EPA United States Environmental Protection Agency

Ground Water Issue

Ground Water Sample Preservation at In-Situ Chemical Oxidation Sites – Recommended Guidelines

Saebom Ko[1], Scott G. Huling[2,*], Bruce Pivetz[3]

Table of Contents

Figures

Tables

[1] National Research Council, Robert S. Kerr Environmental Research Center, P.O. Box 1198, Ada, OK, 74820; Phone: (580) 436-8742; ko.saebom@epa.gov

[2,*] (Corresponding Author) U.S. Environmental Protection Agency, National Risk Management Research Laboratory, Robert S. Kerr Environmental Research Center, P.O. Box 1198, Ada OK, 74820; Phone: (580) 436-8610; huling.scott@epa.gov

[3] Shaw Environmental & Infrastructure, Inc., Robert S. Kerr Environmental Research Center, P.O. Box 1198, Ada, OK, 74820; Phone: (580) 436-8998; E-mail: pivetz.bruce@epa.gov

1. INTRODUCTION

In-situ chemical oxidation (ISCO) involves the introduction of a chemical oxidant into the subsurface for the purpose of transforming ground water and/or soil contaminants into less harmful chemical by-products (Huling and Pivetz, 2006; Rivas, 2006; Ferrarese *et al.,* 2008; Kao *et al.,* 2008). Often, ground water samples collected specifically to analyze organic contaminants may contain the oxidant and the organic contaminants in a "binary mixture" (Huling *et al.,* 2011a; Johnson *et al.,* 2012). When organic contaminants and oxidants are commingled in the ground water sample, there is significant potential for oxidative transformation of contaminants to occur after the sample is collected and the results of the sample analysis to become non-representative of in-situ conditions at the time of sampling. Consequently, the quality of the ground water sample may be compromised and a false negative result may occur.

An integral component of ISCO is the collection and analysis of ground water samples to assess ISCO treatment performance. A technical issue faced by Remedial Project Managers is the collection and analysis of representative, high quality ground water samples that can be used to support a site assessment and remedial performance monitoring at sites where ISCO is being deployed. The purpose of this *Issue Paper* is to provide background information and general guidelines involving methods and procedures that can be used to detect whether an oxidant (i.e., permanganate or persulfate) is present in ground water, to approximate the oxidant concentration, and to estimate and deliver the volume or mass of preservative, specifically ascorbic acid, required to preserve the binary mixture ground water sample. The focus of this *Issue Paper* is on permanganate and persulfate, two oxidants that can persist for long periods of time in the subsurface and therefore represent the greatest potential for binary mixture ground water samples. An Appendix to this *Issue Paper* (Recommended Operating Procedures - Preservation of Ground Water Samples at ISCO Sites Using Ascorbic Acid) provides specific details regarding the preservation procedures for use by EPA Regional personnel, contractors, and other environmental professionals engaged in ground water sample collection and analysis.

The guidelines are also applicable to bench-scale studies where oxidants are used to investigate the feasibility of ISCO treatment. For

example, aqueous samples collected from bench-scale soil reactors are analyzed for organic contaminants, but may also contain the oxidant amended to the reactor to destroy the contaminant. Consequently, the guidelines described below also extend to bench-scale studies where the potential for binary mixture aqueous samples may occur, and are analyzed for organic contaminants.

1.1. Reasons to Sample and Analyze Binary Mixtures

It is often desirable for oxidants in ground water to fully react prior to collecting and analyzing ground water samples for organic contaminants. However, there are circumstances where the collection and analysis of binary mixture ground water samples may not be avoided. These reasons vary widely and some examples include the need to:

(1) conduct an immediate preliminary assessment of ISCO to validate in-progress treatment performance,
(2) establish design parameters from interim ISCO pilot-scale studies needed to design full-scale ISCO deployment,
(3) assess the potential redistribution of the ground water contaminant plume as affected by ISCO activities, and
(4) evaluate reaction kinetics during oxidative treatment.

Rapid turnaround of field data and information may be needed to meet specified milestones and deadlines for full-scale remedy selection, design, construction, and implementation. In addition, regulatory-driven goals and associated timelines may require rapid completion of pilot-scale testing and full-scale deployment of ISCO. Therefore, a significant emphasis may be placed on the collection of ground water samples at ISCO sites prior to complete reaction of the oxidant (Huling *et al.,* 2011a).

1.2. Binary Mixtures of Oxidant and Organic Contaminants in Ground Water Samples

Heterogeneous distribution of oxidant and contaminants, and hydraulic conductivity variations in heterogeneous aquifers are two main causes of binary mixtures (Figure 1) (Huling *et al.,* 2011a). For example, oxidants and contaminants can enter a monitoring well screen from different lithologic zones. These solutes may be captured as separate solutes from different lithologic zones, or as separate or commingled solutes from the same lithologic zone. Insufficient contact time (i.e., reaction time) between the oxidant and contaminants prior to, or after, entering the well leads to binary mixtures in the ground water sample.

Commingling of organic contaminants and oxidants in the ground water sample impacts the quality of the ground water sample, but may also impact the analytical instruments used to measure the concentration of analyte(s) in the ground water sample (Johnson *et al.,* 2012). Although rarely reported and documented, the impact of oxidants on analytical instruments is exclusively reported for permanganate and predominantly involves instrument malfunction resulting from MnO_2(s)-clogged lines and ports. No information was found that documented the impact of hydrogen peroxide or persulfate on analytical instruments despite numerous studies where binary mixtures were analyzed.

1.3. Impact of Binary Mixtures – Previous Studies

A detailed study involving the impact of residual persulfate on the quality of ground water samples was performed (Huling *et al.,* 2011a). A significant decline (49 to 100 percent (%)) in volatile organic compound (VOC) concentrations was measured in unpreserved binary mixture samples using gas chromatography (GC) purge and trap, and GC mass spectroscopy (MS) headspace analytical methods. In that study, preservation of the binary mixture samples was achieved through the addition of ascorbic acid and resulted in 99 to 100% VOC average recovery relative to oxidant-free control samples. Adding high concentrations of ascorbic acid (42 to 420 millimolar (mM)) to the samples did not interfere in the measurement of the VOCs and did not negatively impact the analytical instruments. These results indicated that if persulfate is present in the sample, and the binary sample is not appropriately preserved, the quality of the sample will be compromised. A companion study involving the impact of permanganate on the quality of ground water samples and analytical instruments, and the use of ascorbic acid yielded similar results (Johnson *et al.,* 2012). The results of these studies (Huling *et al.,* 2011a; Johnson *et al.,* 2012) serve as the basis for the guidelines provided in this *Issue Paper*.

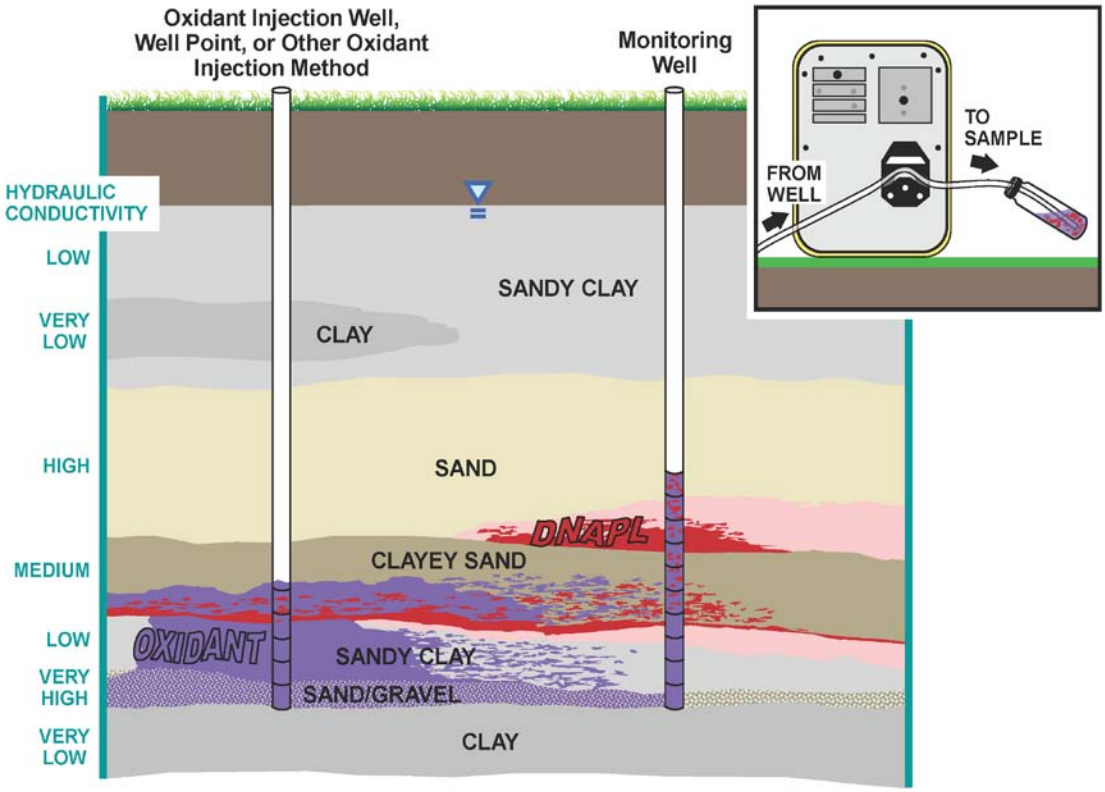


Figure 1. Conceptual model of hydrogeologic, and oxidant and contaminant fate and transport conditions that contribute to binary mixture ground water samples. The oxidant illustrated in purple, conceptually represents any oxidant (permanganate, persulfate) used for in-situ chemical oxidation (Huling *et al.,* 2011a).

The analytical methods used in these studies are commonly used in commercial analytical laboratories. The analytes, including benzene, toluene, xylene (BTX), perchloroethylene (PCE), and trichloroethylene (TCE), are representative of contaminants commonly found at hazardous waste sites. Similarly, empirical results were obtained in the analysis of binary mixtures comprised of persulfate and pentachlorophenol (PCP) by high performance liquid chromatography (HPLC) where significant loss of PCP was measured in unpreserved samples relative to persulfate-free control samples and ascorbic acid-preserved samples (data not included). Currently, we do not have a firm explanation for a viable mechanism responsible for persulfate activation and PCP oxidation in these samples.

Overall, results are applicable to a broad set of analytical methods, analytes, and site conditions. It is unclear to what extent these results extend to analytical methods and contaminants that were not tested in these studies, however. Additional specific studies are needed in cases where different analytical methods and ground water contaminants are involved.

Specifically, analysis involved the measurement of (1) BTX, PCE, and TCE using the GC/MS headspace method, and (2) BTX using the GC purge and trap method (Huling *et al.,* 2011a). The GC/MS headspace method is involved in EPA Method Nos. 8260C and 5021A. The automated headspace GC/MS method is used to confirm the identity and quantity of purgeable VOCs in water samples in 40 mL volatile organic analysis (VOA) vials. This method is used to quantify over sixty VOCs in drinking water, including aromatics, haloalkenes, haloalkanes, haloaromatics, and fuel oxygenates. This automated method involves the transfer of an aqueous sub-sample (10 mL) to a sealed headspace vial which is heated from room temperature to 80 degrees Celsius (°C) in 30 minutes. A sample of the headspace gas is then transferred to the capillary column in the GC. After separation on the GC column and introduction into the MS, the VOCs are identified and

quantified using the MS. We propose that contaminant loss occurs during the heating step of the sub-sample where residual persulfate is thermally activated resulting in VOC oxidation.

The automated purge and trap GC (Agilent, Model 6890, Wilmington, DE) method was used to quantify BTX in water samples (40 mL VOA vials). This method is most similar to EPA Methods 602 and 8020, but shares similarities with several other EPA methods that involve purge and trap, including: EPA 501, 502.2, 503.1, 524.2, 601, 602, 624, 8010, 8020, 8021, 8240, and 8260. In this method, a sub-sample (10 mL) is transferred to a sparge chamber and purged with helium (6 minutes). The VOCs are transferred to a K VOCARB 3000 Encon trap and dry purged with helium to remove water vapor. The VOCs are thermally desorbed and transferred to the GC column for separation and measurement. Sample transfer is through a heated 1.9 mm×1.0 m Silcosteel (Restek, Bellefonte, PA) transfer line coupled directly to the analytical column. Following separation on the column, the presence of VOCs is determined and quantified with photoionization and flame ionization detectors. It was proposed that the contaminant loss was due to the helium sparging step where aerosols are formed containing persulfate and are transfered to the VOC granular activated carbon trap (Huling *et al.,* 2011a). Subsequently, during the VOC thermal desorption step where the trap is heated from room temperature to 260 °C (25 min), the persulfate residing in the trap is thermally activated resulting in the oxidation of the VOCs immobilized and concentrated on the trap. Similarly, highly efficient oxidation of organics immobilized in solid media (i.e., granular activated carbon) by thermally activated persulfate has been demonstrated (Huling *et al.,* 2011b).

The impact of residual permanganate was evaluated in water samples prepared in the lab using a multi-component standard, and in ground water samples collected at ISCO sites (Johnson *et al.,* 2012). Binary mixture aqueous samples were prepared that contained a 52-component standard of organic compounds and permanganate. Ascorbic acid was added to the binary mixture which reacted rapidly with the MnO_4^-, preserved the sample, and limited the reaction between MnO_4^- and the organic compounds. Consequently, the concentrations of the majority of the compounds in the multi-component standard were within the control limits established for quality assurance. However, despite timely efforts to preserve the laboratory-prepared binary mixture samples, the quality of the sample was impacted; concentrations were generally lower than oxidant-free controls, and the concentration of several compounds (*cis*-1,3-dichloropropene, styrene, *trans*-1,2-dichloroethene, *trans*-1,3-dichloropropene, vinyl chloride) fell below the applicable lower control limit.

Concentrations of VOCs measured in field-preserved binary mixture ground water samples were greater than in replicate samples refrigerated in the field and preserved with ascorbic acid upon arrival at the lab (Johnson *et al.,* 2012). These results indicate that the VOCs reacted in transit despite refrigeration. Excess ascorbic acid did not negatively impact the quality of the simulated ground water samples containing a 52-component stock standard, or actual ground water samples collected from two field sites, and did not negatively impact the GC/MS instruments used in the analysis.

2. GROUND WATER SAMPLE COLLECTION, OXIDANT MEASUREMENT, AND OXIDANT NEUTRALIZATION/SAMPLE PRESERVATION

Specific details regarding the procedures used in amending ground water samples with ascorbic acid are provided in the Appendix entitled, "Recommended Operating Procedures - Preservation of Ground Water Samples at ISCO Sites Using Ascorbic Acid".

It is recommended that a representative ground water sample be collected at the well head in a test vial for the specific purpose of measuring the oxidant concentration. Ground water sample collection for this purpose should follow the normal ground water sampling protocol established at the site. This initial screening ground water sample is not collected for the purpose of measuring organic contaminant concentrations. If contaminant analysis of the ground water sample is desired, additional samples must be subsequently collected and preserved, if necessary. Normal sampling procedures appropriate for site conditions and regulatory acceptance are recommended. Sample preservation and handling requirements are based on the type of analyses being performed and should be specified in project-specific documents such as the quality assurance project plan, field sampling

plan, or in general EPA documents such as the Resource Conservation and Recovery Act (RCRA) guidance document (U.S. EPA, 1992) or EPA SW-846 (U.S. EPA, 1982). Additional direction on ground water sampling techniques can be found in Yeskis and Zavala (2002).

2.1. Permanganate (MnO_4^-)

Data and information presented below are reported in terms of the permanganate anion (MnO_4^-; 118.9 grams per mole (g/mol)). Permanganate is purchased either as sodium permanganate ($NaMnO_4$; 141.9 g/mol) or potassium permanganate ($KMnO_4$; 158.0 g/mol) and as a result conversion to the permanganate anion concentration is needed to determine sample preservation needs as per the *Issue Paper*. Specifically, the ratios 118.9/141.9 (g-mole/g-mole) and 118.9/158.0 (g-mole/g-mole) are used to convert $NaMnO_4$ and $KMnO_4$, respectively to MnO_4^-.

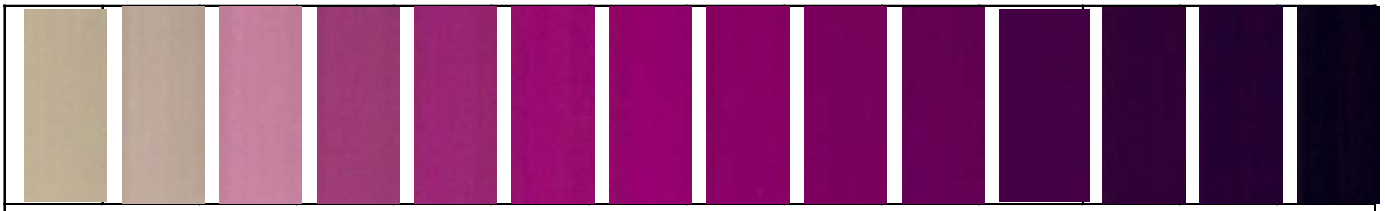
2.1.1. Analysis by Visual Observation

The characteristic pink or purple color of MnO_4^- in a 40 mL VOA vial can be used as a general guideline to estimate the concentration by using the MnO_4^- colorimetric scale (Table 1). This method should be used with caution because ground water turbidity and colloidal manganese dioxide solids (MnO_2(s)) can affect sample color and result in deviations from the tabulated color scale. Field filtration can help minimize these interferences, but may not fully remove all color if sub-micron colloidal and/or dissolved constituents are present.

2.1.2. Spectrophotometric Analysis

The permanganate concentration can be determined using commercially available field test kits (SenSafe™, 2011; CHEMetrics, 2011). Additionally, an accurate measurement of the permanganate concentrations can be determined using a field spectrophotometer (maximum absorbance wavelength (λ) = 525 nanometers (nm) (A_{525})) and a calibration curve involving a linear correlation between MnO_4^- concentration and A_{525} (Figure 2, Table 1). Filtered samples (0.2-0.45 micron) may be required to eliminate background colloidal or suspended solid materials that can absorb light at 525 nm and interfere with permanganate measurement. Volatilization of

Table 1. Permanganate concentration, spectrophotometric absorbance at 525 nm, and required amount of ascorbic acid required to neutralize the oxidant in a 40 mL vial. The color scale represents actual photos of MnO_4^- vials and is included for conceptual guidance. Actual colors vary based on background lighting, and color printers. Additionally, photographs of low concentrations (i.e., clear solutions) do not accurately capture transparency.



$[MnO_4^-]$ (mg/L) (millimolar in parentheses)													
0 (0)	0.75 (0.01)	3.8 (0.03)	7.5 (0.06)	11.3 (0.09)	18.8 (0.16)	30.1 (0.25)	37.6 (0.32)	56.4 (0.47)	75.3 (0.63)	113 (0.95)	151 (1.27)	188 (1.58)	376 (3.16)
Absorbance[1], wavelength (λ) = 525 nm													
0	0.011	0.059	0.134	0.197	0.329	0.516	0.627	NL	NL	NL	NL	NL	NL
Ascorbic Acid Stock Solution (M) [2]													
-	0.015	0.015	0.15	0.15	0.15	0.15	0.15	1.5	1.5	1.5	1.5	1.5	1.5
Volume of Ascorbic Acid solution (µL)													
0	30	150	30	46	76	121	152	23	30	46	61	76	152
Mass of Ascorbic Acid (mg)													
0	0.08	0.4	0.79	1.21	2.1	3.32	4.17	6.1	7.9	12.2	16.1	20.1	40.2

(1) $[MnO_4^-]$ (mg/L) = 58.8 × A_{525}; A_{525} is the absorbance at 525 nm; non-linear above 38 mg/L MnO_4^-.
(2) To minimize sample dilution, the ascorbic acid stock solution used was 0.015, 0.15, and 1.5 M.

contaminants is not a concern since the initial screening ground water sample is used specifically to determine the concentration of permanganate.

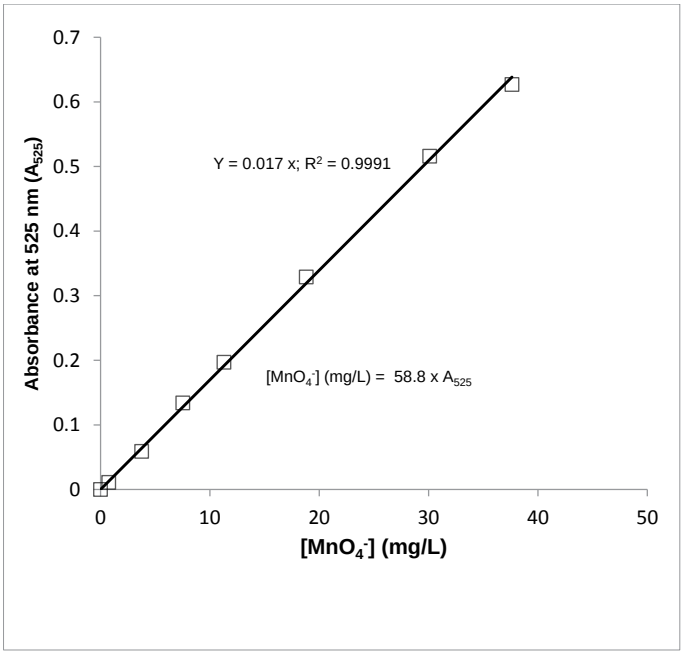


Figure 2. Calibration curve of MnO_4^- concentration versus absorbance at wavelength (λ) of 525 nm.

2.1.3. Results

If MnO_4^- is not detected in the ground water sample, it is recommended that normal ground water sampling and analysis procedures be used. If MnO_4^- is detected, there are two general options to consider. The first option is to delay the collection and analysis of the ground water sample for a sufficient time allowing the MnO_4^- concentration to fully diminish in the subsurface, if desired. In some cases, MnO_4^- persistence is lengthy and this option is not possible (as discussed above in Section 1.1). Due to the site-specific time-dependency of contaminant mass transfer and transport, the time required to approach chemical equilibrium in ground water will likely require additional time after the oxidant is fully consumed. Subsequently, ground water sampling would follow routine guidelines and requirements. The second option is to collect and preserve the ground water sample (i.e., neutralize the oxidant) prior to analysis to minimize the impact of the commingled oxidant. The second option may be desirable for a number of reasons described in Section 1.1.

2.1.4. Oxidant Neutralization and Sample Preservation

Given the MnO_4^- concentration, the volume of ascorbic acid stock solution (0.015, 0.15, or 1.5 mol/L), or weight of crystalline ascorbic acid (176.12 g/mol) required to preserve the binary mixture is determined (Table 1). Sample preservation involves the addition of the appropriate amount of ascorbic acid to preserve a binary mixture in a 40 mL VOA vial. In a lab study (Johnson *et al.,* 2012), the mass of ascorbic acid required to neutralize MnO_4^- ranging in concentration from 1-750 milligrams per liter (mg/L) was determined empirically. The average molar ratio (n=14) was 1.64 mol ascorbic acid/mol MnO_4^- and values ranged from 1.45 to 1.75 mol/mol. Therefore, the weight of ascorbic acid that corresponded with the MnO_4^- colorimetric scale was conservatively based on a stoichiometric ratio of 1.8 mol ascorbic acid/mol MnO_4^-, since, as noted below, no negative side-effects were noted with over-dosing. Detailed recommended operating procedures are provided in the Appendix to estimate the volume of crystalline ascorbic acid or ascorbic acid stock solution required to neutralize the MnO_4^-. Once the oxidant is neutralized, it is recommended that normal ground water sample handling and procedures be followed.

The recommended volume and mass of ascorbic acid included in Table 1 is a guideline. The addition of ascorbic acid will rapidly reduce the MnO_4^- concentration and eliminate the pink/purple color. The formation of colloidal or particulate MnO_2(s) (i.e., Mn^{+4}) may occur causing a brown tinge appearance of the solution. Incremental amendment of ascorbic acid is required to further reduce the Mn^{+4} to Mn^{+2}, and eliminate the brownish tinge color. Mn^{+2} is highly soluble and the most desirable form of Mn to minimize the impact of colloidal or particulate matter on the laboratory analytical instruments. Overall, Table 1 is used as a guideline but the actual amount of ascorbic acid to be added should be based on the amount required to fully eliminate the MnO_4^- and MnO_2(s), and to achieve a clear solution.

Excess ascorbic acid did not have a negative impact on the quality of the ground water sample involving GC and GC/MS analysis of a broad range of organic chemicals (Johnson *et al.,* 2012). The volume of ascorbic acid solution added to the sample vial should be recorded so

appropriate dilution calculations can be performed to obtain an accurate estimate of the contaminant concentrations. Pre-amending sample vials with ascorbic acid is also an option and is discussed further in Section 7.F of the Appendix. Other sample preservation requirements are based on the analyses being performed and are specified in the quality assurance project plan, field sampling plan, RCRA guidance document (U.S. EPA, 1992) or EPA SW-846 (U.S. EPA, 1982). Additional direction on ground water sampling techniques can be found in Yeskis and Zavala (2002)

2.2. Persulfate ($S_2O_8^{2-}$)

The data and information below are presented in terms of the persulfate anion ($S_2O_8^{2-}$; 192.0 g/mol). However, persulfate is predominantly purchased as sodium persulfate ($Na_2S_2O_8$; 238.1 g/mol). As a result, conversion of sodium persulfate to persulfate anion concentrations is necessary to determine sample preservation needs as per the *Issue Paper*. Specifically, the ratio of 192.0/238.1 (g-mol/g-mol) is used to convert $Na_2S_2O_8$ to $S_2O_8^{2-}$. Persulfate is colorless and requires field measurement at the well head to determine its presence and concentration in the ground water sample.

2.2.1. Analysis by Field Test Kit Colorimetry

Field test kits are commercially available to measure persulfate concentration in aqueous samples (CHEMetrics, 2011; FMC, 2012). CHEMetrics persulfate test kits are available for two sodium persulfate concentration ranges (0-7, 7-70 mg/L). Given the high concentrations of persulfate injected into the subsurface at ISCO sites, significant dilution may be required in the use of these test kits. FMC commercial test kits are dependent on whether the persulfate activator is base or thermal (test kit "K"), or whether persulfate is activated by iron chelates or H_2O_2 (test kit "C") (FMC, 2012). The lower detection limit of persulfate using the current FMC test kits is 500 mg/L, a sufficient quantity of oxidant to significantly impact the concentrations of VOCs and the quality of the sample. Based on the current detection limit using the FMC test kit, it is recommended that the minimum amount of ascorbic acid added to the sample vessel should conservatively account for 500 mg/L persulfate.

2.2.2. Analysis by Spectrophotometric Analysis (Ferrous Ammonium Sulfate (FAS) Method)

A spectrophotometric method can be used to analyze the persulfate concentration in aqueous samples. The ground water sample should be filtered (0.2-0.45 micron) to eliminate background material (i.e., turbidity) that may interfere with $S_2O_8^{2-}$ analysis. A small volume of de-ionized (DI) water (0.9 mL) and sulfuric acid (H_2SO_4) (10 mL, 2.5 normal (N)) (or, add 10.9 mL of 2.3 N H_2SO_4) is placed in a 20 mL glass or plastic test vessel. These can be prepared prior to transport to the field. A blank is prepared by mixing 1 mL DI water with H_2SO_4 (10 mL, 2.5 N). The filtered sample (0.1 mL) is placed in the test vessel, followed by the addition of ferrous ammonium sulfate (FAS) ($Fe(SO_4)_2(NH_4)_2 \cdot 6H_2O$) (0.1 mL, 0.4 N) (prepared immediately before use). Adding a couple drops of H_2SO_4 (conc.) to the FAS reagent increases the stability of the ferrous iron for several more hours (5 to 10 hours). The mixture is swirled/mixed and allowed to react for 30 to 40 minutes. Subsequently, the mixture is amended with ammonium thiocyanate (NH_4SCN) (0.2 mL, 0.6 N) and the absorbance of the solution is analyzed immediately with a spectrophotometer at a wavelength of λ = 450 nm (A_{450}) (Huang *et al.,* 2002; Huling *et al.,* 2011a; b). The general colorimetric scale provided below can be used to estimate the persulfate concentration in a ground water sample (Table 2) analyzed by the FAS method. Alternatively, a calibration curve involving a linear correlation between $S_2O_8^{2-}$ concentration and A_{450} can be used to determine a more precise estimate of the persulfate concentration (Figure 3).

2.2.3. Results

If $S_2O_8^{2-}$ is not detected in the ground water sample, it is recommended to proceed using normal ground water sampling and analysis procedures. If $S_2O_8^{2-}$ is detected, there are two general options to consider. The first is to delay collection and analysis of the ground water sample for sufficient time which allows the persulfate concentration to fully diminish in the subsurface, if desired. Due to the site-specific time-dependency of contaminant mass transfer and transport, the time required to approach chemical equilibrium in ground water will likely require additional time after the oxidant is fully consumed. Subsequently, ground water sampling would follow routine guidelines. The second option is to collect and

Table 2. Persulfate concentrations resulting from the ferrous ammonium sulfate analytical method involving the spectrophotometric measurement (λ = 450 nm) of the solution, and the required amount of ascorbic acid required to neutralize the oxidant in a 40 mL vial. The color scale represents actual photos of $S_2O_8^{2-}$ vials and is included for conceptual guidance. Actual colors vary based on background lighting, and color printers. Additionally, photographs of low concentrations (i.e., clear solutions) do not accurately capture transparency.

$[S_2O_8^{2-}]$ (mg/L) (millimolar in parentheses)													
0 0	80 (0.42	200 (1.1)	400 (2.1)	610 (3.2)	810 (4.2)	1210 (6.3)	1610 (8.4)	2020 (10.5)	2420 (12.6)	2820 (14.7)	3230 (16.8)	3630 (18.9)	4030 (21.0)
Absorbance[(1)], wavelength (λ) = 450 nm													
0	0.011	0.019	0.04	0.062	0.076	0.121	0.164	0.204	0.245	0.275	0.313	0.349	0.397
Volume of Ascorbic Acid solution (mL)													
0	0.04	0.11	0.22	0.34	0.45	0.67	0.89	1.12	1.34	1.57	1.79	2.02	2.24
Mass of Ascorbic Acid (176.12 g/mol) (g)													
0	0.01	0.03	0.06	0.09	0.12	0.18	0.24	0.3	0.35	0.41	0.47	0.53	0.59

(1) Solubility of ascorbic acid in water = 330 g/L (1.87 mol/L); 80% solubility (1.5 mol/L) used as stock solution; $[S_2O_8^{2-}]$ (mg/L) = 10,000 × A_{450}; where A_{450} is the absorbance at 450 nm.

preserve the ground water sample prior to analysis to minimize the impact of persulfate on the ground water sample. The second option may be desirable for a number of reasons described in Section 1.1.

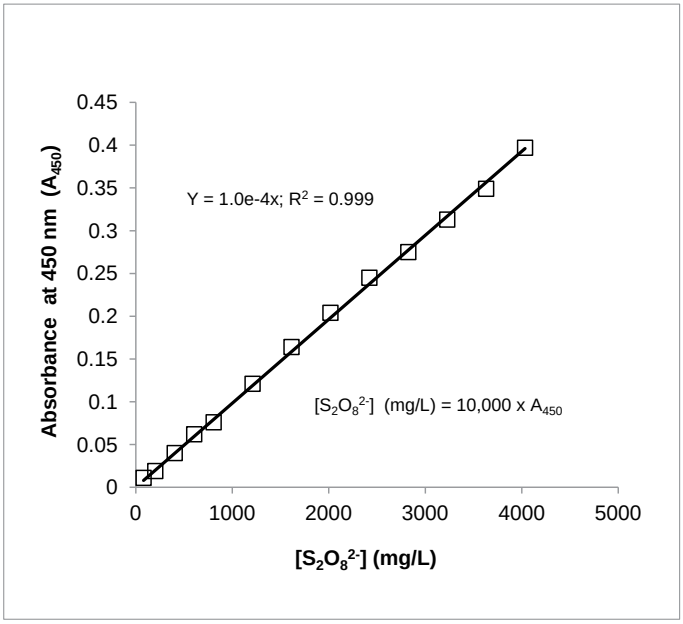


Figure 3. Calibration curve for $S_2O_8^{2-}$ concentration versus absorbance at wavelength 450 nm using the ferrous ammonium sulfate method.

2.2.4. *Oxidant Neutralization and Sample Preservation*

Guidelines for the volume of ascorbic acid stock solution (1.5 mol/L) or the weight of crystalline ascorbic acid (176.1 g/mol) required to preserve the binary mixture in a 40 mL sample vial are provided (Table 2). The mass of ascorbic acid that corresponds with the persulfate colorimetric scale is based on a stoichiometric ratio of 4 mol ascorbic acid/mol persulfate and was determined empirically in a laboratory study (Huling *et al.,* 2011a). Detailed recommended operating procedures are provided in the Appendix to estimate the volume of crystalline ascorbic acid or ascorbic acid stock solution required to neutralize the $S_2O_8^{2-}$. This stoichiometric ratio is in excess of the ideal stoichiometry for mineralization of persulfate by ascorbic acid. Excess ascorbic acid (4 – 40 mol ascorbic acid/mol persulfate) did not have a negative impact on the quality of the ground water sample involving GC and GC/MS analysis of BTX, TCE, and PCE (Huling *et al.,* 2011a). The basis for this quantity of ascorbic acid is to achieve favorable reaction kinetics between $\cdot SO_4^-$ and ascorbic acid, relative to the reaction between the sulfate radical ($\cdot SO_4^-$) and the VOCs. Following oxidant neutralization, it is recommended that other approved sample preservation and handling methods

in ground water sample handling be performed. For example, acidification of the sample is normally carried out to minimize biochemical and reduction reactions. Other sample preservation requirements are based on the analyses being performed and are specified in the quality assurance project plan, field sampling plan, RCRA guidance document (U.S. EPA, 1992) or EPA SW-846 (U.S. EPA, 1982). Additional direction on ground water sampling techniques can be found in Yeskis and Zavala (2002).

3. ADDITIONAL INFORMATION

It is recommended that the analytical laboratory be notified that the aqueous samples contain residual persulfate or permanganate and were preserved with ascorbic acid. The volume of ascorbic acid solution added to the sample should be recorded so the appropriate calculations can be used to correct for dilutions. If MnO_2(s) has settled on the bottom of the VOA vial, it is important that the sample not be disturbed prior to analysis. This precaution in sample handling prevents the suspension of the MnO_2(s) particles and the potential for accidental injection into the analytical instruments.

Other preservatives have been used to successfully neutralize these oxidants, but may negatively impact the quality of the sample (Huling *et al.,* 2011a). Despite efforts used to neutralize the oxidant and to preserve the quality of the ground water sample, the presence of oxidant in ground water samples introduces uncertainty in the precise measurement of contaminant concentrations in the subsurface. This is attributed to the potential impact of the oxidant on contaminant concentrations in the ground water sample prior to neutralization, the transient nature of contaminant fate and transport in the subsurface where ISCO activities were deployed, and the site-specific oxidant injection and hydrogeologic conditions contributing to binary mixtures. Consequently, additional ground water sample collection and analysis will likely be required to achieve an accurate evaluation of post-ISCO performance, and regulatory adherence with US EPA ground water compliance monitoring requirements.

Numerous examples exist where elevated permanganate and VOC concentrations have been measured in ground water samples collected over extended periods of time at hazardous waste sites. It can be concluded from a simple kinetic analysis that long term VOC persistence can primarily be explained by spatial separation between the ground water containing the oxidant and contaminant (Figure 1) (Johnson *et al.,* 2012). Ground water samples derived from wells screened over spatially separate vertical intervals indicate an in-well mixture of ground water containing either oxidants or contaminants. Limited contact between the oxidant and contaminant within the same lithologic unit can be due to specific mass transfer or mass transport conditions including the dissolution of non-aqueous phase liquids (NAPLs) or slow diffusion of contaminants from low permeability materials. These fate and transport conditions indicate the oxidant has not been uniformly delivered to the contaminated zone(s). A critical analysis of screened intervals, injection intervals, contaminated intervals, oxidant and contaminant transport characteristics, and ground water sample results from analyzing preserved binary mixtures, could provide valuable insight for the development of a more accurate site conceptual model that could be used to design and deploy a more effective oxidant delivery system.

4. REFERENCES

CHEMetrics. 2011. http://www.chemetrics.com/Persulfate.

Ferrarese, E., Andreottola, G., and Oprea, I.A. 2008. Remediation of PAH-contaminated sediments by chemical oxidation. *J. Haz. Mat.* 152(1), 128-139.

FMC Environmental Solutions. 2012. Field Measurement http://environmental.fmc.com/solutions/soil-ground-remediation/field-measurement.

Huang, K.C., Couttenye, R.A., and Hoag, G.E. 2002. Kinetics of heat-assisted persulfate oxidation of methyl *tert*-butyl ether (MTBE). *Chemosphere* 49(4), 413-420.

Huling, S.G., and Pivetz, B. 2006. In-Situ Chemical Oxidation – Engineering Issue. US Environmental Protection Agency, National Risk Management Research Laboratory, R.S. Kerr Environmental Research Center, Ada, OK. EPA/600/R-06/072. http://www.epa.gov/nrmrl/gwerd/publications.html#oxidation.

Huling, S.G., Ko, S., and Pivetz, B. 2011a. Ground water sampling at ISCO sites – Binary mixtures of volatile organic compounds and persulfate. *Ground Water Monit. Remed.* 31(2), Spring 72-79.

Huling, S.G., Ko, S., Park, S., and Kan, E. 2011b. Persulfate-driven oxidation of contaminant-spent granular activated carbon. *J. Haz. Mat.* 192(3), 1484–1490.

Johnson, K.T., Wickham-St. Germain, M., Ko, S. and Huling, S.G. 2012. Binary Mixtures of Permanganate and Chlorinated Volatile Organic Compounds in Groundwater Samples: Sample Preservation and Analysis. *Ground Water Monit. Remed.,* 32(3), Summer 84–92.

Kao, C.M., Huang, K.D., Wang, J.Y., Chen, T.Y., and Chien, H.Y. 2008. Application of potassium permanganate as an oxidant for in-situ oxidation of trichloroethylene-contaminated groundwater: A laboratory and kinetics study. *J. Haz. Mat.*153(3), 919-927.

Rivas, F.J. 2006. Polycyclic aromatic hydrocarbons sorbed on soils: A short review of chemical oxidation based treatments. *J. Haz. Mat.* 138(2), 234-251.

SenSafe, 2011. *http://www.sensafe.com/product.php?recordID=481138*.

U.S. EPA. 1982. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, EPA SW-846. Office of Solid Waste and Emergency Response, Washington, D.C. *http://www.epa.gov/epawaste/hazard/testmethods/sw846/online/index.htm*.

U.S. EPA. 1992. RCRA Ground-Water Monitoring: Draft Technical Guidance. Office of Solid Waste, Washington, DC EPA/530/R-93/001, NTIS PB 93-139350.

Yeskis, D., and Zavala, B. 2002. Ground-Water Sampling Guidelines for Superfund and RCRA Project Managers – Ground Water Forum Issue Paper. Office of Solid Waste and Emergency Response, Washington, D.C. EPA 542-S-02-001 May 2002. *http://www.epa.gov/tio/tsp/download/gw_sampling_guide.pdf*.

5. ACKNOWLEDGEMENTS

This Ground Water Issue Paper was prepared for the U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory. The authors were Dr. Saebom Ko (National Research Council), Dr. Scott G. Huling (U.S. EPA) and Dr. Bruce E. Pivetz (Shaw Environmental & Infrastructure Inc.). The authors acknowledge the U.S. EPA Ground Water Forum members for their valuable input and peer review comments. The authors also wish to acknowledge the valuable input and peer review comments provided by Dr. Phil Block (FMC Corp.), Dr. Daniel Cassidy (Western Michigan University), Dr. Wilson Clayton (TriHydro Corporation), Mr. Tom Palaia (CH2M Hill), and Mr. Mike Wireman (U.S. EPA Region 8). The authors thank Ms. Kathy Tynsky (SRA International) for graphics preparation and Ms. Martha Williams (SRA International) for desktop publishing. A portable document format (PDF) version of this document is available for viewing or downloading from *http://www.epa.gov/nrmrl/gwerd/publications.html* (please refer to "In Situ Chemical Oxidation; "Issue Paper"; or "2012").

Appendix Recommended Operating Procedures - Preservation of Ground Water Samples at ISCO Sites Using Ascorbic Acid

Table of Contents

1. PURPOSE (SCOPE AND APPLICATION)

The commingling of organic contaminants and oxidants in ground water or aqueous samples represents a condition in which there is significant potential for oxidative transformation of the contaminants after the sample is collected. Consequently, the quality of the ground water or aqueous sample may be compromised and a false negative result may occur. These recommended operating procedures describe the steps used to preserve ground water samples containing the oxidants permanganate (MnO_4^-), or persulfate ($S_2O_8^{2-}$) and organic contaminants of concern (COCs) prior to analysis. It is applicable for ground water samples containing volatile and non-volatile organic contaminants to be analyzed by gas chromatography (GC), or gas chromatography-mass spectroscopy (GC-MS), using either the purge and trap or headspace sample introduction methods, and high performance liquid chromatography (HPLC).

These procedures are also applicable to bench-scale studies where oxidants are used to investigate the feasibility of ISCO treatment. For example, aqueous samples collected from bench-scale soil reactors are analyzed for organic contaminants, but may also contain the oxidant amended to the reactor to destroy the contaminant. Consequently, the guidelines and general procedures described below also extend to bench-scale studies where the potential for binary mixture aqueous samples may occur, and are analyzed for organic contaminants.

2. METHOD SUMMARY

Based on the measured or estimated oxidant concentration in a ground water or aqueous sample, a specific quantity of the preservative, ascorbic acid, is added to the ground water or aqueous sample to either neutralize or to limit the impact of the residual oxidant on the quality of the sample. Tables 1 and 2 in the *Issue Paper* are used as guidelines to estimate the amount of ascorbic acid to add to a 40 mL VOA vial to preserve binary mixture ground water and/or aqueous samples.

3. REAGENTS

Ascorbic Acid ($C_6H_8O_6$; 176.1 g mol^{-1})

De-ionized (DI) water

Ferrous amonium sulfate (FAS) reagents – sulfuric acid (H_2SO_4), ferrous ammonium sulfate ($Fe(SO_4)_2(NH_4)_2{\cdot}6H_2O$), ammonium thiocyanate (NH_4SCN).

4. EQUIPMENT/APPARATUS

Pipette, volumetric flasks, spectrophotometer (or field test kits)

SenSafe™ or CHEMetrics field test kits for permanganate measurement (if used), or direct measurement.

CHEMetrics or FMC field test kits for persulfate measurement (if used), or measurement using FAS method.

5. HEALTH AND SAFETY PRECAUTIONS

The Materials Safety Data Sheet for ascorbic acid indicates potentially acute health effects: slightly hazardous in case of skin contact (irritant), of eye contact (irritant), of ingestion, of inhalation. In case of skin contact: wash

with soap and water. Cover the irritated skin with an emollient. Get medical attention if irritation develops. Cold water may be used. Other guidelines are available based on exposure (http://www.sciencelab.com/msds.php?msdsId=9922972). It is recommended to wear gloves and safety glasses during all of the procedures described herein due to the potential for exposure to oxidants, impacted ground water sample, and other chemicals involved in these procedures. Always consult site-specific health and safety plans prior to sampling.

6. INTERFERENCES

Colloidal and/or suspended solids in ground water samples may adsorb light and interfere with the measurement of oxidant concentration. For this reason, the ground water sample may require filtration (0.2-0.45 µm) to eliminate background material (i.e., turbidity).

7. PROCEDURES

A. Ascorbic Acid

Prepare ascorbic acid stock solution either in the lab prior to ground water sampling, or in the field. The appropriate use of these stock solutions is dependent on concentrations of the oxidant measured in the ground water samples. The stock solution should be stored in a refrigerator or cooler until used, and discarded after 150 days.

High Concentration Stock Solution: 1.5 M ascorbic acid (e.g., add 264 g of ascorbic acid (MW=176.1 g/mol) to 1L volumetric flask and fill with DI water). This stock solution can be diluted in the preparation of 0.015 and 0.15 M ascorbic acid stock solutions.

Medium Concentration Stock Solution: 0.15 M ascorbic acid: Dilute 1.5 M ascorbic acid stock solution 1:10 (e.g., dilute 100 mL of 1.5 M stock solution to 1L with DI water).

Low Concentration Stock Solution: 0.015 M ascorbic acid: Dilute 1.5 M ascorbic acid stock solution 1:100 (e.g., dilute 10 mL of 1.5 M stock solution to 1L with DI water).

B. Sample Filtration

Filter the ground water or aqueous sample using 0.2–0.45 µm filter (as needed in accordance with the site QAPP or Sampling and Analysis Plan) to eliminate background material (i.e., turbidity) that may interfere with oxidant analysis.

C. Concentration Measurement

Determine the oxidant concentrations (permanganate or persulfate) through one of three methods below.

1) Commercially available test kits
   a. Permanganate: SenSafe™ or CHEMetrics
   b. Persulfate: CHEMetrics or FMC
2) UV-VIS absorbance
   a. Permanganate (direct measurement): wavelength = 525 nm
   b. Persulfate (Ferrous Ammonium Sulfate method): wavelength = 450 nm (Huang *et al.,* 2002; Huling *et al.,* 2011)
3) Colorimetric scales presented in Tables 1 and 2.

Based on the oxidant concentration determined, ascorbic acid stock solution is added to an empty sample vial according to Tables 1 and 2.

D. Quality Assurance and Quality Control (QA/QC)

Quality control includes regularly scheduled analysis of method blanks and sample replicates, and the verification of stock solutions of known concentration via the analysis for concentrations of secondary solutions prepared from the stocks. Results of the analyses of method blanks, replicate analyses, and the verification of stock solution concentrations are logged and maintained in record books specific to the research being conducted. The frequency, control limits, and corrective actions should be appropriately developed for specific applications.

E. Calculations

1) Concentration conversion
   a. Permanganate.

The concentrations of permanganate (MnO_4^-) have been presented in terms of the permanganate anion (118.9 g/mol) (Table 1). However, permanganate is purchased either as sodium permanganate ($NaMnO_4$; 141.9 g/mol) or potassium permanganate ($KMnO_4$; 158.0 g/mol) and as a result conversion to permanganate anion concentrations may be desired to determine

adequate sample preservation needs. Specifically, the ratios 118.9/141.9 (0.84) and 118.9/158.0 (0.75) are used to convert $NaMnO_4$ and $KMnO_4$ respectively, to MnO_4^- (Table A1).

Because 1 mmole of either sodium or potassium permanganate produces 1 mmole of permanganate (Eqs 1 and 2), the molar concentrations of sodium and potassium permanganate are the same as permanganate (Table 3).

$$NaMnO_4 \rightarrow Na^+ + MnO_4^- \quad (1)$$

$$KMnO_4 \rightarrow K^+ + MnO_4^- \quad (2)$$

Converting sodium and potassium permanganate concentrations from mg/L to millimolar, and calculating their permanganate equivalence,

X mg/L $NaMnO_4$ =
(X mg/L) × (1 mmol/141.9 mg) =
X/141.9 mM $NaMnO_4$ =
X/141.9 mM MnO_4^- X/141.9 mM MnO_4^- =
((X/141.9) mmol/L) × (118.9 mg/mmol) =
0.84X mg/L MnO_4^-

NOTE: 1 mmol = 0.001 mol; mM= mmol/L

Y mg/L $KMnO_4$ =
(Y mg/L) × (1 mmol/158.0 mg) =
Y/158.0 mM $KMnO_4$ =
Y/158.0 mM MnO_4^-

Y/158.0 mM MnO_4^- =
((Y/158.0) mmol/L) × (118.9 mg/mmol) =
0.75Y mg/L MnO_4^-

NOTE: 1 mmol = 0.001 mol; mM= mmol/L

b. Persulfate.

The concentration of persulfate is presented in terms of the persulfate anion ($S_2O_8^{2-}$; 192.0 g/mol) (Table A2). However, persulfate is purchased as sodium persulfate ($Na_2S_2O_8$; 238.1 g/mol) and as a result a conversion may be desired to correct for the anionic form of the oxidant and to determine adequate sample preservation needs. Specifically, the ratio of 192.0/238.1 (0.81) is used to convert $Na_2S_2O_8$ to $S_2O_8^{2-}$. Persulfate is colorless and requires field measurement at the well head to determine its presence and concentration in the ground water sample.

Converting sodium persulfate concentrations from mg/L to millimolar, and calculating the persulfate equivalence,

$$Na_2S_2O_8 \rightarrow 2Na^+ + S_2O_8^{2-} \quad (3)$$

Z mg/L $Na_2S_2O_8$ =
(Z mg/L) × (1 mmole/238.1 mg) =
Z/238.1 mM $Na_2S_2O_8$ =
Z/238.1 mM $S_2O_8^{2-}$

Z/238.1 mM $S_2O_8^{2-}$ =
(Z/238.1) mmole/L) × (192 mg/mmole) =
0.81Z mg/L $S_2O_8^{2-}$

2) Required volume and mass of ascorbic acid to neutralize oxidants.

a. Permanganate.

1.8 mole ascorbic acid per mole of permanganate was empirically determined to effectively neutralize permanganate in an aqueous sample containing VOCs (Johnson *et al.*, 2012). Therefore, the mass balance equation (Eq 4) can be set up as follows,

$$1.8C_{MnO4-}V_{MnO4-} = C_{H2A}V_{H2A} \quad (4)$$

Where,
C_{MnO4-} = permanganate concentration determined in step 7.C,

Table A1. Corresponding concentration of sodium permanganate and potassium permanganate to permanganate.

$NaMnO_4$	mg/L	0.90	4.5	9.0	13.5	22.4	35.9	44.9	67.3	89.9	135	180	224	449
	mM	0.006	0.032	0.063	0.095	0.16	0.25	0.32	0.47	0.63	0.95	1.27	1.58	3.16
$KMnO_4$	mg/L	1.00	5.0	10.0	15.0	25.0	40.0	50.0	74.9	100	150	201	250	500
	mM	0.006	0.032	0.063	0.095	0.16	0.25	0.32	0.47	0.63	0.95	1.27	1.58	3.16
MnO_4^-	mg/L	0.75	3.8	7.5	11.3	18.8	30.1	37.9	56.4	75.3	113	151	188	376
	mM	0.006	0.032	0.063	0.095	0.16	0.25	0.32	0.47	0.63	0.95	1.27	1.58	3.16

Table A2. Corresponding concentration of sodium persulfate to persulfate ($S_2O_8^{2-}$).

$Na_2S_2O_8$	mg/L	99	248	496	756	1004	1500	1996	2504	3000	3496	4004	4500	4996
	mM	0.42	1.0	2.1	3.2	4.2	6.3	8.4	10.5	12.6	14.7	16.8	18.9	21.0
$S_2O_8^{2-}$	mg/L	80	200	400	610	810	1210	1610	2020	2420	2820	3230	3630	4030
	mM	0.42	1.0	2.1	3.2	4.2	6.3	8.4	10.5	12.6	14.7	16.8	18.9	21.0

V_{MnO4-} = volume of permanganate solution in the VOA vial (0.04 L),

C_{H2A} = ascorbic acid concentration (0.015, 0.15 or 1.5 M), and

V_{H2A} = volume of ascorbic acid required to neutralize permanganate.

V_{H2A} can be calculated (Eq 5) through rearranging Eq. (4)

$$\mathbf{V_{H2A} = (1.8 \times C_{MnO4-} \times V_{MnO4-})/C_{H2A}} \quad (5)$$

For example, a 40 mL permanganate concentration of 1.27mM (151 mg/L) is neutralized using 1.5 M ascorbic acid. The volume of stock solution and mass of ascorbic acid can be calculated as follows.

$$V_{H2A} = (1.8 \times 1.27 \text{ mmol/L} \times 0.04\text{L}/1.5 \text{ mol/L}) \times (1 \text{ mol}/1000 \text{ mmol}) \times (10^6 \text{ µL}/1\text{L}) = 61 \text{ µL}$$

$$M_{H2A} = 1.5 \text{ mol/L} \times 61 \text{ µL} \times (1\text{L}/10^6 \text{ µL}) \times (176.12 \text{ g/mol}) \times (1000 \text{ mg/g}) = 16.1 \text{ mg}$$

Where,

M_{H2A} = mass of ascorbic acid

The formation of colloidal or particulate MnO_2(s) (i.e., Mn^{+4}) may occur causing a brown tinge appearance of the solution. Incremental amendment of ascorbic acid may be required to further reduce the Mn^{+4} to Mn^{+2}, and eliminate the brownish tinge color. Mn^{+2} is highly soluble and the most desirable form of Mn to minimize the impact of colloidal or particulate matter on the laboratory analytical instruments. Overall, Table 1 is used as a guideline but the actual amount should be based on the amount required to fully eliminate the MnO_4^- and MnO_2(s), and to achieve a clear solution. The volume of ascorbic acid solution added to the sample vial should be recorded so appropriate dilution calculations can be performed to obtain an accurate estimate of the contaminant concentrations.

b. Persulfate.

4 mole of ascorbic acid per mole of persulfate was empirically determined to effectively limit the impact of the oxidant on VOCs in aqueous samples (Huling *et al.*, 2011). Therefore, the mass balance equation (Eq 6) can be set up as follows,

$$4C_{S2O82-}V_{S2O82-} = C_{H2A}V_{H2A} \quad (6)$$

Where,

C_{S2O82-} = persulfate concentration determined in step 7.C,

V_{S2O82-} = volume of persulfate solution in the VOA vial 0.04 L,

C_{H2A} = ascorbic acid concentration (1.5 M),

V_{H2A} = volume of ascorbic acid required to neutralize persulfate

V_{H2A} can be calculated (Eq 7) through rearranging Eq. (6)

$$\mathbf{V_{H2A} = (4 \times C_{S2O82-} \times V_{S2O82-})/C_{H2A}} \quad (7)$$

For example, persulfate concentration is 10.5 mM (2020 mg/L) and neutralized using 1.5 M ascorbic acid. The volume of stock solution and mass of ascorbic acid can be calculated as follows.

$$V_{H2A} = (4 \times 10.5 \text{ mmol/L} \times 0.04\text{L} / 1.5 \text{ mol/L}) \times (1 \text{ mol}/1000 \text{ mmol}) \times (1000 \text{ mL}/1\text{L}) = 1.12 \text{ mL}$$

$$M_{H2A} = 1.5 \text{ mol/L} \times 1.12 \text{ mL} \times (1 \text{ L}/1000 \text{ mL}) \times (176.12 \text{ g/mol}) = 0.3 \text{ g}$$

Where,

M_{H2A} = mass of ascorbic acid

The volume of ascorbic acid solution added to the sample vial should be recorded so appropriate dilution calculations can be performed to obtain an accurate estimate of the contaminant concentrations.

F. Pre-amending Sample Vials With Preservative

Pre-amending the 40 mL sample vials prior to performing ground water sample collection in the field is one step that may help simplify sample preservation procedures. The advantage is that all sample vials are

amended with the preservative in a uniform manner, and this reduces the number of steps and time required during ground water sampling activities in the field. Specifically, this would involve amending the sample vial with an appropriate quantity of ascorbic acid using the procedures recommended above. Successful sample preservation would be immediately obvious in the case with permanganate binary mixtures as the pink/purple color would disappear and the sample would become clear. A persistent pink/purple or brown tinge color would indicate the need for additional preservative. The immediate visual feedback would not occur in the preservation of persulfate binary mixtures due to the absence of oxidant coloration. Success of the preservation method will most likely require prior knowledge of oxidant concentrations in ground water samples to support the selection of an appropriate quantity of preservative. A quality assurance step could include the collection of duplicate samples, and subsequent analysis for persulfate, when time permits, to confirm that a sufficient quantity of preservative was amended. Other appropriate quality assurance steps could be developed.

8. REFERENCES

Huang, K.C., Couttenye, R.A., and Hoag, G.E. 2002. Kinetics of heat-assisted persulfate oxidation of methyl *tert*-butyl ether, *Chemosphere* 49(4), 413-420.

Huling, S.G., Ko, S., and Pivetz, B. 2011. Ground water sampling at ISCO sites – binary mixtures of volatile organic compounds and persulfate. *Ground Water Monit. Remed.* 31(2), Spring 72-79.

Johnson, K.T., Wickham-St. Germain, M., Ko, S. and Huling, S.G. 2012. Binary Mixtures of Permanganate and Chlorinated Volatile Organic Compounds in Groundwater Samples: Sample Preservation and Analysis. *Ground Water Monit. Remed.*, 32(3), Summer 84–92.

9. DISCLAIMER

This recommended operating procedure has been prepared for general use. This is not an official approved U.S. Environmental Protection Agency method and has not undergone the Agency's peer review process.

United States
Environmental Protection
Agency

Please make all necessary changes on the below label, detach or copy, and return to the address in the upper left-hand corner.

If you do not wish to receive these reports CHECK HERE ☐; detach, or copy this cover, and return to the address in the upper left-hand corner.

PRESORTED STANDARD
POSTAGE & FEES PAID
EPA
PERMIT No. G-35

National Risk Management
Research Laboratory
Cincinnati, OH 45268

Official Business
Penalty for Private Use
$300

EPA/600/R-12/049
August 2012