.01 (1993).

6. Code of Federal Regulations 40, Ch. 1, Pt. 136, Appendix B.

7. Hautman, D.P. & Bolyard, M. Analysis of Oxyhalide Disinfection By-products and other Anions of Interest in Drinking Water by Ion Chromatography. Jour. of Chromatog., 602, (1992), 65-74.

8. Standard Methods for the Examination of Water and Wastewater, Method 4500-ClO_2,C "Amperometric Method I" (for the determination of Chlorine Dioxide), 19th Edition of Standard Methods (1995).

17. TABLES, DIAGRAMS, FLOWCHARTS AND VALIDATION DATA

TABLE 1A. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN REAGENT WATER FOR THE COMMON ANIONS (PART A).

ANALYTE	PEAK # (1)	RETENTION TIME (MIN.)	MDL DETERMINATION Fort Conc, mg/L	Number of Replicates	DI MDL mg/L
Fluoride	1	2.53	0.020	7	0.009
Chloride	2	4.67	0.020	7	0.004
Nitrite-N	3	6.01	0.010	7	0.001
Surrogate: DCA	4	7.03			
Bromide	5	8.21	0.040	7	0.014
Nitrate-N	6	9.84	0.010	7	0.008
ortho-Phosphate-P	7	11.98	0.040	7	0.019
Sulfate	8	13.49	0.040	7	0.019

Standard Conditions:

Ion Chromatograph: Dionex DX500
Columns : Dionex AG9-HC / AS9-HC, 2 mm
Detector: Suppressed Conductivity Detector, Dionex CD20
Suppressor: ASRS-I, external source electrolytic mode, 100 mA current
Eluent: 9.0 mM Na_2CO_3
Eluent Flow: 0.40 mL/min
Sample Loop: 10 uL

System Backpressure: 2800 psi
Background Conductivity: 22 uS

Recommended method total analysis time: 25 minutes

(1) See Figure 1

TABLE 1B. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN BOTH REAGENT WATER AND HIGH IONIC STRENGTH WATER FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B).

			MDL DETERMINATION			
ANALYTE	PEAK # (1)	RETENTION TIME (MIN.)	Fort Conc, ug/L	Number of Replicates	DI MDL ug/L	HIW(2) MDL ug/L
Chlorite	1	3.63	2.00	7	0.89	0.45
Bromate	2	4.19	2.00	7	1.44	1.28
Surrogate: DCA	4	7.28				
Bromide	5	8.48	2.00	7	1.44	2.51
Chlorate	6	9.28	2.00	7	1.31	0.78

Standard Conditions:

Ion Chromatograph: Dionex DX500
Columns : Dionex AG9-HC / AS9-HC, 2 mm
Detector: Suppressed Conductivity Detector, Dionex CD20
Suppressor: ASRS-I, external source electrolytic mode, 100 mA current
Eluent: 9.0 mM Na_2CO_3
Eluent Flow: 0.40 mL/min
Sample Loop: 50 uL

System Backpressure: 2800 psi
Background Conductivity: 22 uS

Recommended method total analysis time: 25 minutes

(1) See Figure 2 and 3

(2) HIW indicates High Ionic Strength Water which is a simulated drinking water prepared from reagent water and fortified with chloride at 100 mg/L, carbonate at 100 mg/L, nitrate at 10.0 mg/L as nitrogen, phosphate at 10.0 mg/L as phosphorous, and sulfate at 100 mg/L.

TABLE 1C. CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN REAGENT WATER FOR THE INORGANIC DISINFECTION BY-PRODUCTS USING AN ALTERNATE 4 mm AS9-HC COLUMN (PART B).

ANALYTE	PEAK #	RETENTION TIME (MIN.)	MDL DETERMINATION		
			Fort Conc, ug/L	Number of Replicates	DI MDL ug/L
Chlorite	1	4.43	2.00	7	1.44
Bromate	2	5.10	2.00	7	1.32
Surrogate: DCA	4	8.82			
Bromide	5	10.11	2.00	7	0.98
Chlorate	6	10.94	2.00	7	2.55

Standard Conditions:

Ion Chromatograph: Dionex DX500
Columns : Dionex AG9-HC / AS9-HC, 4 mm
Detector: Suppressed Conductivity Detector, Dionex CD20
Suppressor: ASRS-I, external source electrolytic mode, 300 mA current
Eluent: 9.0 mM Na_2CO_3
Eluent Flow: 1.25 mL/min
Sample Loop: 200 uL

System Backpressure: 1900 psi
Background Conductivity: 21 uS

Recommended method total analysis time: 25 minutes

TABLE 2A. SINGLE-OPERATOR PRECISION AND RECOVERY FOR THE COMMON ANIONS (PART A).

ANALYTE	MATRIX	UNFORT MATRIX CONC., mg/L	FORT CONC mg/L	# OF REPLC	MEAN mg/L	MEAN %REC	SD(n-1)	%RSD
Fluoride	RW	<MDL[1]	2.00	9	1.79	89.7	0.02	1.18
	SW	0.139	2.00	9	1.75	80.4	0.01	0.56
	GW	0.280	2.00	9	1.97	84.3	0.02	0.85
	CDW	0.807	2.00	9	2.59	89.0	0.01	0.46
Chloride	RW	0.029	50.0	9	49.4	98.7	0.03	0.10
	SW	12.1	50.0	9	58.7	93.3	0.04	0.10
	GW	56.6	50.0	9	100.	---[2]	0.22	0.22
	CDW	16.0	50.0	9	64.9	97.8	0.11	0.16
Nitrite-N	RW	<MDL	1.00	9	0.851	85.1	0.00	0.51
	SW	<MDL	1.00	9	0.780	78.0	0.00	0.40
	GW	0.013	1.00	9	0.879	86.6	0.01	0.77
	CDW	<MDL	1.00	9	0.720	72.0	0.00	0.55
Bromide	RW	<MDL	0.500	9	0.480	96.1	0.00	0.92
	SW	0.028	0.500	9	0.469	88.1	0.00	0.94
	GW	0.153	0.500	9	0.634	96.3	0.00	0.52
	CDW	<MDL	0.500	9	0.431	86.2	0.01	1.28
Nitrate-N	RW	<MDL	10.0	9	9.50	95.0	0.01	0.14
	SW	2.12	10.0	9	10.9	87.7	0.03	0.30
	GW	0.016	10.0	9	9.64	96.3	0.03	0.27
	CDW	1.64	10.0	9	10.9	92.4	0.04	0.41
Phosphate-P	RW	<MDL	10.0	9	9.62	96.2	0.01	0.14
	SW	<MDL	10.0	9	8.70	87.0	0.02	0.18
	GW	<MDL	10.0	9	6.12	61.2	0.28	4.66
	CDW	<MDL	10.0	9	9.15	91.5	0.04	0.42
Sulfate	RW	<MDL	50.0	9	44.8	89.5	0.05	0.11
	SW	47.8	50.0	9	92.1	88.6	0.21	0.23
	GW	105	50.0	9	154	---[2]	0.60	0.39
	CDW	57.8	50.0	9	105	---[2]	0.33	0.32
Surrogate:	RW	----	5.00	9	5.12	102.3	0.50	0.49
	SW	----	5.00	9	5.09	102.3	1.12	1.09
	GW	----	5.00	9	5.16	101.8	0.67	0.66
	CDW	----	5.00	9	5.17	103.1	1.36	1.32

RW = Reagent Water GW = Ground Water
SW = Surface Water CDW = chlorine dioxide treated finished drinking water

(1) <MDL indicates less than method detection limit.
(2) Not calculated since amount fortified was less than unfortified native matrix concentration (See 9.4.1.1.).

TABLE 2B. SINGLE-OPERATOR PRECISION AND RECOVERY FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B).

ANALYTE	MATRIX	UNFORT CONC. ug/L	FORT CONC ug/L	# OF REPLC	MEAN ug/L	MEAN %REC	SD(n-1)	%RSD
Chlorite	RW	<MDL[1]	100	9	96.2	96.2	0.95	0.99
			500	9	523	105	3.13	0.60
	HIW	<MDL	100	9	102	102	2.19	2.15
			500	9	520	104	3.64	0.70
	SW	<MDL	100	9	91.4	91.4	1.22	1.33
			500	9	495	99.0	7.54	1.52
	GW	<MDL	100	9	92.9	92.9	1.65	1.77
			500	9	490	98.1	3.40	0.69
	ClW	<MDL	100	9	87.4	87.4	0.59	0.68
			500	9	485	97.1	6.36	1.31
	CDW	292	100	9	396	---[2]	1.64	0.41
			500	9	811	104	4.00	0.49
	O3W	<MDL	100	9	84.4	84.4	0.46	0.54
			500	9	481	96.1	3.24	0.67
Bromate	RW	<MDL	5.00	9	5.04	101	0.45	8.86
			25.0	9	26.5	106	1.71	6.47
	HIW	<MDL	5.00	9	4.88	97.5	0.95	19.5
			25.0	9	25.6	102	1.37	5.37
	SW	<MDL	5.00	9	4.46	89.2	0.58	13.0
			25.0	9	26.3	105	1.10	4.18
	GW	<MDL	5.00	9	5.10	102	0.50	9.75
			25.0	9	22.2	88.9	1.29	5.81
	ClW	<MDL	5.00	9	4.63	92.6	0.77	16.7
			25.0	9	25.1	100	1.64	6.55
	CDW	<MDL	5.00	9	4.14	82.7	0.62	15.1
			25.0	9	25.1	101	1.28	5.09
	O3W	1.45	5.00	9	5.49	80.9	0.61	11.1
			25.0	9	24.1	90.6	1.13	4.69

RW = Reagent Water
HIW = High Ionic strength Water [see note (2) in Table 1B]
SW = Surface Water
GW = Groundwater
ClW = Chlorinated drinking water
CDW = Chlorine dioxide treated drinking water
O3W = Ozonated drinking water

(1) <MDL indicates less than method detection limit.
(2) Not calculated since amount fortified was less than unfortified native matrix concentration (See 9.4.1.1.).

TABLE 2B. SINGLE-OPERATOR PRECISION AND RECOVERY FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B) (contd.).

ANALYTE	MATRIX	UNFORT CONC. ug/L	FORT CONC ug/L	# OF REPLC	MEAN ug/L	MEAN %REC	SD(n-1)	%RSD
Bromide	RW	<MDL[1]	20.0	9	20.9	104	0.80	3.82
			100	9	107	107	0.60	0.56
	HIW	3.24	20.0	9	21.8	92.5	0.79	3.63
			100	9	105	102	1.05	1
	SW	31.0	20.0	9	51.3	---[2]	0.97	1.9
			100	9	140.	109	1.88	1.35
	GW	151	20.0	9	172	---[2]	0.78	0.45
			100	9	265	---[2]	2.18	0.82
	ClW	16.3	20.0	9	39.3	115	0.64	1.62
			100	9	125	109	2.00	1.6
	CDW	11.5	20.0	9	34.4	115	0.76	2.22
			100	9	125	113	1.24	0.99
	O3W	39.8	20.0	9	65.4	---[2]	3.67	5.61
			100	9	153	113	1.00	0.65
Chlorate	RW	<MDL	100	9	98.3	98.3	0.80	0.82
			500	9	520	104	4.15	0.8
	HIW	<MDL	100	9	86.1	86.1	1.47	1.7
			500	9	502	100.	4.52	0.9
	SW	3.18	100	9	102	98.3	1.57	1.55
			500	9	513	102	7.11	1.39
	GW	<MDL	100	9	93.5	93.5	2.00	2.14
			500	9	510	102	3.84	0.75
	ClW	34.4	100	9	136	102	1.01	0.74
			500	9	549	103	3.11	0.57
	CDW	121	100	9	223	---[2]	3.20	1.44
			500	9	651	106	3.50	0.54
	O3W	6.15	100	9	106	100	1.20	1.13
			500	9	523	103	2.45	0.47

RW = Reagent Water
HIW = High Ionic strength Water [see note (2) in Table 1B]
SW = Surface Water
GW = Groundwater
ClW = Chlorinated drinking water
CDW = Chlorine dioxide treated drinking water
O3W = Ozonated drinking water

(1) <MDL indicates less than method detection limit.
(2) Not calculated since amount fortified was less than unfortified native matrix concentration (See 9.4.1.1.).

TABLE 2B. SINGLE-OPERATOR PRECISION AND RECOVERY FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B)(contd.).

ANALYTE	MATRIX	FORT CONC mg/L	# OF REPLC	MEAN mg/L	MEAN %REC	SD(n-1)	%RSD
Surrogate: DCA	RW	5.00	9	5.11	102	0.93	0.91
(see NOTE below)				4.98	99.5	0.69	0.69
	HIW	5.00	9	5.00	100	0.79	0.79
				4.96	99.2	1.76	1.78
	SW	5.00	9	4.95	98.9	0.70	0.7
				4.99	99.8	1.60	1.61
	GW	5.00	9	5.12	102	0.50	0.49
				5.13	103	0.50	0.49
	ClW	5.00	9	5.15	103	1.73	1.68
				5.13	103	1.12	1.09
	CDW	5.00	9	5.01	100	1.02	1.02
				5.04	101	1.08	1.07
	O3W	5.00	9	4.99	99.8	0.70	0.7
				5.11	101	0.53	0.52

RW = Reagent Water
HIW = High Ionic strength Water [see note (2) in Table 1B]
SW = Surface Water
GW = Groundwater
ClW = Chlorinated drinking water
CDW = Chlorine dioxide treated drinking water
O3W = Ozonated drinking water

NOTE: The surrogate DCA was fortified at 5 mg/L but due to concerns about measuring trace concentrations of bromide with such high concentration of the neighboring surrogate peak, the recommended fortified concentration for the surrogate has been reduced to 1.00 mg/L.

TABLE 3A. STABILITY STUDY RESULTS FOR THE COMMON ANIONS (PART A).

ANALYTE	Preservative	Matrix	UNFORT CONC. mg/L	FORT CONC mg/L	Analyte % Recovery Day 0	Day 14	Day 28	See Note
Fluoride	None	RW	<MDL	2.00	89.8	88.3	88.4	
		SW	0.140	2.00	79.9	80.2	80.0	
		GW	0.280	2.00	84.7	87.8	87.0	
		CDW	0.929	2.00	82.9	83.6	81.6	
Chloride	None	RW	<MDL	50.0	98.8	99.1	98.1	
		SW	12.0	50.0	93.4	93.5	92.8	
		GW	56.6	50.0	87.6	87.6	86.5	
		CDW	16.0	50.0	97.9	98.4	97.8	
Nitrite-N	None	RW	<MDL	1.00	85.2	85.5	83.6	
		SW	<MDL	1.00	77.8	76.6	11.9	(1)
		GW	<MDL	1.00	88.2	85.4	56.1	(1)
		CDW	<MDL	1.00	71.9	71.7	73.9	(2)
Bromide	None	RW	<MDL	0.500	95.5	97.0	96.2	
		SW	0.028	0.500	87.5	88.3	86.7	
		GW	0.153	0.500	96.9	96.0	96.1	
		CDW	<MDL	0.500	85.7	87.1	89.2	(2)
Nitrate-N	None	RW	<MDL	10.0	94.9	94.7	94.2	
		SW	2.12	10.0	87.6	87.0	88.7	
		GW	<MDL	10.0	96.5	96.5	95.5	
		CDW	1.64	10.0	92.3	93.3	91.9	
Phosphate-P	None	RW	<MDL	10.0	96.3	95.8	95.2	
		SW	<MDL	10.0	86.9	86.4	85.1	
		GW	<MDL	10.0	62.8	93.1	89.5	(3)
		CDW	<MDL	10.0	91.6	91.4	90.8	
Sulfate	None	RW	<MDL	50.0	89.6	89.3	89.1	
		SW	47.8	50.0	89.0	89.0	88.1	
		GW	105	50.0	97.5	97.3	96.5	
		CDW	57.8	50.0	94.3	94.9	93.8	

NOTES:

(1) Degradation apparent.

(2) Analyte recovery will be adversely effected by reactions with free chlorine.

(3) Phosphate recovery on day 0 is believed to have been adversely effected by biological degradation since the sample sat in the autosampler for 18 hrs prior to analysis

TABLE 3B STABILITY STUDY RESULTS FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B).

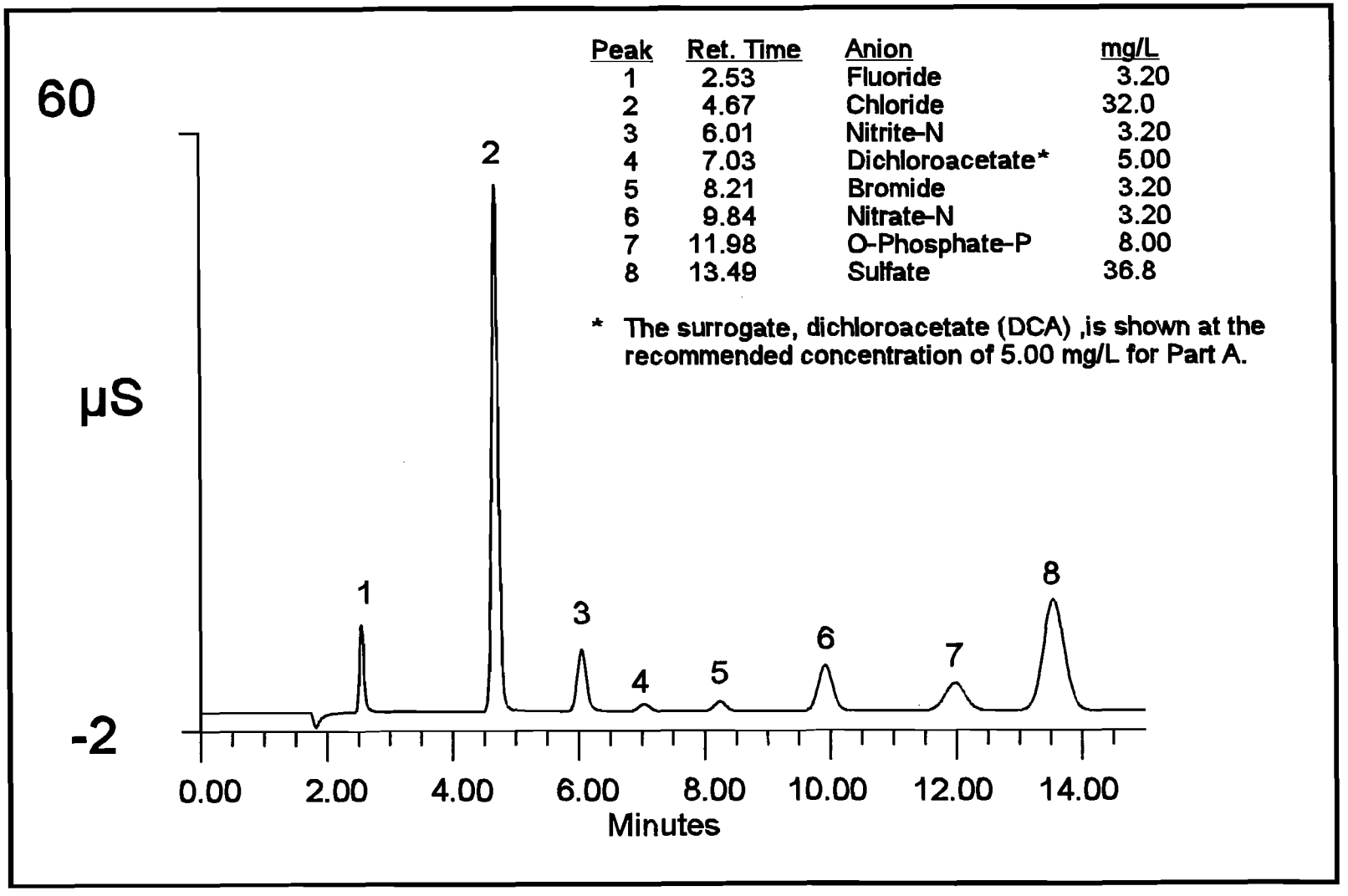
ANALYTE	Preservative	Matrix	UNFORT CONC. ug/L	FORT CONC ug/L	Analyte % Recovery Day 0	Day 3	Day 10	Day 30	See Note
Chlorite	None	RW	<MDL	500	99.8	100	104	94.3	
		HIW	<MDL	500	99.3	98.5	106	89.3	
		SW	<MDL	500	92	88.5	82.	75.1	(1)
		GW	<MDL	500	93.9	94.5	96.	91.7	
		ClW	<MDL	500	93.7	NA[1]	90.	84.7	(2,3)
		CDW	286	500	98.6	101	91.	77.5	(1,3)
		O3W	<MDL	500	10	NA	82.	90.5	(2)
Chlorite	EDA	RW	<MDL	500	101	101	104	95.3	
		HIW	<MDL	500	98.4	98.7	104	95.4	
		SW	<MDL	500	98.3	97.3	97.	92.7	
		GW	<MDL	500	97.7	97.1	97.	92.6	
		ClW	<MDL	500	98.9	NA	96.	92.6	(2)
		CDW	297	500	103	107	102	94.5	
		O3W	<MDL	500	105	NA	96.	91.9	(2)
Bromate	None	RW	<MDL	25.0	93.6	94.1	110	96.1	
		HIW	<MDL	25.0	100	86.0	105	87.7	
		SW	<MDL	25.0	98.7	95.1	105	102	
		GW	<MDL	25.0	79.4	92.4	77.	82.2	
		ClW	<MDL	25.0	102	NA	101	103	(2)
		CDW	<MDL	25.0	104	96.8	98.	92.1	
		O3W	2.27	25.0	87.3	NA	84.	99.9	(2)
Bromate	EDA	RW	<MDL	25.0	97.3	95.3	99.	102	
		HIW	<MDL	25.0	86.9	86.1	107	91.2	
		SW	<MDL	25.0	100	104	103	94.9	
		GW	<MDL	25.0	83.2	101	88.	88.3	
		ClW	<MDL	25.0	105	NA	101	102	(2)
		CDW	<MDL	25.0	117	97.3	98.	83.9	
		O3W	2.32	25.0	92.6	NA	84.	88.9	(2)

See bottom of next page for explanation of notes

TABLE 3B. STABILITY STUDY RESULTS FOR THE INORGANIC DISINFECTION BY-PRODUCTS (PART B)(contd.)

ANALYTE	Preservative	Matrix	UNFORT CONC. ug/L	FORT CONC ug/L	Analyte % Recovery Day 0	Day 3	Day 10	Day 30	See Note
Bromide	None	RW	<MDL	100	99.4	97.2	107	101	
		HIW	<MDL	100	102	103	105	105	
		SW	30.6	100	102	97.1	107	99.1	
		GW	149	100	97.7	95.3	109	100	
		ClW	4.73	100	8.9	NA(1)	37.	11.4	(2,3)
		CDW	<MDL	100	5.78	23.1	38.	51.3	(3)
		O3W	30.4	100	98.3	NA	120	108	(2)
Bromide	EDA	RW	<MDL	100	98.4	98.6	107	100	
		HIW	<MDL	100	104	103	106	105	
		SW	30.5	100	99.5	98.2	107	100	
		GW	149	100	100	97	114	97.7	
		ClW	11.9	100	101	NA	115	97.4	(2,3)
		CDW	6.14	100	101	96.5	119	110	(3)
		O3W	31.0	100	97.3	NA	122	102	(2)
Chlorate	None	RW	<MDL	500	102	102	105	97.4	
		HIW	<MDL	500	96.5	97.8	101	95.4	
		SW	5.84	500	99.8	97.8	100	96	
		GW	<MDL	500	99.5	98.7	101	99.8	
		ClW	37.8	500	102	NA	104	98.2	(2)
		CDW	125	500	102	99.9	104	99.6	
		O3W	8.34	500	100	NA	103	97.3	(2)
Chlorate	EDA	RW	<MDL	500	104	98.6	103	97.3	
		HIW	<MDL	500	97.3	103	100	95	
		SW	6.70	500	99.7	98.2	99.	95.6	
		GW	<MDL	500	102	97	101	99.3	
		ClW	38.2	500	101	NA	102	96.1	(2)
		CDW	123	500	102	96.5	105	97.7	
		O3W	8.62	500	98.4	NA	103	96.4	(2)

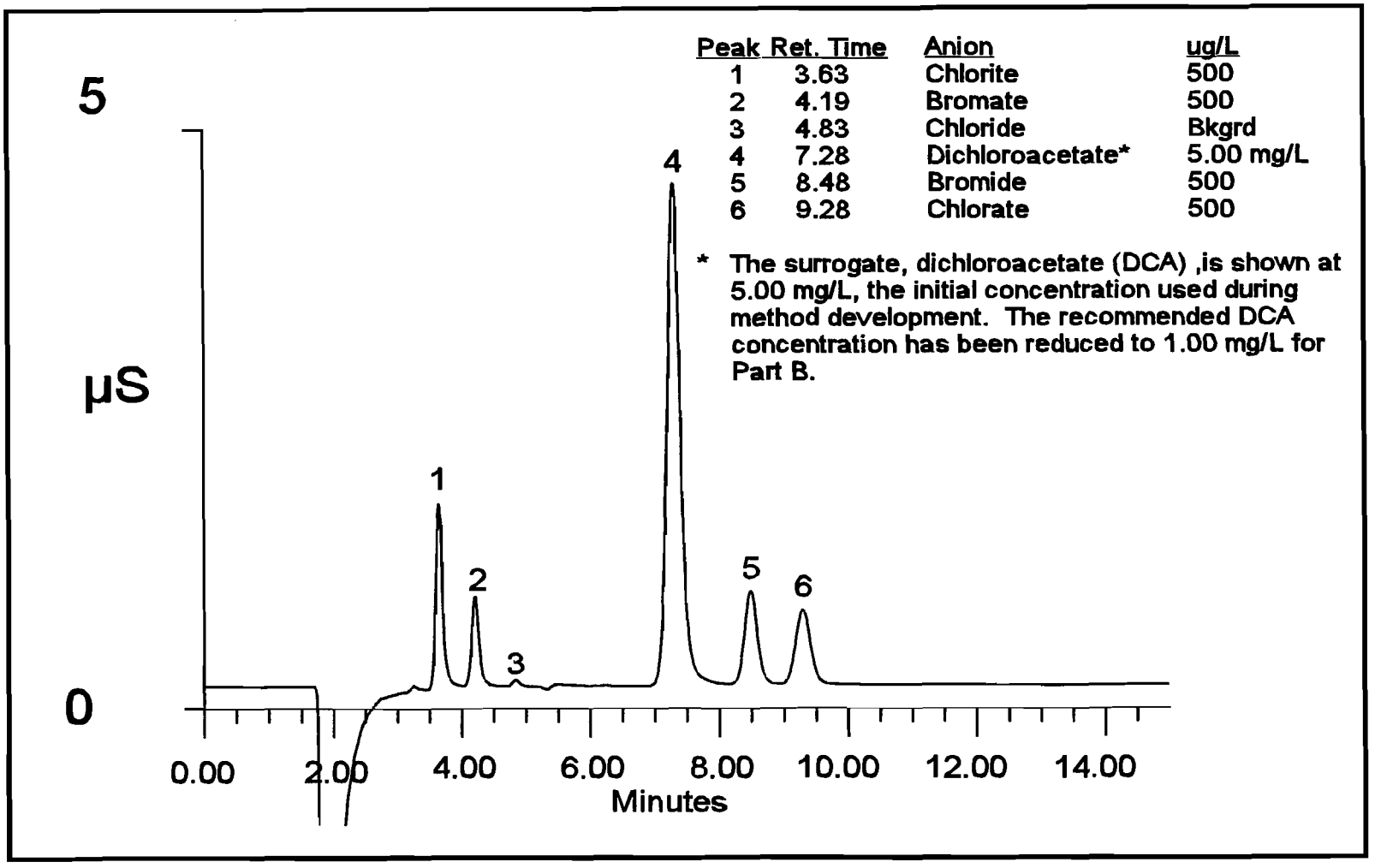
NOTES:
(1) Degradation in the unpreserved matrix is apparent.
(2) NA indicates "NOT ANALYZED"
(3) Analyte recovery will be adversely effected by reactions with free chlorine.



Peak	Ret. Time	Anion	mg/L
1	2.53	Fluoride	3.20
2	4.67	Chloride	32.0
3	6.01	Nitrite-N	3.20
4	7.03	Dichloroacetate*	5.00
5	8.21	Bromide	3.20
6	9.84	Nitrate-N	3.20
7	11.98	O-Phosphate-P	8.00
8	13.49	Sulfate	36.8

* The surrogate, dichloroacetate (DCA) ,is shown at the recommended concentration of 5.00 mg/L for Part A.

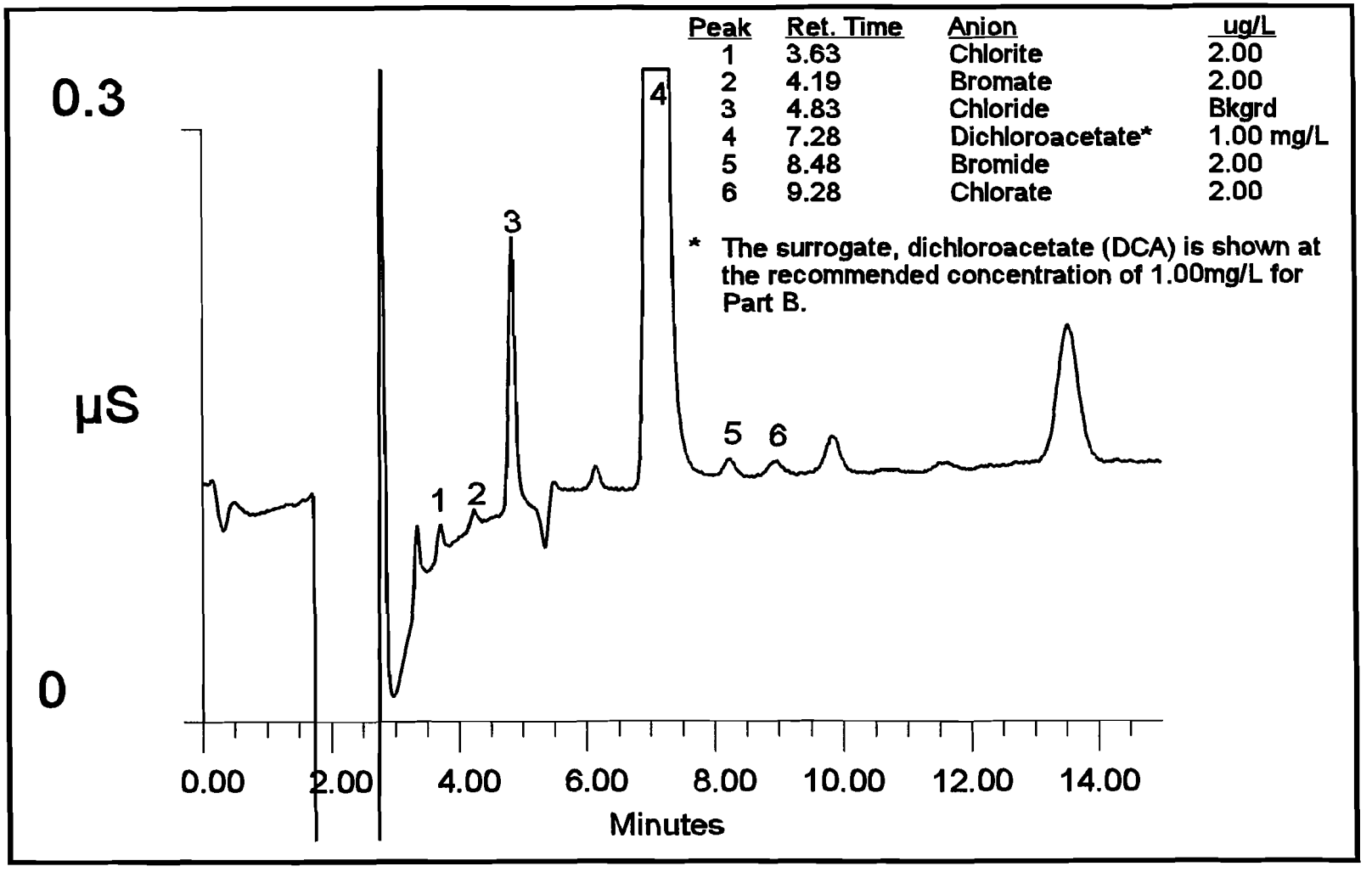
Figure 1. Chromatogram showing separation of the Part A common anions on the AS9-HC column. See Table 1A for analysis conditions.



Peak	Ret. Time	Anion	ug/L
1	3.63	Chlorite	500
2	4.19	Bromate	500
3	4.83	Chloride	Bkgrd
4	7.28	Dichloroacetate*	5.00 mg/L
5	8.48	Bromide	500
6	9.28	Chlorate	500

* The surrogate, dichloroacetate (DCA) ,is shown at 5.00 mg/L, the initial concentration used during method development. The recommended DCA concentration has been reduced to 1.00 mg/L for Part B.

Figure 2 Chromatogram showing separation of the Part B inorganic DBPs and bromide on the AS9-HC column. See Table 1B for analysis conditions.



Peak	Ret. Time	Anion	ug/L
1	3.63	Chlorite	2.00
2	4.19	Bromate	2.00
3	4.83	Chloride	Bkgrd
4	7.28	Dichloroacetate*	1.00 mg/L
5	8.48	Bromide	2.00
6	9.28	Chlorate	2.00

* The surrogate, dichloroacetate (DCA) is shown at the recommended concentration of 1.00mg/L for Part B.

Figure 3. Chromatogram of the inorganic DBPs and bromide (Part B) during the MDL determination in reagent water. See Table 1B for analysis conditions.

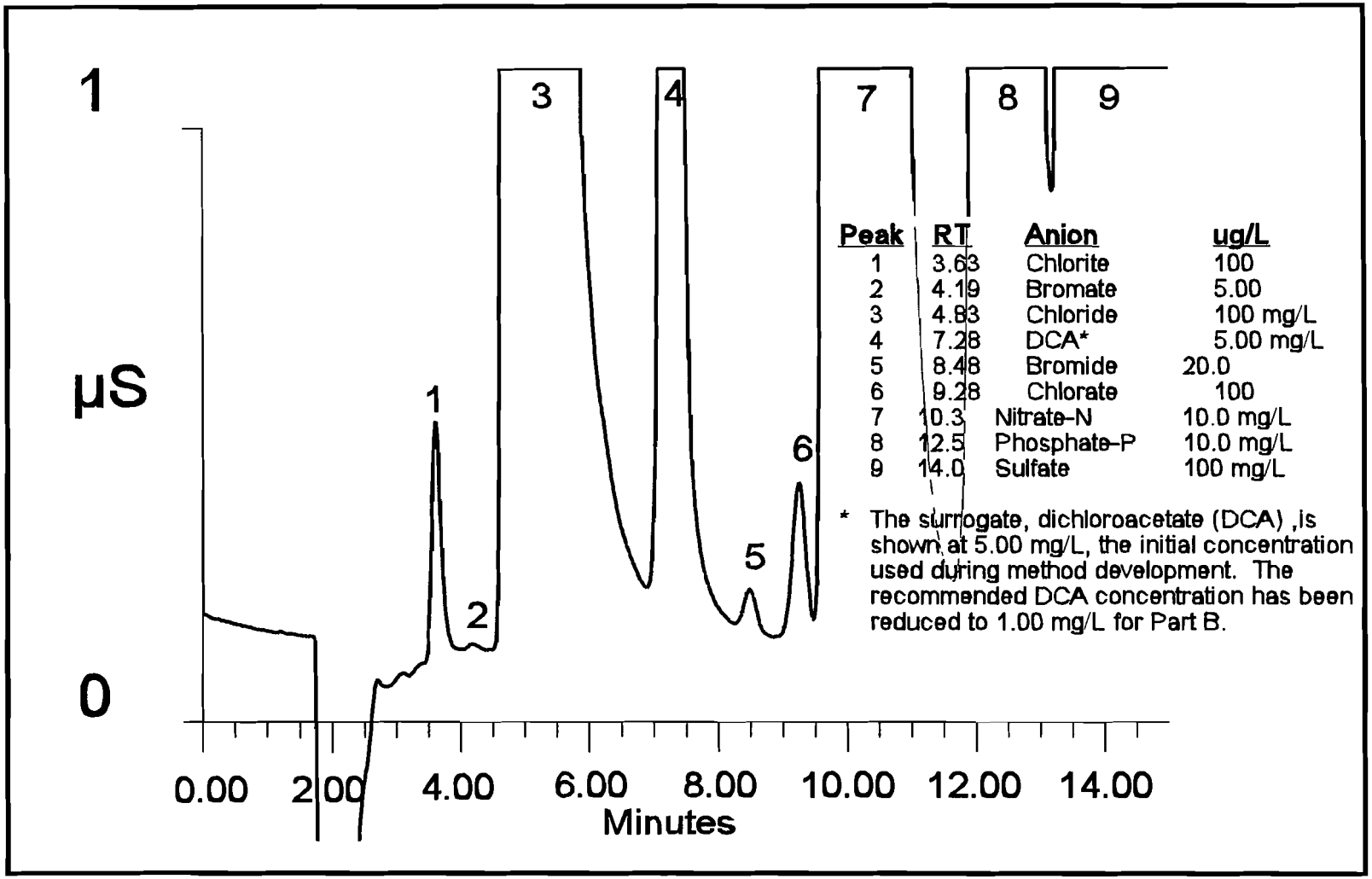


Figure 4. Chromatogram of the inorganic DBPs and bromide (Part B) in high ionic strength water (HIW). See Table 1B for analysis conditions.

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SULFIDE

Method 376.2 (Colorimetric, Methylene Blue)

STORET NO. Total 00745
Dissolved 00746

1. Scope and Application
   1.1 This method is applicable to the measurement of total and dissolved sulfides in drinking, surface and saline waters, domestic and industrial wastes.
   1.2 Acid insoluble sulfides are not measured by this method. Copper sulfide is the only common sulfide in this class.
   1.3 The method is suitable for the measurement of sulfide in concentrations up to 20 mg/l.
2. Summary of Method
   2.1 Sulfide reacts with dimethyl-p-phenylenediamine (p-aminodimethyl aniline) in the presence of ferric chloride to produce methylene blue, a dye which is measured at a wavelength maximum of 625 nm.
3. Comments
   3.1 Samples must be taken with a minimum of aeration. Sulfide may be volatilized by aeration and any oxygen inadvertently added to the sample may convert the sulfide to an unmeasurable form. Dissolved oxygen should not be present in any water used to dilute standards.
   3.2 The analysis must be started immediately.
   3.3 Color and turbidity may interfere with observations of color or with photometric readings.
4. Apparatus
   4.1 Matched test tubes, approximately 125 mm long and 15 mm O.D.
   4.2 Droppers, delivering 20 drops/ml. To obtain uniform drops, hold dropper in vertical position and allow drops to form slowly.
   4.3 Photometer, use either 4.3.1 or 4.3.2.
      4.3.1 Spectrophotometer, for use at 625 nm with cells of 1 cm and 10 cm light path.
      4.3.2 Filter photometer, with filter providing transmittance near 625 nm.
5. Reagents
   5.1 Amino-sulfuric acid stock solution: Dissolve 27 g N,N-dimethyl-p-phenylenediamine oxalate (p-aminodimethylaniline) in a cold mixture of 50 ml conc. H_2SO_4 and 20 ml distilled water in a 100 ml volumetric flask. Cool and dilute to the mark. If dark discard and purchase fresh reagent. Store in dark glass bottle.
   5.2 Amino-sulfuric acid reagent: Dissolve 25 ml amino-sulfuric acid stock solution (5.1) with 975 ml of 1 + 1 H_2SO_4 (5.4). Store in a dark glass bottle. This solution should be clear.
   5.3 Ferric chloride solution: Dissolve 100 g $FeCl_3 \cdot 6H_2O$ in 40 ml distilled water.

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5.4 Sulfuric acid solution, H_2SO_4, 1+1

5.5 Diammonium hydrogen phosphate solution: Dissolve 400 g $(NH_4)_2HPO_4$ in 800 ml distilled water.

5.6 Methylene blue solution I: Dissolve 1.0 g of methylene blue in distilled water in a 1 liter volumetric flask and dilute to the mark. Use U.S.P. grade or one certified by the Biological Stain Commission. The dye content reported on the label should be 84% or more. Standardize (5.8) against sulfide solutions of known strength and adjust concentration so that 0.05 ml (1 drop) equals 1.0 mg/l sulfide.

5.7 Methylene blue solution II: Dilute 10.00 ml of adjusted methylene blue solution I (5.6) to 100 ml with distilled water in a volumetric flask.

5.8 Standardization of methylene blue I solution:

5.8.1 Place several grams of clean, washed crystals of sodium sulfide $Na_2S \cdot 9H_2O$ in a small beaker.

5.8.2 Add somewhat less than enough water to cover the crystals.

5.8.3 Stir occasionally for a few minutes. Pour the solution into another vessel. This reacts slowly with oxygen but the change is insignificnat over a few hours. Make the solution daily.

5.8.4 To 1 liter of distilled water add 1 drop of solution and mix.

5.8.5 Immediately determine the sulfide concentration by the methylene blue procedure (6) and by the titrimetric iodide procedure (Method 376.1, this manual).

5.8.6 Repeat using more than one drop of sulfide solution or less water until at least five tests have been made in the range of 1 to 8 mg/l sulfide.

5.8.7 Calculate the average percent error of the methylene blue procedure (6) as compared to the titrimetric iodide procedure (Method 376.1).

5.8.8 Adjust by dilution or by adding more dye to methylene blue solution I (5.6).

6. Procedure

6.1 Color development

6.1.1 Transfer 7.5 ml of sample to each of two matched test tubes using a special wide tipped pipet or filling to a mark on the test tubes.

6.1.2 To tube A add 0.5 ml amine-sulfuric acid reagent (5.2) and 0.15 ml (3 drops) $FeCl_3$ solution (5.3).

6.1.3 Mix immediately by inverting the tube only once.

6.1.4 To tube B add 0.5 ml 1+1 H_2SO_4 (5.4) and 0.15 ml (3 drops) $FeCl_3$ solution (5.3) and mix.

6.1.5 Color will develop in tube A in the presence of sulfide. Color development is usually complete in about 1 minute, but a longer time is often required for the fading of the initial pink color.

6.1.6 Wait 3 to 5 minutes.

6.1.7 Add 1.6 ml $(NH_4)_2HPO_4$ solution (5.5) to each tube.

6.1.8 Wait 3 to 5 minutes and make color comparisons. If zinc acetate was used wait at least 10 minutes before making comparison.

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6.2 Color comparison

6.2.1 Visual

6.2.1.1 Add methylene blue solution I (5.6) and/or II (5.7) (depending on sulfide concentration and accuracy desired) dropwise to tube B (6.1.4) until the color matches that developed in the first tube.

6.2.1.2 If the concentration exceeds 20 mg/l, repeat 6.2.1.1 using a portion of the sample diluted to one tenth.

6.2.2 Photometric

6.2.2.1 Use a 1 cm cell for 0.1 to 2.0 mg/l. Use a 10 cm cell for up to 20 mg/l.

6.2.2.2 Zero instrument with portion of sample from tube B (6.1.4).

6.2.2.3 Prepare calibration curve from data obtained in methylene blue standardization (5.8), plotting concentraton obtained from titrimetric iodide procedure (Method 376.1) versus absorbance. A straight line relationship can be assumed from 0 to 1.0 mg/l.

6.2.2.4 Read the sulfide concentration from the calibration curve.

7. Calculations

7.1 Visual comparison: With methylene blue solution I (5.6), adjusted so that 0.05 ml (1 drop) = 1.0 mg/l sulfide and a 7.5 ml sample

mg/l sulfide = number drops methylene blue solution I (5.6) + 0.1 x [number of drops methylene blue solution II (5.7)].

7.2 Photometric: see 6.2.2.4

8. Precision and Accuracy:

8.1 The precision has not been determined. The accuracy is about ±10%.

Bibliography

1. Standard Methods for he Examination of Water and Wastewater, 14th edition, p. 503, Method 428C (1975).

METHOD 5030B

PURGE-AND-TRAP FOR AQUEOUS SAMPLES

1.0 SCOPE AND APPLICATION

1.1 This method describes a purge-and-trap procedure for the analysis of volatile organic compounds (VOCs) in aqueous samples and water miscible liquid samples. It also describes the analysis of high concentration soil and waste sample extracts prepared in Method 5035. The gas chromatographic determinative steps are found in Methods 8015 and 8021. The method is also applicable to GC/MS Method 8260.

1.2 Method 5030 can be used for most volatile organic compounds that have boiling points below 200°C and are insoluble or slightly soluble in water. Volatile water-soluble compounds can be included in this analytical technique; however, quantitation limits (by GC or GC/MS) are approximately ten times higher because of poor purging efficiency. The method is also limited to compounds that elute as sharp peaks from a GC column packed with graphitized carbon lightly coated with a carbowax or a coated capillary column. Such compounds include low molecular weight halogenated hydrocarbons, aromatics, ketones, nitriles, acetates, acrylates, ethers, and sulfides.

1.3 Method 5030, in conjunction with Method 8015 (GC/FID), may be used for the analysis of the aliphatic hydrocarbon fraction in the light ends of total petroleum hydrocarbons, e.g., gasoline. For the aromatic fraction (BTEX), use Method 5030 and Method 8021 (GC/PID). A total determinative analysis of gasoline fractions may be obtained using Methods 8021 GC/PID) in series with Method 8015.

1.4 Water samples can be analyzed directly for volatile organic compounds by purge-and-trap extraction and gas chromatography. Higher concentrations of these analytes in water can be determined by direct injection of the sample into the chromatographic system or by dilution of the sample prior to the purge-and-trap process.

1.5 This method is restricted to use by or under the supervision of trained analysts. Each analyst must demonstrate the ability to generate acceptable results with this method.

2.0 SUMMARY OF METHOD

2.1 Aqueous Samples: An inert gas is bubbled through a portion of the aqueous sample at ambient temperature, and the volatile components are efficiently transferred from the aqueous phase to the vapor phase. The vapor is swept through a sorbent column where the volatile components are adsorbed. After purging is completed, the sorbent column is heated and backflushed with inert gas to desorb the components onto a gas chromatographic column.

2.2 High Concentration Extracts from Method 5035: An aliquot of the extract prepared in Method 5035 is combined with organic free reagent water in the purging chamber. It is then analyzed by purge-and-trap GC or GC/MS following the normal aqueous method.

3.0 INTERFERENCES

3.1 Impurities in the purge gas, and from organic compounds out-gassing from the plumbing ahead of the trap, account for the majority of contamination problems. The analytical system must be demonstrated to be free from contamination under the conditions of the analysis by running laboratory reagent blanks. The use of non-polytetrafluoroethylene (non-PTFE) plastic coating, non-PTFE thread sealants, or flow controllers with rubber components in the purging device must be avoided, since such materials out-gas organic compounds which will be concentrated in the trap during the purge operation. These compounds will result in interferences or false positives in the determinative step.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly methylene chloride and fluorocarbons) through the septum seal of the sample vial during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and handling protocols serves as a check on such contamination.

3.3 Contamination by carryover can occur whenever high-concentration and low-concentration samples are analyzed sequentially. Whenever an unusually concentrated sample is analyzed, it should be followed by an analysis of organic-free reagent water to check for cross-contamination. The trap and other parts of the system are subject to contamination. Therefore, frequent bake-out and purging of the entire system may be required.

3.4 The laboratory where volatiles analysis is performed should be completely free of solvents. Special precautions must be taken to determine methylene chloride. The analytical and sample storage areas should be isolated from all atmospheric sources of methylene chloride. Otherwise random background levels will result. Since methylene chloride will permeate through PTFE tubing, all GC carrier gas lines and purge gas plumbing should be constructed of stainless steel or copper tubing. Laboratory workers' clothing previously exposed to methylene chloride fumes during common liquid/liquid extraction procedures can contribute to sample contamination. The presence of other organic solvents in the laboratory where volatile organics are analyzed will also lead to random background levels and the same precautions must be taken.

4.0 APPARATUS AND MATERIALS

4.1 Microsyringes - 10-µL, 25-µL, 100-µL, 250-µL, 500-µL, and 1,000-µL. These syringes should be equipped with a 20-gauge (0.006 in ID) needle having a length sufficient to extend from the sample inlet to within 1 cm of the glass frit in the purging device. The needle length will depend upon the dimensions of the purging device employed.

4.2 Syringe valve - Two-way, with Luer ends (three each), if applicable to the purging device.

4.3 Two 5-mL glass hypodermic syringes with Luer-Lok tip (other sizes are acceptable depending on sample volume used).

4.4 Volumetric flasks, Class A - 10-mL and 100-mL, with ground-glass stoppers.

4.5 Vials - 2-mL, for GC autosampler.

4.6 Purge-and-trap device

The purge-and-trap device consists of three separate pieces of equipment: the sample purger, the trap, and the desorber. Several complete devices are commercially available.

4.6.1 The recommended purging chamber is designed to accept 5-mL samples with a water column at least 3 cm deep. The gaseous headspace between the water column and the trap must have a total volume of less than 15 mL. The purge gas must pass through the water column as finely divided bubbles with a diameter of less than 3 mm at the origin. The purge gas must be introduced no more than 5 mm from the base of the water column. The sample purger, illustrated in Figure 1, meets these design criteria. Alternate sample purge devices may be used, provided equivalent or improved performance is demonstrated.

4.6.2 The trap used to develop this method was 25 cm long with an inside diameter of 0.105 in. Starting from the inlet, the trap contains the following amounts of adsorbents: 1/3 of 2,6-diphenylene oxide polymer, 1/3 of silica gel, and 1/3 of coconut charcoal. It is recommended that 1.0 cm of methyl silicone-coated packing be inserted at the inlet to extend the life of the trap (see Figures 2 and 3). If it is not necessary to analyze for dichlorodifluoromethane or other fluorocarbons of similar volatility, the charcoal can be eliminated and the polymer increased to fill 2/3 of the trap. If only compounds boiling above 35°C are to be analyzed, both the silica gel and charcoal can be eliminated and the polymer increased to fill the entire trap. Before initial use, the trap should be conditioned overnight at 180°C by backflushing with an inert gas flow of at least 20 mL/min. Vent the trap effluent to the hood, not to the analytical column. Prior to daily use, the trap should be conditioned for 10 min at 180°C with backflushing. The trap may be vented to the analytical column during daily conditioning; however, the column must be run through the temperature program prior to analysis of samples.

4.6.3 The desorber must be capable of rapidly heating the trap to 180°C for desorption. The polymer section of the trap should not be heated higher than 180°C, and the remaining sections should not exceed 220°C during bake-out mode. The desorber design illustrated in Figures 2 and 3 meet these criteria.

4.6.4 The purge-and-trap device may be assembled as a separate unit or may be coupled to a gas chromatograph, as shown in Figures 4 and 5.

4.6.5 Trap Packing Materials

4.6.5.1 2,6-Diphenylene oxide polymer - 60/80 mesh, chromatographic grade (Tenax GC or equivalent).

4.6.5.2 Methyl silicone packing - OV-1 (3%) on Chromosorb-W, 60/80 mesh or equivalent.

4.6.5.3 Silica gel - 35/60 mesh, Davison, grade 15 or equivalent.

4.6.5.4 Coconut charcoal - Prepare from Barnebey Cheney, CA-580-26, or equivalent, by crushing through 26 mesh screen.

4.6.5.5 Alternate Trap Materials

A number of hydrophobic carbon molecular sieve and graphitized carbon black materials have been developed. Various combinations of these materials have been shown to provide retention properties similar to the Tenax\Silica gel\Carbon trap. Alternate trap construction with such materials is allowed, provided that the adsorption and desorption characteristics obtained achieve equivalent or better method sensitivity and precision in comparison to the performance documented in the Determinative Method.

4.6.5.5.1 The following alternatives have been shown to be viable for most analytes of concern:

7.6-cm Carbopack™ B/1.3-cm Carboseive™ S-III
VOCARB 3000 - 10.0-cm Carbopack™ B/6.0-cm Carboxin ™ 1000/1.0-cm Carboxin™ 1001
VOCARB 4000 - 8.5-cm Carbopack™ C/10.0-cm Carbopack ™ B/6.0-cm Carboxin™ 1000/1.0-cm Carboxin™ 1001

These combinations require rapid heating to desorption temperatures of 245°C to 270°C (follow manufacturer's instructions). At these increased temperatures, catalytic and thermal decomposition of analytes has been reported. The VOCARB 4000 combination has also been demonstrated to catalytically break down 2-chloroethyl vinyl ether, and to partially decompose 2,2-dichloropropane. Bromoform and bromomethane have shown some thermal decomposition.

4.6.5.5.2 The amount of thermal decomposition products formed must be routinely tracked by daily monitoring of the formation of chloromethane and bromomethane. A daily check standard containing surrogates, internal standards, and 20 µg/L bromoform must be analyzed prior to the analysis of the daily check standard. If levels of chloromethane or bromomethane exceed 0.5 µg/L, then the trap may be too contaminated with salts or tightly bound contamination for analysis to continue. The trap must be replaced and the system recalibrated.

NOTE: Even newly constructed traps may have become contaminated prior to their first use from airborne vapors. These highly adsorptive materials must be kept tightly sealed in an area of minimum organic vapor contamination.

4.7 Heater or heated oil bath - capable of maintaining the purging chamber to within 1°C, over a temperature range from ambient to 100°C.

4.8 Capillary GC Columns - Any GC column that meets the performance specifications of the determinative method may be used. See the specific determinative method for recommended columns, conditions and retention times.

4.8.1 The wide-bore columns have the capacity to accept the standard gas flows from the trap during thermal desorption, and chromatography can begin with the onset of thermal desorption. Depending on the pumping capacity of the MS, an additional interface between the end of the column and the MS may be required. An open split interface , an all-glass jet

separator, or a cryogenic (Sec. 4.8.2) device are acceptable interfaces. The type of interface and its adjustments can have a significant impact on the method detection limits. Other interfaces can be used if the performance specifications described in this method can be achieved.

4.8.2 A system using a narrow-bore column will require lower gas flows of approximately 2 - 4 mL/minute. Because of these low desorption flows, early eluting analytes need to be refocussed to elute in a narrow band. This refocussing may be carried out by using a cryogenic interface. This type of interface usually uses liquid nitrogen to condense the desorbed sample components in a narrow band on an uncoated fused silica precolumn. When all components have been desorbed form the trap, the interface is rapidly heated under a stream of carrier gas to transfer the analytes to the analytical column. The end of the analytical column should be placed within a few mm of the MS ion source. A potential problem with this interface is blockage of the interface by ice caused by desorbing water from the trap. This condition will result in a major loss in sensitivity and chromatographic resolution. Low surrogate compound recoveries can be a sign that this is occurring.

5.0 REAGENTS

5.1 Organic-free reagent water - All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.2 See the determinative method and Method 5000 for guidance on internal and surrogate standards.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 Refer to the introductory material to this chapter, Organic Analytes, Sec. 4.1. Samples should be stored in capped bottles, with minimum headspace, at 4°C or less in an area free of solvent fumes. The size of any bubble caused by degassing upon cooling the sample should not exceed 5 - 6 mm. When a bubble is present, also observe the cap and septum to ensure that a proper seal was made at time of sampling. Is there any evidence of leakage? If the sample was improperly sealed, the sample should be discarded.

6.2 All samples should be analyzed within 14 days of collection. Samples not analyzed within this period must be noted and data are considered minimum values.

7.0 PROCEDURE

7.1 The purge-and-trap technique for aqueous samples is found in Sec. 7.2 and guidance for analysis of solvent extracts from the High Concentration Method in Method 5035 is found in Sec. 7.3. The gas chromatographic determinative steps are found in Methods 8015 and 8021. The method is also applicable to GC/MS Method 8260. For the analysis of gasoline, use Method 8021 with GC/PID for BTEX in series with Method 8015 with the GC/FID detector for hydrocarbons.

7.2 This section provides guidance on the analysis of aqueous samples and samples that are water miscible, by purge-and-trap analysis.

7.2.1 Initial calibration

Prior to using this introduction technique for any GC method, the system must be calibrated. General calibration procedures are discussed in Method 8000, while the specific determinative methods and Method 5000 give details on preparation of standards. The GC/MS methods require instrument tuning prior to proceeding with calibration.

7.2.1.1 Assemble a purge-and-trap device that meets the specification in Sec. 4.6. Condition the Tenax trap overnight at 180°C (condition other traps at the manufacturers recommended temperature) in the purge mode with an inert gas flow of at least 20 mL/min. Prior to use, condition the trap daily for 10 min while backflushing at 180°C with the column at 220°C.

7.2.1.2 Connect the purge-and-trap device to a gas chromatograph or gas chromatograph/mass spectrometer system.

7.2.1.3 Prepare the final solutions containing the required concentrations of calibration standards, including surrogate standards, directly in the purging device. Add 5.0 mL of organic-free reagent water to the purging device. The organic-free reagent water is added to the purging device using a 5-mL glass syringe (a 10-mL or 25-mL syringe may be used if preferred) fitted with a 15-cm 20-gauge needle. The needle is inserted through the sample inlet shown in Figure 1. The internal diameter of the 14-gauge needle that forms the sample inlet will permit insertion of the 20-gauge needle. Next, using a 10-µL or 25-µL micro-syringe equipped with a long needle (Sec. 4.1), take a volume of the secondary dilution solution containing appropriate concentrations of the calibration standards. Add the aliquot of calibration solution directly to the organic-free reagent water in the purging device by inserting the needle through the sample inlet. When discharging the contents of the micro-syringe, be sure that the end of the syringe needle is well beneath the surface of the organic-free reagent water. Similarly, add 10.0 µL of the internal standard solution. Close the 2-way syringe valve at the sample inlet. (The calibration standard, internal standard and surrogate standard may be added directly to the organic free reagent water in the syringe prior to transferring the water to the purging device, see Sec. 7.2.4.7).

7.2.1.4 Follow the purge-and-trap analysis as outlined in Sec. 7.2.4.

7.2.1.5 Calculate response factors (RF) or calibration factors (CF) for each analyte of interest using the procedure described in Method 8000.

7.2.1.6 The average CF (external standards) or RF (internal standards) must be calculated for each compound. For GC/MS analysis, a system performance check must be made before this calibration curve is used (see Method 8260). If the purge-and-trap procedure is used with Method 8021, evaluate the response for the following four compounds: chloromethane; 1,1-dichloroethane; bromoform; and 1,1,2,2-tetrachloroethane. They are used to check for proper purge flow and to check for degradation caused by contaminated lines or active sites in the system.

7.2.1.6.1 Chloromethane: This compound is the most likely compound to be lost if the purge flow is too fast.

7.2.1.6.2 Bromoform: This compound is one of the compounds most likely to be purged very poorly if the purge flow is too slow. Cold spots and/or active sites in the transfer lines may adversely affect response.

7.2.1.6.3 1,1,2,2-Tetrachloroethane and 1,1-dichloroethane: These compounds are degraded by contaminated transfer lines in purge-and-trap systems and/or active sites in trapping materials.

7.2.1.7 The analytes in Method 8021 normally are not as strongly affected by small changes in purge flow or system contamination. When analyzing for very late eluting compounds with Method 8021 (i.e., hexachlorobutadiene, 1,2,3-trichlorobenzene, etc.), cross contamination and memory effects from a high concentration sample or even the standard are a common problem. Extra rinsing of the purge chamber after analysis normally corrects this. The newer purge-and-trap systems often overcome this problem with better bakeout of the system following the purge-and-trap process. Also, the charcoal traps retain less moisture and decrease the problem.

7.2.2 Calibration verification: Refer to Method 8000 for details on calibration verification.

7.2.2.1 To prepare a calibration standard, inject an appropriate volume of a primary dilution standard to an aliquot of organic free reagent water in a volumetric flask, a gas tight syringe, or to a purge device, and inject an appropriate amount of internal standard to the organic free reagent water. Be sure the same amount of internal standard is added to each standard and sample. The volume of organic free reagent water used for calibration must be the same volume used for sample analysis (normally 5 mL). The surrogate and internal standard solutions must be added with a syringe needle long enough to ensure addition below the surface of the water. Assemble the purge-and-trap device as outlined in 4.6. Follow the guidance for the purge-and-trap procedure in Sec. 7.2.4. Ongoing GC or GC/MS calibration criteria must be met as specified in Method 8000 before analyzing samples.

7.2.3 Sample screening

7.2.3.1 Screening of the sample prior to purge-and-trap analysis may provide guidance on whether sample dilution is necessary and may prevent contamination of the purge-and-trap system.

7.2.3.2 SW-846 contains two screening techniques that may be utilized: the automated headspace sampler (Method 5021) connected to a gas chromatograph equipped with a photoionization detector in series with an electrolytic conductivity detector; and extraction of the samples with hexadecane (Method 3820) and analysis of the extract on a gas chromatograph equipped with a flame ionization detector and/or electron capture detector. In addition, other appropriate screening techniques may be employed at the discretion of the analyst.

7.2.4 Sample introduction and purging

7.2.4.1 All samples and standard solutions must be allowed to warm to ambient temperature before analysis.

7.2.4.2 Assemble the purge-and-trap device. The operating conditions for the GC and GC/MS are given in Sec. 7.0 of the specific determinative method to be employed. Whole oven cooling may be needed for certain GC columns and/or certain GC/MS systems to achieve adequate resolution of the gases. Normally a 30 meter wide-bore column will require cooling the GC oven to 25°C or below for resolution of the gases.

7.2.4.3 GC or GC/MS calibration verification criteria must be met (Method 8000) before analyzing samples.

7.2.4.4 Adjust the purge gas flow rate (nitrogen or helium) to 25-40 mL/min (also see Table 1 for guidance on specific analyte groups), on the purge-and-trap device. Optimize the flow rate to provide the best response for chloromethane and bromoform, if these compounds are analytes. Excessive flow rate reduces chloromethane response, whereas insufficient flow reduces bromoform response.

7.2.4.5 Remove the plunger from a 5-mL syringe and attach a closed syringe valve. Open the sample or standard bottle, which has been allowed to come to ambient temperature, and carefully pour the sample into the syringe barrel to just short of overflowing. Replace the syringe plunger and compress the sample. Open the syringe valve and vent any residual air while adjusting the sample volume to 5.0 mL. This process of taking an aliquot destroys the validity of the liquid sample for future analysis; therefore, if there is only one VOA vial, the analyst should fill a second syringe at this time to protect against possible loss of sample integrity. Alternatively, carefully transfer the remaining sample into a 20-mL VOA vial. Seal the vial with zero headspace. The second sample is maintained only until such time when the analyst has determined that the first sample has been analyzed properly. Filling one 10- or 25-mL syringe would allow the use of only one syringe. If a second analysis is needed from a syringe, it must be analyzed within 24 hrs. Care must be taken to prevent air from leaking into the syringe.

7.2.4.6 The following procedure is appropriate for diluting purgeable samples. All steps must be performed without delays until the diluted sample is in a gas-tight syringe.

7.2.4.6.1 Dilutions may be made in volumetric flasks (10-mL to 100-mL). Select the volumetric flask that will allow for the necessary dilution. Intermediate dilutions may be necessary for extremely large dilutions.

7.2.4.6.2 Calculate the approximate volume of organic-free reagent water to be added to the volumetric flask selected and add slightly less than this quantity of organic-free reagent water to the flask.

7.2.4.6.3 Inject the proper aliquot of samples from the syringe prepared in Sec. 7.2.4.5 into the flask. Aliquots of less than 1 mL are not recommended. Dilute the sample to the mark with organic-free reagent water. Cap the flask, invert, and shake three times. Repeat the above procedure for additional dilutions.

7.2.4.6.4 Fill a 5-mL syringe with the diluted sample as in Sec. 7.2.4.5.

7.2.4.7 Add 10.0 µL of surrogate spiking solution (found in each determinative method, Sec. 5.0) and, if applicable, 10.0 µL of internal standard spiking solution through the valve bore of the syringe; then close the valve. The surrogate and internal standards may be mixed and added as a single spiking solution. Matrix spiking solutions, if indicated, should be added (10.0 µL) to the sample at this time.

7.2.4.8 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valves and inject the sample into the purging chamber.

7.2.4.9 Close both valves and purge the sample for the time and at the temperature specified in Table 1. For GC/MS analysis using Method 8260, purge time is 11 minutes at ambient temperature.

7.2.5 Sample desorption

The procedures employed for sample desorption depend on the type of GC interface used. Procedures for non-cryogenic and cryogenic interfaces are described below. Analysts should also consult the instructions from the manufacturer of the purge-and-trap system and the supplier of the trap packing material.

7.2.5.1 Non-cryogenic interface - After the recommended 11-minute purge (see Table 1 for guidance on purge times for specific analyte groups), place the purge-and-trap system in the desorb mode and preheat the trap to 180°C (or other temperature recommended for the specific trap packing material) without a flow of carrier gas passing through the trap.

NOTE: Some purge-and-trap systems are capable of performing a moisture removal step (e.g., dry purge) which can eliminate excess moisture from the trap and gas lines by purging the trap just prior to the desorption step. However, the utility of a moisture removal step depends on the nature of the trap packing material. In general, when using a carbon-based, hydrophobic trap packing, this step may prevent moisture from entering the GC system and affecting chromatography, but may require that the trap be cooled to keep the temperature at or below 25°C. However, for packings that are less hydrophobic or hydrophilic (such as silica gel), a moisture removal step may actually create more significant problems, including loss of sensitivity, poor chromatography, and premature failure of the trap packing material, through the release of increasing amounts of water into the GC system during the course of an analytical shift. The problem may be evident as erratic responses for the early-eluting internal standards and surrogates over the course of the day. Optimum results may be achieved through the proper choices of: the moisture control device, the trap packing material, trap temperature during moisture removal, and carrier gas flow. The use of trap back pressure control may also be necessary. Consult instructions from both the manufacturer of the purge-and-trap system and the supplier of the trap packing material before employing a moisture removal step.

Start the flow of the carrier gas, begin the GC temperature program, and start GC data acquisition. The carrier gas flow rate will depend on the trap employed. A flow rate of 15 mL/min is used for the standard silica gel trap (Sec. 4.6.2), while 10 mL/min may

be adequate for other traps. Continue the carrier gas flow for about 4 min, or as recommended by the manufacturer. Desorption times as low as 1.5 min may be adequate for analytes in Method 8015.

7.2.5.2 Cryogenic interface - After the 11 minute purge, place the purge-and-trap system in the desorb mode, make sure the cryogenic interface is -150°C or lower, and rapidly heat the trap to 180°C (temperature may vary depending on the trap material) while backflushing with an inert gas at 4 mL/minute for about 5 minutes (1.5 min is normally adequate for analytes in Method 8015). At the end of the 5-minute desorption cycle, rapidly heat the cryogenic trap to 250°C; simultaneously begin the temperature program of the gas chromatograph and start the data acquisition.

7.2.6 Trap Reconditioning

7.2.6.1 After desorbing the sample, recondition the trap by returning the purge-and-trap device to the purge mode. Wait 15 seconds, then close the syringe valve on the purging device to begin gas flow through the trap. The trap temperature should be maintained at 180°C for Methods 8021 and 8260, and 210°C for Method 8015. Trap temperatures up to 220°C may be employed. However, the higher temperatures will shorten the useful life of the trap. (Trap temperatures may vary depending on the trap material). After approximately 7 min, turn off the trap heater and open the syringe valve to stop the gas flow through the trap. When cool, the trap is ready for the next sample.

7.2.6.2 While the trap is being desorbed into the gas chromatograph, empty the purging chamber. Wash the chamber with a minimum of two 5 mL flushes of organic free reagent water (or methanol followed by organic free reagent water) to avoid carryover of volatile organics into subsequent analyses.

7.2.7 Interpretation and calculation of data

7.2.7.1 If the initial analysis of a sample or a dilution of the sample has a concentration of analytes that exceeds the initial calibration range, the sample must be reanalyzed at a higher dilution. When a sample is analyzed that has saturated response from a compound, this analysis must be followed by the analysis of organic free reagent water. If the blank analysis is not free of interferences, the system must be decontaminated. Sample analysis may not resume until a blank can meet the organic-free reagent water criteria specified in Chapter One.

7.2.7.2 All dilutions should keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve. Proceed to Method 8000 and the specific determinative method for details on calculating analyte response.

7.2.8 Analysis of water-miscible liquids

7.2.8.1 Water-miscible liquids are analyzed as water samples after first diluting them at least 50-fold with organic-free reagent water.

7.2.8.2 Initial and serial dilutions can be prepared by pipetting 2 mL of the sample into a 100-mL volumetric flask and diluting to volume with organic-free reagent water. Transfer immediately to a 5-mL gas-tight syringe.

7.2.8.3 Alternatively, prepare dilutions directly in a 5-mL syringe filled with organic-free reagent water by adding at least 20.0 µL, but not more than 100.0 µL of liquid sample. The sample is ready for addition of surrogate and, if applicable, internal and matrix spiking standards.

7.3 This section provides guidance on the analysis of solvent extracts from High Concentration Samples prepared by Method 5035.

7.3.1 The GC or GC/MS system should be set up as in Sec. 7.0 of the specific determinative method. This should be done prior to the addition of the solvent extract to organic-free reagent water.

7.3.2 Table 2 can be used to determine the volume of solvent extract to add to the 5 mL of organic-free reagent water for analysis. If a screening procedure was followed, use the estimated concentration to determine the appropriate volume. Otherwise, estimate the concentration range of the sample from the low-concentration analysis to determine the appropriate volume. If the sample was submitted as a high-concentration sample, start with 100.0 µL. All dilutions must keep the response of the major constituents (previously saturated peaks) in the upper half of the linear range of the curve.

7.3.3 Remove the plunger from a 5.0-mL Luer-lok type syringe equipped with a syringe valve and fill until overflowing with organic-free reagent water. Replace the plunger and compress the water to vent trapped air. Adjust the volume to 4.9 mL. Pull the plunger back to 5.0 mL to allow volume for the addition of the sample extract and of standards. Add 10.0 µL of internal standard solution. Also add the volume of solvent extract determined in Sec. 7.3.2 and a volume of the same solvent used in Method 5035 to total 100.0 µL (excluding methanol in standards).

7.3.4 Attach the syringe-syringe valve assembly to the syringe valve on the purging device. Open the syringe valve and inject the water/methanol sample into the purging chamber.

7.3.5 Proceed with the analysis as outlined in the specific determinative method. Analyze all reagent blanks on the same instrument as that used for the samples. The standards and blanks should also contain 100.0 µL of methanol to simulate the sample conditions.

7.4 Sample analysis

The samples prepared by this method may be analyzed by Methods 8015, 8021, and 8260. Refer to these methods for appropriate analysis conditions. For the analysis of gasoline, use Method 8021 with GC/PID for BTEX in series with Method 8015 with the GC/FID detector for hydrocarbons.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures and Method 5000 for sample preparation QC procedures.

8.2 Before processing any samples, the analyst should demonstrate through the analysis of an organic-free reagent water method blank that all glassware and reagents are interference free. Each time a set of samples is extracted, or there is a change in reagents, a method blank should be

processed as a safeguard against chronic laboratory contamination. The blank samples should be carried through all stages of the sample preparation and measurement.

8.3 Standard quality assurance practices should be used with this method. Field duplicates should be collected to validate the precision of the sampling technique. Each analysis batch of 20 or less samples must contain: a reagent blank; either a matrix spike/matrix spike duplicate or a matrix spike and duplicate sample analysis; and a laboratory control sample, unless the determinative method provides other guidance.

8.4 Surrogate standards should be added to all samples when specified in the appropriate determinative method

9.0 METHOD PERFORMANCE

Refer to the determinative methods for performance data.

10.0 REFERENCES

1. U.S. EPA 40 CFR Part 136, "Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Final Rule and Interim Final Rule and Proposed Rule," October 26, 1984.

2. Bellar, T., "Measurement of Volatile Organic Compounds in Soils Using Modified Purge-and-Trap and Capillary Gas Chromatography/Mass Spectrometry", U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, November, 1991.

TABLE 1

PURGE-AND-TRAP OPERATING PARAMETERS

	Analysis Method	
	8015	8021/8260
Purge gas	N_2 or He	N_2 or He
Purge gas flow rate (mL/min)	20	40
Purge time (min)	15.0 ±0.1	11.0 ±0.1
Purge temperature (°C)	85 ±2	Ambient
Desorb temperature (°C)	180	180
Backflush inert gas flow (mL/min)	20-60	20-60[1]
Desorb time (min)	1.5	4

[1] The desorption flow rate for Method 8021 with a wide bore capillary column will optimize at approximately 10 to 15 mL/minute.

TABLE 2

QUANTITY OF METHANOL EXTRACT REQUIRED FOR ANALYSIS OF HIGH-CONCENTRATION SOILS/SEDIMENTS

Approximate Concentration Range	Volume of Methanol Extract[a]
500-10,000 µg/kg	100 µL
1,000-20,000 µg/kg	50 µL
5,000-100,000 µg/kg	10 µL
25,000-500,000 µg/kg	100 µL of 1/50 dilution[b]

Calculate appropriate dilution factor for concentrations exceeding this table.

[a] The volume of methanol added to 5 mL of water being purged should be kept constant. Therefore, add to the 5 mL syringe whatever volume of methanol is necessary to maintain a volume of 100 µL added to the syringe.

[b] Dilute an aliquot of the methanol extract and then take 100 µL for analysis.

FIGURE 1
EXAMPLE OF PURGING DEVICE

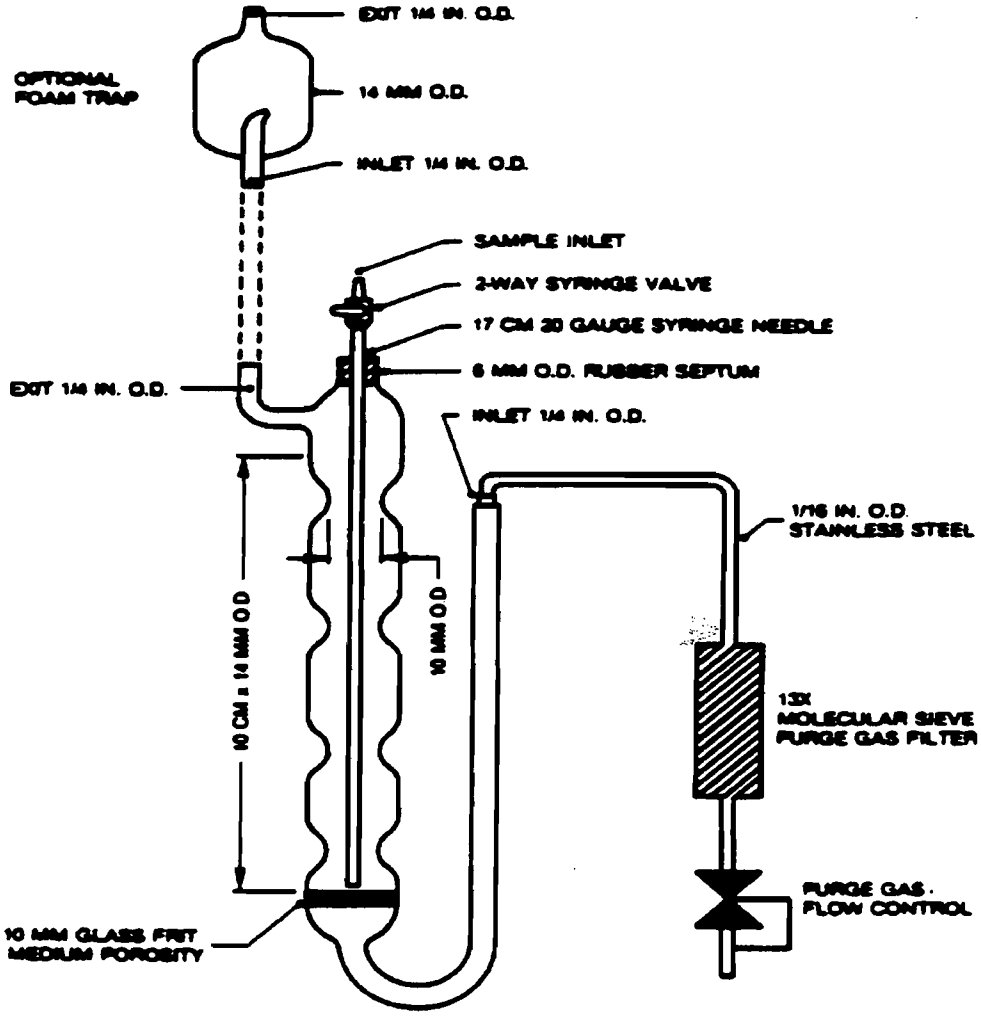


FIGURE 2
EXAMPLE OF TRAP PACKINGS AND CONSTRUCTION
TO INCLUDE DESORB CAPABILITY

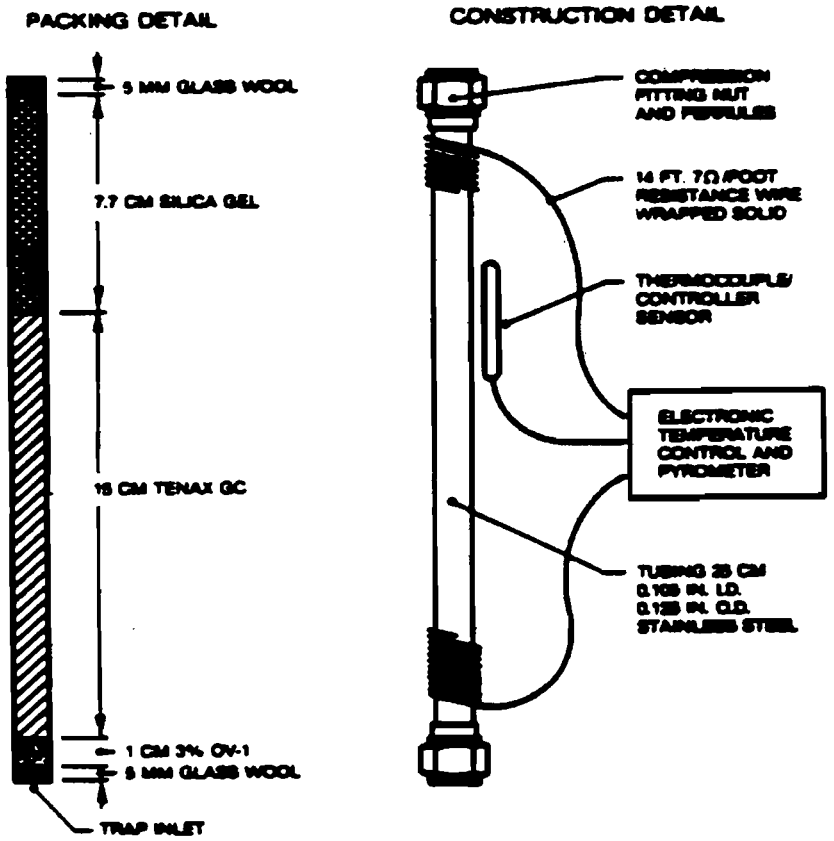


FIGURE 3
SCHEMATIC OF TYPICAL PURGE AND TRAP DEVICE
PURGE MODE

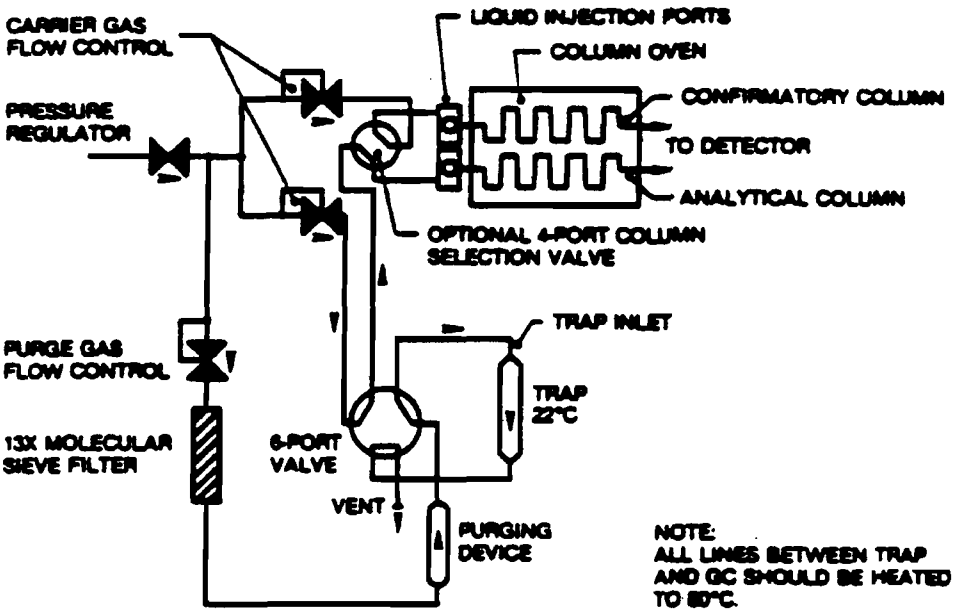
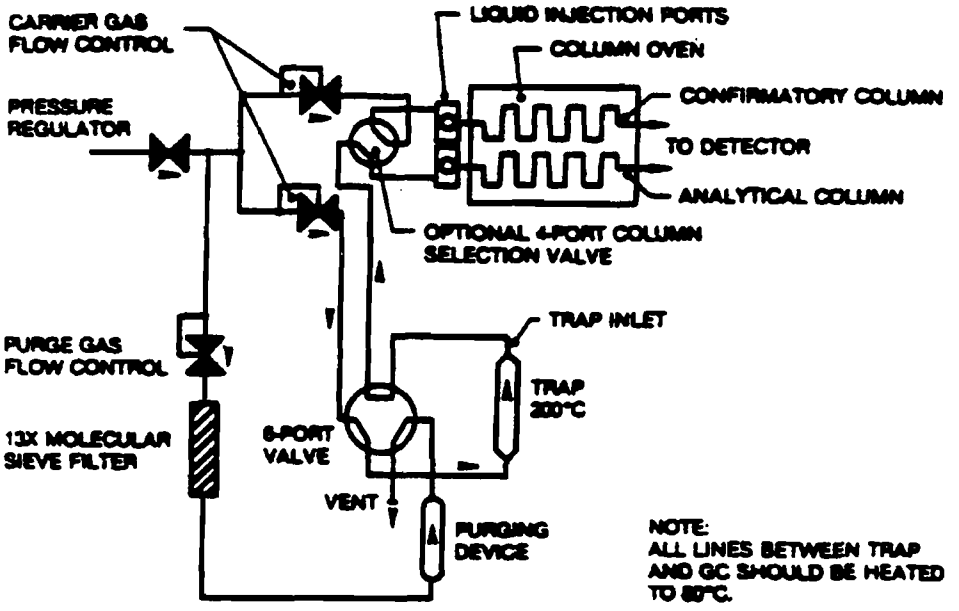
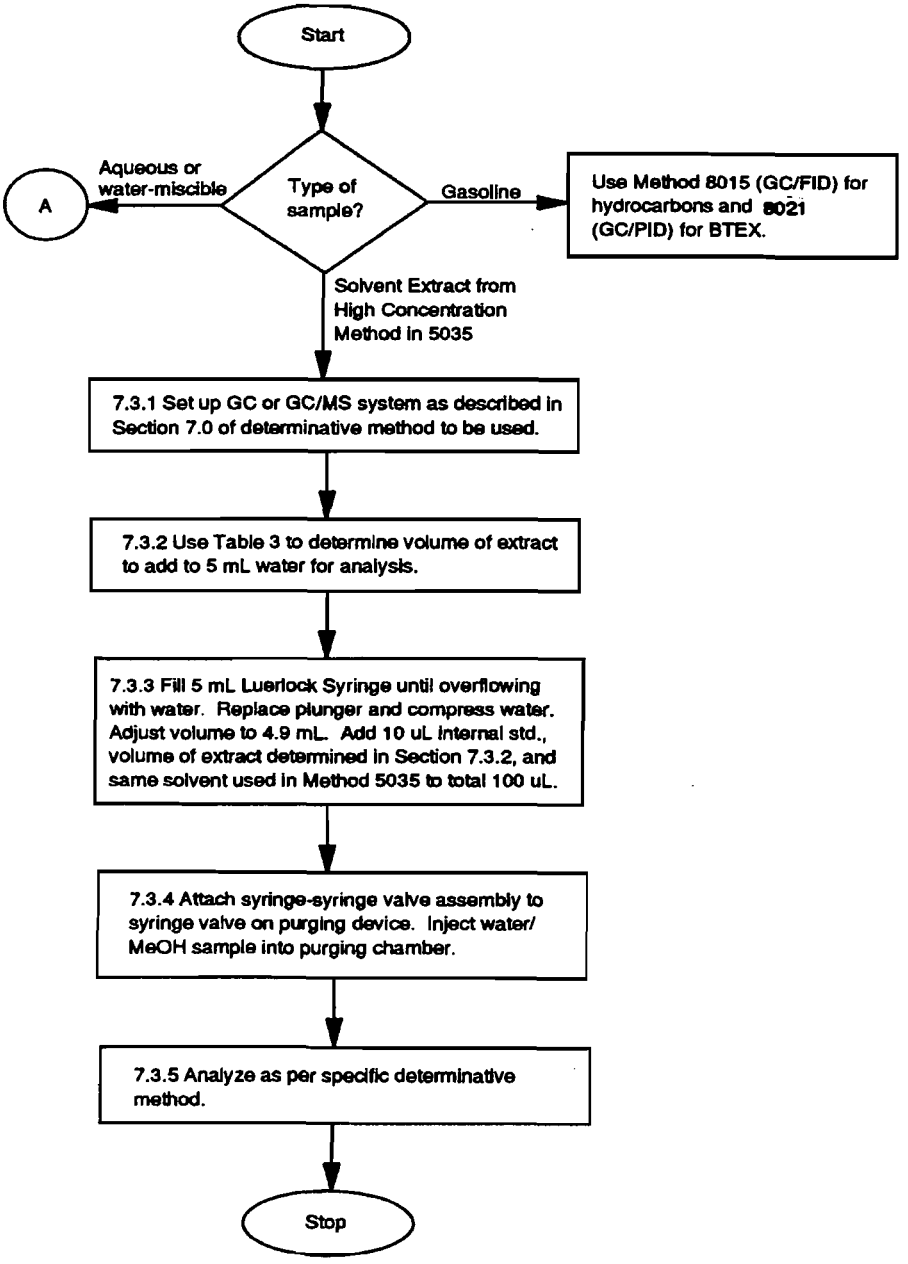
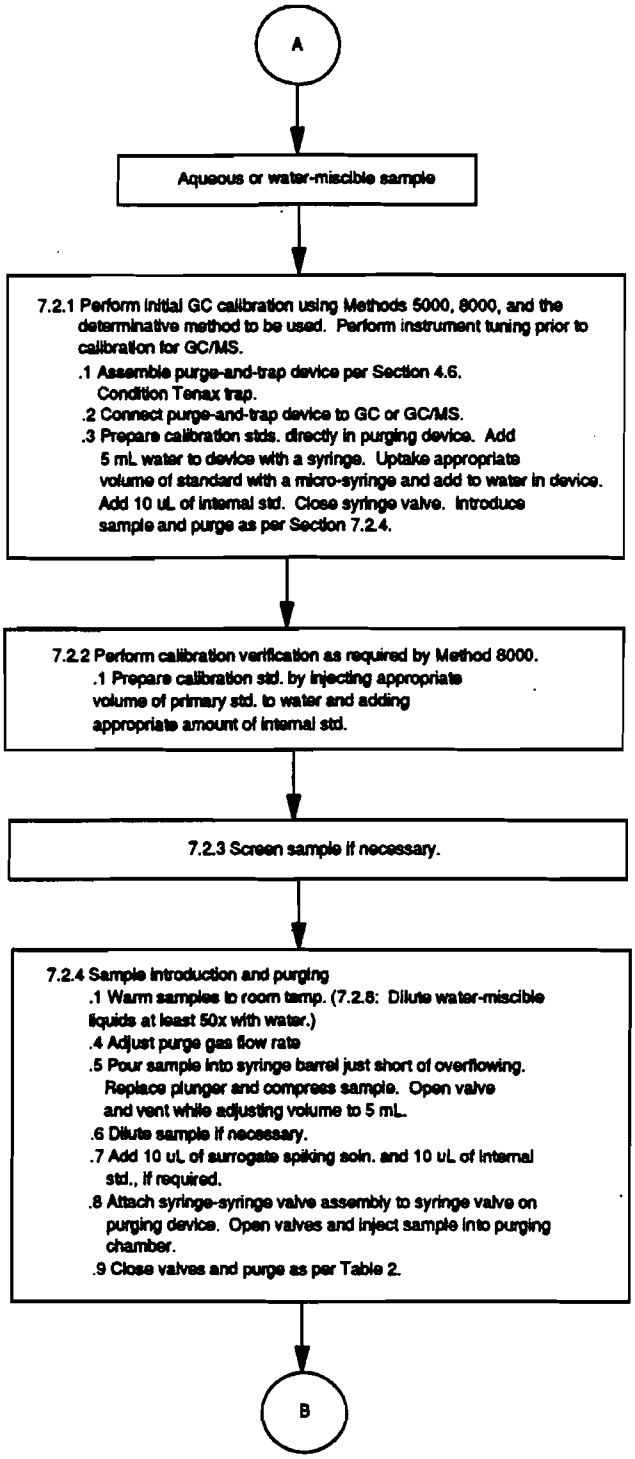


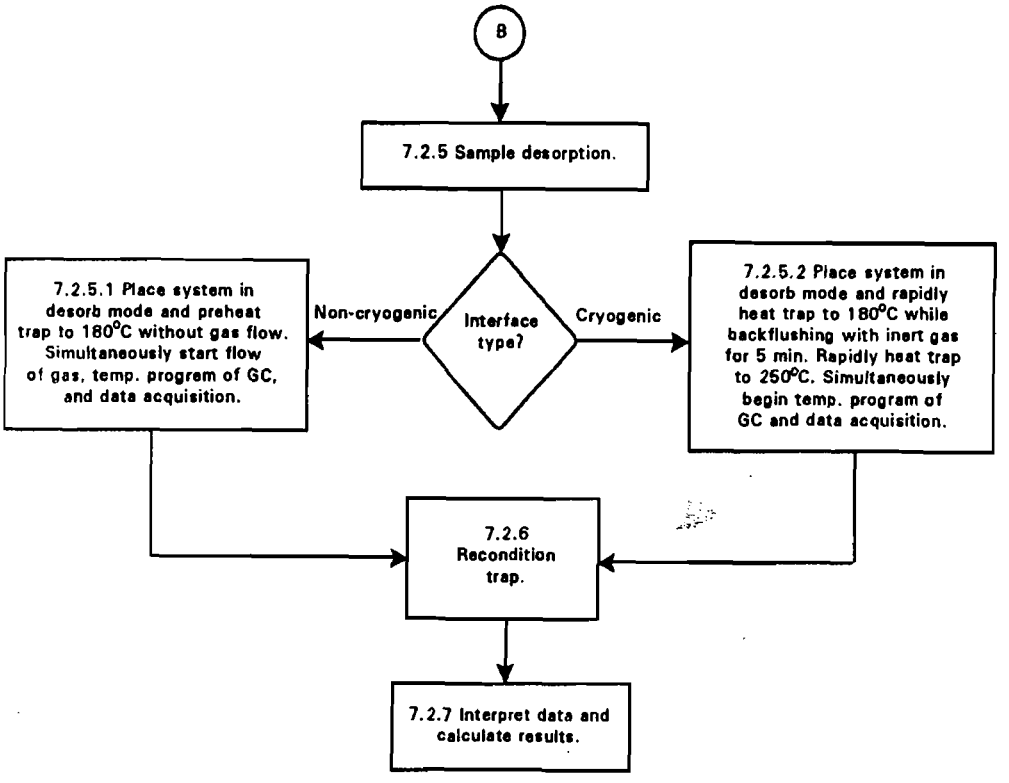
FIGURE 4
SCHEMATIC OF TYPICAL PURGE AND TRAP DEVICE
DESORB MODE



METHOD 5030B
PURGE-AND-TRAP FOR AQUEOUS SAMPLES




A
Aqueous or water-miscible sample
7.2.1 Perform initial GC calibration using Methods 5000, 8000, and the determinative method to be used. Perform instrument tuning prior to calibration for GC/MS.
.1 Assemble purge-and-trap device per Section 4.6. Condition Tenax trap.
.2 Connect purge-and-trap device to GC or GC/MS.
.3 Prepare calibration stds. directly in purging device. Add 5 mL water to device with a syringe. Uptake appropriate volume of standard with a micro-syringe and add to water in device. Add 10 uL of internal std. Close syringe valve. Introduce sample and purge as per Section 7.2.4.
7.2.2 Perform calibration verification as required by Method 8000.
.1 Prepare calibration std. by injecting appropriate volume of primary std. to water and adding appropriate amount of internal std.
7.2.3 Screen sample if necessary.
7.2.4 Sample introduction and purging
.1 Warm samples to room temp. (7.2.8: Dilute water-miscible liquids at least 50x with water.)
.4 Adjust purge gas flow rate
.5 Pour sample into syringe barrel just short of overflowing. Replace plunger and compress sample. Open valve and vent while adjusting volume to 5 mL.
.6 Dilute sample if necessary.
.7 Add 10 uL of surrogate spiking soln. and 10 uL of internal std., if required.
.8 Attach syringe-syringe valve assembly to syringe valve on purging device. Open valves and inject sample into purging chamber.
.9 Close valves and purge as per Table 2.
B


B
7.2.5 Sample desorption.
Interface type?
Non-cryogenic
Cryogenic
7.2.5.1 Place system in desorb mode and preheat trap to 180°C without gas flow. Simultaneously start flow of gas, temp. program of GC, and data acquisition.
7.2.5.2 Place system in desorb mode and rapidly heat trap to 180°C while backflushing with inert gas for 5 min. Rapidly heat trap to 250°C. Simultaneously begin temp. program of GC and data acquisition.
7.2.6 Recondition trap.
7.2.7 Interpret data and calculate results.

METHOD 8021B

AROMATIC AND HALOGENATED VOLATILES BY GAS CHROMATOGRAPHY USING PHOTOIONIZATION AND/OR ELECTROLYTIC CONDUCTIVITY DETECTORS

1.0 SCOPE AND APPLICATION

1.1 Method 8021 is used to determine volatile organic compounds in a variety of solid waste matrices. This method is applicable to nearly all types of samples, regardless of water content, including ground water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The following compounds can be determined by this method:

		Appropriate Technique			
Analyte	CAS No.[a]	Purge-and -Trap	Direct Injection	Vac Distln	Head Space
Allyl chloride	107-05-1	b	b	nd	nd
Benzene	71-43-2	b	b	b	b
Benzyl chloride	100-44-7	pp	b	nd	nd
Bis(2-chloroisopropyl) ether	108-60-1	b	b	nd	nd
Bromoacetone	598-31-2	pp	b	nd	nd
Bromobenzene	108-86-1	b	nd	nd	nd
Bromochloromethane	74-97-5	b	b	nd	b
Bromodichloromethane	75-27-4	b	b	b	b
Bromoform	75-25-2	b	b	b	b
Bromomethane	74-83-9	b	b	b	b
Carbon tetrachloride	56-23-5	b	b	b	b
Chlorobenzene	108-90-7	b	b	b	b
Chlorodibromomethane	124-48-1	b	b	b	b
Chloroethane	75-00-3	b	b	b	b
2-Chloroethanol	107-07-03	pp	b	nd	nd
2-Chloroethyl vinyl ether	110-75-8	b	b	b	nd
Chloroform	67-66-3	b	b	b	b
Chloromethyl methyl ether	107-30-2	pp	pc	nd	nd
Chloroprene	126-99-8	b	nd	nd	nd
Chloromethane	74-87-3	b	b	b	b
4-Chlorotoluene	106-43-4	b	b	nd	nd
1,2-Dibromo-3-chloropropane	96-12-8	pp	b	nd	b
1,2-Dibromoethane	106-93-4	b	nd	nd	b
Dibromomethane	74-95-3	b	b	b	b
1,2-Dichlorobenzene	95-50-1	b	nd	nd	b
1,3-Dichlorobenzene	541-73-1	b	nd	nd	b
1,4-Dichlorobenzene	106-46-7	b	nd	nd	b
Dichlorodifluoromethane	75-71-8	b	b	b	b
1,1-Dichloroethane	75-34-3	b	b	b	b
1,2-Dichloroethane	107-06-2	b	b	b	b

Analyte	CAS No.[a]	Appropriate Technique			
		Purge-and -Trap	Direct Injection	Vac Distln	Head Space
1,1-Dichloroethene	75-35-4	b	b	b	b
cis-1,2-Dichloroethene	156-59-2	b	nd	nd	nd
trans-1,2-Dichloroethene	156-60-5	b	b	b	b
1,2-Dichloropropane	78-87-5	b	nd	b	b
1,3-Dichloro-2-propanol	96-23-1	pp	b	nd	nd
cis-1,3-dichloropropene	10061-01-5	b	b	b	nd
trans-1,3-dichloropropene	10061-02-6	b	b	b	nd
Epichlorhydrin	106-89-8	pp	b	nd	nd
Ethylbenzene	100-41-4	b	b	b	b
Hexachlorobutadiene	87-68-3	b	nd	nd	b
Methylene chloride	75-09-2	b	b	b	b
Naphthalene	91-20-3	b	nd	nd	b
Styrene	100-42-5	b	b	b	b
1,1,1,2-Tetrachloroethane	630-20-6	b	nd	nd	b
1,1,2,2-Tetrachloroethane	79-34-5	b	b	b	b
Tetrachloroethene	127-18-4	b	b	b	b
Toluene	108-88-3	b	b	b	b
1,2,4-Trichlorobenzene	120-82-1	b	nd	nd	b
1,1,1-Trichloroethane	71-55-6	b	b	b	b
1,1,2-Trichloroethane	79-00-5	b	b	b	b
Trichloroethene	79-01-6	b	b	b	b
Trichlorofluoromethane	75-69-4	b	b	b	b
1,2,3-Trichloropropane	96-18-4	b	b	b	b
Vinyl chloride	75-01-4	b	b	b	b
o-Xylene	95-47-6	b	b	b	b
m-Xylene	108-38-3	b	b	b	b
p-Xylene	106-42-3	b	b	b	b

[a] Chemical Abstract Service Registry Number.
b Adequate response by this technique.
i Inappropriate technique for this analyte.
nd Not Determined
pc Poor chromatographic behavior.
pp Poor purging efficiency resulting in high EQLs. May require heated purge (e.g., 40°C) or a more appropriate sample preparation technique, e.g., azeotropic distillation, equilibrium headspace or vacuum distillation, for good method performance.

1.2 Method detection limits (MDLs) are compound dependent and vary with purging efficiency and concentration. The MDLs for selected analytes are presented in Table 1. The applicable concentration range of this method is compound and instrument dependent but is approximately 0.1 to 200 µg/L. Analytes that are inefficiently purged from water will not be detected when present at low concentrations, but they can be measured with acceptable accuracy and precision when present in sufficient amounts. Determination of some structural isomers (i.e., xylenes) may be hampered by coelution.

1.3 The estimated quantitation limit (EQL) of Method 8021A for an individual compound is approximately 1 µg/kg (wet weight) for soil/sediment samples, 0.1 mg/kg (wet weight) for wastes, and 1 µg/L for ground water (see Table 3). EQLs will be proportionately higher for sample extracts and samples that require dilution or reduced sample size to avoid saturation of the detector.

1.4 This method is restricted for use by, or under the supervision of, analysts experienced in the use of gas chromatographs for measurement of purgeable organics at low µg/L concentrations and skilled in the interpretation of gas chromatograms. Each analyst must demonstrate the ability to generate acceptable results with this method.

1.5 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined. Each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are available for the information of the analyst (References 4 and 6).

1.6 The following method analytes have been tentatively classified as known or suspected human or mammalian carcinogens: benzene, carbon tetrachloride, 1,4-dichlorobenzene, 1,2-dichloroethane, hexachlorobutadiene, 1,1,2,2-tetrachloroethane, 1,1,2-trichloroethane, chloroform, 1,2-dibromoethane, tetrachloroethene, trichloroethene, and vinyl chloride. Pure standard materials and stock standard solutions of these compounds should be handled in a hood. A NIOSH/MESA approved toxic gas respirator should be worn when the analyst handles high concentrations of these toxic compounds.

1.7 Other non-RCRA compounds which are amenable to analysis by Method 8021 include:

Analyte	CAS No.[a]
n-Butylbenzene	104-51-8
sec-Butylbenzene	135-98-8
tert-Butylbenzene	98-06-6
2-Chlorotoluene	95-49-8
1,3-Dichloropropane	142-28-9
2,2-Dichloropropane	594-20-7
1,1-Dichloropropene	563-58-6
Isopropylbenzene	98-82-8
p-Isopropyltoluene	99-87-6
n-Propylbenzene	103-65-1
1,2,3-Trichlorobenzene	87-61-6
1,2,4-Trimethylbenzene	95-63-6
1,3,5-Trimethylbenzene	108-67-8

[a] Chemical Abstract Service Registry Number

2.0 SUMMARY OF METHOD

2.1 Method 8021 provides gas chromatographic conditions for the detection of halogenated and aromatic volatile organic compounds. Samples can be analyzed using direct injection (Method 3585 for oily matrices) or purge-and-trap (Method 5030/5035), headspace (Method 5021), or vacuum distillation (Method 5032). Groundwater samples may be analyzed using Method 5030, Method

5021, or Method 5032. A temperature program is used in the gas chromatograph to separate the organic compounds. Detection is achieved by a photoionization detector (PID) and an electrolytic conductivity detector (HECD) in series. The GC system may also be set up to use a single detector when an analyst is looking for only halogenated compounds (HECD) or aromatic compounds (PID).

2.2 Tentative identifications are obtained by analyzing standards under the same conditions used for samples and comparing resultant GC retention times. Confirmatory information can be gained by comparing the relative response from the two detectors. Concentrations of the identified components are measured by relating the response produced for that compound to the response produced by a compound that is used as an internal standard.

3.0 INTERFERENCES

3.1 Refer to the appropriate 5000 Series method and Method 8000.

3.2 Samples can be contaminated by diffusion of volatile organics (particularly chlorofluorocarbons and methylene chloride) through the sample container septum during shipment and storage. A trip blank prepared from organic-free reagent water and carried through sampling and subsequent storage and handling can serve as a check on such contamination.

3.3 Sulfur dioxide is a potential interferant in the analysis for vinyl chloride.

4.0 APPARATUS AND MATERIALS

4.1 Sample introduction apparatus - Refer to Sec. 4.0 of the appropriate 5000 Series method for a listing of the equipment for each sample introduction technique.

4.2 Gas Chromatograph - capable of temperature programming; equipped with variable-constant differential flow controllers, subambient oven controller, photoionization and electrolytic conductivity detectors connected with a short piece of uncoated capillary tubing, 0.32-0.5 mm ID, and data system.

4.2.1 Primary Column - 60-m x 0.75 mm ID VOCOL wide-bore capillary column with 1.5-µm film thickness (Supelco) or equivalent.

4.2.2 Confirmation column - 60-m x 0.53 ID SPB-624 wide-bore capillary column with 3.0-µm film thickness (Supelco) has been suggested as one possible option. Other columns that will provide appropriate resolution of the target compoundsmay also be employed for confirmation, or confirmation may be performed using GC/MS.

4.2.3 Photoionization detector (PID) (Tracor Model 703, or equivalent).

4.2.4 Electrolytic conductivity detector (HECD) (Tracor Hall Model 700-A, or equivalent).

4.3 Syringes - 5 mL glass hypodermic with Luer-Lok tips.

4.4 Syringe valves - 2-way with Luer ends [polytetrafluoroethylene (PTFE) or Kel-F].

4.5 Microsyringe - 25-µL with a 2-in. x 0.006-in. ID, 22° bevel needle (Hamilton #702N or equivalent).

4.6 Microsyringes - 10-, 100-µL.

4.7 Syringes - 0.5-, 1.0-, and 5-mL, gas-tight with shut-off valve.

4.8 Bottles - 15-mL, PTFE-lined with screw-cap or crimp top.

4.9 Analytical balance - 0.0001 g.

4.10 Volumetric flasks, Class A - Appropriate sizes with ground glass stoppers.

5.0 REAGENTS

5.1 Reagent grade inorganic chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all inorganic reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Organic-free reagent water. All references to water in this method refer to organic-free reagent water, as defined in Chapter One.

5.3 Methanol, CH_3OH - Pesticide quality or equivalent, demonstrated to be free of analytes. Store away from other solvents.

5.4 Vinyl chloride, (99.9% pure), CH_2=CHCl. Vinyl chloride is available from Ideal Gas Products, Inc., Edison, New Jersey and from Matheson, East Rutherford, New Jersey, as well as from other sources. Certified mixtures of vinyl chloride in nitrogen at 1.0 and 10.0 ppm (v/v) are available from several sources.

5.5 Stock standards - Stock solutions may either be prepared from pure standard materials or purchased as certified solutions. Prepare stock standards in methanol using assayed liquids or gases, as appropriate. Because of the toxicity of some of the organohalides, primary dilutions of these materials of the toxicity should be prepared in a hood.

NOTE: If direct injection is used, the solvent system of standards must match that of the sample. It is not necessary to prepare high concentration aqueous mixed standards when using direct injection.

5.5.1 Place about 9.8 mL of methanol in a 10-mL tared ground glass stoppered volumetric flask. Allow the flask to stand, unstoppered, for about 10 minutes until all alcohol-wetted surfaces have dried. Weigh the flask to the nearest 0.1 mg.

5.5.2 Add the assayed reference material, as described below.

5.5.2.1 Liquids: Using a 100-µL syringe, immediately add two or more drops of assayed reference material to the flask; then reweigh. The liquid must fall directly into the alcohol without contacting the neck of the flask.

5.5.2.2 Gases: To prepare standards for any compounds that boil below 30°C (e.g., bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, vinyl chloride), fill a 5-mL valved gas-tight syringe with the

reference standard to the 5.0-mL mark. Lower the needle to 5 mm above the methanol meniscus. Slowly introduce the reference standard above the surface of the liquid. The heavy gas rapidly dissolves in the methanol. This may also be accomplished by using a lecture bottle equipped with a septum. Attach PTFE tubing to the side-arm relief valve and direct a gentle stream of gas into the methanol meniscus.

5.5.3 Reweigh, dilute to volume, stopper, and then mix by inverting the flask several times. Calculate the concentration in milligrams per liter (mg/L) from the net gain in weight. When compound purity is assayed to be 96% or greater, the weight may be used without correction to calculate the concentration of the stock standard. Commercially prepared stock standards may be used at any concentration if they are certified by the manufacturer or by an independent source.

5.5.4 Transfer the stock standard solution into a bottle with a PTFE-lined screw-cap or crimp top. Store, with minimal headspace, at -10°C to -20°C and protect from light. Standards should be returned to the freezer as soon as the analyst has completed mixing or diluting the standards to prevent the evaporation of volatile target compounds.

5.5.5 Frequency of Standard Preparation

5.5.5.1 Standards for the permanent gases should be monitored frequently by comparison to the initial calibration curve. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for gases usually need to be replaced after one week or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Dichlorodifluoromethane and dichloromethane will usually be the first compounds to evaporate from the standard and should, therefore, be monitored very closely when standards are held beyond one week.

5.5.5.2 Standards for the non-gases should be monitored frequently by comparison to the initial calibration. Fresh standards should be prepared if this check exceeds a 20% drift. Standards for non-gases usually need to be replaced after six months or as recommended by the standard manufacturer, unless the acceptability of the standard can be documented. Standards of reactive compounds such as 2-chloroethyl vinyl ether and styrene may need to be prepared more frequently.

5.6 Prepare secondary dilution standards, using stock standard solutions, in methanol, as needed, that contain the compounds of interest, either singly or mixed together. The secondary dilution standards should be prepared at concentrations such that the aqueous calibration standards prepared in Sec. 5.8 will bracket the working range of the analytical system. Secondary dilution standards should be stored with minimal headspace for volatiles and should be checked frequently for signs of degradation or evaporation, especially just prior to preparing calibration standards from them. Secondary standards for gases should be replaced after one week unless the acceptability of the standard can be documented. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations. The analyst should also handle and store standards as stated in Sec. 5.5.4 and return them to the freezer as soon as standard mixing or diluting is completed to prevent the evaporation of volatile target compounds.

5.7 Calibration standards - There are two types of calibration standards used for this method: initial calibration standards and calibration verification standards. When using premixed certified solutions, store according to the manufacturer's documented holding time and storage temperature recommendations.

5.7.1 Initial calibration standards should be prepared at a minimum of five concentrations from the secondary dilution of stock standards (see Secs. 5.5 and 5.6) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. At least one of the calibration standards should correspond to a sample concentration at or below that necessary to meet the data quality objectives of the project. The remaining standards should correspond to the range of concentrations found in typical samples but should not exceed the working range of the GC system. Initial calibration standards should be mixed from fresh stock standards and dilution standards when generating an initial calibration curve. See Sec. 7.0 of Method 8000 for guidance on initial calibration.

5.7.2 Calibration verification standards should be prepared at a concentration near the mid-point of the initial calibration range from the secondary dilution of stock standards (see Secs. 5.5 and 5.6) or from a premixed certified solution. Prepare these solutions in organic-free reagent water. See Sec. 7.0 of Method 8000 for guidance on calibration verification.

5.7.3 It is the intent of EPA that all target analytes for a particular analysis be included in the initial calibration and calibration verification standard(s). These target analytes may not include the entire list of analytes (Sec. 1.1) for which the method has been demonstrated. However, the laboratory shall not report a quantitative result for a target analyte that was not included in the calibration standard(s).

5.7.4 The calibration standards should also contain the internal standards chosen for the analysis if internal standard calibration is used.

5.8 In order to prepare accurate aqueous standard solutions, the following precautions must be observed:

NOTE: Prepare calibration solutions for use with direct injection analyses in water at the concentrations required.

5.8.1 Do not inject more than 20 µL of alcoholic standards into 100 mL of water.

5.8.2 Use a 25-µL Hamilton 702N micro syringe or equivalent (variations in needle geometry will adversely affect the ability to deliver reproducible volumes of methanolic standards into water).

5.8.3 Rapidly inject the alcoholic standard into the filled volumetric flask. Remove the needle as fast as possible after injection.

5.8.4 Mix aqueous standards by inverting the flask three times.

5.8.5 Fill the sample syringe from the standard solution contained in the expanded area of the flask (do not use any solution contained in the neck of the flask).

5.8.6 Never use pipets to dilute or transfer samples or aqueous standards.

5.8.7 Standards should be stored and handled according to guidance in Secs. 5.5.4 and 5.5.5.

5.9 Internal standards - It is recommended that a spiking solution containing fluorobenzene and 2-bromo-1-chloropropane in methanol be prepared, using the procedures described in Secs. 5.5

and 5.6. It is further recommended that the secondary dilution standard be prepared at a concentration of 5 mg/L of each internal standard compound. The addition of 10 µL of such a standard to 5.0 mL of sample calibration standard would be equivalent to 10 µg/L. External standard quantitation may also be used.

5.10 Surrogate standards -The analyst should monitor both the performance of the analytical system and the effectiveness of the method in dealing with each sample matrix by spiking each sample, standard, and reagent blank with two or more surrogate compounds. A combination of 1,4-dichlorobutane and bromochlorobenzene is recommended to encompass the range of the temperature program used in this method. From stock standard solutions prepared as in Sec. 5.5, add a volume to give 750 µg of each surrogate to 45 mL of organic-free reagent water contained in a 50-mL volumetric flask, mix, and dilute to volume for a concentration of 15 ng/µL. Add 10 µL of this surrogate spiking solution directly into the 5-mL syringe with every sample and reference standard analyzed. If the internal standard calibration procedure is used, the surrogate compounds may be added directly to the internal standard spiking solution (Sec. 5.9).

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

See the introductory material to this chapter, Organic Analytes, Sec. 4.1.

7.0 PROCEDURE

7.1 Volatile compounds are introduced into the gas chromatograph either by direct injection (Method 3585 for oily matrices) or purge-and-trap (Methods 5030/5035), headspace (Method 5021), or by vacuum distillation (Method 5032). Methods 5030, 5021, or 5032 may be used directly on groundwater samples. Methods 5035, 5021, or 5032 may be used for low-concentration contaminated soils and sediments. For high-concentration soils or sediments (>200 µg/kg), methanolic extraction, as described in Method 5035, may be necessary prior to purge-and-trap analysis. For guidance on the dilution of oily waste samples for direct injection refer to Method 3585.

7.2 Gas chromatography conditions (Recommended)

7.2.1 Set up the gas chromatograph system so that the photoionization detector (PID) is in series with the electrolytic conductivity detector (HECD). It may be helpful to contact the manufacturer of the GC for guidance on the proper installation of dual detector systems.

NOTE: Use of the dual detector system is not a requirement of the method. The GC system may also be set up to use a single detector when the analyst is looking for just halogenated compounds (using the HECD) or for just aromatic compounds (using the PID).

7.2.2 Oven settings:

Carrier gas (Helium) Flow rate:	6 mL/min.
Temperature program	
Initial temperature:	10°C, hold for 8 minutes at
Program:	10°C to 180°C at 4°C/min
Final temperature:	180°C, hold until all expected compounds have eluted.

7.2.3 The carrier gas flow is augmented with an additional 24 mL of helium flow before entering the photoionization detector. This make-up gas is necessary to ensure optimal response from both detectors.

7.2.4 These halogen-specific systems eliminate misidentifications due to non-organohalides which are coextracted during the purge step. A Tracor Hall Model 700-A detector was used to gather the single laboratory accuracy and precision data presented in Table 2. The operating conditions used to collect these data are:

Reactor tube:	Nickel, 1/16 in OD
Reactor temperature:	810°C
Reactor base temperature:	250°C
Electrolyte:	100% n-Propyl alcohol
Electrolyte flow rate:	0.8 mL/min
Reaction gas:	Hydrogen at 40 mL/min
Carrier gas plus make-up gas:	Helium at 30 mL/min

7.2.5 A sample chromatogram obtained with this column is presented in Figure 1. This column was used to develop the method performance statements in Sec. 9.0. Estimated retention times and MDLs that can be achieved under these conditions are given in Table 1. Other columns or element specific detectors may be used if the requirements of Sec. 8.0 are met.

7.3 Calibration - Refer to Method 8000 for proper calibration techniques. Use Table 1 and especially Table 2 for guidance on selecting the lowest point on the calibration curve.

7.3.1 Calibration must take place using the same sample introduction method that will be used to analyze actual samples (see Sec. 7.4.1).

7.3.2 The procedure for internal or external calibration may be used. Refer to Method 8000 for a description of each of these procedures.

7.4 Gas chromatographic analysis

7.4.1 Introduce volatile compounds into the gas chromatograph using either Methods 5030/5035 (purge-and-trap method) or the direct injection method (see Sec. 7.4.1.1), by Method 5021 (headspace) or by Method 5032 (vacuum distillation). If the internal standard calibration technique is used, add 10 µL of internal standard to the sample prior to purging.

7.4.1.1 Direct injection - In very limited applications (e.g., aqueous process wastes) direct injection of the sample into the GC system with a 10 µL syringe may be appropriate. The detection limit is very high (approximately 10,000 µg/L), therefore, it is only permitted where concentrations in excess of 10,000 µg/L are expected or for water-soluble compounds that do not purge. The system must be calibrated by direct injection (bypassing the purge-and-trap device).

7.4.1.2 Refer to Method 3585 for guidance on the dilution and direct injection of waste oil samples.

7.4.1.3 Samples may be purged at temperatures above those being recommended as long as all calibration standards, samples, and QC samples are purged at the same temperature and acceptable method performance is demonstrated.

7.4.2 Follow Sec. 7.0 in Method 8000 for instructions on the analysis sequence, appropriate dilutions, establishing daily retention time windows, identification criteria, and calibration verification. Include a mid-concentration standard after each group of 10 samples in the analysis sequence.

7.4.3 Table 1 summarizes the estimated retention times on the two detectors for a number of organic compounds analyzable using this method.

7.4.4 Record the sample volume purged or injected and the resulting peak sizes (in area units or peak heights).

7.4.5 Calculation of concentration is covered in Method 8000.

7.4.6 Second column confirmation

A 60-m x 0.53 ID SPB-624 wide-bore capillary column with 3.0-µm film thickness (Supelco) has been suggested as one possible option for confirming compound identifications. Other columns that will provide appropriate resolution of the target compoundsmay also be employed for confirmation, or confirmation may be performed using GC/MS.

7.4.7 If the response for a peak is off-scale, i.e., beyond the calibration range of the standards, prepare a dilution of the sample with organic-free reagent water. The dilution must be performed on a second aliquot of the sample which has been properly sealed and stored prior to use.

7.4.8 For target compounds that boil below 30°C at 1 atm pressure (e.g., bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, and vinyl chloride), analysts may use a calibration verification acceptance criteria of within ± 20% difference from the initial calibration response.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One and Method 8000 for specific quality control (QC) procedures. Quality control procedures to ensure the proper operation of the various sample preparation and/or sample introduction techniques can be found in Methods 3500 and 5000. Each laboratory should maintain a formal quality assurance program. The laboratory should also maintain records to document the quality of the data generated.

8.2 Quality control procedures necessary to evaluate the GC system operation are found in Method 8000, Sec. 7.0 and includes evaluation of retention time windows, calibration verification and chromatographic analysis of samples.

8.3 Initial Demonstration of Proficiency - Each laboratory must demonstrate initial proficiency with each sample preparation and determinative method combination it utilizes, by generating data of acceptable accuracy and precision for target analytes in a clean matrix. The laboratory must also repeat the following operations whenever new staff are trained or significant changes in instrumentation are made. See Method 8000, Sec. 8.0 for information on how to accomplish this demonstration.

8.4 Sample Quality Control for Preparation and Analysis - The laboratory must also have procedures for documenting the effect of the matrix on method performance (precision, accuracy,

and detection limit). At a minimum, this includes the analysis of QC samples including a method blank, a matrix spike, a duplicate, and a laboratory control sample (LCS) in each analytical batch and the addition of surrogates to each field sample and QC sample.

8.4.1 Documenting the effect of the matrix should include the analysis of at least one matrix spike and one duplicate unspiked sample or one matrix spike/matrix spike duplicate pair. The decision on whether to prepare and analyze duplicate samples or a matrix spike/matrix spike duplicate must be based on a knowledge of the samples in the sample batch. If samples are expected to contain target analytes, then laboratories may use one matrix spike and a duplicate analysis of an unspiked field sample. If samples are not expected to contain target analytes, laboratories should use a matrix spike and matrix spike duplicate pair.

8.4.2 A Laboratory Control Sample (LCS) should be included with each analytical batch. The LCS consists of an aliquot of a clean (control) matrix similar to the sample matrix and of the same weight or volume. The LCS is spiked with the same analytes at the same concentrations as the matrix spike. When the results of the matrix spike analysis indicate a potential problem due to the sample matrix itself, the LCS results are used to verify that the laboratory can perform the analysis in a clean matrix.

8.4.3 See Method 8000, Sec. 8.0 for the details on carrying out sample quality control procedures for preparation and analysis.

8.5 Surrogate recoveries - The laboratory must evaluate surrogate recovery data from individual samples versus the surrogate control limits developed by the laboratory. See Method 8000, Sec. 8.0 for information on evaluating surrogate data and developing and updating surrogate limits.

8.6 Calibration verification acceptance criteria - For target compounds that boil below 30°C at 1 atm pressure (e.g., bromomethane, chloroethane, chloromethane, dichlorodifluoromethane, trichlorofluoromethane, and vinyl chloride), analysts may use a calibration verification acceptance criteria of within ± 20% difference from the initial calibration response.

8.7 It is recommended that the laboratory adopt additional quality assurance practices for use with this method. The specific practices that are most productive depend upon the needs of the laboratory and the nature of the samples. Whenever possible, the laboratory should analyze standard reference materials and participate in relevant performance evaluation studies.

9.0 METHOD PERFORMANCE

9.1 Method detection limits for these analytes have been calculated from data collected by spiking organic-free reagent water at 0.1 µg/L. These data are presented in Table 1.

9.2 This method was tested in a single laboratory using organic-free reagent water spiked at 10 µg/L. Single laboratory precision and accuracy data for each detector are presented for the method analytes in Table 2.

10.0 REFERENCES

1. "Volatile Organic Compounds in Water by Purge-and-Trap Capillary Column Gas Chromatography with Photoionization and Electrolytic Conductivity Detectors in Series",

Method 502.2, Rev. 2.0 (1989); Methods for the Determination of Organic Compounds in Drinking Water", U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Cincinnati, OH, EPA/600/4-88/039, December, 1988.

2. "The Determination of Halogenated Chemicals in Water by the Purge and Trap Method", Method 502.1; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, OH 45268, September, 1986.

3. "Volatile Aromatic and Unsaturated Organic Compounds in Water by Purge and Trap Gas Chromatography", Method 503.1; U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, OH, September, 1986.

4. Glaser, J.A., Forest, D.L., McKee, G.D., Quave, S.A., Budde, W.L. "Trace Analyses for Wastewaters", Environ. Sci. Technol., 1981, 15, 1426.

5. Bellar, T.A., Lichtenberg, J.J. "The Determination of Synthetic Organic Compounds in Water by Purge and Sequential Trapping Capillary Column Gas Chromatography", U.S. Environmental Protection Agency, Environmental Monitoring and Support Laboratory: Cincinnati, OH, 45268.

TABLE 1

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS WITH PHOTOIONIZATION DETECTION (PID) AND HALL ELECTROLYTIC CONDUCTIVITY DETECTOR (HECD) DETECTORS

Analyte	PID Ret. Time[a] minute	HECD Ret. Time minute	PID MDL µg/L	HECD MDL µg/L
Dichlorodifluoromethane	-[b]	8.47		0.05
Chloromethane	-	9.47		0.03
Vinyl Chloride	9.88	9.93	0.02	0.04
Bromomethane	-	11.95		1.1
Chloroethane	-	12.37		0.1
Trichlorofluoromethane	-	13.49		0.03
1,1-Dichloroethene	16.14	16.18	ND[c]	0.07
Methylene Chloride	-	18.39		0.02
trans-1,2-Dichloroethene	19.30	19.33	0.05	0.06
1,1-Dichloroethane	-	20.99		0.07
2,2-Dichloropropane	-	22.88		0.05
cis-1,2-Dichloroethane	23.11	23.14	0.02	0.01
Chloroform	-	23.64		0.02
Bromochloromethane	-	24.16		0.01
1,1,1-Trichloroethane	-	24.77		0.03
1,1-Dichloropropene	25.21	25.24	0.02	0.02
Carbon Tetrachloride	-	25.47		0.01
Benzene	26.10	-	0.009	
1,2-Dichloroethane	-	26.27		0.03
Trichloroethene	27.99	28.02	0.02	0.01
1,2-Dichloropropane	-	28.66		0.006
Bromodichloromethane	-	29.43		0.02
Dibromomethane	-	29.59		2.2
Toluene	31.95	-	0.01	
1,1,2-Trichloroethane	-	33.21		ND
Tetrachloroethene	33.88	33.90	0.05	0.04
1,3-Dichloropropane	-	34.00		0.03
Dibromochloromethane	-	34.73		0.03
1,2-Dibromoethane	-	35.34		0.8
Chlorobenzene	36.56	36.59	0.003	0.01
Ethylbenzene	36.72	-	0.005	
1,1,1,2-Tetrachloroethane	-	36.80		0.005
m-Xylene	36.98	-	0.01	
p-Xylene	36.98	-	0.01	
o-Xylene	38.39	-	0.02	
Styrene	38.57	-	0.01	
Isopropylbenzene	39.58	-	0.05	
Bromoform	-	39.75		1.6
1,1,2,2-Tetrachloroethane	-	40.35		0.01
1,2,3-Trichloropropane	-	40.81		0.4

TABLE 1(cont.)

CHROMATOGRAPHIC RETENTION TIMES AND METHOD DETECTION LIMITS (MDL) FOR VOLATILE ORGANIC COMPOUNDS WITH PHOTOIONIZATION DETECTION (PID) AND HALL ELECTROLYTIC CONDUCTIVITY DETECTOR (HECD) DETECTORS

Analyte	PID Ret. Time[a] minute	HECD Ret. Time minute	PID MDL µg/L	HECD MDL µg/L
n-Propylbenzene	40.87	-	0.004	
Bromobenzene	40.99	41.03	0.006	0.03
1,3,5-Trimethylbenzene	41.41	-	0.004	
2-Chlorotoluene	41.41	41.45	ND	0.01
4-Chlorotoluene	41.60	41.63	0.02	0.01
tert-Butylbenzene	42.92	-	0.06	
1,2,4-Trimethylbenzene	42.71	-	0.05	
sec-Butylbenzene	43.31	-	0.02	
p-Isopropyltoluene	43.81	-	0.01	
1,3-Dichlorobenzene	44.08	44.11	0.02	0.02
1,4-Dichlorobenzene	44.43	44.47	0.007	0.01
n-Butylbenzene	45.20	-	0.02	
1,2-Dichlorobenzene	45.71	45.74	0.05	0.02
1,2-Dibromo-3-Chloropropane		48.57		3.0
1,2,4-Trichlorobenzene	51.43	51.46	0.02	0.03
Hexachlorobutadiene	51.92	51.96	0.06	0.02
Naphthalene	52.38	-	0.06	
1,2,3-Trichlorobenzene	53.34	53.37	ND	0.03
Internal Standards				
Fluorobenzene	26.84	-		
2-Bromo-1-chloropropane	-	33.08		

[a] Retention times determined on 60 m x 0.75 mm ID VOCOL capillary column. Program: Hold at 10°C for 8 minutes, then program at 4°C/min to 180°C, and hold until all expected compounds have eluted.

[b] Dash (-) indicates detector does not respond.

[c] ND = Not determined

TABLE 2

SINGLE LABORATORY ACCURACY AND PRECISION DATA
FOR VOLATILE ORGANIC COMPOUNDS IN WATER[d]

	Photoionization Detector		Hall Electrolytic Conductivity Detector	
Analyte	Standard Recovery,[a] %	Deviation of Recovery	Standard Recovery,[a] %	Deviation of Recovery
Benzene	99	1.2	-[b]	-
Bromobenzene	99	1.7	97	2.7
Bromochloromethane	-	-	96	3.0
Bromodichloromethane	-	-	97	2.9
Bromoform	-	-	106	5.5
Bromomethane	-	-	97	3.7
n-Butylbenzene	100	4.4	-	-
sec-Butylbenzene	97	2.6	-	-
tert-Butylbenzene	98	2.3	-	-
Carbon tetrachloride	-	-	92	3.3
Chlorobenzene	100	1.0	103	3.7
Chloroethane	-	-	96	3.8
Chloroform	-	-	98	2.5
Chloromethane	-	-	96	8.9
2-Chlorotoluene	ND[c]	ND	97	2.6
4-Chlorotoluene	101	1.0	97	3.1
1,2-Dibromo-3-chloropropane	-	-	86	9.9
Dibromochloromethane	-	-	102	3.3
1,2-Dibromoethane	-	-	97	2.7
Dibromomethane	-	-	109	7.4
1,2-Dichlorobenzene	102	2.1	100	1.5
1,3-Dichlorobenzene	104	1.7	106	4.3
1,4-Dichlorobenzene	103	2.2	98	2.3
Dichlorodifluoromethane	-	-	89	5.9
1,1-Dichloroethane	-	-	100	5.7
1,2-Dichloroethane	-	-	100	3.8
1,1-Dichloroethene	100	2.4	103	2.9
cis-1,2 Dichloroethene	ND	ND	105	3.5
trans-1,2-Dichloroethene	93	3.7	99	3.7
1,2-Dichloropropane	-	-	103	3.8
1,3-Dichloropropane	-	-	100	3.4
2,2-Dichloropropane	-	-	105	3.6
1,1-Dichloropropene	103	3.6	103	3.4
Ethylbenzene	101	1.4	-	-
Hexachlorobutadiene	99	9.5	98	8.3
Isopropylbenzene	98	0.9	-	-
p-Isopropyltoluene	98	2.4	-	-

TABLE 2 (cont.)

SINGLE LABORATORY ACCURACY AND PRECISION DATA
FOR VOLATILE ORGANIC COMPOUNDS IN WATER[d]

Analyte	Photoionization Detector		Hall Electrolytic Conductivity Detector	
	Standard Recovery,[a] %	Deviation of Recovery	Standard Recovery,[a] %	Deviation of Recovery
Methylene chloride	-	-	97	2.8
Naphthalene	102	6.3	-	-
n-Propylbenzene	103	2.0	-	-
Styrene	104	1.4	-	-
1,1,1,2-Tetrachloroethane	-	-	99	2.3
1,1,2,2-Tetrachloroethane	-	-	99	6.8
Tetrachloroethene	101	1.8	97	2.4
Toluene	99	0.8	-	-
1,2,3-Trichlorobenzene	106	1.9	98	3.1
1,2,4-Trichlorobenzene	104	2.2	102	2.1
1,1,1-Trichloroethane	-	-	104	3.4
1,1,2-Trichloroethane	-	-	109	6.2
Trichloroethene	100	0.78	96	3.5
Trichlorofluoromethane	-	-	96	3.4
1,2,3-Trichloropropane	-	-	99	2.3
1,2,4-Trimethylbenzene	99	1.2	-	-
1,3,5-Trimethylbenzene	101	1.4	-	-
Vinyl chloride	109	5.4	95	5.6
o-Xylene	99	0.8	-	
m-Xylene	100	1.4	-	-
p-Xylene	99	0.9	-	-

[a] Recoveries and standard deviations were determined from seven samples and spiked at 10 µg/L of each analyte. Recoveries were determined by internal standard method using a purge-and-trap. Internal standards were: Fluorobenzene for PID, 2-Bromo-1-chloropropane for HECD.

[b] Detector does not respond

[c] ND = Not determined

[d] This method was tested in a single laboratory using water spiked at 10 µg/L (see Reference 8).

TABLE 3

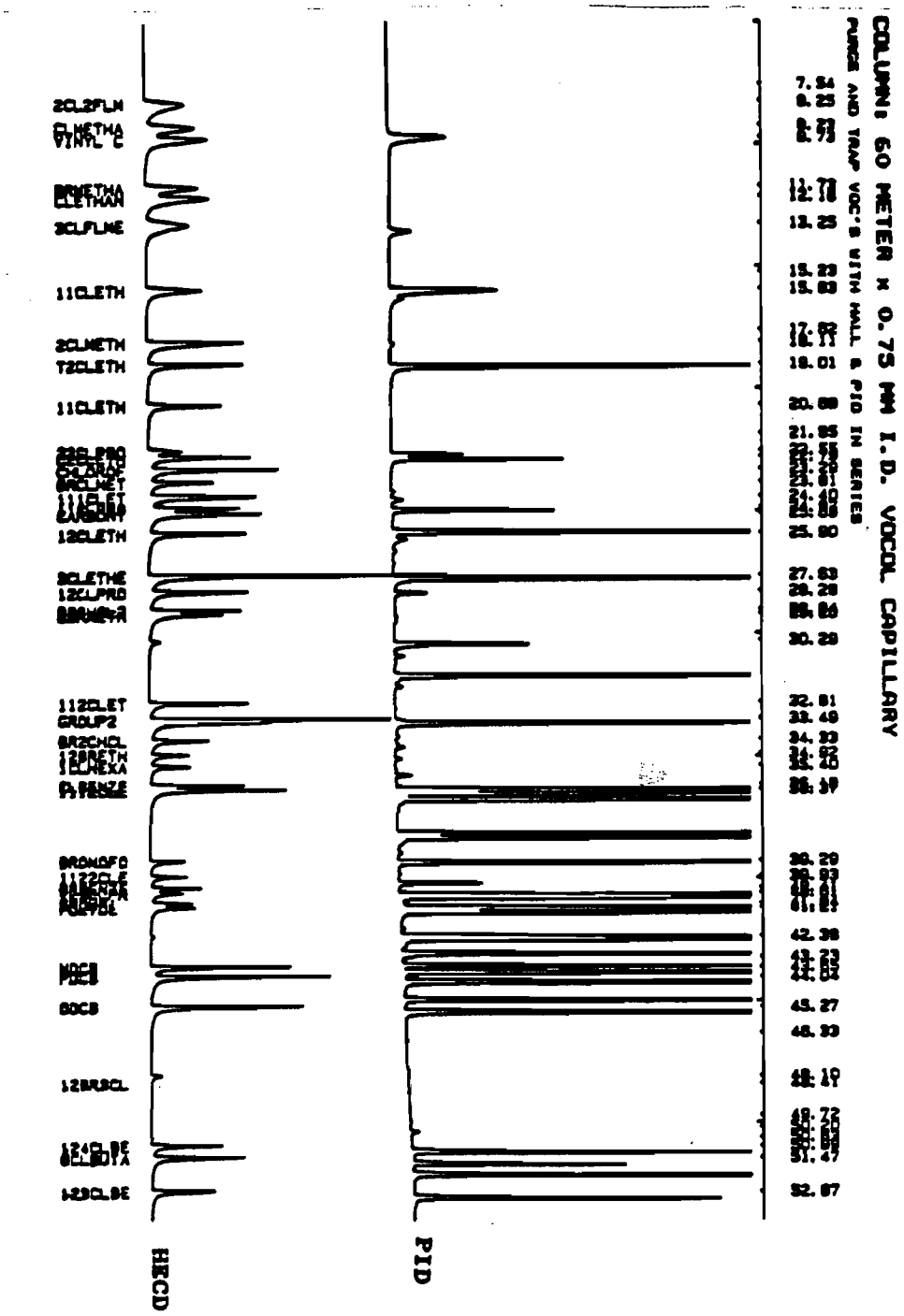
DETERMINATION OF ESTIMATED QUANTITATION LIMITS (EQL) FOR VARIOUS MATRICES[a]

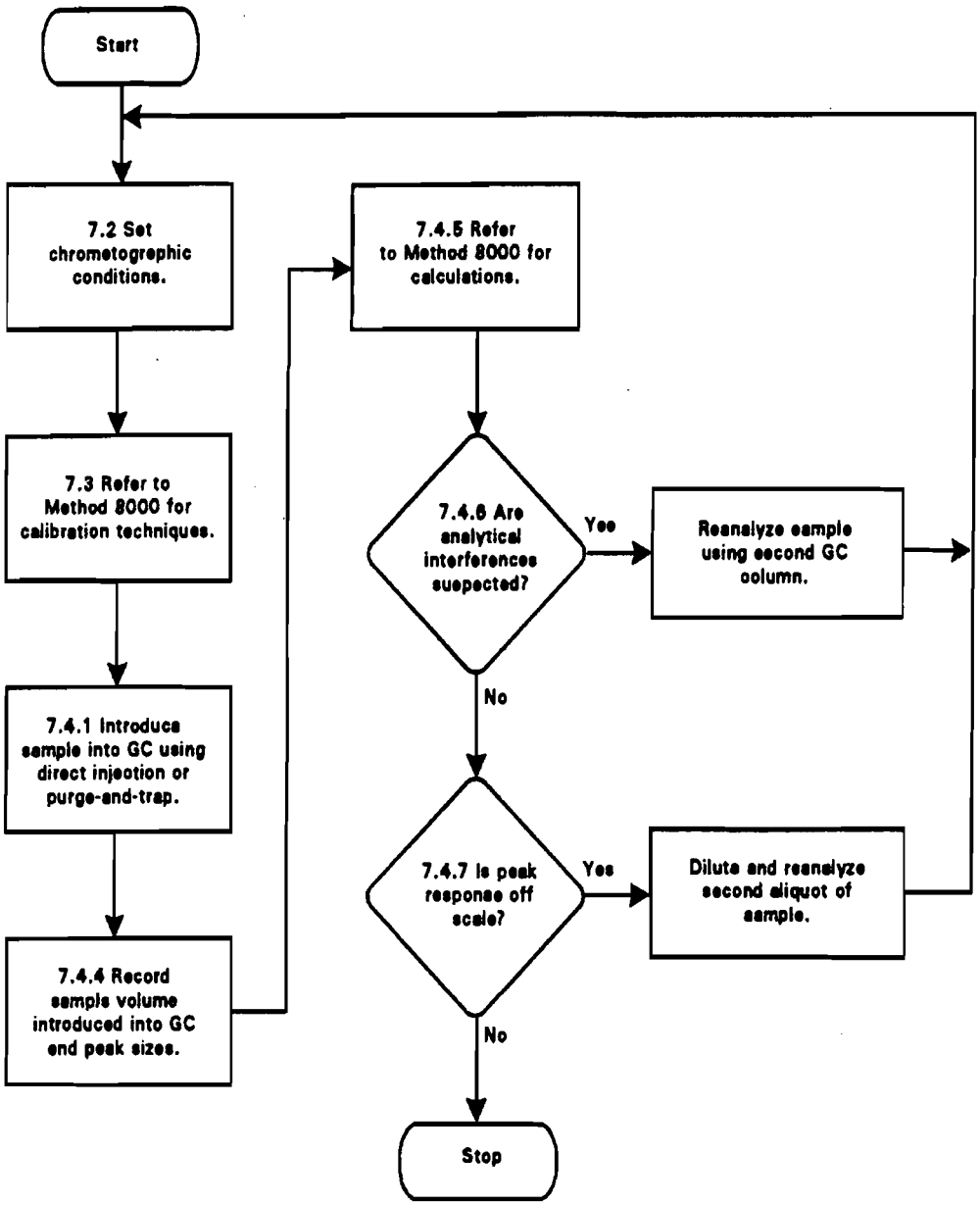
Matrix	Factor[b]
Ground water	10
Low-concentration soil	10
Water miscible liquid waste	500
High-concentration soil and sludge	1250
Non-water miscible waste	1250

[a] Sample EQLs are highly matrix dependent. The EQLs listed herein are provided for guidance and may not always be achievable.

[b] EQL = [Method detection limit (Table 1)] X [Factor (Table 2)]. For non-aqueous samples, the factor is on a wet-weight basis.

FIGURE 1
GAS CHROMATOGRAM OF VOLATILE ORGANICS




Start
7.2 Set chromatographic conditions.
7.3 Refer to Method 8000 for calibration techniques.
7.4.1 Introduce sample into GC using direct injection or purge-and-trap.
7.4.4 Record sample volume introduced into GC and peak sizes.
7.4.5 Refer to Method 8000 for calculations.
7.4.6 Are analytical interferences suspected?
Yes
Reanalyze sample using second GC column.
No
7.4.7 Is peak response off scale?
Yes
Dilute and reanalyze second aliquot of sample.
No
Stop

METHOD 9056

DETERMINATION OF INORGANIC ANIONS BY ION CHROMATOGRAPHY

1.0 SCOPE AND APPLICATION

1.1 This method addresses the sequential determination of the anions chloride, fluoride, bromide, nitrate, nitrite, phosphate, and sulfate in the collection solutions from the bomb combustion of solid waste samples, as well as all water samples.

1.2 The method detection limit (MDL), the minimum concentration of a substance that can be measured and reported with 99% confidence that the value is above zero, varies for anions as a function of sample size and the conductivity scale used. Generally, minimum detectable concentrations are in the range of 0.05 mg/L for F^- and 0.1 mg/L for Br^-, Cl^-, NO_3^-, NO_2^-, PO_4^{3-}, and SO_4^{2-} with a 100-µL sample loop and a 10-µmho full-scale setting on the conductivity detector. Similar values may be achieved by using a higher scale setting and an electronic integrator. Idealized detection limits of an order of magnitude lower have been determined in reagent water by using a 1-µmho/cm full-scale setting (Table 1). The upper limit of the method is dependent on total anion concentration and may be determined experimentally. These limits may be extended by appropriate dilution.

2.0 SUMMARY OF METHOD

2.1 A small volume of combustate collection solution or other water sample, typically 2 to 3 mL, is injected into an ion chromatograph to flush and fill a constant volume sample loop. The sample is then injected into a stream of carbonate-bicarbonate eluent of the same strength as the collection solution or water sample.

2.2 The sample is pumped through three different ion exchange columns and into a conductivity detector. The first two columns, a precolumn or guard column and a separator column, are packed with low-capacity, strongly basic anion exchanger. Ions are separated into discrete bands based on their affinity for the exchange sites of the resin. The last column is a suppressor column that reduces the background conductivity of the eluent to a low or negligible level and converts the anions in the sample to their corresponding acids. The separated anions in their acid form are measured using an electrical-conductivity cell. Anions are identified based on their retention times compared to known standards. Quantitation is accomplished by measuring the peak height or area and comparing it to a calibration curve generated from known standards.

3.0 INTERFERENCES

3.1 Any species with a retention time similar to that of the desired ion will interfere. Large quantities of ions eluting close to the ion of interest will also result in an interference. Separation can be improved by adjusting the eluent concentration and/or flow rate. Sample dilution and/or the use of the

method of standard additions can also be used. For example, high levels of organic acids may be present in industrial wastes, which may interfere with inorganic anion analysis. Two common species, formate and acetate, elute between fluoride and chloride.

3.2 Because bromide and nitrate elute very close together, they are potential interferences for each other. It is advisable not to have Br^-/NO_3^- ratios higher than 1:10 or 10:1 if both anions are to be quantified. If nitrate is observed to be an interference with bromide, use of an alternate detector (e.g., electrochemical detector) is recommended.

3.3 Method interferences may be caused by contaminants in the reagent water, reagents, glassware, and other sample processing apparatus that lead to discrete artifacts or elevated baseline in ion chromatograms.

3.4 Samples that contain particles larger than 0.45 µm and reagent solutions that contain particles larger than 0.20 µm require filtration to prevent damage to instrument columns and flow systems.

3.5 If a packed bed suppressor column is used, it will be slowly consumed during analysis and, therefore, will need to be regenerated. Use of either an anion fiber suppressor or an anion micromembrane suppressor eliminates the time-consuming regeneration step through the use of a continuous flow of regenerant.

4.0 APPARATUS AND MATERIALS

4.1 Ion chromatograph, capable of delivering 2 to 5 mL of eluent per minute at a pressure of 200 to 700 psi (1.3 to 4.8 MPa). The chromatograph shall be equipped with an injection valve, a 100-µL sample loop, and set up with the following components, as schematically illustrated in Figure 1.

4.1.1 Precolumn, a guard column placed before the separator column to protect the separator column from being fouled by particulates or certain organic constituents (4 x 50 mm, Dionex P/N 030825 [normal run], or P/N 030830 [fast run], or equivalent).

4.1.2 Separator column, a column packed with low-capacity pellicular anion exchange resin that is styrene divinylbenzene-based has been found to be suitable for resolving F^-, Cl^-, NO_2^-, PO_4^{-3}, Br^-, NO_3^-, and SO_4^{-2} (see Figure 2) (4 x 250 mm, Dionex P/N 03827 [normal run], or P/N 030831 [fast run], or equivalent).

4.1.3 Suppressor column, a column that is capable of converting the eluent and separated anions to their respective acid forms (fiber, Dionex P/N 35350, micromembrane, Dionex P/N 38019 or equivalent).

4.1.4 Detector, a low-volume, flowthrough, temperature-compensated, electrical conductivity cell (approximately 6 µL volume, Dionex, or equivalent) equipped with a meter capable of reading from 0 to 1,000 µseconds/cm on a linear scale.

4.1.5 Pump, capable of delivering a constant flow of approximately 2 to 5 mL/min throughout the test and tolerating a pressure of 200 to 700 psi (1.3 to 4.8 MPa).

4.2 Recorder, compatible with the detector output with a full-scale response time in 2 seconds or less.

4.3 Syringe, minimum capacity of 2 mL and equipped with a male pressure fitting.

4.4 Eluent and regenerant reservoirs, suitable containers for storing eluents and regenerant. For example, 4 L collapsible bags can be used.

4.5 Integrator, to integrate the area under the chromatogram. Different integrators can perform this task when compatible with the electronics of the detector meter or recorder. If an integrator is used, the maximum area measurement must be within the linear range of the integrator.

4.6 Analytical balance, capable of weighing to the nearest 0.0001 g.

4.7 Pipets, Class A volumetric flasks, beakers: assorted sizes.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One. Column life may be extended by passing reagent water through a 0.22-µm filter prior to use.

5.3 Eluent, 0.003M $NaHCO_3$/0.0024M Na_2CO_3. Dissolve 1.0080 g of sodium bicarbonate (0.003M $NaHCO_3$) and 1.0176 g of sodium carbonate (0.0024M Na_2CO_3) in reagent water and dilute to 4 L with reagent water.

5.4 Suppressor regenerant solution. Add 100 mL of 1N H_2SO_4 to 3 L of reagent water in a collapsible bag and dilute to 4 L with reagent water.

5.5 Stock solutions (1,000 mg/L).

5.5.1 Bromide stock solution (1.00 mL = 1.00 mg Br^-). Dry approximately 2 g of sodium bromide (NaBr) for 6 hours at 150°C, and cool in a desiccator. Dissolve 1.2877 g of the dried salt in reagent water, and dilute to 1 L with reagent water.

5.5.2 Chloride stock solution (1.00 mL = 1.00 mg Cl^-). Dry sodium chloride (NaCl) for 1 hour at 600°C, and cool in a desiccator. Dissolve 1.6484 g of the dry salt in reagent water, and dilute to 1 L with reagent water.

5.5.3 Fluoride stock solution (1.00 mL = 1.00 mg F^-). Dissolve 2.2100 g of sodium fluoride (NaF) in reagent water, and dilute to 1 L with reagent water. Store in chemical-resistant glass or polyethylene.

5.5.4 Nitrate stock solution (1.00 mL = 1.00 mg NO_3^-). Dry approximately 2 g of sodium nitrate ($NaNO_3$) at 105°C for 24 hours. Dissolve exactly 1.3707 g of the dried salt in reagent water, and dilute to 1 L with reagent water.

5.5.5 Nitrite stock solution (1.00 mL = 1.00 mg NO_2^-). Place approximately 2 g of sodium nitrate ($NaNO_2$) in a 125 mL beaker and dry to constant weight (about 24 hours) in a desiccator containing concentrated H_2SO_4. Dissolve 1.4998 g of the dried salt in reagent water, and dilute to 1 L with reagent water. Store in a sterilized glass bottle. Refrigerate and prepare monthly.

NOTE: Nitrite is easily oxidized, especially in the presence of moisture, and only fresh reagents are to be used.

NOTE: Prepare sterile bottles for storing nitrite solutions by heating for 1 hour at 170°C in an air oven.

5.5.6 Phosphate stock solution (1.00 mL = 1.00 mg PO_4^{3-}). Dissolve 1.4330 g of potassium dihydrogen phosphate (KH_2PO_4) in reagent water, and dilute to 1 L with reagent water. Dry sodium sulfate (Na_2SO_4) for 1 hour at 105°C and cool in a desiccator.

5.5.7 Sulfate stock solution (1.00 mL = 1.00 mg SO_4^{2-}). Dissolve 1.4790 g of the dried salt in reagent water, and dilute to 1 L with reagent water.

5.6 Anion working solutions. Prepare a blank and at least three different working solutions containing the following combinations of anions. The combination anion solutions must be prepared in Class A volumetric flasks. See Table 2.

5.6.1 Prepare a high-range standard solution by diluting the volumes of each anion specified in Table 2 together to 1 L with reagent water.

5.6.2 Prepare the intermediate-range standard solution by diluting 10.0 mL of the high-range standard solution (see Table 2) to 100 mL with reagent water.

5.6.3 Prepare the low-range standard solution by diluting 20.0 mL of the intermediate-range standard solution (see Table 2) to 100 mL with reagent water.

5.7 Stability of standards. Stock standards are stable for at least 1 month when stored at 4°C. Dilute working standards should be prepared weekly, except those that contain nitrite and phosphate, which should be prepared fresh daily.

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Analyze the samples as soon as possible after collection. Preserve by refrigeration at 4°C.

7.0 PROCEDURE

7.1 Calibration

7.1.1 Establish ion chromatographic operating parameters equivalent to those indicated in Table 1.

7.1.2 For each analyte of interest, prepare calibration standards at a minimum of three concentration levels and a blank by adding accurately measured volumes of one or more stock standards to a Class A volumetric flask and diluting to volume with reagent water. If the working range exceeds the linear range of the system, a sufficient number of standards must be analyzed to allow an accurate calibration curve to be established. One of the standards should be representative of a concentration near, but above, the method detection limit if the system is operated on an applicable attenuator range. The other standards should correspond to the range of concentrations expected in the sample or should define the working range of the detector. Unless the attenuator range settings are proven to be linear, each setting must be calibrated individually.

7.1.3 Using injections of 0.1 to 1.0 mL (determined by injection loop volume) of each calibration standard, tabulate peak height or area responses against the concentration. The results are used to prepare a calibration curve for each analyte. During this procedure, retention times must be recorded.

7.1.4 The working calibration curve must be verified on each working day, or whenever the anion eluent strength is changed, and for every batch of samples. If the response or retention time for any analyte varies from the expected values by more than ± 10%, the test must be repeated, using fresh calibration standards. If the results are still more than ± 10%, an entirely new calibration curve must be prepared for that analyte.

7.1.5 Nonlinear response can result when the separator column capacity is exceeded (overloading). Maximum column loading (all anions) should not exceed about 400 ppm.

7.2 Analyses

7.2.1 Sample preparation. When aqueous samples are injected, the water passes rapidly through the columns, and a negative "water dip" is observed that may interfere with the early-eluting fluoride and/or chloride ions. The water dip should not be observed in the combustate samples; the collecting solution is a concentrated eluent solution that will "match" the eluent strength when diluted to 100-mL with reagent water according to the bomb combustion procedure. Any dilutions required in analyzing other water samples should be made with the eluent solution. The water dip, if present, may be removed by adding concentrated eluent to

all samples and standards. When a manual system is used, it is necessary to micropipet concentrated buffer into each sample. The recommended procedures follow:

(1) Prepare a 100-mL stock of eluent 100 times normal concentration by dissolving 2.5202 g $NaHCO_3$ and 2.5438 g Na_2CO_3 in 100-mL reagent water. Protect the volumetric flask from air.

(2) Pipet 5 mL of each sample into a clean polystyrene micro-beaker. Micropipet 50 µL of the concentrated buffer into the beaker and stir well.

Dilute the samples with eluent, if necessary, to concentrations within the linear range of the calibration.

7.2.2 Sample analysis.

7.2.2.1 Start the flow of regenerant through the suppressor column.

7.2.2.2 Set up the recorder range for maximum sensitivity and any additional ranges needed.

7.2.2.3 Begin to pump the eluent through the columns. After a stable baseline is obtained, inject a midrange standard. If the peak height deviates by more than 10% from that of the previous run, prepare fresh standards.

7.2.2.4 Begin to inject standards starting with the highest concentration standard and decreasing in concentration. The first sample should be a quality control reference sample to check the calibration.

7.2.2.5 Using the procedures described in Step 7.2.1, calculate the regression parameters for the initial standard curve. Compare these values with those obtained in the past. If they exceed the control limits, stop the analysis and look for the problem.

7.2.2.6 Inject a quality control reference sample. A spiked sample or a sample of known content must be analyzed with each batch of samples. Calculate the concentration from the calibration curve and compare the known value. If the control limits are exceeded, stop the analysis until the problem is found. Recalibration is necessary.

7.2.2.7 When an acceptable value has been obtained for the quality control sample, begin to inject the samples.

7.2.2.8 Load and inject a fixed amount of well-mixed sample. Flush injection loop thoroughly, using each new sample.

Use the same size loop for standards and samples. Record the resulting peak size in area or peak height units. An automated constant volume injection system may also be used.

7.2.2.9 The width of the retention time window used to make identifications should be based on measurements of actual retention time variations of standards over the course of a day. Three times the standard deviation of a retention time can be used to calculate a suggested window size for a compound. However, the experience of the analyst should weigh heavily in the interpretation of chromatograms.

7.2.2.10 If the response for the peak exceeds the working range of the system, dilute the sample with an appropriate amount of reagent water and reanalyze.

7.2.2.11 If the resulting chromatogram fails to produce adequate resolution, or if identification of specific anions is questionable, spike the sample with an appropriate amount of standard and reanalyze.

NOTE: Nitrate and sulfate exhibit the greatest amount of change, although all anions are affected to some degree. In some cases, this peak migration can produce poor resolution or misidentification.

7.3 Calculation

7.3.1 Prepare separate calibration curves for each anion of interest by plotting peak size in area, or peak height units of standards against concentration values. Compute sample concentration by comparing sample peak response with the standard curve.

7.3.2 Enter the calibration standard concentrations and peak heights from the integrator or recorder into a calculator with linear least squares capabilities.

7.3.3 Calculate the following parameters: slope (s), intercept (I), and correlation coefficient (r). The slope and intercept define a relationship between the concentration and instrument response of the form:

$$y_i = s_i x_i + I \quad (1)$$

where:

y_i = predicted instrument response
s_i = response slope
x_i = concentration of standard i
I = intercept

Rearrangement of the above equation yields the concentration corresponding to an instrumental measurement:

$$x_j = (y_j - I)/s_j \quad (2)$$

where:

x_j = calculated concentration for a sample
y_j = actual instrument response for a sample
s_j and I are calculated slope and intercept from calibration above.

7.3.4 Enter the sample peak height into the calculator, and calculate the sample concentration in milligrams per liter.

8.0 QUALITY CONTROL

8.1 All quality control data should be maintained and available for easy reference and inspection. Refer to Chapter One for additional quality control guidelines.

8.2 After every 10 injections, analyze a midrange calibration standard. If the instrument response has changed by more than 5%, recalibrate.

8.3 Analyze one in every ten samples in duplicate. Take the duplicate sample through the entire sample preparation and analytical process.

8.4 A matrix spiked sample should be run for each analytical batch or twenty samples, whatever is more frequent, to determine matrix effects.

9.0 METHOD PERFORMANCE

9.1 Single-operator accuracy and precision for reagent, drinking and surface water, and mixed domestic and industrial wastewater are listed in Table 3.

9.2 Combustate samples. These data are based on 41 data points obtained by six laboratories who each analyzed four used crankcase oils and three fuel oil blends with crankcase in duplicate. The oil samples were combusted using Method 5050. A data point represents one duplicate analysis of a sample. One data point was judged to be an outlier and was not included in the results.

9.2.1 Precision. The precision of the method as determined by the statistical examination of interlaboratory test results is as follows:

<u>Repeatability</u> - The difference between successive results obtained by the sample operator with the same apparatus under constant operating conditions on identical test material would exceed, in the long run, in the normal and correct operation of the test method, the following values only in 1 case in 20 (see Table 4):

*where x is the average of two results in µg/g.

$$Repeatability = 20.9\sqrt{x}*$$

Reproducibility - The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would exceed, in the long run, the following values only in 1 case in 20:

$$Reproducibility = 42.1\sqrt{x}*$$

*where x is the average value of two results in µg/g.

9.2.2 Bias. The bias of this method varies with concentration, as shown in Table 5:

Bias = Amount found - Amount expected

10.0 REFERENCES

1. Environmental Protection Agency. Test Method for the Determination of Inorganic Anions in Water by Ion Chromatography. EPA Method 300.0. EPA-600/4-84-017. 1984.

2. Annual Book of ASTM Standards, Volume 11.01 Water D4327, Standard Test Method for Anions in Water by Ion Chromatography, pp. 696-703. 1988.

3. Standard Methods for the Examination of Water and Wastewater, Method 429, "Determination of Anions by Ion Chromatography with Conductivity Measurement," 16th Edition of Standard Methods.

4. Dionex, IC 16 Operation and Maintenance Manual, PN 30579, Dionex Corp., Sunnyvale, CA 94086.

5. Method detection limit (MDL) as described in "Trace Analyses for Wastewater," J. Glaser, D. Foerst, G. McKee, S. Quave, W. Budde, Environmental Science and Technology, Vol. 15, Number 12, p. 1426, December 1981.

6. Gaskill, A.; Estes, E. D.; Hardison, D. L.; and Myers, L. E. Validation of Methods for Determining Chlorine in Used Oils and Oil Fuels. Prepared for U.S. Environmental Protection Agency Office of Solid Waste. EPA Contract No. 68-01-7075, WA 80. July 1988.

TABLE 1.
CHROMATOGRAPHIC CONDITIONS AND METHOD DETECTION LIMITS IN REAGENT WATER

Analyte	Retention[a] time min	Relative retention time	Method[b] detection limit, mg/L
Fluoride	1.2	1.0	0.005
Chlorine	3.4	2.8	0.015
Nitrite-N	4.5	3.8	0.004
o-Phosphate-P	9.0	7.5	0.061
Nitrate-N	11.3	9.4	0.013
Sulfate	21.4	17.8	0.206

Standard conditions:

Columns - As specified in 4.1.1-4.1.3
Detector - As specified in 4.1.4
Eluent - As specified in 5.3

Sample loop - 100 µL
Pump volume - 2.30 mL/min

Concentrations of mixed standard (mg/L):

Fluoride 3.0
Chloride 4.0
Nitrite-N 10.0
o-Phosphate-P 9.0
Nitrate-N 30.0
Sulfate 50.0

[a]The retention time given for each anion is based on the equipment and analytical conditions described in the method. Use of other analytical columns or different elutant concentrations will effect retention times accordingly.

[b]MDL calculated from data obtained using an attentuator setting of 1-µmho/cm full scale. Other settings would produce an MDL proportional to their value.

TABLE 2.
PREPARATION OF STANDARD SOLUTIONS FOR INSTRUMENT CALIBRATION

	High Range Standard[1]	Anion concentration mg/L	Intermediate-range standard, mg/L (see 5.6.2)	Low-range standard, mg/L (see 5.6.3)
Fluoride (F^-)	10	10	1.0	0.2
Chloride (Cl^-)	10	10	1.0	0.2
Nitrite (NO_2^-)	20	20	2.0	0.4
Phosphate (PO_4^{3-})	50	50	5.0	1.0
Bromide (Br^-)	10	10	1.0	0.2
Nitrate (NO_3^-)	30	30	3.0	0.6
Sulfate (SO_4^{2-})	100	100	10.0	2.0

[1]Milliliters of each stock solution (1.00 mL = 1.00 mg) diluted to 1 L (see sec. 5.6.1).

TABLE 3.
SINGLE-OPERATOR ACCURACY AND PRECISION

Analyte	Sample type	Spike mg/L	Number of replicates	Mean recovery, %	Standard deviation, mg/L
Chloride	RW	0.050	7	97.7	0.0047
	DW	10.0	7	98.2	0.289
	SW	1.0	7	105.0	0.139
	WW	7.5	7	82.7	0.445
Fluoride	RW	0.24	7	103.1	0.0009
	DW	9.3	7	87.7	0.075
	SW	0.50	7	74.0	0.0038
	WW	1.0	7	92.0	0.011
Nitrate-N	RW	0.10	7	100.9	0.0041
	DW	31.0	7	100.7	0.356
	SW	0.50	7	100.0	0.0058
	WW	4.0	7	94.3	0.058
Nitrite-N	RW	0.10	7	97.7	0.0014
	DW	19.6	7	103.3	0.150
	SW	0.51	7	88.2	0.0053
	WW	0.52	7	100.0	0.018
o-Phosphate-P	RW	0.50	7	100.4	0.019
	DE	45.7	7	102.5	0.386
	SW	0.51	7	94.1	0.020
	WW	4.0	7	97.3	0.04
Sulfate	RW	1.02	7	102.1	0.066
	DW	98.5	7	104.3	1.475
	SW	10.0	7	111.6	0.709
	WW	12.5	7	134.9	0.466

RW = Reagent water. SW = Surface water.
DW = Drinking water. WW = Wastewater.

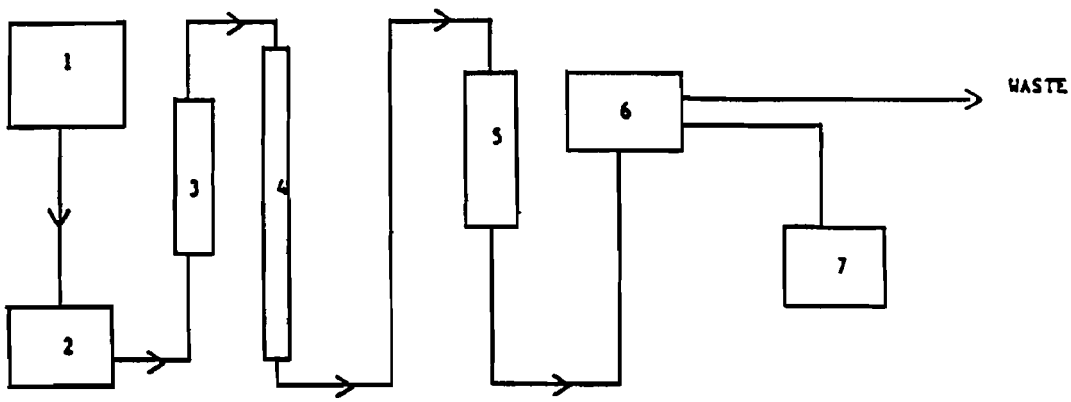
TABLE 4.
REPEATABILITY AND REPRODUCIBILITY FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY

Average value, µg/g	Repeatability, µg/g	Reproducibility, µg/g
500	467	941
1,000	661	1,331
1,500	809	1,631
2,000	935	1,883
2,500	1,045	2,105
3,000	1,145	2,306

TABLE 5.
RECOVERY AND BIAS DATA FOR CHLORINE IN USED OILS BY BOMB OXIDATION AND ION CHROMATOGRAPHY

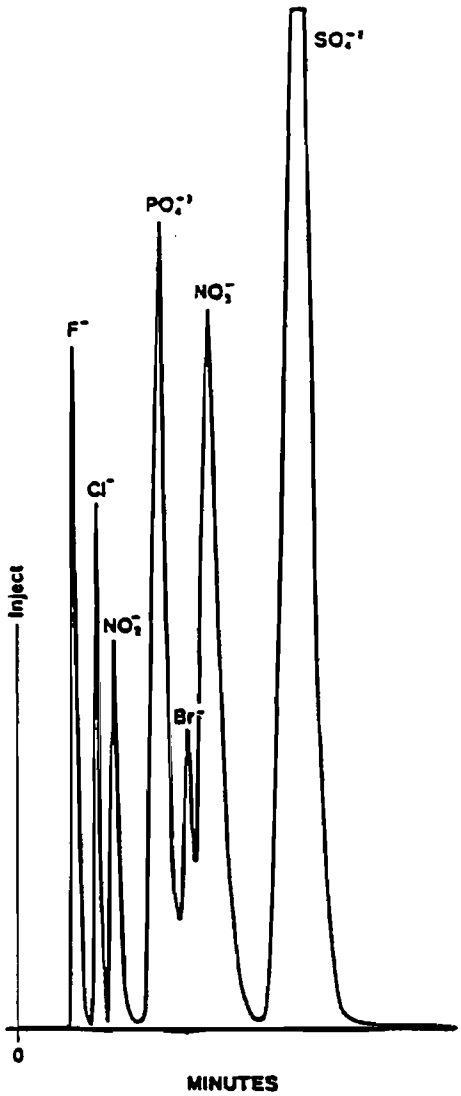
Amount Expected µg/g	Amount found µg/g	Bias, µg/g	Percent, bias
320	567	247	+77
480	773	293	+61
920	1,050	130	+14
1,498	1,694	196	+13
1,527	1,772	245	+16
3,029	3,026	-3	0
3,045	2,745	-300	-10

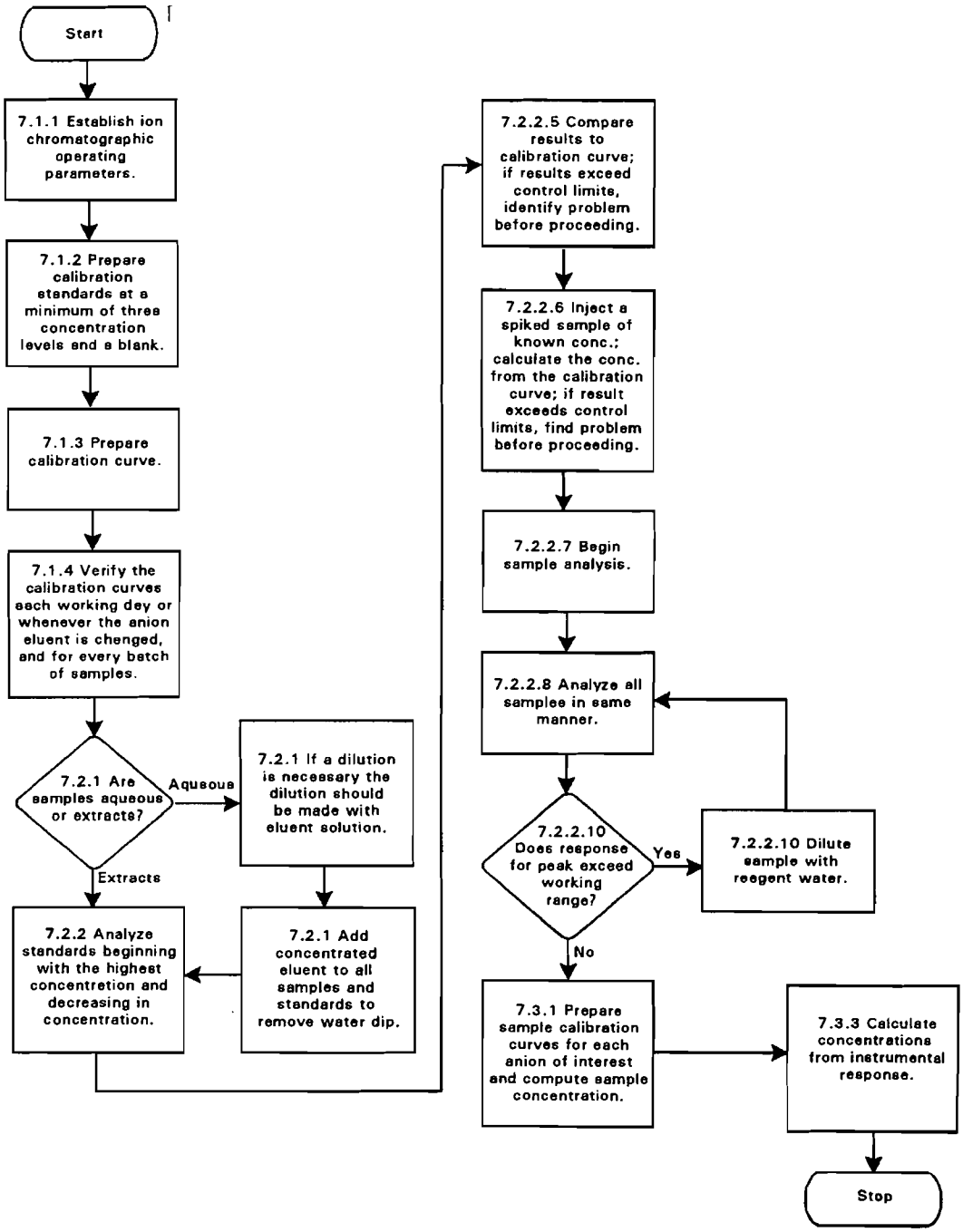
FIGURE 1
SCHEMATIC OF ION CHROMATOGRAPH



(1) Eluent reservoir
(2) Pump
(3) Precolumn
(4) Separator column
(5) Suppressor column
(6) Detector
(7) Recorder or integrator, or both

FIGURE 2
TYPICAL ANION PROFILE




Start
7.1.1 Establish ion chromatographic operating parameters.
7.1.2 Prepare calibration standards at a minimum of three concentration levels and a blank.
7.1.3 Prepare calibration curve.
7.1.4 Verify the calibration curves each working day or whenever the anion eluent is changed, and for every batch of samples.
7.2.1 Are samples aqueous or extracts?
Aqueous
Extracts
7.2.1 If a dilution is necessary the dilution should be made with eluent solution.
7.2.1 Add concentrated eluent to all samples and standards to remove water dip.
7.2.2 Analyze standards beginning with the highest concentration and decreasing in concentration.
7.2.2.5 Compare results to calibration curve; if results exceed control limits, identify problem before proceeding.
7.2.2.6 Inject a spiked sample of known conc.; calculate the conc. from the calibration curve; if result exceeds control limits, find problem before proceeding.
7.2.2.7 Begin sample analysis.
7.2.2.8 Analyze all samples in same manner.
7.2.2.10 Does response for peak exceed working range?
Yes
7.2.2.10 Dilute sample with reagent water.
No
7.3.1 Prepare sample calibration curves for each anion of interest and compute sample concentration.
7.3.3 Calculate concentrations from instrumental response.
Stop

APPENDIX C

Environmental Security Technology Certification Program (ESTCP)

Quality Assurance Project Plan

In Situ Catalytic Groundwater Treatment Using Palladium Catalyst and Horizontal Flow Treatment Wells

Naval Facilities Engineering Service Center
Stanford University
Air Force Institute of Technology
Lawrence Livermore National Laboratory

May 18, 2001

Final Version
Revision 2.0

1. Purpose and Scope of This Plan

This Quality Assurance Project Plan (QAPP) pertains to the demonstration of the technology entitled "In Situ Catalytic Groundwater Treatment Using Palladium Catalyst and Horizontal Flow Treatment Wells," hereafter referred to as the Pd/HFTW technology. This technology demonstration is sponsored by the Environmental Security Technology Certification Program (ESTCP) of the United States Department of Defense. The technology demonstration will be performed at Site 19 of the Edwards Air Force Base in southeastern California. The Pd/HFTW technology is designed to remove trichloroethylene (TCE) and other halogenated organic contaminants from groundwater by catalytically dehalogenating the compounds of concern. The technology and the demonstration site have been described in detail in the Demonstration Plan.

The purpose of this QAPP is to delineate the approach for monitoring the demonstration to ensure that the facilities, equipment, personnel, methods, practices, records, and controls are in conformance with ESTCP-approved data quality objectives.

2. Quality Assurance Responsibilities

This demonstration project represents a collaboration of the following agencies and organizations:

- Stanford University: project design, management, and implementation
- U.S. Navy, Naval Facilities Engineering Service Center (NFESC): project oversight and project support
- U.S. Department of Defense, Environmental Security Technology Certification Program (ESTCP): project sponsor
- Edwards Air Force Base: site host
- Air Force Institute of Technology: modeling activities
- Lawrence Livermore National Laboratories: reactor design and fabrication
- Earth Tech: contractor to Edwards Air Force Base

The Quality Assurance (QA) Officer for this project will be Dr. Jeffrey Cunningham of Stanford University, as stated in Section 3.9 of the Demonstration Plan. Sample collection will be conducted by Stanford University, NFESC, and Earth Tech. Sample analysis will be conducted in the Water Quality Laboratory of the Department of Civil and Environmental Engineering at Stanford University.

The overall role of the QA Officer is to ensure that the data produced during this demonstration project are of sufficient type, quantity, and quality that the cost and performance of the Pd/HFTW technology can be assessed accurately. The QA Officer shall perform the following specific duties.

- Maintain copies of all protocols pertaining to the demonstration.

- Ascertain that equipment used in the generation, measurement, or assessment of data is of appropriate design and adequate capacity to function properly, and is suitably located for operation, inspection, cleaning, and maintenance.
- Verify that equipment is periodically inspected, cleaned, and maintained, and that equipment used for the generation, measurement, or assessment of data is tested, calibrated, and/or standardized.
- Maintain records of all inspection, maintenance, testing, calibrating, and/or standardizing operations, including the date(s) of the operations and a description of wheter the maintenance operations were routine and followed standard operating procedures.
- Maintain records of non-routine repairs performed on equipment as a result of failure and/or malfunction, documenting the nature of the defect, how and when the defect was discovered, and any remedial action recommended or taken in response to the defect.
- Inspect the Pd/HFTW system at adequate intervals to evaluate its integrity. Write a report of each periodic inspection, including the date of the inspection, the phase or segment of the demonstration inspected, any problems found, actions recommended and taken to resolve existing problems, and, if necessary, scheduled date for reinspection.
- Document any deviations from approved protocols or standard operating procedures.
- Review the final demonstration report to ensure that it accurately describes the methods and standard operating procedures, and that the reported results accurately reflect the raw data of the demonstration.

3. Data Quality Parameters and Indicators

The following parameters will be used to assess the quality of collected data:

(1) Accuracy: the degree of agreement between measurements and the actual or true values of the sample
(2) Precision: the degree of mutual agreement among a number of individual measurements
(3) Completeness: the amount of valid or useful data obtained, relative to the number of valid measurements that should have been collected (i.e., that were planned for collection)
(4) Representativeness: the degree to which the measurements accurately and precisely represent the parameters for the conditions of operation.

Accuracy, the degree of agreement between measurement and the actual or true value of the sample, will be determined by analysis of spike recoveries. Either surrogate spikes or quality control checks (QCCs) can be used. Surrogate spike compounds are normally analytes not found within the sample matrix but added to each individual sample for the data validation of accuracy. QCCs are spiked samples prepared from commercially available stock solutions having at least five target analytes and are generally used to evaluate loss of instrument sensitivity and are thus of low concentration. Accuracy as measured by spike recovery is expressed as percent recovery (%R):

$$\%R = 100\ (C_M/C_S)$$

where C_M is the measured concentration of analyte and C_S is the spiked concentration of analyte. For this demonstration project, surrogate spikes will be added to samples and %R tabulated for all ground water samples. Perchloroethylene (PCE) is a good candidate for a surrogate spike compound because it is chemically similar to TCE and the other analytes in this project, and should not cause any artificial changes in the concentrations of the other analytes.

Precision, the degree of mutual agreement among a number of individual measurements, is commonly determined by analysis of duplicate and replicate samples. Duplicate samples are collected in a common container and then transferred to two or more individual containers, while replicate samples are collected sequentially in individual containers. For this demonstration project, replicate samples will be used. Precision can be expressed as percent relative difference (%RD):

$$\%RD = 100\ (C1 - C2)/((C1 + C2)/2)$$

where C1 and C2 are the individual measurements for the duplicate or replicate samples. When large data sets are collected from a system which is in "steady state," precision can also be evaluated by the percent relative standard deviation (%RSD):

$$\%RSD = 100\ (\sigma/\mu)$$

where σ is the standard deviation and μ is the mean value. The analysis of precision based upon %RSD will be watched, but unless steady-sate conditions are known to exist, it will be considered secondary.

Table 3-1: Accuracy and Precision Objectives for Groundwater Samples

Analytes	Method of Analysis	Accuracy (%R)	Precision (%RD)
TCE, *cis*-DCE, *trans*-DCE, 1,1-DCE, and VC	Modified EPA methods 5030B (purge-and-trap) and 8021B (gas chromatography with photoionization detection)	85 –115%	20%
Sulfate	Modified EPA method 300.1 and/or 9056 (anion chromatography)	85 – 115%	20%
Sulfide	Modified EPA method 376.2 (colorimetric, methylene blue)	85 – 115%	20%

Note: Percent relative difference (%RD) for precision measurement is based on intralaboratory analysis of replicate samples.

Completeness is a measure of the amount of valid data obtained from a measurement system, expressed as a percentage of the number of valid measurements that should have been collected

(i.e., measurements that were planned to be collected). Ideally, then, completeness would be 100%. The reasons why completeness sometimes does not achieve 100% include mechanical failure, electrical failure, operator errors, lack of needed resources to implement planned sample collection, collection of irrelevant samples, or failure to collect samples from an important region of the demonstration site (e.g., one or more strata in a stratified aquifer). For this demonstration project, the objective is at least 90% completeness.

Representativeness, the degree to which the measurement accurately and precisely represents the parameter for the condition or operation, is not easily quantifiable. Within the subsurface environment, stratification of the aquifer solids (e.g., clay lenses embedded in sandy zones) can produce micro-environments which have entirely different redox potentials when compared to the bulk ground water surrounding them. The use of multi-level sampling points within a single borehole both allows the detection of these micro-environments and also produces sufficient data for statistical analysis of the bulk ground water chemical concentrations. Proper sample collection, shipping, and storage are required to ensure representative results are obtained. Sampling and analysis procedures will be reviewed regularly to ensure representativeness.

4. Calibration Procedures

Groundwater samples will be collected at the test site and analyzed in the Water Quality Laboratory (Department of Civil and Environmental Engineering) at Stanford University, or at another qualified laboratory. The Field Sampling Plan (FSP) is provided as Appendix C of the Demonstration Plan. Analyses will be conducted to measure the concentrations of trichloroethylene (TCE), *cis*-dichloroethylene (*cis*-DCE), *trans*-DCE, 1,1-DCE, and vinyl chloride (VC) in the collected groundwater. Aqueous concentrations will be measured according to procedures adapted from EPA standard methods 5030B (purge-and-trap for aqueous samples) and 8021B (aromatic and halogenated volatiles by gas chromatography using photoionization and/or electrolytic conductivity detectors), which are summarized as follows:

1. Sample aliquots of 5.0 mL are taken from the sample collection vial with an auto-pipette.
2. VOCs are stripped from the water and concentrated into a helium carrier gas stream with a Tekmar 4000 Head Space Concentrator (purge-and-trap).
3. Concentrations of the individual VOCs are determined with a Hewlett Packard 5890 gas chromatograph and photo-ionization detection (PID) or electro-conductivity detection (ElCD).

EPA standard methods 5030B and 8021B are provided in Appendix D of the Demonstration Plan.

The analytical method is calibrated using an external standard solution of TCE, *cis*-DCE, *trans*-DCE, and 1,1-DCE. Vinyl chloride is added (neat phase) to the standard solution immediately prior to analysis of the standard solution to prevent losses of vinyl chloride from the standard solution during storage. Concentrations of the analytes in the standard solution are: 978 μg/L TCE, 688 μg/L *cis*-DCE, 592 μg/L *trans*-DCE, 912 μg/L 1,1-DCE, and 800 μg/L VC. The

standard solution and a blank sample are analyzed prior to the first sample analysis and again after each eight sample analyses in order to maintain calibration of the analytical instrumentation.

Samples will also, on occasion, be analyzed for sulfate concentration and sulfide concentration. Sulfate concentration will be measured according to procedures adapted from EPA standard methods 300.1 (Determination of Inorganic Anions in Drinking Water by Ion Chromatography) and 9056 (Determination of Inorganic Anions by Ion Chromatography). Sulfide concentration will be measured according to procedurs adapted from EPA standard method 376.2 (Colorimetric Analysis with Methylene Blue). EPA standard methods 300.1, 376.2, and 9056 are provided in Appendix D of the Demonstration Plan. The ion chromatography method is calibrated using external standard solutions of sulfate, nitrate, and bromide. A stock solution consisting of 9139 mg/L SO_4^{2-}, 7256 mg/L NO_3^-, and 4014 mg/L Br^- is diluted to 1:100 and to 1:1000. This yields two external standard solutions which are used to calibrate the ion chromatograph. The standard solutions and a blank are analyzed prior to each sample analysis session

5. Demonstration Procedures

Initial design parameters will be specified during the preliminary design phase of this project, as discussed in Section 3.6.1.3 of the Demonstration Plan. However, it is expected that, during the initial few weeks or months of system operation, variables such as the pumping rate, hydrogen addition rate, regenerant dose, etc., might have to be adjusted for field conditions. During this time, the reactors may need to be taken off-line on a regular basis. Therefore, the reactors will initially be operated above-ground, i.e., not placed down the wells. This will greatly facilitate taking the reactors off-line, performing maintenance, altering system variables, etc. Once the system has been demonstrated to achieve a consistent TCE removal without frequent maintenance or operator intervention, the reactors will be placed down the wells for *in situ* treatment. At that point, the system will be operated continuously except for occasional inspection.

Four months are allotted for completion of this system adjustment. During this time, samples will be collected and analyzed on a weekly basis, and the pumping rate will also be monitored on a weekly basis. This will establish the baseline operating conditions for the Pd/HFTW system, and will establish the TCE conversion and mass destruction rate when operating at the baseline conditions.

Throughout the technology demonstration, a Field Notebook will be maintained at the demonstration site. All relevant observations, actions, and procedures, including sample collection and maintenance, are required to be logged in the Field Notebook. Measurements of the groundwater pumping rate will also be logged in the Field Notebook on a weekly basis during the first four months of the demonstration, and on a bi-weekly basis thereafter.

6. Data Format, Storage, and Archiving Procedures

The majority of the data collected during this technology demonstration will be in the form of aqueous contaminant concentrations in the collected groundwater samples. The groundwater samples will be analyzed using a Tekmar 4000 Head Space Concentrator (purge-and-trap) and a Hewlett Packard 5890 gas chromatograph (GC) with a photo-ionization detector (PID), as described in Section 4, above, and in the Field Sampling Plan (Appendix C of the Demonstration Plan).

The GC/PID output is analyzed by a computer hardware/software system, the PE Nelson Model 2600 Chromatography Data System (Perkin Elmer Nelson Systems, Inc., Cupertino, CA), commonly referred to as simply the "Nelson system." The Nelson system acquires raw chromatography data from the GC/PID equipment using a PE Nelson 900 Series Intelligent Interface, which digitizes the analog output of the GC/PID. The Nelson system then analyzes (integrates) the peaks of the chromatograms, stores the digitized raw data and calculated results, and prints out the chromatograms on a connected dot-matrix printer. The Nelson system gives the operator the option of manually interpreting the peaks of the chromatogram, which is useful if compounds co-elute from the GC or if compounds are present in very low concentrations.

All results from the GC analysis will be stored in three ways:

(1) Raw chromatograms will be stored digitally, in a compressed format, on the hard drive of the computer which houses the Nelson system, and/or stored on floppy disks if the computer memory becomes too full. The compressed files can be retrieved using the Nelson software.
(2) Hard copies of the chromatograms will be printed out on the dot-matrix printer and stored in a binder for the duration of the technology demonstration.
(3) Results from the Nelson system and/or manual analyses of the chromatograms will be entered by hand into a computer spreadsheet, using a common software package like Microsoft Excel, and stored on the hard drive of a computer at Stanford University.

Groundwater pumping rates will be determined by field equipment and will be recorded in the Field Notebook. Pumping rates will be recorded weekly during the first four months of the demonstration, and bi-weekly thereafter. Any data recorded in the Field Notebook must be recorded directly, promptly, legibly, and in indelible ink. Data entries in the Field Notebook must indicate the date of the observation or measurement, the name of the person making the observation, and, if different, the name of the person recording the measurement.

All raw data, documentation, records, protocols, and reports generated as a result of the technology demonstration will be retained by the QA Officer. The QA Officer will archive these materials in a manner that facilitates their expedient retrieval upon request. Storage conditions for archived materials must provide minimum deterioration of documents and electronic media (e.g., extremes of temperature and humidity must be avoided, disks cannot be stored near strong magnetic fields, etc.).

APPENDIX D

APPENDIX F: Health and Safety Plan (HASP)

Environmental Security Technology Certification Program
(ESTCP)

Health and Safety Plan

In Situ Catalytic Groundwater Treatment Using Palladium Catalyst and Horizontal Flow Treatment Wells

Site 19, Operable Unit No. 1
Main Base Flightline

Naval Facilities Engineering Service Center
Stanford University
Air Force Institute of Technology
Lawrence Livermore National Laboratory

June 15, 2001

Final Version
Revision 2.0

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Appendix: Stanford University Injury and Illness Prevention Plan (IIPP)
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Appendix: Material Safety Data Sheets (MSDS)

Signatures Page

My signature below signifies that I have read and understood this Health and Safety Plan (HASP) for the project entitled "In Situ Catalytic Groundwater Treatment Using Palladium Catalyst and Horizontal Flow Treatment Wells," to be performed at Edwards Air Force Base in southeastern California. I understand the content of this HASP and agree to comply with the provisions contained herein.

Name (print)	Signature	Organization	Date
Name (print)	Signature	Organization	Date
Name (print)	Signature	Organization	Date
Name (print)	Signature	Organization	Date
Name (print)	Signature	Organization	Date
Name (print)	Signature	Organization	Date

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List of Abbreviations and Acronyms

ACGIH	American Conference of Governmental Industrial Hygienists
CFR	Code of Federal Regulations
CGI	combustible gas indicator
CNS	central nervous system
CRZ	Contamination Reduction Zone
ESTCP	Environmental Security Technology Certification Plan
HASP	Health and Safety Plan
HAZMAT	hazardous materials
HazWOpER	Hazardous Waste Operations and Emergency Response
HFTW	horizontal flow treatment well
IDLH	immediately dangerous to life or health
IIPP	Injury and Illness Prevention Plan
LEL	lower explosive limit
MSDS	material safety data sheet
NFESC	Naval Facilities Engineering Service Center
NIOSH	National Institute for Occupational Safety and Health
OSHA	Occupational Safety and Health Administration
Pd	palladium
PEL	permissible exposure limit (provided by OSHA)
PPE	personal protective equipment
REL	recommended exposure limit (provided by NIOSH)
SSHO	Site Safety and Health Officer
TCE	trichloroethene, also called trichloroethylene
TLV	threshold limit value (provided by ACGIH)
TWA	time-weighted average
UEL	upper explosive limit
WBGT	wet-bulb globe thermometer

1. Introduction

The purpose of this Health and Safety Plan (HASP) is to protect the health and safety of personnel involved in this technology demonstration, and the public in the vicinity of the demonstration, in accordance with the federal regulations 29 CFR 1910.120. This HASP pertains to the demonstration of technology entitled "In Situ Catalytic Groundwater Treatment Using Palladium Catalyst and Horizontal Flow Treatment Wells," hereafter referred to as the Pd/HFTW technology. The technology demonstration will be performed at Site 19 of the Edwards Air Force Base in southeastern California. The technology and the site history and conditions are described in the Demonstration Plan. Key activities that will be performed by demonstration personnel include:

- Installing necessary equipment in treatment wells
- Collecting groundwater samples from monitoring wells and treatment wells
- Changing tanks of hydrogen gas
- Reading and recording measurements made by instrumentation at the demonstration site
- Performing routine maintenance on pumps or other equipment.

The HASP discusses proper health and safety measures to be followed during the performance of these and other project activities.

The organizations involved in this technology demonstration include:

- Stanford University: project design, management, and implementation
- U.S. Navy, Naval Facilities Engineering Service Center (NFESC): project oversight
- U.S. Department of Defense, Environmental Security Technology Certification Program (ESTCP): project sponsor
- Edwards Air Force Base: site host
- Air Force Institute of Technology: modeling activities
- Lawrence Livermore National Laboratories: reactor design and fabrication
- Earth Tech: contractor to Edwards Air Force Base

Personnel associated with these organizations will be expected to adhere to this HASP when performing duties associated with the Pd/HFTW technology demonstration. In addition, all Stanford University personnel must be in compliance with the provisions of Stanford's Injury and Illness Prevention Program (IIPP).

In the event of a conflict between the requirements of this HASP and the requirements of applicable federal, state, or local regulations, the more stringent will apply.

2. Key Personnel

The Pd/HFTW technology is designed to operate with limited operator intervention. Many of the necessary field duties (e.g., collecting groundwater samples, changing gas tanks) will be performed by a single individual. The key personnel duties are defined according to this anticipated work structure.

2.1 Project Managers

The Project Managers for this technology demonstration will be Carmen Lebron of NFESC and Martin Reinhard of Stanford University. The health and safety duties of the Project Managers include:

- Management of the project
- Preparation of the demonstration plan, preparation of the HASP, and designation of field personnel
- Executing the Demonstration Plan and schedule
- Access permission for visitors, new hires, etc., and coordination activities with appropriate officials
- Confirmation of each team member's suitability for work based on employee's training and physical condition
- Informing field personnel of their duties
- Coordination with the Site Safety and Health Officer (SSHO) on safety and health requirements
- Preparation of final reports
- Liaison with public officials.

The Project Managers may temporarily delegate one or more of these duties to appropriately-trained personnel, but shall retain the final responsibility for the proper conduction of these duties.

2.2 Site Safety and Health Officer (SSHO)

The Site Safety and Health Officer (SSHO) for this technology demonstration will be the senior Stanford University investigator who has completed 40-hour Hazardous Waste Operations and Emergency Response (HazWOpER) training. It is anticipated that the SSHO for this demonstration will be Gary Hopkins, with an alternate choice of Jeffrey Cunningham. The health and safety duties of the SSHO include:

- Managing the safety and health programs for the site
- Determining appropriate protection levels
- Periodically inspecting protective clothing and equipment
- Monitoring and evaluating HASP implementation
- Monitoring and inspecting protective clothing and equipment to ensure that they are properly maintained
- Verifying each team member's suitability for work based on the employee's training and physical condition
- Participating in the preparation and implementation of the HASP

- Conducting periodic inspections to verify that the HASP is being properly implemented
- Ensuring that planned work requirements adhere to established health and safety procedures
- Ensuring that personnel are (1) aware of the provisions of this HASP; (2) instructed in the work practices necessary to ensure safety; (3) aware of planned procedures for dealing with emergencies; and (4) aware of potential hazards associated with site operations
- Enforcing health and safety procedures
- Correcting any work practices or conditions that may result in injury or exposure to hazardous substances
- Knowing emergency procedures, evacuation routes, and the telephone numbers of the ambulance, local hospital, poison control center, fire department, and police department
- Preparing any necessary accident, injury, or incident reports.

Because the Pd/HFTW technology is designed to operate with limited operator intervention, many of the necessary field duties (e.g., collecting groundwater samples, changing gas tanks) will be performed by a lone individual, without the SSHO on site. However, the SSHO retains ultimate responsibility for the duties described above.

2.3 Field Personnel

The Field Personnel involved in the technology demonstration are responsible for the following health and safety duties:

- Reading, understanding, and complying with the requirements of this HASP
- Taking reasonable precautions to prevent injury to themselves, fellow employees, and the public in the vicinity of the technology demonstration
- Implementing the HASP
- Reporting to the SSHO any deviations from the anticipated conditions described in the HASP and/or the Demonstration Plan
- Performing only those tasks for which they have been properly trained, and can perform safely
- Reporting any accidents or unsafe conditions to the SSHO
- Attending all required safety briefings and adhering to procedures specified therein
- Notifying local public emergency officials when necessary
- Knowing emergency procedures, evacuation routes, and the telephone numbers of the ambulance, local hospital, poison control center, fire department, and police department
- Maintenance of a daily site log documenting field activities, including sample collection.

3. Hazard Assessment

3.1 Control of Potential Hazards

The purpose of this section of the HASP is to identify the risks associated with conduction of this technology demonstration, and to describe the actions that should be taken to mitigate those risks.

Table 3-1: Control of Potential Hazards

Potential Hazard or Risk	Potentially Encountered During	Control(s)
Dermal or ocular exposure to contaminated groundwater	Direct contact with contaminated water during sample collection or sample transport; Secondary contact with contaminated clothing or equipment	Use of Level D personal protective equipment (Section 5); No eating, drinking, or smoking in the exclusion zone or contamination reduction zone (Section 9); Proper decontamination procedures (Section 10); Wash hands and face thoroughly with soap and water after work and before eating, drinking, or smoking
Ingestion of contaminated groundwater	Via eating, drinking or smoking after or during site work	No eating, drinking, or smoking in the exclusion zone or contamination reduction zone (Section 9); Proper decontamination procedures (Section 10); Wash hands and face thoroughly with soap and water after work and before eating, drinking, or smoking
Heat-related disorders	General site work on hot or sunny days	Monitoring for signs or symptoms; Use of work-rest cycles (Section 6); Sun block and/or sun-protective clothing (Section 5)
Frostbite and/or hypothermia	General site work on cold or rainy days	Monitoring for signs and symptoms; Insulating clothing; Limit duration of work cycles in extreme conditions (Section 6)
Ingestion or dermal exposure to regenerant solution (peroxide or hypochlorite)	General site work	Use of Level D personal protective equipment (Section 5); Proper storage of chemicals; Proper decontamination procedures (Section 10)

3.2 Use of Compressed Hydrogen Gas

This technology demonstration employs tanks of compressed hydrogen gas (approximately 258 cubic feet at 2400 psi). This presents potential hazards because hydrogen is a flammable gas at ambient conditions, with a lower explosive limit (LEL) of approximately 4% and an upper explosive limit (UEL) of approximately 75%. Also, the rupture of a compressed gas cylinder can result in explosion, and the cylinder can become a dangerous projectile. However, when proper handling methods are used and proper precautions are taken, compressed hydrogen gas can be used just as safely in the field as it is in the laboratory.

Hydrogen gas will be delivered to contaminated groundwater using a bubble-less permeable membrane. Hydrogen gas flow rate will be approximately 30 mL per liter of groundwater pumped, delivered at approximately 40 psi. Table 3-2 shows the system alarms that will be installed to minimize the risks associated with using compressed hydrogen gas.

Table 3-2: System Alarms

Abnormal Event	Possible Cause	Alarm	System Response
Hydrogen gas concentration above 10% of LEL at well head	H_2 leak in module or plumbing; High H_2 pressure; Low water pressure or water flow rate	Hydrogen alarm	Shut down
Loss of hydrogen gas flow to water stream	Plugged hydrogen delivery membrane	Hydrogen flow alarm; Membrane differential pressure alarm	Shut down
Loss of water flow or pressure	Submersible pump failure; Leak in system	Water flow alarm; Membrane differential pressure alarm	Shut down
High pressure differential across hydrogen delivery membrane	High H_2 pressure setting at tank regulator; High flow setting at flow controller; Plugged delivery membrane	Membrane differential pressure alarm	Shut down

Table continued on following page

Table 3-2: System Alarms, Continued

Abnormal Event	Possible Cause	Alarm	System Response
Low pressure differential across hydrogen delivery membrane	Low pressure setting at regulator; low setting at flow controller; Depleted H_2 supply	Membrane differential pressure alarm	Shut down

3.3 Eyewashes, Safety Showers, and Fire Extinguishers

Eyewashes, safety showers, and fire extinguishers will be present on site in conspicuous locations. Personnel will be shown the location of this safety equipment prior to beginning work at the site.

3.4 Chemical Storage

Any chemicals used in this technology demonstration must be stored properly. The only chemical likely to be stored at the demonstration site is the regenerant solution used to maintain the activity of the palladium catalyst. This will be a solution of either peroxide or hypochlorite. The material safety data sheets (MSDSs) for both of these chemicals are provided as Appendices to this HASP. Proper storage includes separating the chemicals from any non-compatible materials or chemicals, e.g., peroxide will not be stored in close proximity to the tanks of compressed hydrogen gas.

4. Training Requirements

4.1 General Training Requirements

The Code of Federal Regulations 29 CFR 1910.120(e) requires different levels of training, depending on the tasks to be performed. Field personnel in this technology demonstration must complete either the 24-hour or 40-hour Hazardous Waste Operations and Emergency Response (HazWOpER) training, as appropriate, including the required one or three days of supervised on-site field activity. The HazWOpER training must include, at a minimum:

- Hazard identification and communication
- Flammable atmospheres and ignition controls
- Toxic chemical recognition
- Exposure guidelines
- Use of personal protective equipment (PPE)
- Respiratory protection
- Hearing conservation
- Heat stress
- Site decontamination procedures
- Prevention of slip, trip, and fall hazards
- Safe lifting techniques
- Safe work practices.

The SSHO will receive an additional eight (8) hours of training as specified in 29 CFR 1910.120(e)(4). This addresses supervisor responsibilities for establishment and implementation of an employee health and safety program.

All field personnel must renew their HazWOpER training with an eight-hour refresher course annually.

4.2 Site-Specific Training Requirements

Federal regulation 29 CFR 1910.120(b)(4)(iii) specifies that a pre-entry briefing be given to each site worker, manager, supervisor, and/or any other individual associated with the site. Site safety orientation and training meetings will be conducted:

- Before field personnel begin work at the site
- When modifications are made to this HASP
- When additional workers or subcontractors begin field work.

The meetings will be convened by the Site Safety and Health Officer (SSHO). A record of the meetings, including attendees, will be maintained by the SSHO in the health and safety file. During these briefings, project personnel will be:

- Instructed on the contents of applicable portions of this HASP
- Made aware of task-specific physical hazards and other hazards which may be encountered during this technology demonstration

- Informed about (1) the possible routes of chemical exposure; (2) protective clothing; and (3) symptoms and signs of fatigue, chemical exposure, and heat stress
- Made aware of fire prevention measures, fire extinguishment methods, and evacuation procedures
- Required to sign the signatures page of this HASP, indicating their understanding of the HASP and their compliance with the provisions herein.

Also, "tailgate" safety meetings will be conducted in the field by the SSHO to review and discuss the health and safety issues associated with the work, PPE requirements for the specific operations to be performed over the course of the day, problems encountered, and modifications to existing procedures. A copy of all health and safety meetings and/or issues will be maintained by the SSHO. All field personnel are required to attend these meetings.

4.3 Record-Keeping

A health and safety file will be maintained by the Site Safety and Health Officer (SSHO). The file will contain:

- Safety orientation and training meeting records
- Tailgate safety meeting records
- Injury/illness reports (see below)
- Monitoring records
- Applicable records from the Medical Surveillance Plan (see Section 7)
- Exclusion zone control records.

Any injury or work-related illness not limited to a first-aid case will be immediately reported to the Site Safety and Health Officer (SSHO). The SSHO will complete State Form DWC-1 and Stanford Form SU-17 within 24 hours. If the illness or injury results in the loss of one or more work days, Cal OSHA Form 5020 and Stanford Form SU-16 must be completed. In addition, the SSHO will notify the Project Managers. Required forms are appended to this HASP. For serious injuries (i.e., those resulting in hospitalization for more than 24 hours, permanent disfigurement, or death), the accident will be immediately reported to Stanford Environmental Health and Safety (650-723-0448). The Project Managers will also be notified. Copies of any illness and injury report forms completed for this project will be maintained in the health and safety file.

5. Personal Protective Equipment

Careful selection and use of personal protective equipment (PPE) is essential to protect the health and safety of workers. The purpose of PPE is to shield or isolate workers from the chemical, physical, radiological, and biological hazards that may be encountered at the site. The protection level assigned must match the hazard(s) confronted.

For the hazards to be encountered during this technology demonstration, Level D personal protective equipment is appropriate. Level D protection is the lowest level of personal protection allowed on hazardous waste sites. Should site conditions deteriorate unexpectedly so that Level D protection is insufficient, work will cease. The following equipment will be worn, as needed, to provide Level D protection:

- Gloves, latex or nitrile
- Long pants and long-sleeved shirt
- Lab coat or coveralls
- Splash-resistant clothing (e.g., Tyvek, Saranex)
- Boots, preferably with steel toes and a chemical-resistant, non-slip sole
- Safety glasses with side shields, safety goggles, and/or full face shield
- Hard hat
- Hat, sunblock, and/or other protection against direct sunlight
- Hearing protection

The precise equipment required will depend upon the task being performed. For instance, when collecting water samples, workers should wear safety glasses, gloves, long pants and long-sleeved shirt, and boots. Hearing protection, hard hat, and sun protection might or might not be required, depending on site conditions during the sample collection. Site workers are required to have completed OSHA 24-hour or 40-hour HazWOpER training, and will therefore be capable of selecting the proper PPE to provide Level D protection for the particular tasks being performed.

Site workers are expected to store and maintain their own PPE, except for disposable latex and nitrile gloves, which will be provided at the site. Whenever a worker leaves the exclusion zone, the following PPE decontamination procedure will be followed:

- Remove gross debris from clothes, boots, and gloves
- Remove disposable clothing and place in PPE plastic garbage bags
- Clean reusable protective equipment, such as hard hats
- Wash hands and face thoroughly with soap and water.

6. Extreme Temperature Disorders or Conditions

6.1 Temperature Conditions at Edwards Air Force Base

Edwards Air Force Base is located in the Mojave Desert, where temperature conditions of extreme heat and extreme cold are both possible. Table 6-1 shows average daily high and low temperatures. [Source: Edwards Air Force Base web site, http://afttc.edwards.af.mil/climo/SFCCLIMO.TXT, February 7, 2001] Extreme heat or cold conditions are possible at any time of the year, but extreme heat conditions are particularly likely during the months June–September, and extreme cold conditions are particularly likely during the months December–February.

Table 6-1: Average Daily High and Low Temperatures, 1941-1996

	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec
High (°F)	57	61	65	73	81	91	99	97	91	79	66	57
Low (°F)	31	35	39	45	52	59	66	64	57	47	36	30

The added burden of PPE required for hazardous waste operations in a temperature extreme condition, particularly in a condition of extreme heat, increases the potential for worker disorders or conditions that can result in injury or illness. Other factors that could affect a worker's ability to function in extreme temperatures include:

- Physical fitness
- Acclimatization
- Age
- Alcohol consumption, smoking, or other drug use
- Infections, disease, or other health condition.

The potential for both heat and cold related disorders or conditions can occur in many common situations. For example, cold early morning temperatures can give way to warm daily temperatures, resulting in heavy perspiration within protective clothing; then, as temperatures cool again in the evening, the potential for cold related disorders or conditions can occur.

6.2 Heat-Related Disorders

The following are heat-related disorders that site workers should be aware of and will take adequate steps to prevent.

- **Heat Rash**: Caused by continuous exposure to heat or humid air. Can be recognized by the occurrence of small red pimples on the skin. Typically found in sensitive areas of the body where the potential for rubbing can occur (e.g., underarm, groin area.)
- **Heat Cramps**: Caused by heavy sweating and inadequate electrolyte replacement. Signs to look for include muscle spasms and pain in the extremities, such as hands and feet, and in the abdomen.

- **Heat Exhaustion**: Caused by increased stress on various parts of the body, including inadequate blood circulation due to cardiovascular insufficiency or dehydration. Signs to look for include cool moist skin, heavy sweating, dizziness, nausea, and fainting.
- **Heat Stroke**: This is most serious of all heat-related disorders or conditions, since bodily temperature regulation fails and the body temperature rises to critical levels. Immediate action should be taken to cool the body before serious injury or death occurs. Competent medical help should be obtained. Signs to look for include unusually dry skin, reduced perspiration, nausea, dizziness and confusion, and coma.

6.2.1 Monitoring for Heat-Related Disorders

Table 6-2 shows the required frequency of physiological monitoring for fit and acclimatized workers.

Table 6-2: Required Frequency of Physiological Monitoring for Fit and Acclimatized Workers Wearing Normal (Level D) Work Clothing

Temperature	Frequency of Monitoring
90 °F or above	After every 45 minutes of work
87.5 °F – 90 °F	After every 60 minutes of work
82.5 °F – 87.5 °F	After every 90 minutes of work
77.5 °F – 82.5 °F	After every 120 minutes of work
72.5 °F – 77.5 °F	After every 150 minutes of work

The following parameters should be used when monitoring workers.

- **Heart rate**: Count the radial pulse as early as possible in the rest period to ensure a more accurate reading. If the heart rate exceeds 110 beats per minute at the beginning of the rest period, shorten the next work cycle by one-third and keep the rest period at the same length. If, at the end of the following work period, the heart rate still exceeds 110 beats per minute, shorten the work period again by one-third.
- **Oral Temperature**: The utilization of oral temperature applies to the time immediately after the worker leaves the contamination reduction zone. Using a clinical thermometer, take the temperature for three minutes. If the oral temperature exceeds 99.6 °F, shorten the next work cycle by one-third, without a change to the rest period. If the oral temperature still exceeds 99.6 °F at the end of the following work period, shorten the next work cycle by one-third.
- **Ear Canal Readings**: Ear canal readings are a valid method to monitor the temperature of workers who remain in the contamination reduction zone.
- **Body Water Loss**: Measure body weight to see if enough fluids are being consumed to prevent dehydration. If a worker loses 5% or more of his/her body weight due to perspiration, he/she should cease work until body fluids can be replenished.

6.2.2 Prevention of Heat-Related Disorders

The primary method for preventing heat-related disorders is the proper use of work-rest cycles. A site worker should spend a portion of each hour resting. The portion of each hour which should be spent resting is calculated based upon the ambient temperature, the site conditions, the type of clothing being worn by the worker, the physical condition of the worker, and the strenuosity of the work being performed.

Table 6-3: Recommended Work-Rest Cycles for a Fit, Acclimatized Worker Wearing Conventional (Level D) Work Clothes

Work Load	Wet-Bulb Globe Temperature (°C)	Work-Rest Regimen
Light	below 30.0	continuous work
	30.0 – 30.6	45 minutes work, 15 minutes rest each hour
	30.6 – 31.4	30 minutes work, 30 minutes rest each hour
	above 31.4	15 minutes work, 45 minutes rest each hour
Moderate	below 26.7	continuous work
	26.7 – 28.0	45 minutes work, 15 minutes rest each hour
	28.0 – 29.4	30 minutes work, 30 minutes rest each hour
	above 29.4	15 minutes work, 45 minutes rest each hour
Heavy	Below 25.0	continuous work
	25.0 – 25.9	45 minutes work, 15 minutes rest each hour
	25.9 – 27.9	30 minutes work, 30 minutes rest each hour
	above 27.9	15 minutes work, 45 minutes rest each hour

Source: Threshold Limit Values and Biologic Exposure Indices, Second Printing, American Conference of Governmental Hygienists, 1989-1990.

The wet-bulb globe temperature (WBGT) is measured using a wet-bulb globe thermometer, which consists of three separate thermometers: a dry-bulb thermometer, a wet-bulb thermometer, and a globe thermometer. The WBGT is calculated according to:

$$WBGT = 0.7\ T_{wet} + 0.2\ T_{globe} + 0.1\ T_{dry}$$

During rest cycles, body fluids should be replenished, but workers must keep in mind that drinking is prohibited in the exclusion zone and the contamination reduction zone (see Section 9). Therefore, when possible, workers should exit the exclusion zone, wash hands thoroughly, and, once in the support zone, should drink plenty of water or other fluid suitable to maintain body fluids and electrolytes.

Good hygiene will also help to prevent heat-related disorders. Workers should change clothes frequently and shower or bathe daily. Clothing should be permitted to dry during rest periods.

6.3 Cold Exposure

Exposure to cold temperatures increases the likelihood and potential for worker disorders or conditions that could result in injury or illness. The generally recognized cold disorders or conditions are frostbite and hypothermia. Contributing factors to these disorders or conditions are:

- Exposure to humidity
- High winds
- Contact with wetness
- Inadequate clothing
- Poor worker health.

Early recognition of the symptoms of cold exposure stress is essential in preventing serious or permanent disorders or conditions. The following are cold-related disorders that site workers should be aware of and will take adequate steps to prevent:

- **Hypothermia**: The first symptoms of this condition are uncontrollable shivering and the sensation of cold, irregular heart beat, weakened pulse, and change in blood pressure. Severe shaking of rigid muscles may be caused by a burst of body energy and changes in the body's chemistry. Vague or slow, slurred speech, memory lapses, incoherence, and drowsiness are some of the additional symptoms. Symptoms noticed before complete collapse are cool skin, slow and irregular breathing, low blood pressure, apparent exhaustion, and fatigue even after rest. As the core body temperature drops, the victim may become listless and confused, and may make little or no attempt to keep warm. Pain in the extremities can be the first warning of dangerous exposure to cold. If the body core temperature drops to about 85° F, a significant and dangerous drop in the blood pressure, pulse rate, and respiration can occur. In extreme cases, death will occur.
- **Frostbite**: Frostbite can occur, in absence of hypothermia, when the extremities do not receive sufficient heat from central body stores. This can occur because of inadequate circulation and/or insulation. Frostbite occurs when there is freezing of fluids around the cells of the body tissues due to extremely low temperatures. Damage may result, including loss of tissue around the areas of the nose, cheeks, ears, fingers, and toes. This damage can be serious enough to require amputation or result in permanent loss of movement.

In order to prevent cold exposure, the presence of dead air space between the warm body and clothing and the outside air is essential. Many layers of relatively light clothing with an outer shell of windproof material maintains body temperature much better than a single heavy outer garment worn over ordinary indoor clothing. The more air cells each clothing layer has, the more efficient it insulates against body heat loss. Clothing also needs to allow some venting of perspiration. In addition to adequate clothing, whenever possible, full use should be made of windbreaks and heat tents.

Table 6-4 gives the time limits for working in various low temperature ranges.

Table 6-4: Maximum Daily Time Limits for Exposure at Low Temperatures

Temperature Range, adjusted for wind chill ° C	° F	Maximum Daily Exposure
0 to -18	30 to 0	No limit, providing that the person is properly clothed.
-18 to -34	0 to -30	Total work time: 4 hours. Alternate 1 hour in and 1 hour out of the low-temperature area.
-34 to -57	-30 to -70	Two periods of 30 minutes each, at least 4 hours apart. Total low-temperature work time allowed is 1 hour.
-57 to -73	-70 to -100	Maximum permissible work time is 5 minutes during an 8-hour working day. At these extreme temperatures, completely enclosed headgear, equipped with a breathing tube running under the clothing and down the leg to preheat the air, is recommended.

Because of the relatively warm climate conditions at Edwards AFB (see Table 6-1), it is very unlikely that these maximum daily time limits for exposure would be exceeded.

7. Medical Surveillance

The Medical Surveillance Program is designed to ensure that the health of employees working on hazardous waste sites is documented before, during, and at termination of work on the site. The Medical Surveillance Program includes:

- Baseline or pre-assignment examination
- Periodic monitoring
- Examination after illness or injury
- Termination examination
- Maintenance of medical records.

The medical surveillance program is designed to:

- Establish the baseline medical condition of employees and fitness for duty
- Determine the ability to work while wearing protective equipment
- Track the physiological conditions of employees on an established schedule and at termination of the project or employment
- Ensure that documentation of employee exposure and medical conditions is provided and maintained as a part of the employee's medical record.

7.1 Participation in the Medical Surveillance Program

Participation in the Medical Surveillance Program is mandatory for:

- All employees who are exposed to hazardous substances or health hazards above published exposure limits (e.g., OSHA PELs, ACGIH TLVs, NIOSH RELs) without regard to the use of respirators, for 30 days or more per year
- All employees who wear a respirator for 30 days (or fractions of days) or more per year, or as required by 29 CFR 1910.134
- All employees who are injured, become ill, or develop signs or symptoms due to possible overexposure involving hazardous substances or health hazards from an emergency response or hazardous waste operation
- Members of HAZMAT teams.

It is not expected that these conditions will apply to any site workers during this technology demonstration. For all other workers, participation in the Medical Surveillance Program is voluntary.

7.2 Frequency of Medical Exams / Consultations

Participants in the Medical Surveillance Program should receive appropriate medical exams or consultations from a qualified physician at the following times:

- Prior to beginning work at the demonstration site
- Once per year while work at the demonstration site is ongoing
- After any work-related accident, illness, or event that might impair worker health
- After completion of work at the demonstration site.

7.3 Content of Medical Exams / Consultations

Medical examinations should include a medical and work history with special emphasis on symptoms related to exposure to hazardous substances and their health effects, and on fitness for duty when conducting project tasks. The content of the medical examinations will be based on applicable laws, regulations, and known or potential exposure to contaminants. Where possible, the content should be determined by a licensed physician certified in Occupational Medicine by the American Board of Preventive Medicine. However, at a minimum, the physician making the determination should be knowledgeable and experienced in occupational medicine screening and surveillance.

An example of a matrix of medical examination by job task is shown in Table 7-1.

Table 7-1: Example of Periodic Examination Based on Job Task

	Project Management	Data and Sample Collector	Oversight	Equipment Operator	Laborer
Medical and Work History	X	X	X	X	X
Physical Exam	X	X	X	X	X
Pulmonary Function	A	X	A	X	X
X-ray	A	A	A	A	A
EKG	A	X	A	X	X
Eye Exam	A	X	A	X	X
Audiogram	A	X	A	X	X
Urinalysis	A	X	A	X	X
Blood Chemistry	A	X	A	X	X
Heavy Metals	A	X	A	X	X
Other	A	A	A	A	A

X = Recommended
A = As Appropriate

7.3.1 Baseline/Initial Examination

Participating site workers will receive a baseline or initial medical examination based on an activity hazard assessment prior to being assigned to a hazardous or potentially hazardous activity (e.g., exposure to toxic substances or radiological materials, repetitive motion, heat/cold stress). The items listed below are recommended components of the examination.

- Complete medical and work history
- Physical examination
- Pulmonary function test
- Eye examination
- EKG
- Audiogram
- Urinalysis
- Blood chemistry
- Evaluation of stresses related to repetitive motion.

7.3.2 Periodic Evaluation

Participants in the Medical Surveillance Program should be provided with medical examinations every 12 months, unless a physician believes a shorter or longer duration is appropriate. The content of the examination should be:

- Based on applicable laws and regulations
- Determined by a qualified physician
- Designed to detect changes from the baseline examination
- Designed to identify physiological changes.

A hazard assessment, specific employee exposure data, and other relevant information should be provided to the examining physician.

7.3.3 Evaluation After a Work-Related Accident, Illness, or Exposure

Follow-up examinations should be provided as soon as possible to the employee due to any of the following situations:

- Notification to the supervision, management, or physician that the employee has developed signs or symptoms indicating sensitivity or overexposure
- Potential exposure above the permissible exposure limit or published exposure limit
- Lost-time illness of three working days or more
- Any recordable injury to the employee
- Contamination incident.

In the case of injury or illness, the Site Safety and Health Officer (SSHO) or his/her designated alternate is responsible for notifying the physician of the incident and the suspected substance involved. If the substance is unknown, it should be indicated as such.

The examination will be carried out by a licensed occupational medical provider. The scope of the examination will be determined by the physician. The employee will not return to work until the physician certifies that the employee is fit to return to work, activity restrictions are identified, and documentation of fitness for duty is provided.

Table 7-2 identifies the hazardous substances which have the highest probability of being encountered during this technology demonstration, and the potential health effects of exposure to those chemicals.

Table 7-2: Effects of Hazardous Substances

Hazardous Substance	Target Organs	Potential Health Effects	Medical Monitoring
Trichloroethene (TCE)	Liver, kidneys, respiratory system, skin, central nervous system (CNS)	liver disease and kidney injury, CNS depression, dermatitis, cancer, ventricular arrhythmia	History for pre-existing liver disease or decreased lung functions, measurement of liver enzymes and liver function, urine screen, physical exam focusing on nervous system, skin, and respiratory system

7.3.4 Exit Examination

The employer should provide a termination medical examination when an employee is terminated or reassigned to an area or activity where the employee is not exposed to hazardous substances. The termination examination content will be determined by the physician. If termination occurs within six months of a periodic examination, the physician may determine that an additional examination is not necessary. Documentation of the decision not to provide a termination examination, and its basis, will be provided in the medical file for the employee.

7.4 Physician's Written Opinion and Record-Keeping Requirements

The employee will be notified of recommended limitations upon his/her assigned work. The physician should provide a written opinion to the records indicating that the employee has been informed of the results of the exam and of any medical conditions which require further examination or treatment. In addition, the following specific records should be maintained:

- Name and Social Security number of employee
- Physician's written opinion, recommended limitations and results of exam
- Employee medical complaints related to exposure to hazardous substances
- Information provided to the physician from the employer
- Engineering controls, work practices, and PPE for employee protection.

Personnel medical records and exposure monitoring records will be maintained according to the requirements of 29 CFR 1910.120(f)(8) and 29 CFR 1910.20. Access to medical records will be consistent with the requirements of 29 CFR 1910.20. The employee medical records will be held in confidence by the employer to the extent permitted by law.

8. Exposure Monitoring and Air Sampling

Hazardous waste activities generate the potential for employee exposure to, and/or off-site migration of, hazardous concentrations of airborne substances. This section provides the general HASP guidance for the exposure monitoring/air sampling program and specific activities that should take place during this technology demonstration.

The objectives of exposure monitoring/air sampling are to accurately determine:

- Exposure levels for site workers
- Work areas generating the most significant airborne contaminants
- Whether migration is occurring
- Whether modified levels of protection or engineering controls are required.

8.1 Airborne Hazards

During this technology demonstration, site workers and/or the nearby community might be exposed to the following airborne hazards:

- Exposure to volatile organic compounds, primarily trichloroethene (TCE)
- Flammable or explosion hazard created by hydrogen gas
- Noise.

Because all work will be performed outdoors, there is no significant danger of creating an oxygen-deficient atmosphere. TCE and hydrogen can both present short-term hazards (e.g., explosion hazard, acute exposure), but will both disperse without implementation of additional engineering controls. Table 8-1 shows the most important properties of TCE and hydrogen.

Table 8-1: Summary of Properties for Hydrogen and TCE

	Hydrogen	TCE
Physical-Chemical Properties		
Molecular formula	H_2	C_2HCl_3
Molecular weight	2.0	131.4
Melting point	-259.14 °C	-73 °C
Boiling point	-252.87 °C	87.2 °C
Vapor pressure at 20 °C	supercritical at 20 °C	0.079 atm
Hazardous Properties		
Type of hazard	flammable/explosive	flammable; see also Table 7-2
Lower Explosive Limit (LEL)	4%	8% at 77 °F
Upper Explosive Limit (UEL)	75%	10.5% at 77°F
IDLH	not a chemical hazard	1000 ppm (5370 mg/m^3)

IDLH = "immediately dangerous to life or health"

8.2 Chemical Exposure Monitoring

Monitoring must be used to properly characterize any employee exposures, and to provide knowledge of site conditions in enough detail to determine if work should be suspended due to exceedance of action levels. Personal air sampling may be conducted to evaluate employee exposures to hazardous chemicals or environments, and to determine the need to suspend work. Air samples, using a combustible gas indicator (CGI) and/or a Drager tube, will be taken during the activities specified in Table 8-2. Additionally, the treatment wells will be equipped with continuously-monitoring on-line hydrogen sensors. If measured levels are above those indicated in Table 8-2, work will cease.

Table 8-2: Monitoring Program Action Levels

Parameter	Monitoring Zone	Instrument	Reading Interval	Action Level	Response
Hydrogen	Treatment Wells	On-line H_2 detector	Continuous	> 10% of LEL	Shut down treatment wells, allow area to ventilate, check hydrogen addition rate and catalyst activity
Combustible Gas	Monitoring wells	Combustible gas indicator (CGI)	While collecting first sample from each well	< 10% of LEL	Continue Level D work, continue monitoring
Combustible Gas	Monitoring wells	CGI	While collecting first sample from each well	> 10% of LEL	Cease work, move workers out of area, and continue to monitor until below 5% of LEL for at least 15 minutes
TCE	Monitoring wells	Drager tube	While collecting first sample from each well	< 20 ppm	Continue Level D work
TCE	Monitoring wells	Drager tube	While collecting first sample from each well	> 20 ppm	Stop work and allow area to ventilate; test again after 30 minutes

Note: The National Institute for Occupational Safety and Health (NIOSH) considers TCE to be a potential occupational carcinogen, with a recommended exposure limit (REL) of 25 ppm as a 10-hour time-weighted average. The Occupational Saftey and Health Administration (OSHA) lists a time-weighted personal exposure limit (PEL) of either 50 ppm (1989 value, vacated in 1992) or 100 ppm (1993 value) for TCE. (source: NIOSH Pocket Guide to Chemical Hazards, June 1997).

All health and safety monitoring data will be recorded and maintained in the health and safety file kept by the Site Safety and Health Officer (SSHO). All monitoring equipment will be maintained and calibrated in accordance with manufacturer recommendations. All pertinent data will be logged in the health and safety file and maintained on site for the duration of site activities.

8.3 Noise Monitoring

Exposure to excessive noise can cause permanent hearing loss. If an excessively high noise level is believed to exist, protective equipment will be provided and used. The Site Safety and Health Office (SSHO) can arrange for noise testing by a health and safety professional. The SSHO will ensure that employees exposed to levels at or above those listed in Table 8-3 will wear appropriate hearing protection. Hearing protection may be worn at noise levels below this for employee comfort, as long as the equipment does not impair the worker's awareness of the work environment. The selection of the type of hearing protection will depend on comfort, convenience, and attenuation capabilities. Assigned hearing protection must have sufficient capabilities to reduce the noise levels reaching the ear to below the necessary levels.

Table 8-3: Time-Weighted Average (TWA) Noise Levels Allowed for Workers Without Hearing Protection

Continuous Noise		Impact Noise	
Sound Level (dB)	Duration (hours)	dB Peak	Frequency per Day
80	16	140	100
85	8	130	1000
90	4	120	10,000
95	2		
100	1		
105	05 (30 min)		
110	0.25 (15 min)		
115	0.125 (7 min)		
> 115	None		

8.4 Off-Site and Perimeter Monitoring

Off-site and perimeter monitoring will not be routinely conducted as part of this demonstration project. The only significant on-site sources of airborne hazards are from the monitoring wells and from the hydrogen tanks which are used to supply hydrogen to the treatment wells. Even if TCE or hydrogen were detected at hazardous levels at the demonstration site, these compounds will rapidly disperse because the demonstration area is outdoors. Therefore, there is a very small probability of these compounds being transported to off-site at hazardous levels.

If hazardous concentrations of these compounds are found on-site repeatedly, or for a prolonged period of time, then measurements will be taken at the perimeter of the demonstration site to

verify that hazardous concentrations are not reaching the site perimeter. If hazardous concentrations reach the site perimeter, work will be suspended. Because the demonstration site is located on the Flight Line, the following steps will be implemented:

- Call 911.
- Notify the Bioenvironmental Engineering personnel of Edwards AFB.
- Notify personnel working on the flight line in close proximity to the site.

9. Site Control

The site control program at hazardous waste sites is used to control the activities and movement of people and equipment in order to minimize the potential for worker exposure to hazardous substances. The provisions of 29 CFR 1910.120(d) require that an appropriate site control program be developed prior to the implementation of cleanup operations. The overall objective of the site control component of the HASP is to specify procedures to minimize employee exposure and protect the public from hazardous substances and to prevent unauthorized access to the site.

9.1 Establishment of Work Zones

One of the basic elements of an effective site control program is the delineation of work zones at the site. The purpose of establishing work zones is to:

- Reduce the accidental spread of hazardous substances by workers or equipment from the contaminated areas to the clean areas
- Confine work activities to the appropriate areas, thereby minimizing the likelihood of accidental exposures
- Facilitate the location and evacuation of personnel in case of an emergency
- Prevent unauthorized personnel from entering controlled areas.

Although a site may be divided into as many zones as necessary to ensure minimal employee exposure to hazardous substances, the three most frequently identified zones are the exclusion zone (or "hot zone"), the contamination reduction zone, and the support zone (or "clean zone"). Movement of personnel and equipment between these zones should be minimized to prevent cross-contamination.

9.1.1 Site Map

Figure 9-1 shows a map of the treatment wells and monitoring wells at the demonstration area. The exclusion zone, the contamination reduction zone, and the support zone are indicated on the map. During this technology demonstration, the potential for exposure to hazardous chemicals is relatively low; the most likely risks are inhalation of TCE or dermal exposure to TCE-containing groundwater during the collection of water samples. Therefore, the exclusion zone is limited to the area near the treatment and monitoring wells. The use of hydrogen gas also presents a significant hazard risk, but is also limited to the area near the treatment wells.

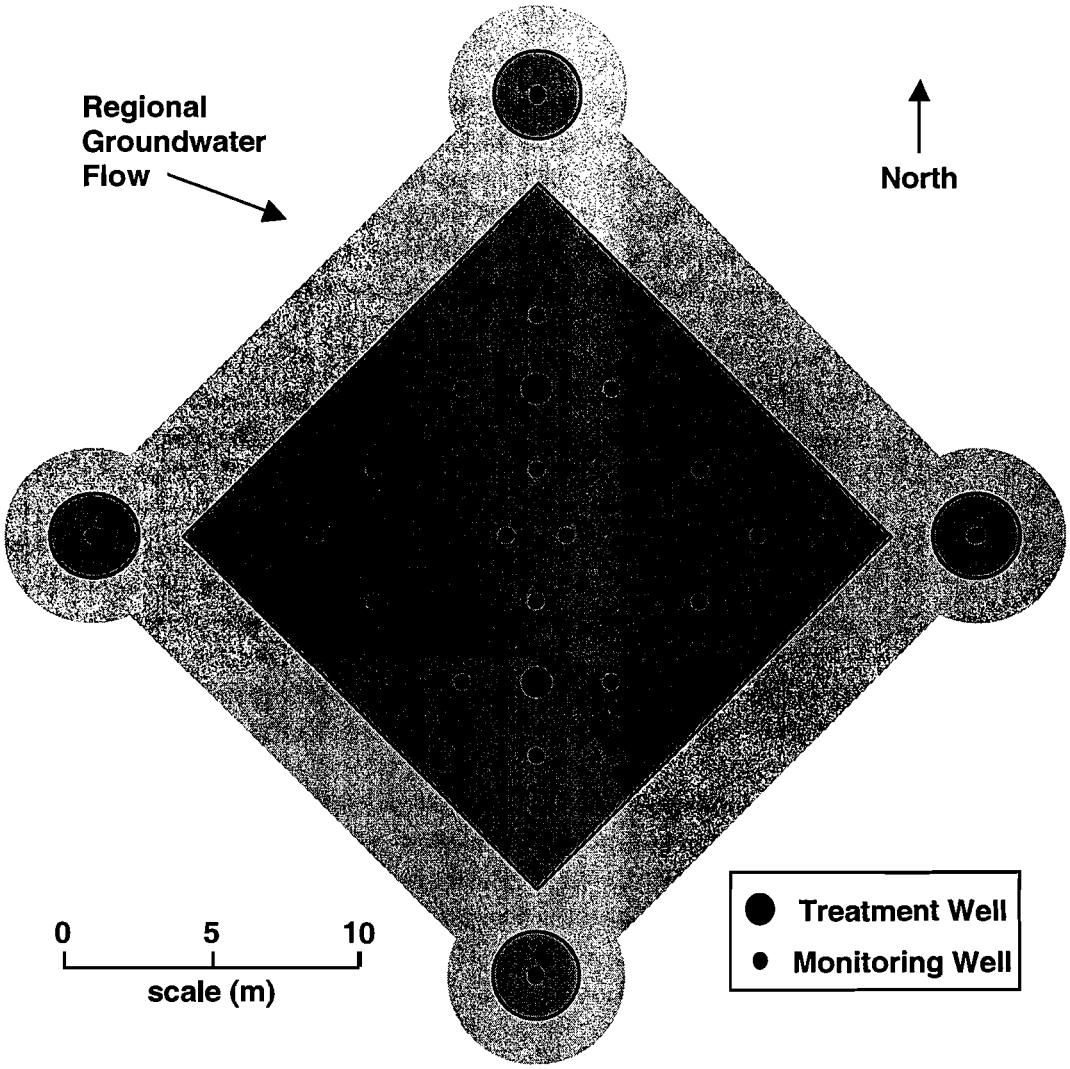

Figure 9-1: Map of Exclusion Zone, Contamination Reduction Zone, and Support Zone for the Demonstration Site: Dark grey represents exclusion zone, light grey represents contamination reduction zone, and white background represents support zone.

9.1.2 Exclusion Zone

The exclusion zone is the area where contamination is either known or expected to occur and where the greatest potential for exposure exists. The outer boundary of the exclusion zone (also called the "hotline") separates the area of contamination from the contamination reduction zone. Factors to consider in establishing the boundary of the exclusion zone include:

- Determination of the extent of hazardous substances based on the hazard assessment (Section 3)
- Providing sufficient space to protect personnel outside the exclusion zone from potential fire or explosion
- Allowing an adequate area within which to conduct site operations
- Reducing the potential for contaminant migration.

Figure 9-1 shows the boundary of the exclusion zone for this technology demonstration. The exclusion zone is limited to the area immediately surrounding the treatment and monitoring wells, because the potential hazards of this demonstration are limited to the areas around the wells and the activities that take place therein.

All persons who enter the exclusion zone will wear the appropriate level of personal protective equipment (PPE) for the degree and types of hazards present (see Chapter 5). If the exclusion zone is subdivided, different levels of PPE may be appropriate. Each subdivision of the exclusion zone will be clearly marked to identify the hazards and the required level of PPE. Clean hard hats, goggles, face shields, and other PPE should be stored in a clean location away from the exclusion zone.

Personnel who enter the exclusion zone, including site visitors, will be noted on exclusion zone control records. These will be maintained as part of the health and safety file.

9.1.3 The Contamination Reduction Zone

The contamination reduction zone is the area in which decontamination procedures take place. It is the transition area between the exclusion zone and the support zone. The purpose of the contamination reduction zone is to reduce the possibility that the support zone will become contaminated or affected by the site hazards. Figure 9-1 shows the contamination reduction zone for this technology demonstration. The boundary between the contamination reduction zone and the support zone is called the contamination control line, which separates the clean areas of the site from those areas used to decontaminate workers and equipment.

A decontamination station will be established within the contamination reduction zone (see also Section 10). All disposable protective clothing will be dropped in plastic garbage bags tagged for PPE for later disposal. The bag will not be used for other non-contaminated trash. If there is a rip or tear in a worker's protective clothing, that individual will remove the torn garment while in the contamination reduction zone. New protective clothing must be donned before the worker can return to the exclusion zone.

9.1.4 The Support Zone

The support zone is the uncontaminated area where workers are unlikely to be exposed to hazardous substances or dangerous conditions. Because the support zone is free from contamination, personnel working within it may wear normal work clothes. Any potentially contaminated clothing or equipment should remain inside the contamination reduction zone or the exclusion zone. The support zone should be in an area that is known to be free of elevated (i.e., higher than background) concentrations of hazardous substances. Because the potential hazards of this technology demonstration are localized, any areas sufficiently far from the treatment and monitoring wells are designated as the support zone, as shown in Figure 9-1.

An area within the support zone will be designated the break area. Eating, drinking, and smoking will be permitted in the support zone only after workers have proceeded through the contamination reduction zone and have washed their hands and faces.

9.2 Communication

The term "internal communication" refers to communication between or among workers operating in the exclusion zone or contamination reduction zone. The term "external communication" refers to communication between onsite and offsite personnel. During this technology demonstration, many operations (e.g., collecting samples, changing tanks of hydrogen) will be performed by individual workers. Therefore, no formalized program is required for internal communication. When more than one worker is at the site concurrently, those workers should agree upon a system of internal communication. Acceptable methods of internal communication include the use of radio, noisemakers, or visual signals.

An external communication system should be maintained in order to coordinate emergency response efforts with offsite responders, report progress or problems to management, and maintain contact with essential offsite personnel. For this technology demonstration, the primary means of external communication will be telephone.

9.3 Medical Assistance

Table 9-1 lists phone numbers for emergency medical assistance and for key personnel. Figures 9-2 and 9-3 show locations of medical facilities. This information will also be posted conspicuously throughout the demonstration site, including near telephones.

Table 9-1: Emergency Telephone Numbers

Security Police	911
Base Fire Department	
Emergency	911
Non-emergency	661-277-4978
Base Paramedic Ambulance Service (30 Hospital Road, Edwards AFB, CA)	
Emergency	911
Non-emergency	661-277-2330
Emergency Room, Antelope Valley Hospital (15th Street West, Lancaster, CA)	
Emergency	911
Non-emergency	661-949-5000
Stanford University, Environmental Health and Safety	650-723-0448
Project Personnel	
Carmen LeBron (Project Manager)	805-982-1616
Martin Reinhard (Project Manager)	650-723-0308
Gary Hopkins (Site Safety and Health Officer)	408-262-2070
Jeff Cunningham (alternate Site Safety and Health Officer)	650-723-5885

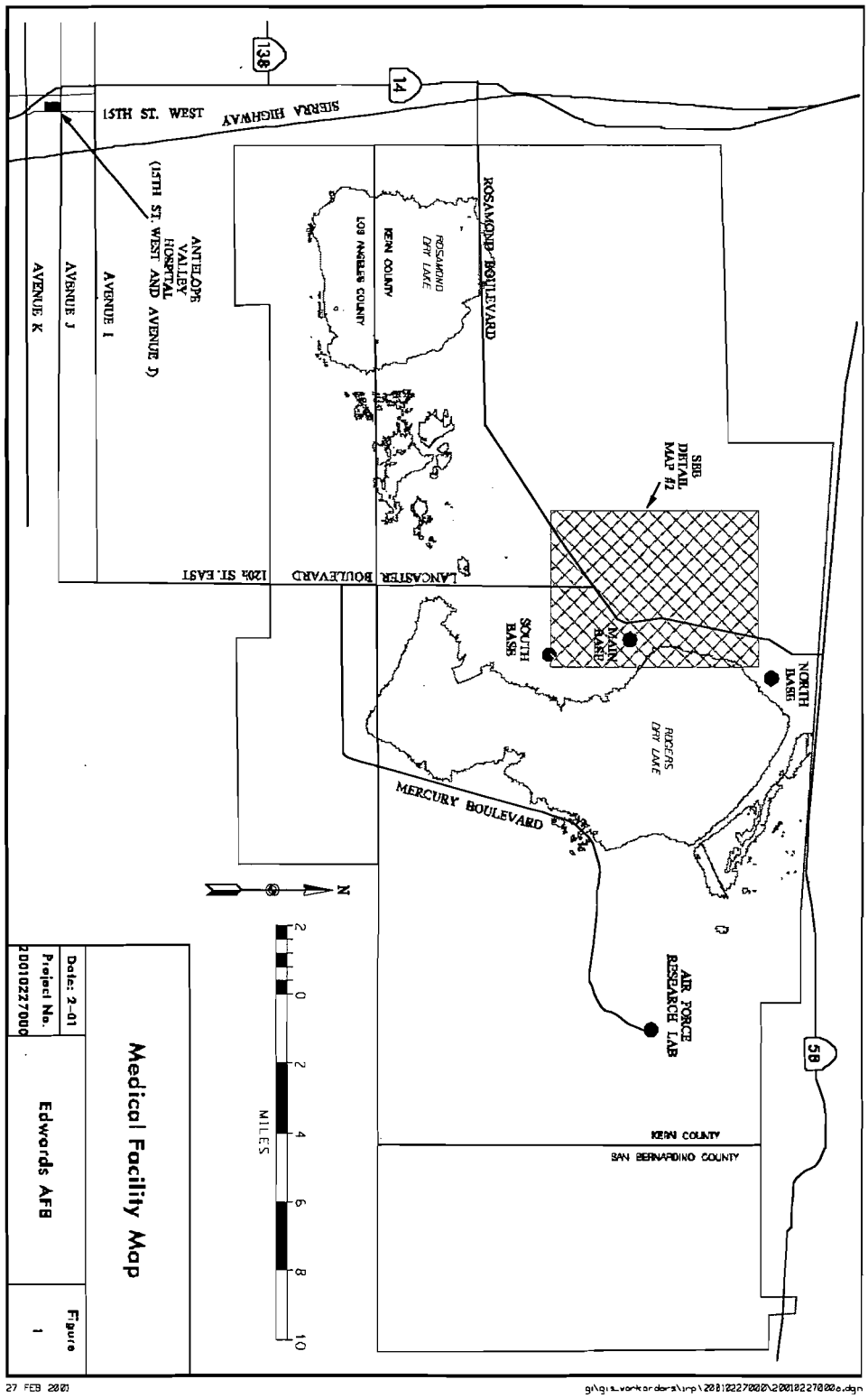

Figure 9-2: Map of Edwards Air Force Base

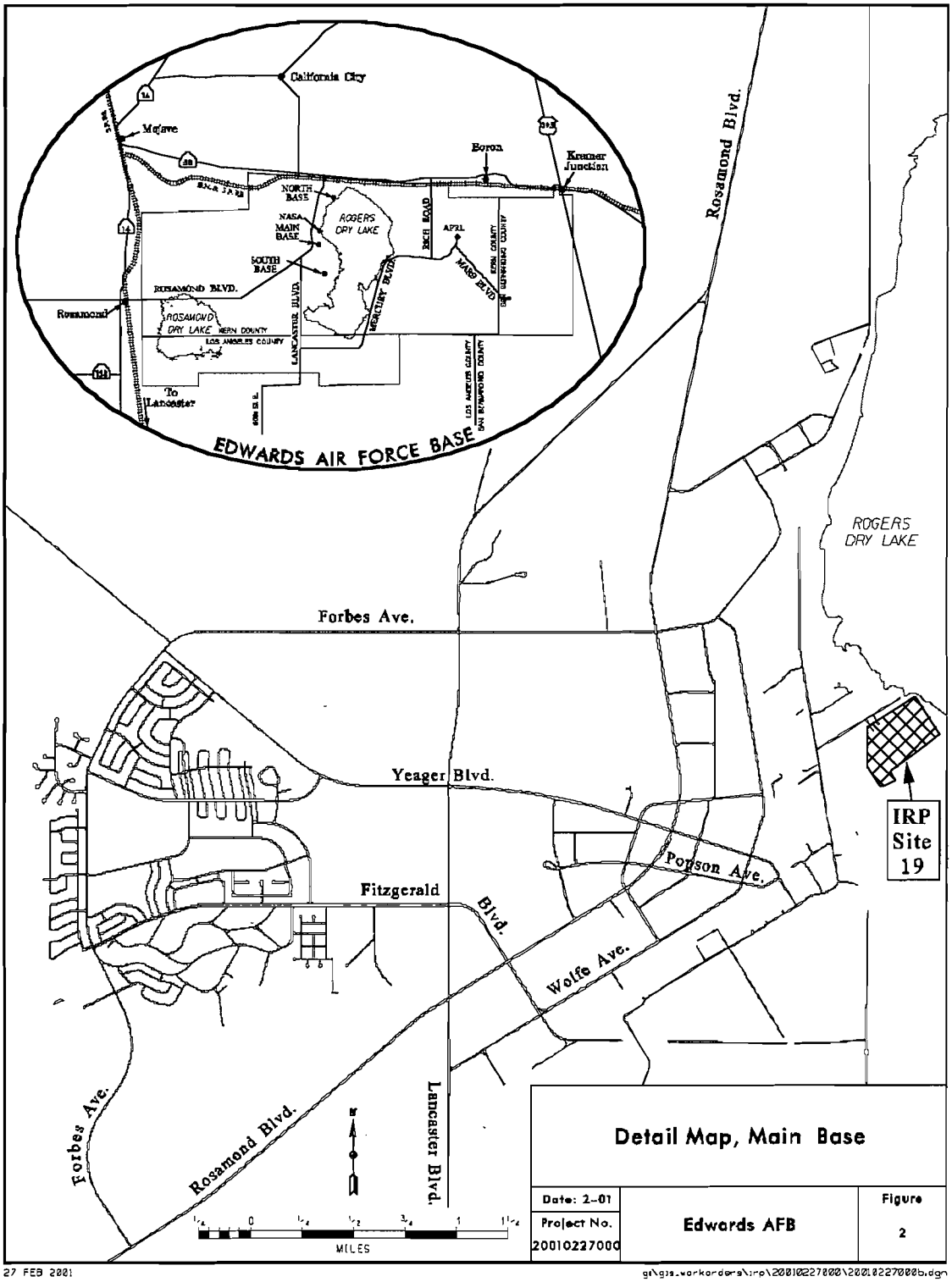

Figure 9-3: Detail Map of Edwards Air Force Base

10. Decontamination

Decontamination involves physically removing contaminants from personnel and equipment and/or chemically converting them into innocuous substances. The extent of decontamination depends on a number of factors, the most important of which is the types of contaminants involved. The more harmful the contaminant, the more extensive and thorough the decontamination. The combination of decontamination, correct donning of protective clothing, and zoning of site work areas, minimizes cross-contamination from the protective clothing to wearer, from equipment to personnel, and from one area to another.

During this technology demonstration, the primary hazard that might require decontamination is the contact of skin, clothing, equipment, or personal protective equipment (PPE) with groundwater that contains trichloroethylene (TCE). The risk of skin contact with contaminated groundwater can be minimized by proper use of PPE. Therefore, the HASP is primarily concerned with the decontamination of equipment, clothing, and PPE which might have contacted contaminated groundwater.

10.1 Use of the Contamination Reduction Zone

The contamination reduction zone will be used to control access into and out of the exclusion zone. Decontamination of personnel and/or equipment will be confined to the contamination reduction zone. Personnel and equipment exiting the exclusion zone are required to go through the contamination reduction zone. Anyone in the contamination reduction zone should be wearing the appropriate level of protection designated for the decontamination crew. Protective clothing, respirators, monitoring equipment, sampling supplies, and other equipment should be maintained in the support area outside of the contamination reduction zone.

A decontamination station will be established within the contamination reduction zone. All disposable protective clothing will be dropped in plastic garbage bags tagged for PPE for later disposal. The bag will not be used for other non-contaminated trash. If there is a rip or tear in a worker's protective clothing, that individual will remove the torn garment while in the contamination reduction zone. New protective clothing must be donned before the worker can return to the exclusion zone

10.2 Decontamination Procedures and Guidelines

All items (including clothing, equipment, liquids) used in the decontamination procedure that cannot be completely decontaminated will be considered hazardous. Clothing and equipment will be collected, treated, stored, and disposed of based on the type and level of contamination according to applicable federal, state and local regulations. Drainage and/or collection systems for contaminated liquids will be established and approved containers will be used. Wash water will be collected for proper disposal. Waste minimization should be a consideration, secondary only to worker safety and health protection requirements.

Any tool, equipment, or material from inside the exclusion zone will be considered contaminated and must be cleaned before it is removed from the demonstration site. Verification that all equipment has been properly decontaminated will be the responsibility of the Site Safety and

Health Officer (SSHO). All contaminated water generated from the cleaning operation will be collected and placed in a properly labeled container for later disposal.

Whenever a person leaves the exclusion zone, the following decontamination procedure will be followed in the contamination reduction zone:

- Remove gross debris from clothes, boots, and gloves
- Remove disposable clothing and place in PPE plastic garbage bags
- Clean reusable protective equipment, such as hard hats
- Wash hands and face thoroughly with soap and water.

Other decontamination rules and guidelines are the following.

- An area within the support zone will be designated the break area. Eating, drinking, and smoking will be permitted in the support zone only after workers have proceeded through the contamination reduction zone and have washed their hands and faces.
- The SSHO shall monitor the effectiveness of the decontamination procedures, and if necessary, shall take appropriate steps to correct any deficiencies noted or to modify the decontamination procedures as needed.
- All disposable protective clothing shall be dropped into a plastic garbage bag tagged for PPE for later disposal. This bag shall not be used for other non-contaminated trash.
- Clean hard hats, goggles, face shields, and other PPE should be stored in a clean location away from the exclusion zone.
- Soiled boots, hard hats, and other equipment will be inspected before use, and will be washed and scrubbed in a detergent/water solution. After cleaning, equipment will be rinsed thoroughly in water and allowed to dry on a clean surface.

10.3 Decontamination During Emergencies

Because the risk of contamination of site workers is expected to be low during this technology demonstration, especially compared to the risk incurred by delay in an emergency medical situation, decontamination procedures may be bypassed or minimized in the event of an emergency. The SSHO will make the decision whether bypassing or minimizing decontamination procedures is appropriate.

11. Emergency Action Plan

There are three major classes of emergency which could occur during this technology demonstration:

- Catastrophic event (fire, explosion, chemical release, hurricane, blizzard, flood, earthquake, etc.), which might require evacuation
- Medical emergency (e.g., illness, physical injury)
- Safety equipment problems.

During an emergency that requires evacuation, employees shall perform only such activities as emergency shut-down or first aid and CPR. Therefore, this emergency action plan is provided instead of an emergency response plan.

11.1 Personnel Responsibilities

If the Site Safety and Health Officer (SSHO) is on site, then he/she will be the primary contact individual and coordinator of all emergency activities. If he/she is not on site, then the primary contact individual and the emergency activity coordinator will be the senior on-site worker with 40-hour HazWOpER training. He or she will be responsible for:

- Evaluating the severity of the emergency
- Implementing appropriate response action
- Summoning appropriate emergency services (fire department, ambulance, etc.)
- Notifying all site personnel and concerned authorities of the emergency situation.

At least one person on site who has been trained in first aid and CPR (preferably the SSHO) will be available to administer emergency medical treatment to any injured workers.

It will be the obligation of the field personnel to inform the SSHO (or the designated individual) of all emergency situations and to abide by their issued response actions. Special medical problems of field personnel such as allergies to insects, plants, specific drugs, etc., will be reported to the SSHO.

11.2 Work Stoppage and Corrective Actions

The SSHO will recommend temporary work stoppage if either of the following conditions are encountered:

- Air monitoring shows concentrations of airborne contaminants exceeding those outlined in Table 8-2
- Emergency conditions directly affect the health and safety of on-site workers or nearby residents or property.

The SSHO is empowered to unilaterally stop work if necessary to meet health and safety guidelines.

11.3 Catastrophic Event Emergencies

In the event of a catastrophic event, such as a fire, explosion, chemical release, hurricane, blizzard, flood, or earthquake, work activities will cease and all project personnel will be evacuated from the site. The evacuation will proceed in a direction opposite of the critically affected area, with all personnel assembling in a predesignated location outside of the demonstration area. A head count of the assembled employees will be taken, and first aid will be administered to any injured individuals.

Airhorns or vehicle horns will be used as signal devices to alert project personnel of emergencies. Designated signals consist of the following:

- Intermittent single blast: signifies a fire or chemical release emergency
- Intermittent double blast: signifies a medical emergency
- Continuous blast: signifies that site evacuation is required.

The contents of this action plan will be reviewed with the field project personnel during safety meetings.

11.4 Medical Emergencies

A medical emergency is defined as a situation that presents a significant threat to the health of project personnel or the members of the nearby community. These emergencies could result from chemical exposure, extreme heat, extreme cold, poisonous insect or snake bites, or accidents. Accidents can result from physical hazards on a site. These hazards can include tripping, catching, or cutting, and may be associated with debris at the demonstration site, heavy equipment, etc. Injuries might include broken bones, sprains, puncture wounds, electrical shock, or cuts. Medical emergencies must be dealt with immediately, and proper care must be administered. This may be in the form of first aid, examination by a qualified physician, or emergency hospitalization.

11.5 Safety Equipment Emergencies

An emergency may develop due to malfunction or other problems associated with health and safety equipment being utilized by field personnel. These equipment problems must be corrected before proceeding with field activities. Health and safety problems that might occur include leaks or tears in protective clothing, or encountering contaminants for which the prescribed PPE is not sufficient.

11.6 Emergency Equipment

Provisions will be made to have appropriate emergency equipment available and in proper working order. This equipment will include a first-aid kit, fire extinguisher, fire blankets, and splints. Equipment should be checked daily before commencing site activities, and defective equipment should be repaired or replaced before performing site work.

12. Spill Containment

During this technology demonstration, the only significant spill hazards are the spillage of catalyst regenerant solution (peroxide or hypochlorite solution) and the spillage of purged or sampled groundwater containing trichloroethylene (TCE). The regenerant solutions are not considered hazardous. Therefore, the scenario which requires greatest attention is the potential spillage of contaminated groundwater collected from the wells. There is very little possibility of spilling a large volume of groundwater, because the amounts collected during well purging and during sampling are small (typically less than 10 liters from each well).

Many potential spills can be avoided through application of proper engineering controls to hazards identified in the assessment. In areas where storage, handling, and transportation activities occur, preplanning to contain the largest volume of material that could be released in the area will minimize worker exposure. The containment measure should be appropriate to the hazardous material(s) identified and should be installed in the area or located nearby. The following examples are measures most frequently used:

- Absorbent materials, (e.g., pads, booms, powders)
- Salvage containers (e.g., overpack drums)
- Bermed, lined pads
- Concrete pad and dike
- Inflatable containment (e.g., "kiddie" pools, bladders)
- Associated equipment (e.g., pumps, hoses, shovels, hoists).

If contaminated groundwater is spilled on the ground at Edwards AFB, a quick response is necessary to limit the affected area as much as possible. Measures such as blocking culverts, digging bell holes or trenches, and building dikes and inverted weirs may be incorporated. Once the spill is contained, any standing fluid will be removed by pumping or vacuuming it into a tank. Absorbent materials will be used to soak up residual groundwater that cannot be vacuumed. The type of absorbent material used must be easy to apply and remove. Soil impacted by the spill will be removed and treated as required.

12.1 Reporting and Initial Personnel Safety

Upon discovery of a hazardous substance spill, personnel will perform the following tasks:

- Immediately summon help by notifying the Site Safety and Health Officer (SSHO) and/or the Project Manager
- Take action to ensure the safety of nearby personnel, including those actions specified in Section 11.2, below
- Proceed to a safe location;
- If anyone is seriously injured, immediately contact emergency medical services
- Keep unauthorized personnel out of the area.

12.2 Initial Spill Action

Factors that limit the employee's response at the site of a spill are:

- Level of training
- Personal safety
- Available personal protective equipment (PPE)
- Knowledge of the substance.

Employees should act to minimize the spill, but should limit their actions to the following.

- Shutting off equipment or pumps
- Closing valves
- Blocking drains within the path of the spill
- Using spill kit materials to dam or impede the flow of the spill.

Unauthorized persons will be excluded from the area.

12.3 Spill Response Evaluation

The identity and hazards of the spilled material should be determined before decisions regarding spill containment and control are made. The SSHO or Project Manager will evaluate the hazards associated with the spill and decide whether project employees or external response organizations should conduct the cleanup. If the Project Manager determines that project response personnel cannot safely perform the spill cleanup, the Project Manager will notify and request the assistance of the site host, and the Emergency Action Plan (see Section 11) will be activated.

12.4 Organizing a Spill Response

If the Project Manager determines that cleanup can be performed safely with project response personnel, the SSHO may act as the spill team leader and designate required procedures. Safety practices for small spill operations closely parallel procedures implemented during routine hazardous materials handling operations. Before work begins, the SSHO will conduct a hazard identification and assessment with response personnel. The following will be discussed and established:

- Levels of PPE and safety procedures
- Safety and work zones
- All steps of the response activities
- Most effective procedures or methods for cleanup
- Means of containment
- Leak or spill control
- Decontamination procedures
- Emergency decontamination.

12.5 Spill Cleanup Procedures

After care of injured personnel, containment of the released hazardous material should be the next consideration to limit its effect on the safety of personnel, the public, and the environment. The SSHO will determine the methods of control which depend upon the nature and extent of the spill. Decontamination will be accomplished in accordance with Section 10. Decontamination and disposal of contaminated materials will meet all regulatory requirements.

12.6 Post-Incident Follow-Up

The Project Manager or SSHO will implement necessary steps to ensure that the incident is properly documented and that spill response equipment is replenished. The Project Manager will direct the necessary corrective actions to prevent recurrence and evaluate the response.

APPENDICES TO HEALTH AND SAFETY PLAN

APPENDIX E

PALLADIUM CATALYSIS IN HORIZONTAL-FLOW TREATMENT WELLS: FIELD-SCALE DESIGN AND LABORATORY STUDY

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ABSTRACT: This paper discusses the field-scale design and associated laboratory experiments for a new groundwater remediation system that combines palladium-catalyzed hydrodehalogenation with the use of dual horizontal-flow treatment wells (HFTWs). Palladium (Pd) catalysts can treat a wide range of halogenated compounds, often completely and rapidly dehalogenating them. The HFTW system recirculates water within the treatment zone and provides the opportunity for multiple treatment passes, thereby enhancing contaminant removal. The combined Pd/HFTW system is scheduled to go on line in mid-2002 at Edwards Air Force Base in southeastern California, with groundwater contaminated with 0.5 to 1.5 mg/L of trichloroethylene (TCE). Laboratory work, performed in conjunction with the field-scale design, provided reaction rates for field-scale design and information on long-term catalyst behavior. The apparent first-order reaction rate constant for TCE was 0.43/min, corresponding to a half-life of 1.6 min. Over the long term (1 to 2 months), the reaction rate decreased, indicating catalyst deactivation. The data show three distinct deactivation rates: a slow rate of 0.03/day over approximately the first month, followed by faster deactivation at 0.16 to 0.19/day. The final, fastest deactivation (0.55/day) was attributed to an artifact of the laboratory setup, which caused unnaturally high sulfide concentrations through bacterial reduction of sulfate to sulfide, a known catalyst poison. Sodium hypochlorite recovered the catalyst activity, and is expected to maintain activity in the field with periodic pulses to regenerate the catalyst and control growth of sulfate-reducing bacteria.

INTRODUCTION

Groundwater contamination is a significant problem at thousands of Department of Defense (DoD) installations and former defense sites. The U.S. Environmental Protection Agency (U.S. EPA) estimated in 1996 that of 8,336 DoD sites needing cleanup, approximately 70% had contaminated groundwater (U.S. EPA, 1997). Volatile organic compounds (VOCs) are the most common groundwater contaminants and are found at approximately 75% of contaminated groundwater sites; the most commonly encountered VOCs are chlorinated solvents such as trichloroethylene (TCE) and tetrachloroethylene (also called perchloroethylene, or PCE). Based on the U.S. EPA estimates, TCE and PCE contaminate the groundwater at over 2,000 DoD installations. The TCE and PCE tend to be mobile and, in aerobic environments, refractory.

This project explores a new remediation strategy for chlorinated hydrocarbons by combining two technologies: Pd-catalyzed hydrodehalogenation and horizontal-flow treatment wells (HFTWs). Palladium (Pd) catalysis is an effective means of removing halogenated contaminants, and the HFTW system creates a zone in which contaminated

water is captured and recirculated. This recirculation leads to higher contaminant removal efficiencies than might otherwise be achieved.

Pd-Catalyzed Hydrodehalogenation. The Pd catalysts are capable of rapidly transforming a wide range of hydrocarbons, including polycyclic aromatic hydrocarbons (PAHs), PCBs, and halogenated methanes, ethylenes, ethanes, benzenes and pesticides (Munakata and Reinhard, 2001). Chlorinated ethylenes react with half-lives of minutes in the presence of dissolved hydrogen gas and a Pd catalyst, even at ambient temperature (Schreier and Reinhard, 1995; Siantar et al., 1996; Lowry and Reinhard, 1999). In the presence of excess hydrogen, dechlorination is complete and is followed by saturation of the double bond, forming ethane and hydrochloric acid (Lowry and Reinhard, 1999).

$$Cl_2C{=}CHCl + 4\,H_2 \xrightarrow{\text{Pd-on-}Al_2O_3} H_3C\text{-}CH_3 + 3\,HCl$$

The formation of hydrochloric acid as a reaction product should not generally represent an obstacle to applying this technology to contaminated groundwater, because reactant TCE concentrations are normally low (less than 30 mg/L), and because groundwaters usually have some natural buffering capacity.

Pd-catalyzed hydrodehalogenation was recently tested in the field (though not in conjunction with HFTWs). A Pd-catalyzed *in situ* groundwater treatment system was used for more than one year at Lawrence Livermore National Laboratory (LLNL) in Livermore, California, beginning in October 1998 (McNab et al., 2000). Two in-well Pd reactors were placed in series, with residence times of 5 minutes in the lower reactor and 6 minutes in the upper reactor. The system was plumbed such that water could enter through the lower reactor (upflow mode) or the upper reactor (downflow mode). In practice, the system was operated for a total of 8 to 10 hours per day: 4 to 5 hours per day in upflow mode followed by 4 to 5 hours per day in downflow mode. During the remaining time, the columns were drained and exposed to air. If the total operating time were increased past 10 hours per day, catalyst deactivation was observed and contaminant removal efficiencies declined. Subsequent experiments by Lowry and Reinhard (2000) show that this behavior is consistent with catalyst deactivation from sulfide produced by sulfate-reducing bacteria; periodic oxygen exposure would inhibit growth of these bacteria. The 14 to 16 hours of daily air exposure were sufficient to maintain catalyst activity for more than one year (the duration of the field test). During this time, the system removed greater than 99% of PCE and TCE, and greater than 98% of carbon tetrachloride (initial concentrations of 0.3 to 0.4 mg/L, 3 to 4 mg/L, and 18 to 21 μg/L, respectively).

The Pd technology offers several potential advantages over currently available treatment alternatives such as conventional pump-and-treat with granular activated carbon (GAC), reactive iron walls, and biological degradation.

- Reaction rates for contaminants can be fast enough for in-well treatment.
- The TCE, PCE, and other chlorinated compounds are destroyed, not merely transferred from the groundwater to another medium (e.g., activated carbon).
- The technology is applicable in deep aquifers.
- The technology is applicable even at high contaminant concentrations, where other treatment technologies might not be feasible.

- There is little or no formation of hazardous by-products such as dichloroethylene (DCE) or vinyl chloride (VC), which can be formed during biological reductive dechlorination.
- Catalytic reductive dehalogenation can be used in groundwater where dissolved oxygen is present, where biological reductive dehalogenation is not feasible
- The technology can destroy PCE, unlike biological cometabolic oxidation.

Horizontal-Flow Treatment Well (HFTW) Technology. The HFTW system consists of two treatment wells installed in an aquifer. Each well is screened over an upper interval and a lower interval. One well pumps in an upflow mode, extracting water through the lower screen and injecting it through the upper screen. The other well pumps in a downflow mode, extracting water through the upper screen and injecting it through the lower screen. In this field project, a Pd reactor will be placed between the upper and lower screens in each well and will treat the contaminated water as it travels between the screened sections in the well. Using this combination of upflow and downflow modes, the two wells create a region of groundwater recirculation within the aquifer. (Figure 1)

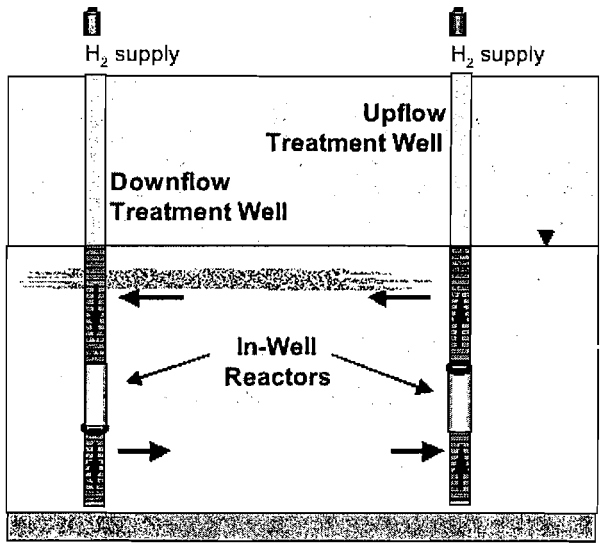

FIGURE 1. Horizontal flow treatment well (HFTW) system.

With this system, groundwater flow is captured by the HFTWs, recirculated through the aquifer, and then released to continue traveling downgradient. If the pump rate is high relative to the regional groundwater flow rate, then some fraction of the captured groundwater will be recirculated by the wells multiple times, and will pass through the in-well Pd reactors multiple times. Recirculation is improved by the presence of an aquitard or confining layer between the upper and lower screens, i.e., if the aquifer is divided into distinct upper and lower zones. This prevents a "short-circuit" flow of the water between the upper and lower screens of the same well. Modeling studies (Christ et al., 1999) have shown that the HFTW technology is also applicable to a single-zone aquifer, provided that the aquifer has a horizontal-to-vertical hydraulic conductivity anisotropy ratio of at least 10:1, which is relatively common. Modeling studies also indicate that the plume width captured can easily be several times the distance between

the two wells. In this way, HFTWs can provide many of the same advantages as "funnel-and-gate" technologies, often at a substantially lower capital installation cost.

FIELD PROJECT

Site Description. This project will be conducted at Edwards Air Force Base (EAFB), which is located in the Mojave Desert in southern California, approximately 60 miles (100 km) north-northeast of Los Angeles. Measured TCE concentrations at the field site range from 0.5 to 1.5 mg/L. The site was previously used for another demonstration project (McCarty et al., 1998); use of this site is advantageous because treatment and monitoring wells have already been installed and the hydrogeology is relatively well characterized.

The geology in the plume consists of unconsolidated alluvial sediments overlying granitic bedrock. The alluvial sediments are primarily fine- to medium-sized sand, with some silt and clay. The fraction of organic carbon is low, about 0.01 to 0.4%. At the project site, the depth to the water table is approximately 9 m and the depth to the underlying weathered bedrock is about 24 m. The aquifer consists of two zones separated by an aquitard. Estimated thicknesses range from 5.7 to 8 m for the upper unconfined aquifer, approximately 2 m for the aquitard, and from 5 to 9 m for the lower confined aquifer (McCarty et al., 1998; Gandhi et al., 2002). There is a head difference of approximately 0.25 m between the two zones, with the upper zone having higher head. The hydraulic gradient is towards the east-southeast, with the magnitude of the gradient between 0.004 and 0.007 (McCarty et al., 1998; Gandhi et al., 2002). Hydraulic conductivity ranges from about 10^{-3} cm/s to 10^{-2} cm/s in both the upper and lower aquifer zones (McCarty et al., 1998; Gandhi et al., 2002). Assuming a hydraulic conductivity of 3.4×10^{-3} cm/s, a gradient of 0.007, and a porosity of 0.30, the regional groundwater velocity is estimated to be about 6.9 cm/day. However, the regional velocity may differ between the upper and lower aquifer zones.

System Design. The system is comprised of three basic components: the well configuration, the reactors, and the operating conditions. The previous project at the site installed two treatment wells, 10 m apart, and 20 monitoring locations. It is economically impractical to monitor all of the wells, so a subset of 10 monitoring locations was selected, based on modeling results (Gandhi et al., 2002). The monitoring locations were chosen such that there are four wells in the HFTW recirculation zone, and one to three wells each, upstream and downstream of the treatment area, in both the upper and lower aquifer.

The reactor design is modeled on the successful Pd reactors installed at LLNL (McNab et. al., 2000), but has been altered based on the conditions at the site and results from laboratory studies. The reactor dimensions are constrained by the well diameter, which is 8 in. (20 cm); the reactor diameter will be 6 in. (15cm). The reactor length will be 54 in. (137 cm), yielding a single reactor empty bed volume of 6.5 gal (25 L); based on laboratory predictions of TCE removal rates, two reactors in series will be used. The reactors will be filled with a dispersed Pd/alumina catalyst (an alumina support onto which Pd clusters are dispersed).

The main operating conditions for the field system are the flow rate and the regeneration method. Operational flow rates will be based on reaction rates determined in

laboratory results. Regeneration/biogrowth control will either use sodium hypochlorite (shown to be an effective regenerant in laboratory tests) or hydrogen peroxide. The regeneration method will examine the effects of the regenerant concentration, the frequency of regeneration, and the duration of each regeneration pulse.

LABORATORY STUDY

Materials and Methods. The catalyst used in the laboratory study is supplied by Precious Metals Corporation (PMC, Sevierville, TN) and is a dispersed Pd metal on an alumina support, 1/16 in. (1.6 mm) in diameter, with a metal loading of 1% Pd by weight. The catalyst was used in a column reactor experiment, in which catalyst was exposed to a continuous flow of EAFB groundwater. The reactor consisted of a stainless steel column, 1.27 cm in diameter and 9.8 cm in length, with an empty bed volume of 10.5 mL. The bottom of the column held 8.0 g of inert 2 mm diameter borosilicate beads, topped with 1.0 g of catalyst; the remaining space was filled with glass wool. The water supply was hydrogen saturated and amended with 1 to 3 mg/L of TCE. The flow rate was held constant at 0.5 mL/min, which yielded a residence time of 1.7 min in the catalyst section of the reactor. This residence time was chosen such that the initial TCE removals would be approximately 50 to 80%; this range provides the maximum sensitivity to changes in the catalyst activity, which allows optimal observation of catalyst deactivation and regeneration. Aqueous samples were taken at the inlet and outlet of the reactor, extracted in hexane, and measured on an HP5890 Series II Gas Chromatograph equipped with an electron capture detector. Regeneration was performed using a sodium hypochlorite solution (Clorox™), diluted as 2 mL or 20 mL in 700 mL of deionized (DI) water (concentrations of ~150 mg/L and ~1500 mg/L, respectively, as free chlorine). In total, regeneration was carried out three times, under the conditions show in Table 1.

TABLE 1. Regeneration conditions.

Regeneration Number	1	2	3
Run Time (days)	40	42	62
Duration (min)	1000	240	1200
Regenerant Conc. (as mg/L free chlorine)	150	1500	1500

Results and Discussion. The results from the operation of the EAFB column are shown in Figure 2. As expected, the system initially removed 50 to 80% of the influent TCE. With no regenerative treatment, activity declined over 40 days; however, regeneration using the sodium hypochlorite solutions restored catalyst activity to original levels (R1 and R2 in Figure 2). Although the third regeneration (R3) appears less effective, this is attributed to an increase in sulfide concentration, rather than to any inherent change in the catalyst itself. The EAFB groundwater has extremely high sulfate concentrations (~700 mg/L) and was stored for over a month under hydrogen pressure, which would allow sulfate-reducing bacteria to grow and produce sulfide; in fact, sulfide was smelled when the EAFB groundwater reservoir was opened at day 67. This result is an artifact of the laboratory setup and should not be seen in the field. Under field conditions, hydrogen is added just before the reactor, so the water will not remain under hydrogen pressure for long periods of time. In response to these results, the laboratory setup was modified so

that the source water is stored under nitrogen pressure and hydrogen is added to the water just before flowing through the reactor.

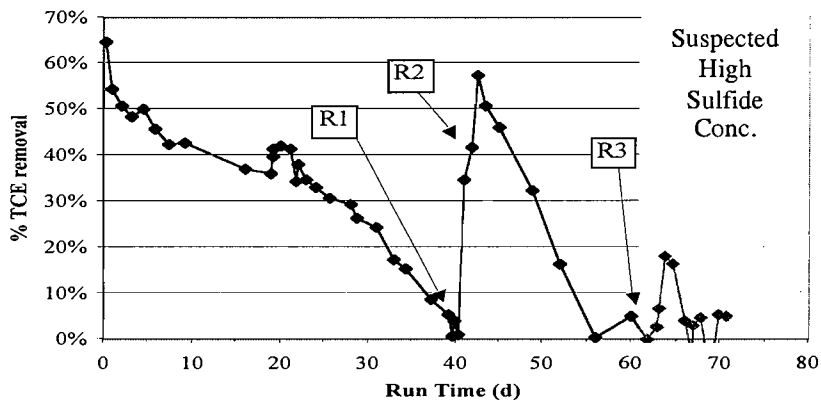

FIGURE 2. TCE removals with EAFB groundwater, residence time of 1.7 min. "R" indicates regeneration using a sodium hypochlorite solution.

Modeling of the data was also performed, to determine the reaction rate and deactivation rate constants. As derived by Levenspiel (1993), the model assumes plug flow, first-order reaction, and first-order deactivation:

$$\ln\ln\frac{C_i}{C_e} = \ln(k\tau) - k_d t$$

where C_e is the effluent concentration (mg/L), C_i is the influent concentration (mg/L), k is the first order reaction rate constant (min^{-1}), k_d is the deactivation rate constant ($days^{-1}$), τ is the average residence time in the reactor (min), and t is the total run time (days). Based on this model, the EAFB data was analyzed (Figure 3).

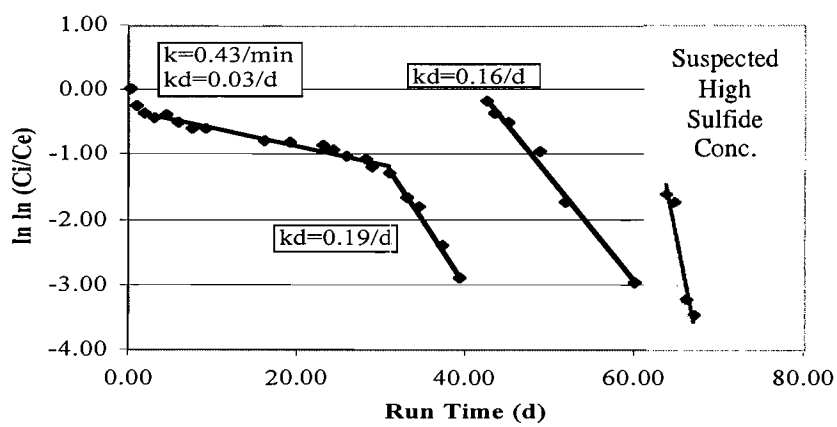

FIGURE 3. Reaction and deactivation kinetics, EAFB groundwater.

The reaction rate constant k is 0.43 min^{-1}, which is comparable to the k of ~0.5 min^{-1} seen with groundwater from Moffett Federal Airfield (Lowry and Reinhard, 2000). It is interesting to note that the reaction rate for TCE is similar in both groundwaters, despite

the fact that they come from different sources. The reaction rate constant of 0.43/min can be used to estimate the residence times needed for a given amount of TCE conversion (Table 2). The shown conversions were selected for the following reasons:

- 99.7%: lowers concentrations to the maximum contaminant level (MCL) of 5 μg/L, assuming the maximum influent concentration (1.5 mg/L).
- 99%: meets the design criteria of 99% removal
- 90%: meets the design criteria of 99% overall removal, assuming recirculation and two passes through each well, on average.

TABLE 2. Required residence times for TCE conversions in a single pass through the reactor.

Conversion	90%	99%	99.7%
Residence Time (min)	4.9	9.8	12

Also similar to the Moffett Federal Airfield (MFA) groundwater data, the deactivation in the EAFB groundwater appears to have an initial slower rate, followed by a faster rate. Lowry and Reinhard (2000) attribute the second, faster rate to bacterial sulfate reduction, which produces the catalyst poison sulfide (measured at a concentration of ~0.1 mg/L in the Lowry/Reinhard experiment). With the EAFB groundwater, the initial deactivation rate constant was 0.03 $days^{-1}$ during the first 30 days, and the second rate was 0.19 $days^{-1}$. After R1/R2, deactivation reoccurred at a very similar rate (0.16 $days^{-1}$). After R3, with the suspected high sulfide concentrations, the deactivation rate was higher (0.55 $days^{-1}$); this is consistent with the k_d of 0.42 $days^{-1}$, seen in Lowry and Reinhard (2000) at a sulfide concentration of 0.4 mg/L. Overall, these deactivation rate results are consistent with sulfide poisoning. It should be noted that the source water in the field (an aerobic aquifer) is expected to be free of sulfide, unlike the laboratory source water, which was stored under hydrogen pressure. It is therefore expected that the deactivation rates will also be relatively low; Lowry and Reinhard (2000) showed that catalyst activity could be maintained in MFA groundwater near the initial high levels, by periodically regenerating the catalyst with sodium hypochlorite. Given the similar behavior of the catalyst in the two groundwaters, it is expected that catalyst activity can be maintained in EAFB groundwater with periodic regeneration.

Implications of the Laboratory Study. Overall, the laboratory results imply that

1) Palladium catalysts can successfully remove TCE from the EAFB groundwater.
2) The TCE reaction rates are similar in groundwaters from MFA and EAFB.
3) The catalyst deactivation behavior is similar between the EAFB and previously studied MFA groundwaters, and is consistent with sulfide poisoning.
4) Sodium hypochlorite can regenerate a fully deactivated catalyst. It is expected to be able to maintain catalyst activity with periodic regeneration in the field.

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Reductive Hydrodechlorination of Trichloroethylene by Palladium-on-Alumina Catalyst: ^{13}C Solid-State NMR Study of Surface Reaction Precursors

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Adsorption of trichloroethylene (TCE) on alumina-supported palladium catalysts (Pd/Al_2O_3) was studied in the presence and absence of hydrogen using ^{13}C-solid state NMR. Carbon-13 NMR spectra indicate that at low coverage strongly adsorbed species are formed while at high coverage additional physisorbed species are present. Carbon-13 spin−echo amplitude data measured as a function of pulse separation, τ, was used to determine the $^{13}C-^{13}C$ intramolecular dipolar coupling and the carbon−carbon bond length of adsorbed species. Results indicate that a substantial fraction of the chemisorbed carbon species had undergone carbon−carbon bond scission forming single-carbon fragments, suggesting that the activation energy for carbon−carbon bond scission is comparable to the heat of adsorption. For the remaining surface species, the double bond is elongated to 1.46 ± 0.03 Å and is suspected to be chemically bonded ethynyl. At room temperature, adding an excess of hydrogen to catalyst that is covered to saturation with TCE precursors produces only in a small amount of ethane, indicating the fraction of surface species that are hydrodehalogenation precursors is small.

Introduction

Catalytic reductive hydrodehalogenation is an innovative technology for the treatment of groundwater contaminated with halogenated hydrocarbons, such as chlorinated solvents and pesticides.[1−3] Treatment involves adding hydrogen to the contaminated water followed by contacting with a palladium (Pd) catalyst.[4] For chlorinated ethylenes, the reaction is rapid even at ambient temperature and pressure and the products formed, ethane and hydrochloric acid, are inconsequential.[5] Optimized, the process is nearly quantitative and competitive to conventional technologies such as air-sparging and activated carbon, which produce secondary waste streams, and biological methods, which can yield toxic byproducts such as dichloroethylene and vinyl chloride.

Unlike ethylene hydrogenation on platinum, which has been investigated in great detail,[6] the surface reaction mechanism for hydrodechlorination has not been established. It has been reported that ethylene forms a π-bond at high ethylene pressures (∼1 atm) and ethylidyne ($M{\equiv}CCH_3$) bonded to Pt at low ethylene pressures (<1 atm). The π-bonded ethylene is then irreversibly hydrogenated through an ethyl intermediate ($M-CH_2-CH_3$) forming ethane, whereas the ethylidyne is simply a "spectator species".[7] The hypothesis tested in this study was that such spectator species are also formed in the catalytic hydrogenation of chlorinated ethylenes on palladium.

The objectives of this study were to (1) elucidate the products of TCE adsorption on a powdered palladium-on-alumina (Pd/Al_2O_3) catalyst and (2) examine the influence of coadsorbed hydrogen. Solid-state NMR has previously been used to study reactions of acetylene, ethylene, and methyl iodide on dispersed metal catalysts.[8−10] A key advantage of solid-state NMR is that results are relevant to reaction conditions: dispersed catalysts and high pressure. Other surface spectroscopic methods such as low energy electron diffraction (LEED), temperature programmed desorption (TPD), and reflection absorption infrared spectroscopy (RAIRS) are limited to the use of single crystals under ultrahigh vacuum (UHV) conditions.

Several studies addressed chlorinated ethylene adsorption on single-crystal palladium surfaces. Bloxham et al. studied the adsorption of *trans*-1,2-dichloroethylene on Pd(110) with TPD, RAIRS, and LEED.[11] They found that, at room temperature, the molecule decomposes and hydrogen evolves at low coverage whereas acetylene and HCl evolve at high coverage. Park et al. and Klier et al. found that at room temperature and above chemisorption of dichloromethane and tetrachloroethylene (PCE) on Pd(100) is completely dissociative for C−Cl bonds whereas C=C bonds remain in tact.[12,13] Jugnet et al. studied adsorption of TCE on PdCu(110) alloy using high-resolution electron energy loss spectroscopy (HREELS)[14] and found that upon sorption at 280 K and higher most of the C−Cl bonds break. Carbon−carbon dissociation does not seem to be favored energetically at T < 280 K. These UHV studies agree in that on single-crystal surfaces there is significant dissociation of C−Cl bonds well

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below room temperature but no carbon−carbon bond scission at room temperature or below.

The direct measurements of the $^{13}C-^{13}C$ dipolar coupling reported here indicate that a significant fraction, e.g., up to 60%, of the TCE molecules undergo carbon−carbon bond scission upon adsorption at room temperature while the remainder of the TCE chemisorbed on the metal is converted to an activated surface species with a carbon−carbon bond length greater than that of a double bond but shorter than that of a single bond. These new species may be in the form of an ethynyl (M≡CCH). Measurement of the ^{13}C spectrum for a sample where hydrogen was coadsorbed on a saturated monolayer of TCE and associated fragments showed only a small amount of conversion to ethane, suggesting that in this case the chemisorbed TCE species are not active for hydrogenation, perhaps in analogy to ethylene hydrogenation.

Materials and Methods

Materials. Pd/η-Al_2O_3 and powdered η-alumina (surface area 200−300 m^2/g) used to prepare Pd/η-Al_2O_3 (5 wt% Pd, 19% dispersion) were obtained from Dr. J. H. Sinfelt (Exxon Research and Engineering Co, Annandale, NJ). ^{13}C-enriched TCE was doubly labeled and 99% pure (Cambridge Isotope Lab, Cambridge, MA).

Sample Preparation. Sample preparation was performed using a gas-handling apparatus, which was attached to a turbo pump station. The gas-handling apparatus consisted of two sections: a quartz furnace tube (0.6 L) to which a 2-mL NMR sample ampule was attached and a glass manifold (1.1 L) to which sources of ultrapure hydrogen, oxygen, and TCE vapor were attached. The two sections were separated by a valve. Pressures were measured to a precision of 0.01 Torr using a Baratron capacitance manometer.[15]

Sample preparation consisted of two steps: catalyst cleaning and exposure to adsorbates.[15] During the cleaning step, the catalyst was heated under vacuum to 570 K in the furnace tube overnight to 10^{-6} Torr and exposed to three sets of alternating 10-min flows of hydrogen and oxygen. Between these flows, the system was re-evacuated again for 5 min to 10^{-5} Torr to avoid an explosion. A final flow of hydrogen was applied to reduce the catalyst followed by cooling to room temperature under vacuum. After that, the furnace tube was detached from the manifold. The sample was shaken into the ampule, and then the furnace tube was re-attached to the manifold and for low-T adsorptions, the ampule was immersed into a liquid nitrogen bath. Prior to exposure to the adsorbate, with the valve separating the two sections closed, the glass manifold section was filled to a desired adsorbate pressure, P_i. The valve between the two sections was then opened and, after allowing about 5−10 min for equilibration, the final adsorbate pressure, P_f, was recorded. The final adsorbate pressure reflected the pressure drop due to both the volume change and to adsorption. The pressure change was used to determine the amount of adsorbate on the catalyst or blank support. In most cases, after adsorption, the system was re-evacuated for at least 5 min to pressures lower than 10^{-3} Torr. Finally, the ampule containing the catalyst or blank support was flame-sealed while submerged in a liquid nitrogen bath to minimize possible reactions during the sealing step.

The amount of irreversibly adsorbed TCE for both catalyst and alumina samples was determined using unlabeled TCE. The sample was exposed to a predetermined amountof TCE vapor. The uptake of total (reversible and irreversible) TCE was calculated from the pressure drop observed during sorption. The sample was evacuated, and the sample was again exposed to TCE vapor. This uptake was attributed to reversible (or physical) sorption and the difference to the total irreversible sorption. The catalyst coverage is defined as the number of irreversibly bound TCE molecules per surface Pd atom. Table 1 summarizes the samples used in this work and details of the preparation procedures. The amount of surface Pd was calculated from the total catalyst mass per sample (∼1 g) and the dispersion. The support was η-Al_2O_3. Sample 1 was prepared by exposing the catalyst to a large excess of TCE for 2 h at 292 K followed by evacuation for 5 min to 10^{-3} Torr and sealing.

Table 1. Summary of Samples Prepared

sample	support	surface Pd (μmol)	^{13}C-TCE (μmol)	H_2 (μmol)	$T_{adsorption}$ (K)	evacuation
1	Pd/η-Al_2O_3	102	972	−	292	yes[a]
2	Pd/η-Al_2O_3	101	230	−	77	no
3	Pd/η-Al_2O_3	72	38	40	77	yes
4	η-Al_2O_3	−	275	−	77	no

[a] Final pressure = 10^{-3} Torr.

Sample 2 was prepared by condensing an excess of TCE at 77 K followed by immediate sealing and equilibration at room temperature. Sample 3 was equilibrated at room temperature for 10 h under vacuum (∼10^{-6} Torr), exposed to hydrogen at 77 K, and flame-sealed. The control sample (Sample 4) was prepared with η-Al_2O_3 by condensing TCE onto 1.00 g of support, respectively) while the ampule was at 77 K. After loading, the samples were immediately sealed. A reference sample of ^{13}C-TCE in deuterated ethanol was also prepared (10% $^{13}C_2$-TCE, 90% CD_3CD_2OH).

NMR Experiments. ^{13}C NMR spectra were obtained using a home-built singly tuned NMR probe with a Chemagnetics 400 MHz spectrometer equipped with a Janis STVP-200 dewar. The spin−echo pulse sequence was used with a typical ^{13}C π pulse length of 5.0 μs. The ^{13}C spin−lattice relaxation time, T_1, was measured using a saturation recovery experiment, and the data were fit to an exponential recovery. All ^{13}C spectra were referenced to 0 ppm via external trimethylsilane (TMS).

The $^{13}C-^{13}C$ bond length was determined from measuring the $^{13}C-^{13}C$ dipolar coupling by fitting the "slow beat data" to the slow beat equation for "unlike" spins shown below.[16] (Spins are considered "unlike" when the difference in their resonance frequencies is much larger than their coupling.) The slow beat data were obtained by measuring the signal intensity, $S(\tau)$, as a function of the evolution time, τ, between the $\pi/2$ and π pulses of the spin−echo.

$$S(\tau) = \alpha\left\langle \cos\left(\left(\frac{\gamma_c^2\hbar}{r^3}\right)(1 - 3\cos^2\theta)\,\tau\right)\right\rangle_{avg} \exp\left(-\frac{2\tau}{T_2}\right) + (1-\alpha)\exp\left(-\frac{2\tau}{T_2'}\right) \quad (1)$$

There are four fitting parameters: α, the fraction of paired nuclei; r, the internuclear distance; and T_2 and T_2', spin−spin relaxation times for the ^{13}C nuclei in $^{13}C-^{13}C$ pairs and those not in $^{13}C-^{13}C$ pairs, respectively. Other parameters are the gyromagnetic constant for carbon, γ_c, and the angle between the internuclear vector and the static field, θ.

Similarly, the existence of carbon−hydrogen bonds was determined by probing the $^{13}C-^{1}H$ dipolar coupling using $^{13}C-^{1}H$ spin−echo double resonance (SEDOR).[17] In a SEDOR experiment, the ^{13}C spin−echo signal intensities with and without the application of a ^{1}H π pulse during the echo evolution are compared. If the carbon has a neighboring hydrogen atom, then applying a ^{1}H π pulse will cause the ^{13}C signal to diminish. The extent of this reduction in ^{13}C signal intensity is a function of the duration between the ^{13}C $\pi/2$ pulse and the ^{1}H π pulse, τ_1, and the fraction of ^{13}C nuclei with a neighboring hydrogen. A home-built two-channel probe was used in these experiments. The typical ^{13}C and ^{1}H π pulse lengths were 7.5 and 11.0 μs, respectively. The probe and the method were validated using three test compounds: methyl iodide (CH_3− model), ethanol (CH_2− model), and TCE (CH− model).

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Results and Discussion

1. TCE Coverage. When 0.812 g of a clean Pd/η-Al_2O_3 catalyst (72.5 μmol of surface Pd) was exposed to 16.7 Torr (2188.0 $\pm$ 0.6 μmol) of TCE for 45 min at 292 K, 792.1 $\pm$ 1.1 μmol of TCE adsorbed. After re-evacuation to 10^{-5} Torr, a second exposure resulted in the adsorption of 773.7 $\pm$ 1.1 μmol of TCE. Therefore, we conclude that 18.4 $\pm$ 1.6 μmol of TCE were irreversibly adsorbed on the catalyst surface. This corresponds to a coverage of 25 $\pm$ 2%, similar to that reported for other ethenes.[18] We repeated the measurements at 233 K where we observed an initial adsorption of 1212.2 $\pm$ 1.1 μmol and a second adsorption of 1174.4 $\pm$ 1.1 μmol. The total irreversible adsorption was 37.8 $\pm$ 1.6 μmol, corresponding to 35 $\pm$ 2% coverage, a significant increase over the result at room temperature. Clearly, there is a large amount of physisorption of TCE on the catalyst at both temperatures. At lower temperatures, the amount of physisorbed TCE is larger.

For the blank support η-Al_2O_3 at 292 K, we observed only physisorption. An evacuation to pressures of 10^{-6} Torr essentially leaves an undetectable amount of sorbed TCE (i.e., $<$0.4 μmol/g). When evacuation is only to 10^{-3} Torr, the amount of TCE remaining on the support depends on the initial exposure: on the order of 1$-$2 μmol of TCE per gram of alumina were left after exposure to 970 μmol of TCE, and less than 0.4 μmol of TCE per gram of alumina was left after an exposure of 490 μmol of TCE.

2. NMR Spectra. 2.1. ^{13}C Spectra of TCE Adsorbed on Alumina. For TCE in deuterated ethanol, we observed two peaks with chemical shifts of 117 and 124 ppm, respectively, which agree well with the published ^{13}C NMR chemical shifts for the monochlorinated and dichlorinated carbons of TCE in deuterated chloroform (116.6 and 123.9 ppm, respectively).[19,20] The room-temperature spectrum for Sample 4 (TCE/η-Al_2O_3) is shown in Figure 1a. There is a feature with a shoulder of width $\sim$8 ppm centered at a chemical shift of 121 ppm. The feature can be fit with two peaks with a chemical shift difference of $\sim$3 ppm, each of width $\sim$3 ppm (see inset to Figure 1a). The similarity in chemical shifts to those observed for TCE in deuterated ethanol implies that TCE adsorbed on alumina has not changed its structure from TCE in solution. Furthermore, the relatively narrow width of the peaks implies that TCE adsorbed on the alumina is nearly as mobile as TCE in solution at room temperature, consistent with physisorption.

The 77 K spectrum for Sample 4 (η-Al_2O_3 + TCE) shown in Figure 1b contains a feature with a distinct shoulder centered at $\sim$117 ppm and is similar to that of TCE in ethanol at the same temperature. We expect TCE to be frozen at this temperature because the freezing point for bulk TCE is 200 K. The asymmetry of the line shape is primarily due to the large chemical shift anisotropy ($\sim$200 ppm or $\sim$20 kHz) with a minor contribution from the ^{13}C$-^{13}$C dipolar coupling tensor (on the order of 25 ppm or 2.5 kHz). Carbon$-$hydrogen couplings (on the order of 25 kHz or 250 ppm for directly bonded carbon$-$hydrogen pairs) also contribute to the overall line width.

Since the spectra of TCE on alumina both at room temperature and at 77 K are similar to that of TCE in ethanol, we conclude that TCE on alumina is physisorbed, i.e., it has weak interactions with the surface rather than strong chemisorption which would broaden the line shape and suppress motion at room temperature. This observation is consistent with the findings from the coverage measurements that showed physisorbed TCE can be removed via pumping.

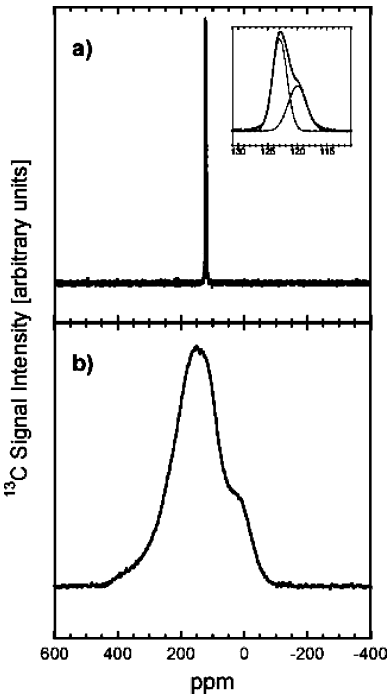

Figure 1. ^{13}C NMR spectra of ^{13}C-TCE adsorbed on blank alumina support (Sample 4) obtained at room temperature (a) and at 77 K (b). Both spectra were acquired with a repetition rate of 2 s. The room-temperature spectrum was the result of the accumulation of 2048 scans. The 77 K spectrum was the result of 2048 scans.

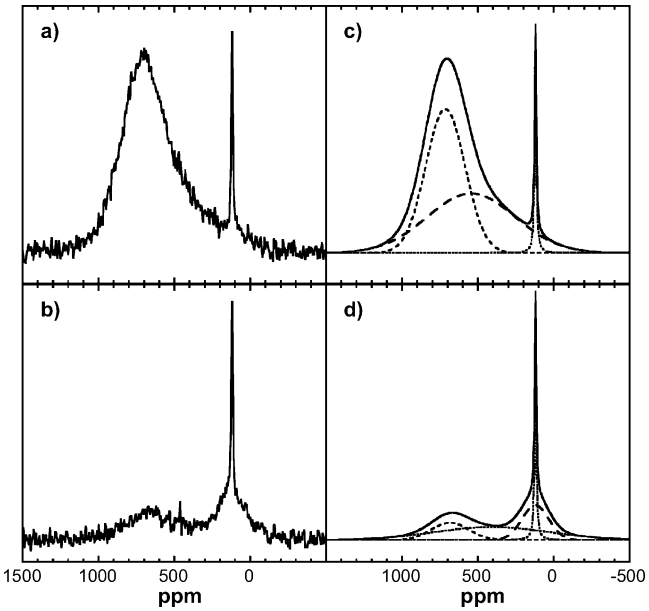

Figure 2. Room temperature ^{13}C NMR spectra and corresponding spectral simulations of ^{13}C-TCE adsorbed on palladium catalyst (Sample 1) for repetition rates of 0.04 (a and c) and 64 s (b and d) with 76 800 and 192 scans, respectively. The integral of the narrow feature at $\sim$121 ppm in (b) constitutes $\sim$15% of the total carbon signal.

2.2. ^{13}C Spectra of TCE Adsorbed on Supported Palladium Catalyst. The spectra for Sample 1 (Pd/η-Al_2O_3 + TCE) shown in Figures 2 and 3 are very different from those for TCE adsorbed on alumina. Also shown are the results of simulations resulting from deconvoluting the spectra into a sum of Gaussian and

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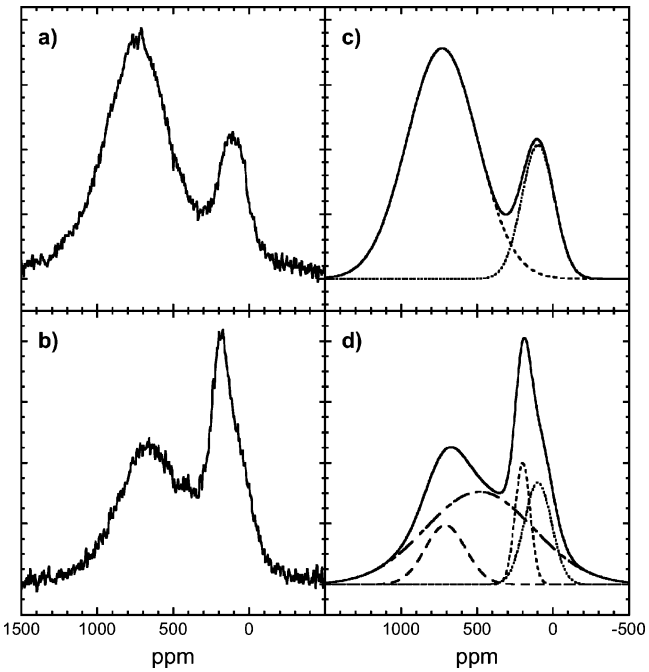

Figure 3. 77 K ^{13}C NMR spectra and corresponding spectral simulations of ^{13}C-TCE adsorbed on palladium catalyst (Sample 1) for repetition rates of 0.04 (a and c) and 32 s (b and d) with 76 800 and 192 scans, respectively.

Lorentzian components. Although we do not expect the spectrum corresponding to any specific species to be a simple Gaussian or Lorentzian, we do expect it to remain fixed. Therefore, deconvolutions can be useful for evaluating qualitative changes in the spectra, e.g., for detecting the presence of new surface species due to changes in the relative spectral intensity in different regions of the total spectrum.

It is clear from both the raw spectra and their corresponding simulations that there are several different types of species present in the catalyst samples. At room temperature, there is a narrow feature at ~121 ppm which is roughly 8 ppm wide. This feature is similar to the peak observed for the sample with TCE physisorbed on alumina. Indeed, a higher-resolution spectrum of the same sample obtained with additional shimming allowed resolution into two peaks located at 118 and 123 ppm, with widths of 2 and 4 ppm, respectively. We therefore assign this narrow feature in Figure 2a to physisorbed TCE, which remained after the final evacuation to 10^{-3} Torr (see discussion above). Focusing on the broad components in Figures 2 and 3, we conclude that there are carbon nuclei which are directly adsorbed to the metal nuclei due to the presence of ^{13}C signal in a chemical shift range that is much greater than would normally be observed for TCE (i.e., chemical shifts much larger than 300 ppm). Such unusually broad line shapes and large downfield shifts have been previously observed for nuclei in species bonding to transition metals and are due to the anisotropic Knight shift and the magnetic susceptibility of the metal clusters.[21] For Pd, this susceptibility effect is on the order of 270 ppm.[22] Thus, we conclude that the carbon signal at chemical shifts above ~300 ppm corresponds to carbon species directly bonded to the metal.

In summary, the spectra for TCE on the supported Pd catalysts suggest the presence of both weakly adsorbed intact TCE and several different strongly adsorbed species with direct bonding to the Pd surface. We expect that the latter species will include a variety of decomposition products and intermediate reaction species. However, direct structural information cannot be obtained from the spectra shown in Figures 1 and 2 and can only be obtained from measurements of internuclear dipolar couplings.

3. ^{13}C T_1 Relaxation Times. The measurement of ^{13}C T_1 relaxation times as a function of chemical shift across the spectrum gives insights into the nature of the interaction of the surface species with the metal surface and also helps unravel the number of different species. For chemical shifts larger than 400 ppm, the T_1 data for Sample 1 (Pd/η-Al_2O_3 + TCE) are reasonably well fit to a single exponential. At 77 K, the T_1 ranges from ~0.2 s at 400 ppm to ~0.1 s at 800 ppm, while at 292 K, the T_1 ranges from 1.2 s at 400 ppm to ~0.4 s at 800 ppm. The decrease in T_1 with increasing chemical shift along with the inverse temperature dependence are consistent with strong metal interactions.[21] For lower chemical shifts, the T_1 data were multiexponential and more difficult to analyze. At 77 K, there is a significant contribution in this spectral region from physisorbed TCE (see Figure 1b), which itself is expected to have multiexponential relaxation behavior. Measurements of the ^{13}C T_1 for TCE on alumina and comparison with the results for Samples 1 and 2, where the latter has a large excess of TCE, showed that, while at room temperature the T_1 for TCE physisorbed on the catalyst is ~1 s, at 77 K, the T_1 increases to a value on the order of several minutes. This will be important in the experiments discussed below since it allows us to suppress the signal due to physisorbed TCE at 77 K by using repetition rates on the order of a few seconds.

4. ^{13}C Slow Beat Data. To gain more insight into the different carbon species chemisorbed on the catalyst surface we acquired ^{13}C slow beat data. First, to confirm that our method is robust, at 77 K we measured the carbon−carbon bond length for TCE adsorbed on alumina, where we expect the physisorbed species to retain the same structure as it does in bulk. We expect only one carbon species resulted when TCE physisorbed onto alumina and therefore the slow beat data for this sample were measured using the echo amplitude, which is the sum of total ^{13}C signal in the sample.

The data obtained in this way yielded a fraction of intact ^{13}C−^{13}C bonds, α, of 89 ± 3% with a carbon bond length of 1.34 ± 0.02 Å, consistent with the double bond of TCE (1.36 ± 0.04 Å).[23] (Figure 4) Since our ^{13}C-TCE is 99% enriched, we expected 98.01% of the carbon atoms to be in ^{13}C−^{13}C pairs, 1.98% in ^{12}C−^{13}C pairs, and 0.01% to be in ^{12}C−^{12}C pairs. The lower-than-expected observed fraction of molecules with intact ^{13}C−^{13}C bonds is possibly due to the clustering of TCE molecules which introduces intermolecular ^{13}C−^{13}C dipolar couplings. (Simulations for a three-spin system consisting of two strongly coupled spins and a third spin slightly further away suggest that the effective α can be reduced, depending on the relative orientation of the internuclear vectors.) In contrast to the 77 K measurement, no oscillation in the slow beat data was observed at room temperature. The molecular motion for TCE physisorbed on alumina at room temperature averages out the dipolar coupling.

For the TCE adsorbed on the catalyst samples, we measured the ^{13}C slow beat both using the echo amplitude, which gives an average for all surface species, and as a function of chemical shift. We also used a relatively short repetition rate of 2 s to suppress the signal from the physisorbed TCE. The echo amplitude

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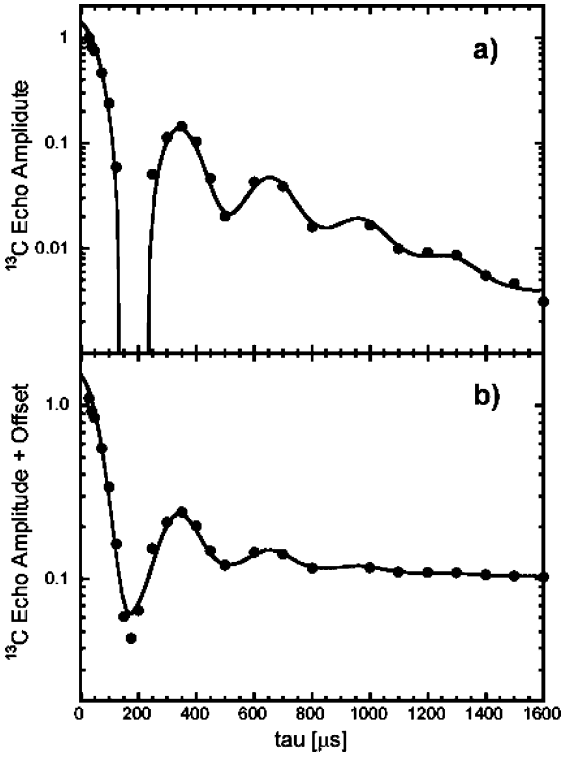

Figure 4. Slow beat data for Sample 4 (η-Al_2O_3 + TCE) along with fits showing that TCE retains its structure when adsorbed onto alumina surface. Points show data. The line shows slow beat simulation with $r(^{13}C-^{13}C) = 1.34$ Å, $T_2 = 520$ μs, $T_2' = 850$ μs, and 89% of the ^{13}C-carbon bonded to another ^{13}C-carbon. At the minimum of the "beat", the intensities gave negative values, and thus, these points are omitted in order to plot with an exponential *y* axis (a). In plot b, the data were shifted vertically by 0.1 (b).

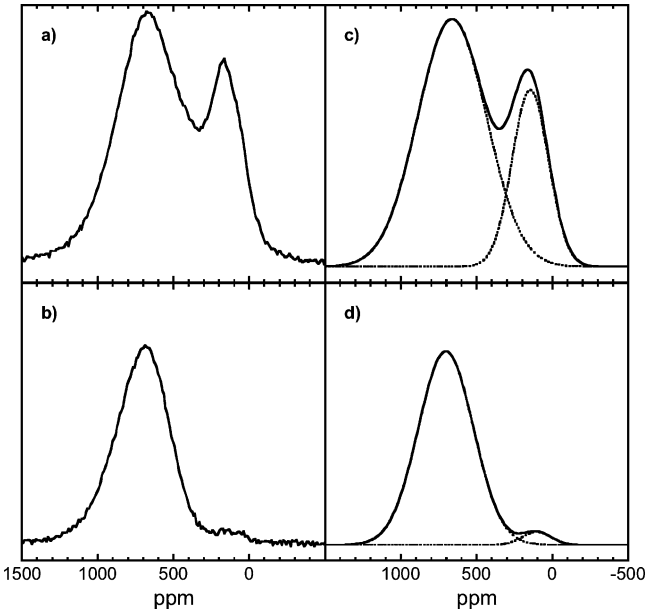

Figure 5. ^{13}C NMR spectra and corresponding simulations from the slow beat experiment for Sample 1 (Pd/η-Al_2O_3 + TCE) at 77 K. The spectra in (a) and (c) correspond to τ of 30 μs, while the spectra in (b) and (d) correspond to a τ of 200 μs.

data were fit using a bond length of 1.46 ± 0.04 Å with 41 ± 3% of the observed carbon signal being associated with carbon−carbon pairs. The spectra assocated with this measurement suggested there was significant variation in the slow beat across the spectrum. Figure 5 compares a spectrum obtained with a τ of 30 μs to a spectrum obtained with a τ of 200 μs. To investigate this further, we measured the slow beat as a function of chemical shift. Figure 6b shows slow beat data measured at 125 ppm where the oscillations in the data are very clear. The slow beat simulation yields a carbon−carbon length of 1.46 ± 0.02 Å, a value between that of a carbon−carbon double bond and a carbon−carbon single bond. The α value of 83% indicates that even at 125 ppm there exist carbon fragments that contribute to the spectral intensity. As the chemical shift increases, the slow beat data begin to show less of an initial decay and the beat near τ of 400 μs, indicative of carbon−carbon bonds, gradually disappears. For example, at 600 ppm, it appears that ∼15% of the carbon atoms are participating in carbon−carbon bonds. Figure 6a shows a plot of the slow beat data measured at 900 ppm. There is no distinct "beat", which suggests there are no intact carbon−carbon bonds. The early part of the data can be fit with a simple exponential decay corresponding to a T_2 of ∼1000 μs. The curvature in the long-τ data is similar to that observed for ^{13}C-enriched carbon monoxide chemisorbed on supported platinum catalysts, where the T_2 decay was exclusively due to intermolecular dipolar couplings.[24] We therefore conclude that the low-field side of the ^{13}C spectrum corresponds to carbon fragments resulting from C−C bond scission. (A similar low-field shift for carbon fragments was previously observed for supported Pt catalysts.[25]) This is consistent with results from ^{13}C T_1 measurements.

We also measured slow beat data as a function of the chemical shift at room temperature. In this case, the narrow width of the 118 ppm feature corresponding to physisorbed TCE allows us to avoid its contribution. At 200 ppm, we observe a characteristic beat and the data is fit using the bond length of 1.46 ± 0.02 Å, the same as that observed at 77 K. This confirms that this new species is immobile, i.e., strongly chemisorbed onto the palladium surface. The room-temperature data measured at chemical shifts above 600 ppm showed no beat, as was observed for the 77 K data.

5. ^{13}C−^{1}H SEDOR. Figure 6 compares ^{13}C spectra of TCE adsorbed on the catalyst (Sample 2: Pd/η-Al_2O_3 + TCE) with and without a ^{1}H pulse. Again, the repetition rate was chosen at 2 s to suppress the signal from excess physisorbed TCE. The ^{13}C signal intensity at high chemical shifts (>500 ppm) is not affected by the application of a ^{1}H pulse, implying that these carbon species are not coupled to a hydrogen atom, whereas the ^{13}C signal intensity for the chemical shifts lower than 500 ppm is visibly affected. From the slow beat results, we have concluded that the carbon at the higher chemical shifts corresponds to carbon fragments. Therefore, from the SEDOR results, we can also conclude that not only are they not bonded to another carbon, but they are also not bonded to a hydrogen atom. Assuming that species with chemical shifts lower than 500 ppm correspond to the two-carbon species, the SEDOR data show that at least a fraction of these carbons are bonded to hydrogen atoms.

It is typical to plot a SEDOR curve, i.e., the SEDOR fraction as a function of τ_1, the time between the application of the first ^{13}C pulse and the ^{1}H pulse. The SEDOR curve will approach an asymptotic value as τ_1 gets large. Different numbers of hydrogen atoms attached to a carbon result in uniquely different SEDOR curves. In our case, the ^{13}C slow beat data show that the T_2 of the surface species is very short. The ^{13}C signal intensity drops

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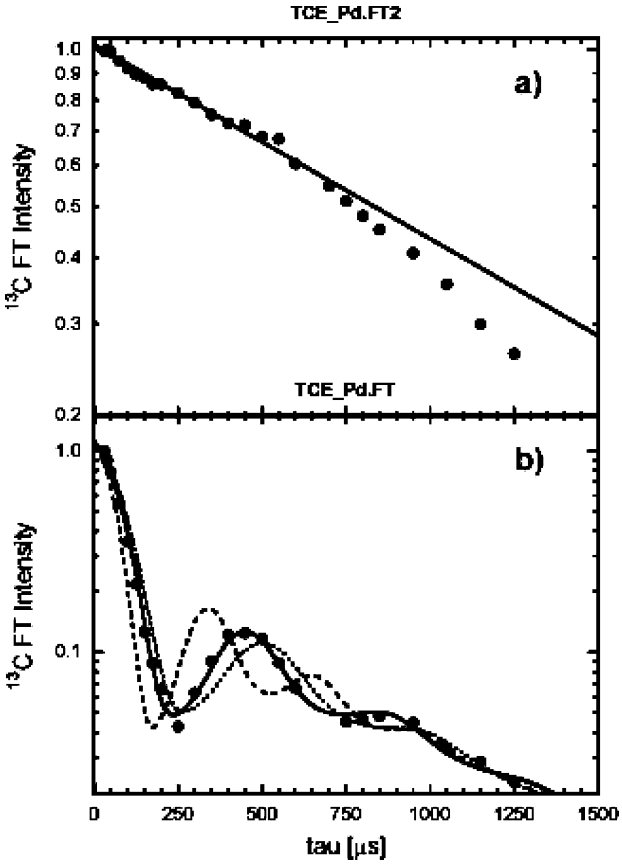

Figure 6. Slow beat data obtained at 77 K for Sample 1 (Pd/η-Al_2O_3 + TCE). Data were obtained by measuring the FT amplitudes in the frequency domain. Data in plot (a), measured at 900 ppm, show no carbon−carbon bonds and only one T_2 value of 1000 μs, whereas the slow beat data measured at 125 ppm (b) give a stretched carbon−carbon bond length of 1.46 Å, $T_2 = 550$ μs, $T_2' = 1150$ μs for 83% of the carbons observed at this chemical shift. The dotted line shows a simulation for paired carbons with double bonds ($r =$ 1.34 Å). The dashed line shows a simulation for paired carbons with single bonds ($r = 1.54$ Å).

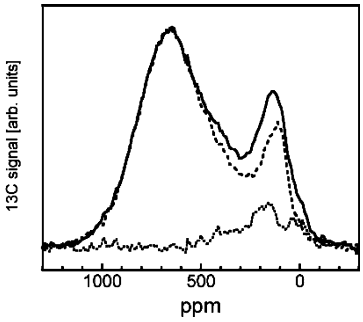

Figure 7. ^{13}C NMR spectra from SEDOR experiments at 77 K. The solid line represents ^{13}C signal without ^{1}H pulse (S_0). The dashed line represents ^{13}C signal with ^{1}H pulse (S); the dotted line represent the difference ($S_0 - S$). Each spectrum is a result of 1024 scans at repetition rate of 2 s, echo delay (τ) of 65 μs, and τ_1 ranging from 15 to 45 μs.

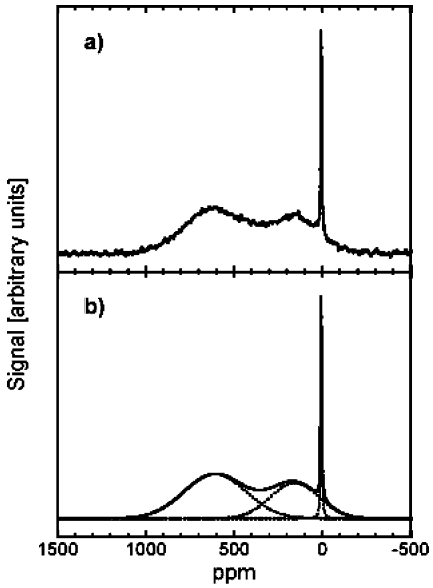

Figure 8. Room-temperature ^{13}C NMR spectrum (a) and corresponding spectral simulation (b) for a sample containing ^{13}C-TCE coadsorbed with hydrogen on palladium catalyst (Sample 3: Pd/η-Al_2O_3 + TCE + H_2) shows three features. The spectrum was the result of the accumulation of 5120 scans with repetition rate of 2 s.

to half of its maximum value when τ is ∼100 μs. Furthermore, for a repetition time of 2 s we found from the fit to the echo amplitudes from the ^{13}C slow beat measurement that most (∼65 ± 5%) of the carbon signal is from isolated fragments. These two factors made it impractical to obtain SEDOR curves with sufficient signal-to-noise to be able to distinguish between CH_3, CH_2, and CH.

6. Reaction of Hydrogen with TCE-Covered Surface. Figure 8 shows the room-temperature spectrum and corresponding spectral simulation for a sample containing TCE coadsorbed with hydrogen on the palladium catalyst (Sample 3: Pd/η-Al_2O_3 + TCE + H_2). This spectrum was obtained 5 months after the sample preparation and storage at room temperature, and we therefore expect the reaction to have already equilibrated.

Comparing this spectrum to those for a sample containing only TCE adsorbed on the palladium catalyst (Figures 2 and 3), it is clear that chemisorbed carbon atoms are still present, while the only product observed is ethane at ∼6 ppm. There is no evidence of any other intermediate products. Under higher resolution, the ethane feature is a clear quartet with a C−H J coupling of ∼120 Hz which indicates high mobility, i.e., ethane is not strongly adsorbed to the surface. The spin lattice relaxation time for the product is ∼0.5 s, slightly shorter than that of physisorbed TCE (∼1 s) but longer than that for the carbon fragments. The integral of the ethane peak accounts for only ∼7% of the total carbon signal. Even if we take into account the fact that a substantial amount of the carbon bonds break upon initial adsorption (we estimate that roughly 60% of the intensity is in the low field region of the spectrum corresponding to carbon fragments), we still expect that a large fraction of the surface species had intact carbon−carbon bonds prior to exposure to hydrogen.

Clearly, many of these chemisorbed surface species were unable to react to form ethane at room temperature, despite the excess hydrogen present in this sample. One possible explanation is that preadsorption of a saturation coverage of TCE at room temperature left a surface that is not favorable toward reaction, e.g., the hydrogen physisorbed at 77 K was unable to find sufficient or appropriate active metal sites. Another important consideration is occupation of surface sites by chlorine atoms, a known deactivator for palladium catalysts.[26−28] Further experiments

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where we vary the sample preparation, e.g., vary the amount of hydrogen coadsorbed, will yield more insights into the hydrogenation mechanism. For example, we will determine whether high hydrogen pressures cause the chemisorbed two-carbon species to react quantitatively and thus vacate the surface completely.[28]

Conclusions

The ^{13}C spectra and ^{13}C slow beat fitting show that when TCE was adsorbed onto a dispersed palladium catalyst at room temperature, at least two types of chemisorbed carbon species formed. (A third species, physisorbed TCE, forms when the sample is exposed to an excess of TCE. However, most of this physisorbed TCE can be removed by evacuation.) One species appears at low field in the ^{13}C spectrum and corresponds to isolated dehydrogenated carbon atoms. These carbon fragments account for nearly 60% of the total chemisorbed carbon. The fraction of broken carbon−carbon bonds is significantly smaller when ethylene or acetylene is adsorbed on dispersed platinum catalyst where only ∼20% of the bonds were fragmented, indicating that the activation energy of the carbon−carbon bond scission for adsorption of TCE on palladium is on the order of the heat of adsorption, ∼7−11 kcal/mol.[29]

A second chemisorbed surface species corresponds to species with an intact carbon−carbon bond of length 1.46 ± 0.02 Å. To put this work into perspective with other findings for adsorbed species on metal surfaces, we surveyed published literature on surface species created by adsorbing ethylene and acetylene. Results are summarized in Table 2.

Common adsorbed species are π-bonded ethylene, σ-bonded ethylene, ethylidyne, ethylidene, vinylidene, and ethynyl. From the ^{13}C slow beat measurements as a function of chemical shift, we determined that species containing carbon−carbon bonds have ^{13}C chemical shifts ranging from −200 to 500 ppm. This suggests that at least one of the two carbons (but probably not both) is directly bonded to the metal surface, i.e., exhibits a Knight shift. Therefore, we eliminate the existence of π-bonded TCE. The SEDOR results suggest that at least one of carbon atoms is bonded to at least one hydrogen atom. Therefore, we can discount the possibility of this chemisorbed carbon species being a completely dehydrogenated C−C pair. The bond length of 1.46 Å measured via the ^{13}C slow beat is closer to 1.44 Å, the expected bond length for σ-bonded ethylene, vinylidene, ethylylidyne, and to 1.45 Å, the expected bond length for ethynyl than to 1.5 Å, the expected bond length for ethylidyne, or to 1.6 Å for ethylidene. Of these, ethynyl is the most likely species because it is the structure TCE would acquire after it has lost all its chlorine atoms upon adsorption. There are few extra hydrogen atoms available to react with the ethynyl to form the species with more hydrogen atoms such as σ-bonded ethylene, vinylidene, or ethylylidyne.

Table 2. Common Surface Species in Ethylene Hydrogenation Compared with Results from This Study

species	bond length (Å)	NMR δ shift (ppm)	PWHM[a] (ppm)
TCE	1.36	117, 124	8
ethylene	1.34	120	N/A
π-bonded ethylene	1.40[30]	60−90[31] 70−90[21,32]	30[31]
σ-bonded ethylene	1.44[30]	(110−220)[33]	N/A
σ-vinyl group		130−170[32]	
ethylidyne ($H_3C-C\equiv M$)	1.49[34] 1.51[30]	(110−220)[33]	N/A
ethylidyne ($H_3C-HC=M$)	1.6	90, 200[31]	20, 80[31]
vinylidene ($H_2C=C=M$) or ethylylidyne ($M\cdots H_2C-C\equiv M$)	1.44[16]	∼120[17]	400
ethynyl ($M-C\equiv M$)	1.45[35]	N/A	N/A
ethane	1.54	7	4
from this study	1.46	∼200−500	∼300

[a] PWHM = peak width at half maxima.

In summary, we believe that upon adsorption the TCE loses hydrogen to leave a dehydrogenated surface species: $C_2HCl_3(g) \rightarrow C_2H(ads) + 3Cl(ads)$. A significant fraction of the dechlorinated surface species further decompose to isolated carbon and hydrogen atoms: $C_2H(ads) \rightarrow 2C(ads) + H(ads)$. The dechlorinated surface species can also react with excess hydrogen to form products, which in this case was only ethane: $C_2H(ads) + 5H(ads) \rightarrow C_2H_6(g)$.

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Palladium-catalyzed Aqueous Hydrodehalogenation in Column Reactors: Modeling of Deactivation Kinetics with Sulfide and Comparison of Regenerants

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Abstract

Palladium (Pd) based catalysts are increasingly important in environmental applications; however, sulfide, a known poison, has been identified as a potential issue in laboratory and field studies. This paper develops a quantitative model for deactivation kinetics with aqueous sulfide; investigates the effects of pH on a catalyzed dehalogenation reaction and sulfide deactivation; and characterizes regeneration with acids, bases, and oxidizing agents. Results show no inherent catalyst deactivation in deionized water. Deactivation increased with sulfide concentration and exposure time. Results also suggest that sulfide diffuses into the Pd bulk during deactivation. This accumulated sulfide then serves as a reservoir and continues to poison the Pd surface after sulfide exposure has ended; as a result, the time required for regeneration increased with increasing sulfide concentrations and exposure times. Deactivation was slowly reversible by

flushing the catalyst with deionized water at pH 10.4. Treatment with 20 mM sodium hypochlorite quickly and completely regenerated the catalyst, and was significantly more effective than hydroxide, hydrochloric acid, hydrogen peroxide, and air-saturated water. These results have important implications for maintaining catalyst activity with Pd or bimetallic catalyst systems.

Keywords

Palladium (Pd), sulfide deactivation kinetics, sulfur diffusion, regeneration, groundwater remediation, trichloroethene (TCE), zero valent iron, bimetallic catalysts.

1. Introduction

Palladium catalysis and bimetallic catalysis are promising technologies for reductive treatment of waters contaminated with halogenated hydrocarbons and oxidized species such as nitrite. It offers several potential advantages: the ability to treat a wide range of pollutants; rapid reaction rates, often on the order of minutes; transformation of contaminants to relatively benign compounds, with little or no formation of hazardous partially halogenated by-products such as vinyl chloride; and applicability in deep aquifers, at high contaminant concentrations, and in the presence of oxygen, where other treatment technologies might be impractical or infeasible [*1*]. Field implementations of this technology have confirmed the ability of Pd to successfully treat halogenated hydrocarbons in groundwater for periods of at least two to three years [*2, 3*]. However, all previous field and laboratory studies using groundwaters have indicated that sulfide and/or sulfur compounds (known catalyst poisons) can deactivate Pd, and that this may be an issue in waters where sulfide is present or can be formed by sulfate-reducing bacteria growing in the hydrogen-rich environment of the Pd process [*2-6*]. Research also implies that oxidizing

agents such as air, hypochlorite, and hydrogen peroxide may make effective regenerants or biocides [*2-5*]. However, reversibility of the deactivation reaction has not been tested, sulfide deactivation rates have not yet been quantified, the factors affecting deactivation and subsequent regeneration requirements have not been characterized, and regeneration options have not been compared. This paper addresses these issues and provides a chemical basis for employing Pd and bimetallic catalysts for the reductive remediation of contaminated waters.

Based on published literature, the following conceptual model is proposed for catalyst activity, deactivation, and regeneration. In the absence of sulfide, the catalyst is expected to deactivate slowly; pH should not affect activity [*4*]. In the presence of sulfide, literature reports that gas phase hydrogen sulfide [7, *8*] and aqueous bisulfide [*9*] dissociatively sorb to Pd, thereby blocking reaction sites and poisoning the catalyst. The structure and concentration of sorbed sulfur atoms on Pd can vary, with poorly ordered adatom structures at low sulfur coverage, growing to ordered structures such as p(2x2) with a S:Pd ratio of 1:4, and increasingly complex structures at higher sulfur coverage, with S:Pd ratios as high as 2:3 [*7-11*]. Increased surface sulfur concentrations are expected to inhibit surface-catalyzed reactions, i.e. reduce catalyst activity. Raising aqueous sulfide concentrations should increase the thermodynamic and kinetic driving forces toward the metal surface, thereby increasing both surface concentrations of sulfur on the Pd and deactivation rates.

Sulfur removal from the catalyst surface is proposed via several mechanisms. Previous literature demonstrated that adsorbed sulfur can be electrochemically removed from a Pd electrode, when hydrogen-producing voltages were applied [*9*]:

$$S_{(ads)} + H_{2(g)} + OH^-_{(aq)} \longrightarrow H_2O + HS^-_{(aq)}$$

Based on this work, surface sorption of sulfur is hypothesized to be reversible at high pH under catalytic conditions as well. Under this hypothesis, the catalyst activity will reach a steady-state level when the rate of sulfur removal by hydroxide equals the rate of sulfide sorption onto the Pd. This level depends on the aqueous sulfide concentration, which determines the rate of sulfur sorption, and the pH, which determines the rate of sulfur removal. If this hypothesis is false, i.e. sulfur sorption is irreversible, the catalyst activity will drop to zero over time.

Electrochemical experiments also showed that adsorbed sulfur was oxidized to sulfate and removed from a Pd electrode surface [*9*]. In the work presented here, oxidation of adsorbed sulfur was tested under catalytic conditions, and regeneration efficiencies were compared using air-saturated water, hypochlorite and hydrogen peroxide. Hypochlorite, with a redox potential of 1.5 eV [*14*], is known to regenerate sulfide-deactivated catalysts [*4*]. The regenerant in the air-saturated water is presumed to be dissolved oxygen (DO), at a theoretical concentration of approximately 0.5 mM [*15*]. Oxygen is the weakest of the three reagents, with a redox potential of 1.2 eV [*14*]; however, DO has been reported to oxidize sulfide to sulfate for both aqueous sodium sulfide and solid pyrite (iron sulfide) [*16*]. Hydrogen peroxide is the strongest oxidant with a redox potential of 1.8 eV [*14*], and is expected to be the best regenerant.

One additional complication is the possibility of sulfur diffusion from the Pd surface into the bulk metal; however, literature states that surface penetration of sulfur into Pd is unknown [*17*]. High-temperature gas-phase experiments indicate that diffusion occurs very slowly or not at all, below approximately 800ºC [*10, 13*]. However, limited ambient-temperature aqueous-phase diffusion of sulfide into Pd was observed in one experiment, although the authors “note that the barriers to interdiffusion appear to be reasonably large” [*12*]. Based on these results, sulfur

diffusion is hypothesized to have an insignificant impact on deactivation and regeneration requirements. If this hypothesis is false, diffusion will create a reservoir of sulfur that can re-diffuse back to the surface and poison the catalyst after regeneration. In this case, regeneration requirements would increase as the amount of sulfur stored in the Pd bulk increased, due to either higher sulfide concentrations (higher diffusive driving force into the Pd) or increased sulfide exposure time (increased time for diffusion).

This work provides the chemical basis for practical use of reductive catalysis for water treatment, by demonstrating constant catalyst activity in the absence of sulfide, the reversibility of sulfide poisoning, the presence of sulfur diffusion and its impacts on increasing regeneration requirements, and the efficacy of hypochlorite as a regenerant. These findings will benefit the growing number of Pd-based catalysts, such as supported Pd [*1-5*], Pd/Fe [*6, 18-20*] and other bimetallic catalysts [*21-24*], as they are applied to the treatment of drinking water, wastewater and groundwater.

2. Experimental Section

2.1 Materials and Analytical Methods

All chemicals were reagent grade and at least 99+% purity, except sodium hypochlorite (6.3% by weight), hydrogen peroxide (31.1% by weight), hydrochloric acid (37.8%), and the catalyst. The catalyst was 1% by weight Pd on γ-alumina and was manufactured by Precious Metals Corporation (now part of Johnson Matthey Catalysts, West Deptford, New Jersey). Specific catalyst characteristics are given elsewhere [*4*].

Catalyst activity was monitored via the removal of trichloroethene (TCE). A 1.0 mL gas-tight syringe with a luer-lok fitting was used to take 0.5 mL aqueous TCE samples, which were extracted in 1.0 mL of hexane containing 2.0 mg/kg PCE as a standard. As described elsewhere [*4*], samples were then analyzed with a gas chromatograph equipped with an electron capture detector, and TCE removals were calculated. Sulfide and regenerant concentrations were quantified using an Orbeco-Hellige spectrophotometer (Orbeco-Hellige, Farmingdale, New York). A sulfur balance was not evaluated due to losses extraneous to the Pd catalyst.

2.2 Reactor Characterization and Calculations

Each column reactor consisted of a 10.5 mL stainless steel tube (1.2 cm in diameter, 9.8 cm long), capped with 3/8" to 1/16" Swagelok reducing unions to prevent catalyst loss. The reactors were packed with 8.0 g of 2.0 mm diameter borosilicate glass beads at the bottom (to disperse flow evenly), 1.0 g of catalyst, and topped with a plug of glass wool. The same catalyst was used for the duration of all of the experiments, i.e. the catalyst was not replaced.

In order to quantitatively model the deactivation kinetics, several catalyst/reactor parameters were determined gravimetrically. Using the following equations, the catalyst bulk density (ρ) was calculated to be 0.80 g/mL, the reactor porosity (η) was 0.70, and the total surface Pd concentration (Pd_T) was calculated to be 5.1 g of surface Pd per liter of reactor water:

$$\rho = \frac{m_{cat} - m_r}{(m_w - m_r)/\rho_w} \tag{1}$$

$$\eta = \frac{m_{packed} - m_{cat}}{m_w - m_r} \tag{2}$$

$$Pd_T = \frac{(W_{Pd})(D_{Pd})(\rho)}{\eta} \tag{3}$$

In these equations, D_{Pd} is the metal dispersion of Pd on the catalyst (previously measured to be 45%), m_{cat} is the mass of a reactor filled with dry catalyst (g), m_{packed} is the mass of a reactor filled with catalyst and water (g), m_r is the mass of an empty reactor (g), m_w is the mass of a reactor filled with water (g), W_{Pd} is the weight percent of Pd (nominally 1% by weight), and ρ_w is the density of water (g/mL). To measure m_{packed}, the catalyst was degassed under vacuum in water (to eliminate gas in water-accessible pores), and the reactor was filled with water before being packed with the catalyst (again, to eliminate possible gas pockets). The flow rate through the column was 0.5 mL/min, which yields a calculated hydraulic residence time of 1.75 minutes.

2.3 Reactor System Configuration and Operating Conditions

The reactor configuration (Fig. 1) consisted of three catalyst columns in parallel, with the associated apparatus for storing and/or preparing the influent feed streams for the columns. All experiments used deionized (DI) water that had been degassed for at least two hours under an aspirator vacuum and amended with TCE, acid, base, and/or sulfide as necessary. Two different reservoir configurations were used for the experiments, which are summarized in Table 1.

The first configuration used a single 19L pressurizable stainless steel tank obtained from Alloy Products (Waukesha, Wisconsin). Water was removed from the reservoir via Pump 1, a Rainin Rabbit 25sc high pressure pump from Varian, Inc. (Palo Alto, CA), and flowed through the hydrogen contactor, a Liqui-Cel 0.75x5 MiniModule Contactor from Celgard, Inc. (Charlotte, North Carolina). The contactor consisted of a bundle of parallel membrane fibers through which the water flowed, surrounded by 160 kPa of hydrogen gas. As the water flowed through the contactor, hydrogen diffused in and saturated it. After the contactor, the flow split into three parallel lines, which were pumped to the reactors at 0.5 mL/min; a fourth line served

as a bleed to relieve excess flow from Pump 1(set to 1.6 mL/min to ensure sufficient flow to the three reactors). Pumps 2-4 were Eldex Duros CC-30-S high pressure pumps from Eldex Laboratories, Inc. (Napa, California).

The second configuration used the "Alternate Feed" system shown in Fig. 1: the feed stream to Pumps 2 to 4 was switched (from the 19L reservoir used in the first configuration) to a series of two 2L borosilicate glass bottles. The primary bottle was kept full by pumping water from the secondary bottle, which was then refilled as necessary. This two-bottle system allowed continuous flow without interruptions to refill the water source, and also maintained sulfide concentrations at relatively constant levels during deactivation experiments.

3. Results and Discussion

3.1 Baseline Activity in Water and Sulfide Deactivation Experiments.

Baseline activity experiments were conducted at pH values comparable to those in the sulfide deactivation experiments: 5.0 ± 0.2 in DI water amended with hydrochloric acid (HCl), 5.3 ± 0.05 in unbuffered DI water, 8.8 ± 0.3 in DI water buffered with 80 mg/L pyrophosphate, and 10.4 ± 0.1 in DI water buffered with 150 mg/L carbonate. The pH in the amended DI waters did not change significantly between the influent and effluent; however, the effluent pH in the unbuffered water dropped to 4.2 ± 0.1, because the TCE dehalogenation reaction releases hydronium ions.

The average TCE removal was 59 ± 3% across all of the baseline experiments (Fig. 2). For clarity, all catalyst activities in this paper are normalized to the level of the fully active catalyst by dividing the measured TCE removal by the maximum removal of 59%, e.g. a fully active

catalyst with 59% removal has 100% relative activity and a fully deactivated catalyst with no removal has 0% relative activity. As can be seen in Fig. 2, pH has essentially no effect on the dehalogenation reaction in DI or amended DI water, as expected. In addition, the activity was constant across the duration of the experiments, i.e. there was no catalyst deactivation. This lack of deactivation contrasts with the previously published results [*4*], which showed deactivation even in DI water. The same batch of catalyst was used for both sets of experiments, but the DI water systems were different; subsequent analyses with x-ray photoelectron spectroscopy indicated that sulfide was the likely cause of the earlier deactivation [*25*]. It can be concluded that there is no inherent deactivation of Pd in clean water and that neither hydroxide nor hydronium ions compete with TCE for reaction sites on the Pd.

3.2 Sulfide Deactivation Experiments.

Twelve deactivation experiments were conducted to determine the effects of sulfide concentration and pH on deactivation; operating conditions are in Table 2, along with data and model fits. Before each deactivation experiment, the catalyst was regenerated with 20 mM sodium hypochlorite (NaOCl) until activity was stable. Hydrogen-saturated sulfide-free DI water (amended with HCl or 150 mg/L carbonate before acidic or alkaline deactivation experiments, respectively) was then run for several days through the column reactors. Experiments were started by amending the water source with sulfide, added as sodium sulfide nonahydrate. Note that the three experiments at 0.03 mg/L sulfide were conducted before protocols for sample analysis were finalized; as a result, these data have a higher degree of variability than the other data sets.

Fig. 3a shows that sulfide concentrations strongly affect the deactivation kinetics: as total sulfide concentrations increase, the catalyst deactivates faster. Fig. 3b shows several effects of pH. The deactivation rate is noticeably slower at the highest pH of 10.4. Fig. 3b and Table 2 also indicate that the catalyst maintains a non-zero level of activity at steady-state at both pH 9.6 and 10.4, and that this steady-state activity increases with increasing pH. Both results (that the steady-state activity is non-zero and increases with increasing pH) support the hypothesis that sulfide sorption is reversible in a pH-dependent reaction; this is explored further in the next section.

3.3 Removal of Surface Sulfur by Hydroxide.

Regeneration by acids and bases was tested after the acidified deactivation experiments at 0.3, 1 and 2 mg/L sulfide. At the start of the regeneration experiment, the sulfide solution flow was stopped; for the remainder of the experiment, only pH-adjusted DI water was pumped through the columns. Sulfide-free DI water was first acidified to pH 5.3 with hydrochloric acid (HCl) and pumped through the column. This was followed by DI water buffered with 150 mg/L carbonate at pH 8.7, and then DI water buffered with 150 mg/L carbonate at pH 10.4.

Table 3 shows an increase in catalyst activity after exposure to DI water at pH 10.4, with no significant activity gained in the pH 5.3 and 8.7 waters. This confirms that sulfur can be removed from the catalyst surface, and that removal increases at high pH levels. Within the catalysts treated at pH 10.4, activity increased most for the catalyst exposed to 0.3 mg/L sulfide and least for the catalyst exposed to 2 mg/L sulfide. This result implies that higher sulfide concentrations result in higher levels of sulfide associated with the catalyst, a concept that is explored further in Section 3.6.

3.4 Modeling Kinetics of TCE Reaction and Sulfide Deactivation.

3.4.1 Conceptual Model.

Based on published literature and the results shown in this paper, the following reactions were proposed as a conceptual model of the chemical reactions:

$$\mathrm{Pd} + a\mathrm{H_2S_{(aq)}} \xrightarrow{k_{2a}} \mathrm{Pd*S_a} + a\mathrm{H_{2(aq)}}$$

$$\mathrm{Pd} + b\mathrm{HS^-_{(aq)}} + b\mathrm{H_2O} \xleftrightarrow[k_3 \;/\; k_{2b}]{} \mathrm{Pd*S_b} + b\mathrm{H_{2(aq)}} + b\mathrm{OH^-_{(aq)}}$$

Both H_2S and bisulfide sorb dissociatively [7-9] to form a surface species, Pd*S. The first reaction is irreversible, based on the complete deactivation shown in Fig. 3a at pH 4.8 (i.e. no detectable reverse reaction with 99% H_2S) and the lack of catalyst recovery in acidic and neutral DI water. As indicated by Fig. 3b and Table 3, the second reaction is reversible and pH dependent, with higher pH levels promoting the reverse reaction. Because hydrogen levels were constant and maintained at full saturation throughout all of the experiments, they were not included as a variable in the mathematical model.

3.4.2 Quantitative Model.

Reaction kinetics for TCE used a previously published first-order plug-flow model [*4*], with the additional assumption of first order dependence with respect to the active Pd concentration. This yields Eq. (4), where k_1 is the first order rate constant in (L water)(g surface Pd)$^{-1}$(min)$^{-1}$, [Pd] is the concentration of active Pd (in g of active surface Pd/L of reactor water), [TCE] is the TCE concentration at the reactor effluent, $[TCE]_0$ is the TCE concentration at the reactor effluent, and τ is the residence time in the reactor in minutes. With the data presented here, k_1.was calculated to be 0.10 ± 0.01 (L water)(g surface Pd)$^{-1}$(min)$^{-1}$, a value consistent with

previous work [*4*] using the same catalyst, which had an equivalent k_1. of 0.12 to 0.17 (L water)(g surface Pd)$^{-1}$(min)$^{-1}$.

$$\ln \frac{TCE}{TCE_0} = -k_1[Pd]\tau \tag{4}$$

The deactivation model was developed by deriving and solving the differential equations for the reactions in the conceptual model, with empirical reaction rate coefficients (with forward rate coefficients $k_{2}a$ and $k_{2}b$, and reverse rate coefficient k_3) and exponents (*m* for H_2S, *n* for HS^-, and *p* for OH^-). The resulting equation (Eq. (5)) was solved for [Pd] as a function of run time (Eq. (6)), with the following conditions: 1) the total amount of surface Pd in the system, Pd_T, is constant and equal to the sum of the active ([Pd]) and inactive ([Pd*S]) Pd species; 2) sulfide and hydroxide concentrations are constant over time; and 3) the initial amount of active Pd at time 0 is Pd_0. This solution for [Pd] was then substituted into Eq. (4), rearranged to solve for the theoretical TCE Removal, and normalized as the relative activity.

$$\frac{d[Pd]}{dt} = -k_{2a}[H_2S]^m[Pd] - k_{2b}[HS^-]^n[Pd] + k_3[Pd*S][OH^-]^p \tag{5}$$

$$[Pd] = \frac{k_3[OH^-]^p}{k_{2a}[H_2S]^m - k_{2b}[HS^-]^n + k_3[OH^-]^p} Pd_T + \left(Pd_0 - \frac{k_3[OH^-]^p}{k_{2a}[H_2S]^m - k_{2b}[HS^-]^n + k_3[OH^-]^p} Pd_T \right) \exp\left[-(k_{2a}[H_2S]^m - k_{2b}[HS^-]^n + k_3[OH^-]^p)t\right] \tag{6}$$

3.4.3 Determining the fitting parameters

The goals in determining the fitting parameters were to find the optimal values for k_{2a}, k_{2b}, k_3, *m*, *n*,and *p*; estimate a confidence interval for those values; and test the values against "new" data that were not used in determining the fitting parameters. The large number of fitting parameters required a correspondingly large number of data points to sufficiently constrain the model to a single set of values; as a result, the model fit used all but the 0.03 mg/L sulfide experiments, which were reserved as test data. Optimal fitting parameters were determined with a least

squares regression, using a Nelder-Mead simplex (direct) method in the program Matlab. Parameter ranges were estimated via a bootstrap simulation with 10000 replications, performed on the residuals of the data, relative to the optimized model. The given ranges are standard deviations of the parameter values obtained from the bootstrap simulations.

The optimized values and ranges are shown in Table 4, while fits to the data are given in Fig. 4 and Table 2. Fig. 4b indicates that the model fits the test data well; the lower R^2 values in Table 2 may be attributable to the high variability caused by the older protocols for sample analysis, as well as the relatively long level tail on the data. The other experiments have fairly high R^2 values, and the predicted steady-state activities are generally well within the standard deviation of the measured activities for all experiments.

3.5 Comparison of Oxidizing Agents as Regenerants.

The experiments comparing oxidizing agents was run after deactivation with 0.03 mg/L sulfide in unbuffered DI water. At the start of the regeneration experiment, the sulfide solution flow was stopped; for the remainder of the experiment, only unbuffered DI water or regenerants were pumped through the columns. On Day 0, the three columns were regenerated for 30 minutes: the first column was exposed to 20 mM hypochlorite, the second to 20 mM H_2O_2, and the third to air-saturated water (0.5 mM DO). Pump problems that were encountered on the second and third columns necessitated a second regeneration on Day 4 for 30 min with 20 mM H_2O_2 and air-saturated water, respectively. On Day 14, the second and third columns were regenerated a final time for 30 minutes with 200 mM H_2O_2 and air-saturated water, respectively.

Hypochlorite is the most effective of the three oxidants, recovering and maintaining catalyst activity for over four months (Fig. 5). The regenerative effects of H_2O_2 and DO are difficult to

evaluate, because the improved catalyst performance after regeneration could be caused by the change to a sulfide-free influent stream and the subsequent slow reverse reaction. At best, these two regenerants recovered approximately 35% of the original catalyst activity; at worst, they had no regenerative power. This poorer performance may be due to slower reaction kinetics, weaker oxygen redox potentials, lower oxidant concentrations for DO, side reactions of the highly reactive H_2O_2 with organic matter [*26*], or H_2O_2 decomposition to oxygen [*27*]. Based on the data in Fig. 5, neither DO nor H_2O_2 is an appropriate regenerant for sulfide-deactivated catalysts; however, H_2O_2 can be useful as a biocide to prevent the growth of sulfate-reducing bacteria, as demonstrated by Schüth, et al. [*3*].

3.6 Regeneration Requirements

The experiments that investigated regeneration requirements were run after deactivation with 2 mg/L sulfide at pH 10.4 and after the five unbuffered deactivation experiments at 0.09, 0.2, 0.5, 1 and 2 mg/L sulfide. Each regeneration used 20 mM NaOCl for 30 minutes, followed by a 0.50 mL/min flow of TCE-amended unbuffered DI water. This cycle of regeneration and DI water was repeated until complete and stable activity was obtained.

Regeneration successfully recovered full catalyst activity after deactivation experiments at all sulfide concentrations; however, the deactivation conditions clearly affected the regeneration requirements (Fig. 6). The catalyst required more regeneration cycles and recovered less activity per cycle after deactivation at higher sulfide concentrations and/or lower pH levels. These results are consistent with the conceptual model: as aqueous sulfide concentrations increase or pH decreases, sulfur concentrations on the Pd surface increase and regeneration is more difficult.

3.7 Sulfur Diffusion.

Fig. 6 also shows continued deactivation of the catalyst after regeneration, despite the lack of sulfide in the influent stream. This suggests a sulfur reservoir in the catalyst. Several sources were considered: the alumina surface, a sulfur multilayer on the Pd surface, and diffusion into the Pd. A set of experiments was conducted to further investigate these possibilities. Prior to the start of these experiments, two columns were run with sulfide-free DI water buffered with 150 mg/L carbonate at pH 10.4. Sulfide at 2 mg/L was then added to the influent of the columns for three and 45 days, respectively. The columns were regenerated with 20 mM hypochlorite on Day 0 for 30 minutes and on Day 4 for 24 hours; at all other times, the columns were run with sulfide-free unbuffered DI water containing approximately 3 mg/L TCE.

Fig. 7 supports the hypothesis of sulfur diffusion into the Pd. With a point-of-zero-charge of 9, the alumina surface was negatively charged and eliminated as a potential sulfide source; however, the deactivation after regeneration remained. After the 24-hour regeneration on Day 4, both catalysts recovered full activity, indicating that all of the sulfur (including any possible multi-layer) was removed from the Pd surface. However, both catalysts continued to deactivate, with faster and more severe deactivation with the longer sulfide exposure. This can be explained by a longer diffusion time, which resulted in a larger sulfur reservoir and faster re-poisoning of the surface after regeneration.

These results are also quantitatively consistent with the single literature observation of sulfur diffusion, which can be used to estimate the amount of sulfur in the Pd. Literature reports sulfide penetration one to two nm into Pd after one day of exposure to a 10 mM aqueous sulfide solution at 25ºC (*12*), which corresponds to an approximate diffusivity of 1 to 4 E-18 m^2/day (Eq. (7)).

This diffusivity can then be used to calculate concentration profiles of sulfide in the bulk Pd, using the analytical solution for diffusion into a semi-infinite solid (Eq. (8)), where D_s is the diffusivity of sulfide through Pd in m^2/day, r = the sulfide diffusion distance in m, $S(r,t)$ = sulfide concentration at time t and distance r into the Pd in mg/L, S_0 = bulk aqueous sulfide concentration in mg/L, and t_d = time of sulfide diffusion in days. Integrating the concentration over depth and taking the ratio between the data at three and 45 days indicates that the catalyst exposed for 45 days contains up to four times the sulfur of the catalyst exposed for three days.

$$D_s = \frac{r^2}{t_D} = \frac{(1 \text{ to } 2 \text{ x } 10^{-9} \text{ m})^2}{(1.0 \text{ day})} = 1 \text{ to } 4 \text{ x } 10^{-18} \text{ m}^2/\text{day} \tag{7}$$

$$\frac{S(r,t)}{S_0} = erfc\left(\frac{r}{\sqrt{4D_S t}}\right) \tag{8}$$

The occurrence of sulfur diffusion into Pd has important ramifications for practical applications. Catalysts that are exposed to higher concentrations of sulfide or are exposed for longer periods of time will require more regeneration, both in terms of the length of a single regeneration cycle to remove sulfur from the surface and also in terms of the total number of cycles (regeneration time) for the catalyst to fully recover from deactivation.

4. Conclusions

Most importantly, hypochlorite was found to be capable of completely regenerating even fully deactivated catalysts and sustaining activity for years; the catalyst used in these experiments successfully provided 100% relative activity over the course of more than two years, despite repeated severe deactivations with sulfide. Contrary to previous results, the data

shown in this paper also indicate that Pd catalysts do not inherently deactivate in deionized water. Deactivation rates increased with sulfide concentration and exposure time, and decreased at high pH (10.4); high pH water was also capable of reversing the deactivation reaction. The kinetic model developed in this paper allows for improved prediction of the deactivation kinetics, which will aid in the evaluation of appropriateness of this technology for a given water quality. The results also indicate that sulfur diffuses into the Pd, and that frequent regeneration will improve operational performance by limiting this diffusion; highly deactivated catalysts will require longer regeneration times. The comparison of regenerants suggests the use of hypochlorite to maintain catalyst activity, as it is a significantly more effective regenerant than HCl, hydroxide, hydrogen peroxide, and air-saturated water.

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Figure Captions

Fig. 1. Column Reactor System. Catalyst columns were fed either from a single source, the 19-L reservoir, or individually via alternate feed bottles. Pumps #2, 3, and 4 each had a set of alternate feed bottles, but for simplicity, only one set is shown in Fig. 1.

Fig. 2. Catalyst does not deactivate in DI water, and activity is not affected by pH. Average relative activities were 100 ± 5% at influent pH 5.0, 100 ± 7% at pH 5.3, 98 ± 6% at pH 8.8, and 101 ± 2% at pH 10.4.

Fig. 3. Deactivation of Pd catalysts as a function of (a) sulfide concentration at constant pH (4.8) and (b) pH at constant sulfide concentration (2 mg/L). In both figures, points represent experimental data, lines represent best fits to the model.

Fig. 4. Model fits to sulfide deactivation of Pd catalysts in unbuffered DI water. (a) Data used for parameter fitting (0.5 mg/L data omitted for clarity) and (b) test data at 0.03 mg/L sulfide. Points represent experimental data; lines represent best fits to the model.

Fig. 5. Comparison of oxidizing agents as regenerants. The catalyst was regenerated at Days 0, 4, and 14 (indicated by the large black circles on the graph).

Fig. 6. Recovery of catalyst activity with successive 20 mM hypochlorite regenerations. The catalyst was regenerated for 30 minutes after each large black circle (e.g. at Days 0, 4, 7, etc.).

Fig. 7. Hypochlorite regeneration following deactivation at pH 10.4. The catalyst was regenerated at Day 0 for 30 min and Day 4 for 24 hours (indicated by black circles on the graph).

Table 1. Reservoir configurations for experiments.

Experiment (# experiments)	Water reservoir	Reservoir pressure
Baseline, unbuffered (1)	19L tank	110 kPa helium
Baseline, buffered (3)	Alternate feed bottles	130 kPa hydrogen
Sulfide deactivation (12)	Alternate feed bottles	130 kPa hydrogen
Sulfide diffusion (2)	Alternate feed bottles	130 kPa hydrogen
Regeneration with acids/bases (3)	19L tank	110 kPa helium
Regeneration with oxidants (3)	Alternate feed bottles	110 kPa helium
After oxidative regeneration	19L tank	110 kPa helium

Table 2. Conditions, data, and model fits for the sulfide deactivation experiments.

Sulfide Conc. (mg/L)	Additive	Influent pH	Influent Sulfide Species (%H_2S, %HS^-, %$S^=$)	Effluent pH	Initial Effluent Sulfide Species (%H_2S, %HS^-, %$S^=$)	Steady-State Relative Activity, After Day 11	Predicted Final Relative Activity	Model Fit (R^2)
0	Various	5.0-10.4	-	4.2-10.5	-	100%± 6%	100%	NM[a]
0.03	None	5.9[b]	93, 7, 0	4.4	100, 0, 0	21 ± 15%	18%	0.35
0.03	None	5.9[b]	93, 7, 0	4.4	100, 0, 0	18 ± 11%	18%	0.62
0.03	None	5.9[b]	93, 7, 0	4.4	100, 0, 0	18 ± 11%	18%	0.59
0.09	None	6.3[b]	83, 17, 0	4.4[a]	100, 0, 0	11 ± 5%	10%	0.96
0.2	None	6.9[b]	58, 42, 0	4.5[a]	100, 0, 0	12%[c]	8%	0.95
0.3	HCl	4.8 ± 0.3	99, 1, 0	4.9 ± 0.3	99, 1, 0	2 ± 5%	3%	0.97
0.5	None	8.5[b]	3, 97, 0	4.8[a]	99, 1, 0	11%[c]	12%	0.93
1	HCl	4.8 ± 0.2	99, 1, 0	4.9 ± 0.2	99, 1, 0	2 ± 3%	1%	0.96
1	None	9.3[b]	1, 99, 0	6.6[a]	72, 28, 0	6 ± 6%	11%	0.91
2	HCl	4.8 ± 0.2	99, 1, 0	4.8 ± 0.2	99, 1, 0	0.5 ± 5%	1%	0.94
2	None	9.6[b]	0, 99, 0	8.8	2, 98, 0	9 ± 4%	8%	0.93
2	150 mg/L Carbonate	10.4 ± 0.1	0, 97, 3	10.4 ± 0.1	0, 97, 3	10 ± 6%	12%	0.81

[a]Not meaningful. R^2 inherently equals zero in this case, where the model is simply the mean of the data.

[b]pH values were not monitored during unbuffered experiments and are estimated assuming complete dehalogenation of 2 mg/L TCE. Catalyst deactivation results in less TCE reacting and higher effluent pH; for a fully deactivated catalyst, influent and effluent pH values and speciation distributions should be the same.

[c]Final activity on Day 9, when the experiment was stopped.

Table 3. Average relative catalyst activities before hydroxide treatment, and after exposure to water at pH 5.3, 8.7 and 10.4.

Sulfide conc during deactivation (mg/L)	Final relative activity during deactivation	Relative activity, pH 5.3 DI water	Relative activity, pH 8.7 DI water	Relative activity, pH 10.4 DI water[a]
0.3	2 ± 5%	0.6 ± 5%	4 ± 7%	20 ± 3%
1	2 ± 3%	1 ± 5%	2 ± 4%	10 ± 3%
2	0.3 ± 5%	0.6 ± 4%	0.2 ± 4%	3 ± 5%

[a]Because the activity changed over time, the average of the last five data points (Day 20-25) is provided.

Table 4. Parameter values and ranges for the mathematical model of sulfide deactivation.

Parameter	Optimal value	Parameter range
k_{2a}	12.4	10.2-14.7
k_{2b}	7.5	5.5-9.1
k_3	0.13	0.11-0.14
m	0.69	0.64-0.73
n	0.68	0.59-0.74
p	0.19	0.16-0.21

Fig. 1

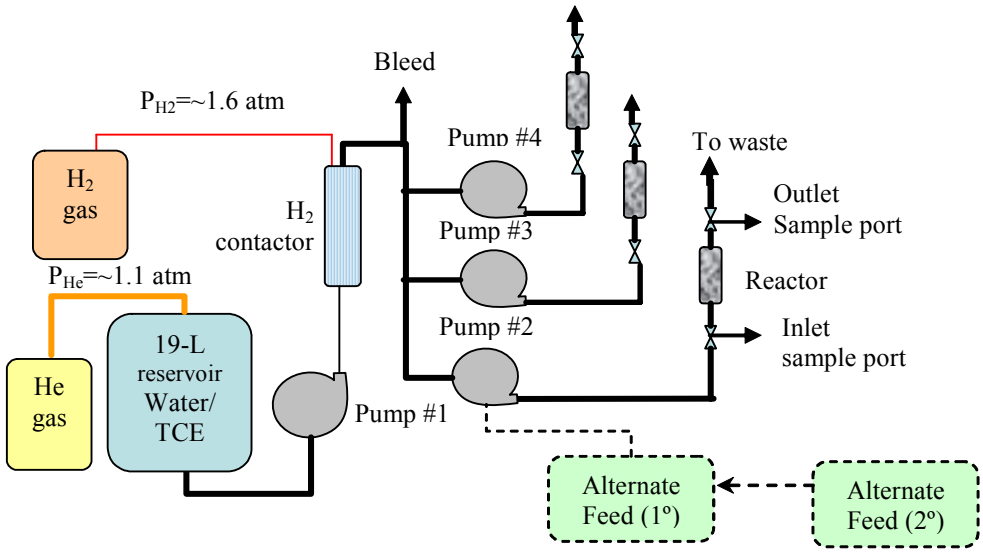

Bleed
P_{H2}=~1.6 atm
Pump #4
To waste
H_2 gas
H_2 contactor
Outlet Sample port
Pump #3
P_{He}=~1.1 atm
Reactor
Pump #2
Inlet sample port
He gas
19-L reservoir Water/ TCE
Pump #1
Alternate Feed (1º)
Alternate Feed (2º)

Fig. 2

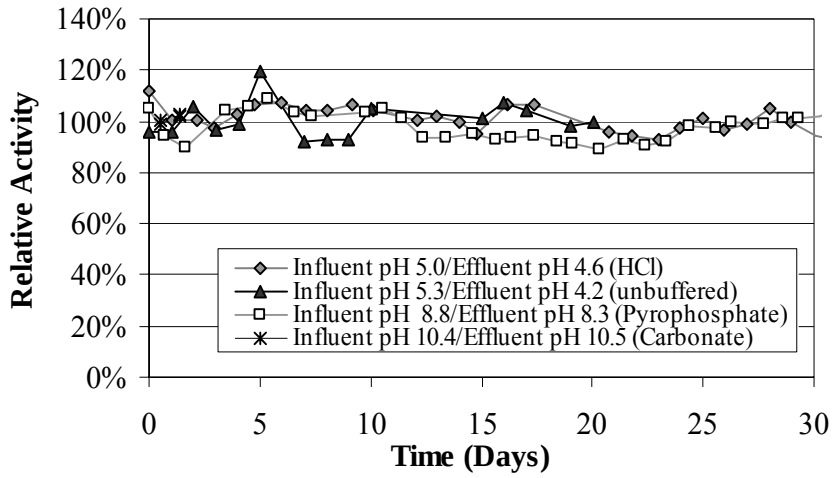

140%
120%
100%
80%
60%
40%
20%
0%
Relative Activity
0
5
10
15
20
25
30
Time (Days)
Influent pH 5.0/Effluent pH 4.6 (HCl)
Influent pH 5.3/Effluent pH 4.2 (unbuffered)
Influent pH 8.8/Effluent pH 8.3 (Pyrophosphate)
Influent pH 10.4/Effluent pH 10.5 (Carbonate)

Fig. 3

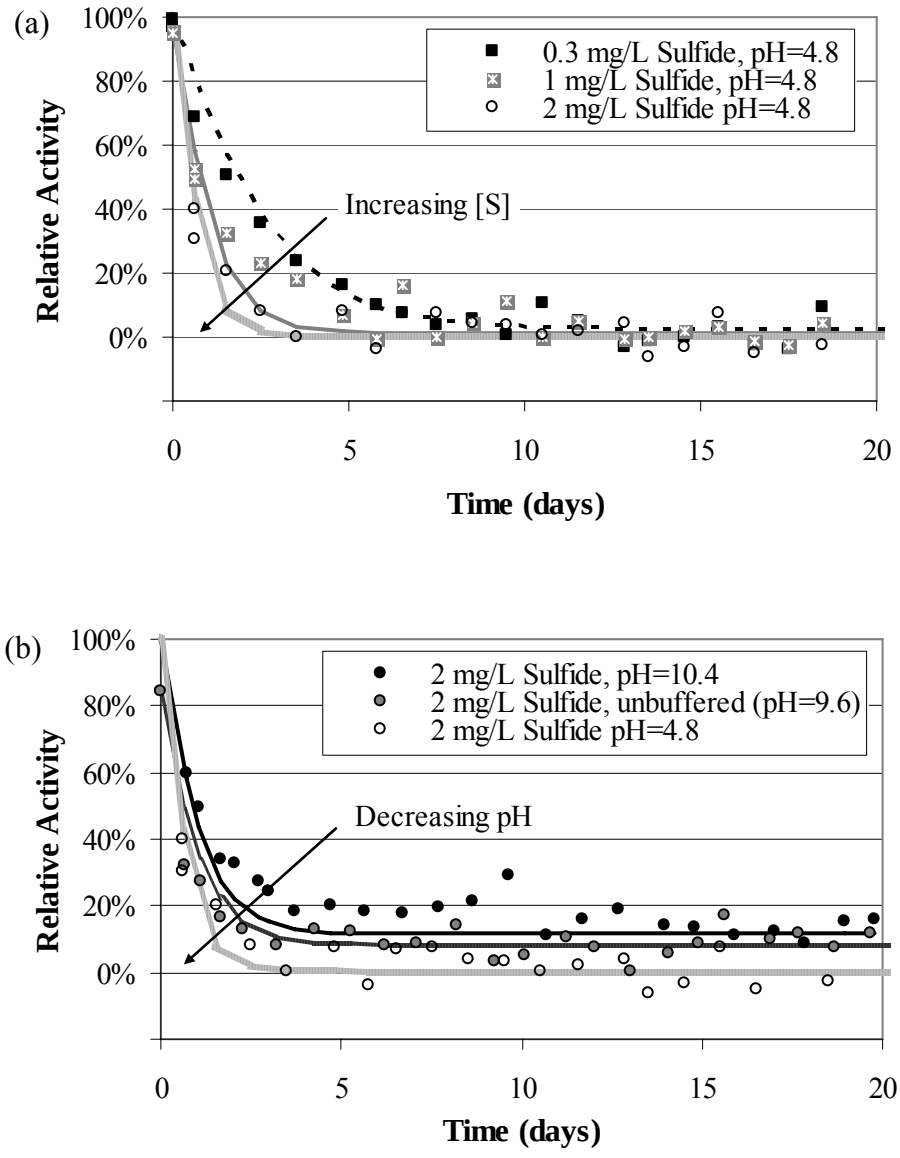

(a)
100%
80%
60%
40%
20%
0%
Relative Activity
0.3 mg/L Sulfide, pH=4.8
1 mg/L Sulfide, pH=4.8
2 mg/L Sulfide pH=4.8
Increasing [S]
0
5
10
15
20
Time (days)
(b)
100%
80%
60%
40%
20%
0%
Relative Activity
2 mg/L Sulfide, pH=10.4
2 mg/L Sulfide, unbuffered (pH=9.6)
2 mg/L Sulfide pH=4.8
Decreasing pH
0
5
10
15
20
Time (days)

Fig. 4

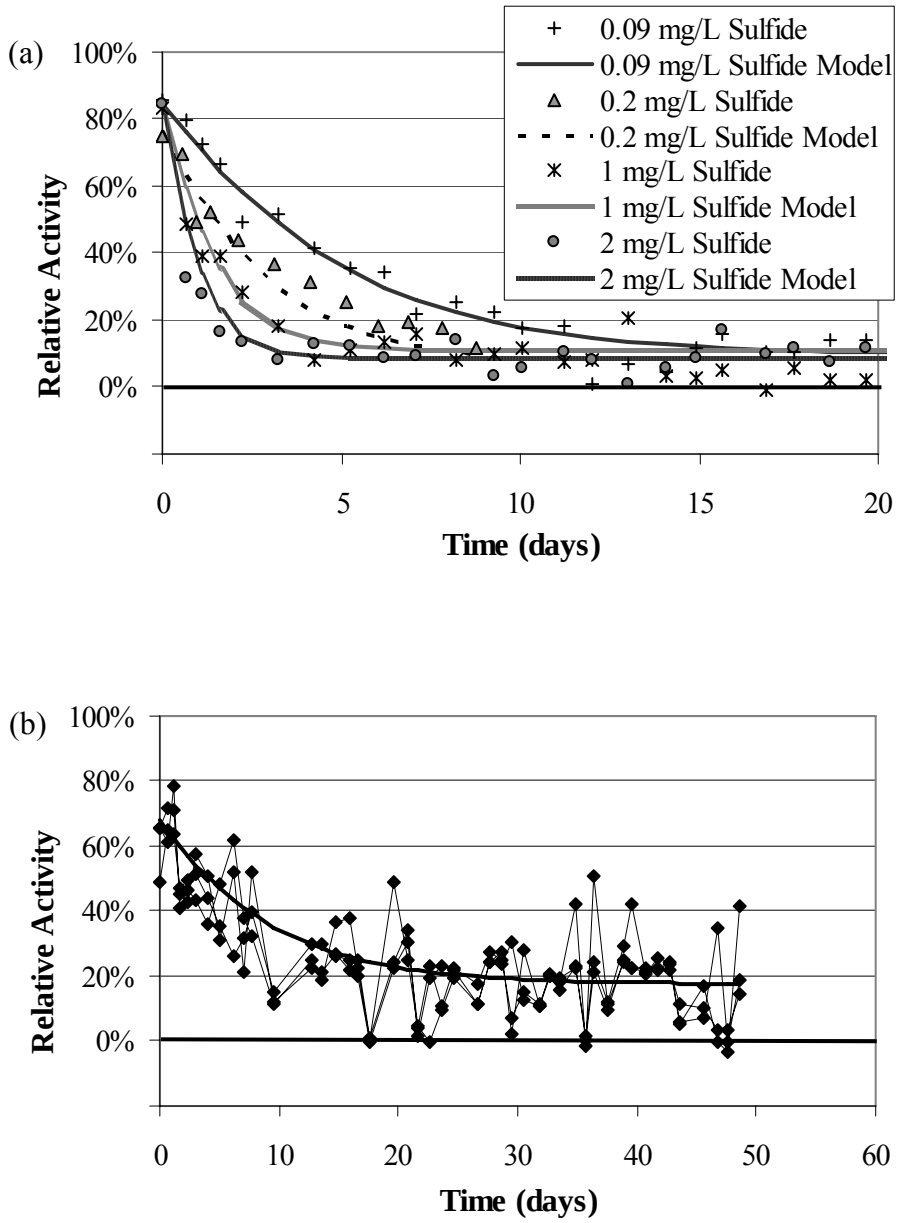

(a)
100%
80%
60%
40%
20%
0%
Relative Activity
0
5
10
15
20
Time (days)
0.09 mg/L Sulfide
0.09 mg/L Sulfide Model
0.2 mg/L Sulfide
0.2 mg/L Sulfide Model
1 mg/L Sulfide
1 mg/L Sulfide Model
2 mg/L Sulfide
2 mg/L Sulfide Model
(b)
100%
80%
60%
40%
20%
0%
Relative Activity
0
10
20
30
40
50
60
Time (days)

Fig. 5

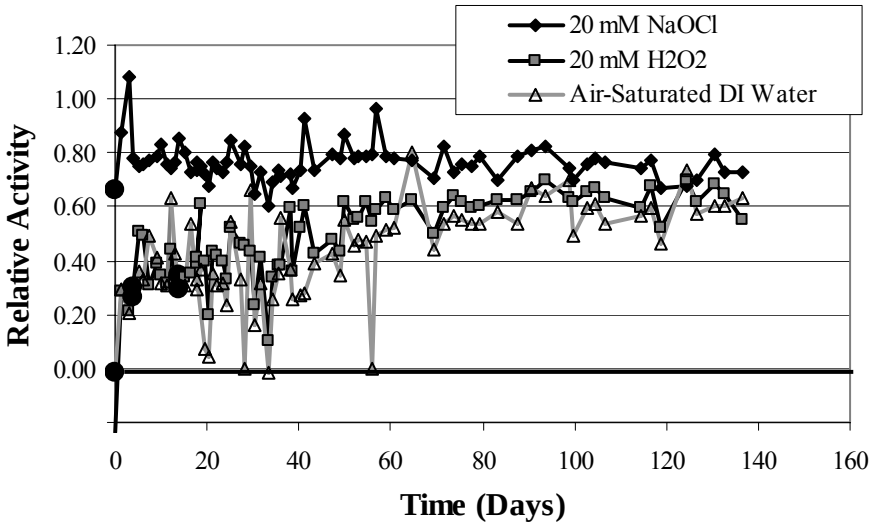

20 mM NaOCl
20 mM H2O2
Air-Saturated DI Water
Relative Activity
1.20
1.00
0.80
0.60
0.40
0.20
0.00
0
20
40
60
80
100
120
140
160
Time (Days)

Fig. 6

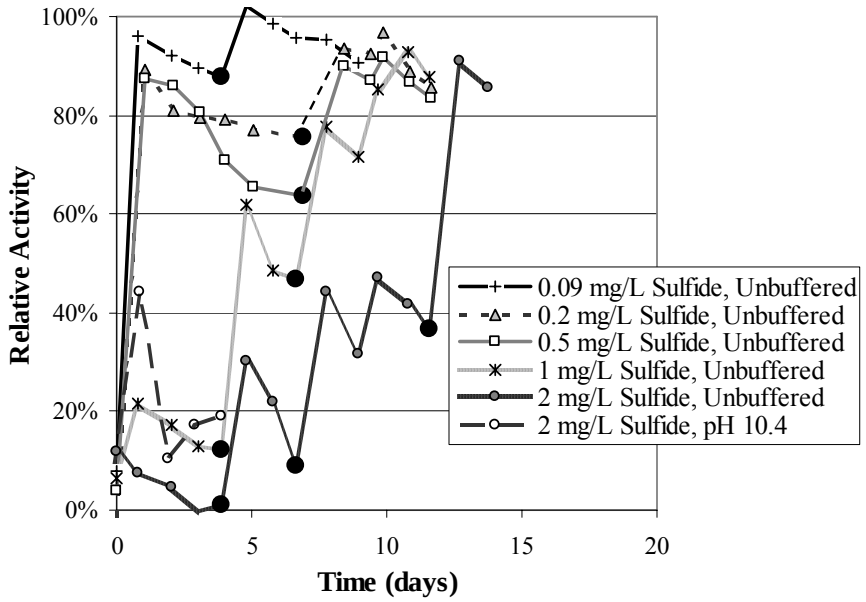
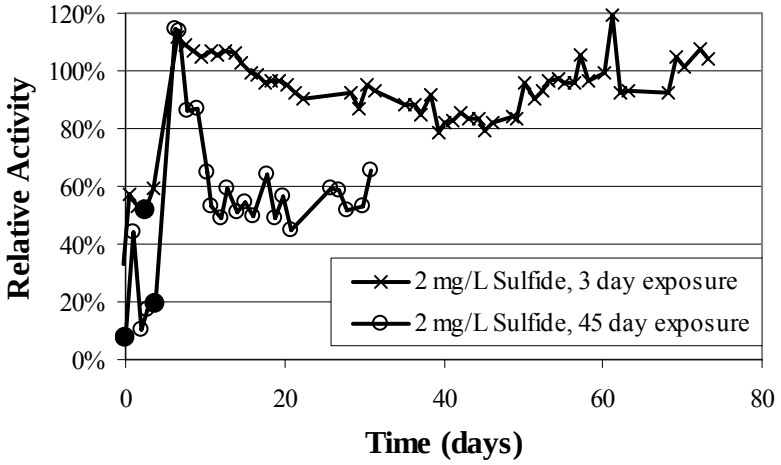

100%
80%
60%
40%
20%
0%
Relative Activity
0
5
10
15
20
Time (days)
0.09 mg/L Sulfide, Unbuffered
0.2 mg/L Sulfide, Unbuffered
0.5 mg/L Sulfide, Unbuffered
1 mg/L Sulfide, Unbuffered
2 mg/L Sulfide, Unbuffered
2 mg/L Sulfide, pH 10.4

Fig. 7


120%
100%
80%
60%
40%
20%
0%
Relative Activity
0
20
40
60
80
Time (days)
2 mg/L Sulfide, 3 day exposure
2 mg/L Sulfide, 45 day exposure