Final Quality Assurance Project Plan (QAPP) Addendum 3

For Use of Passive Flux Meters

Chemplex Parties

March 14, 2025

→ The Power of Commitment

Contents

Appendices

1. Introduction

This Quality Assurance Project Plan (QAPP) Addendum has been prepared by GHD to supplement the Chemplex QAPP dated March 22, 2018. The 2018 QAPP addresses routine groundwater sampling work including sampling methods (GHD, 2018). This QAPP Addendum 3 addresses the use of Passive Flux Meters (PFMs). QAPP Addendum 1 addressed vapor sampling and QAPP Addendum 2 addressed the use of no-purge sampling techniques.

1.1 Passive Flux Meters

Use of PFMs is proposed for the MW-150 location based on initial data collected at this location, with the potential for use at additional locations in the future, depending on effective deployment and retrieval of the PFM and evaluation of the data.

The 2018 QAPP addresses routine groundwater monitoring for volatile organic compounds (VOCs) and polynuclear aromatic hydrocarbons (PAHs) in groundwater. The PFM applies to VOCs and is not intended for PAHs.

This QAPP Addendum provides the framework for additional analysis at the Chemplex site, regarding the implementation of PFMs. The QAPP is a planning document that provides a “blueprint” for obtaining the type and quantity of data needed to support remedial activities and environmental decision making. The QAPP integrates technical and quality aspects of a project and documents all quality assurance (QA), quality control (QC), and technical activities and procedures associated with planning, implementing, and assessing environmental data collection operations.

1.2 Objective of Passive Flux Meters

The objective of employing PFMs is to further characterize potential areas of significant tetrachloroethene (PCE) mass flux. PFMs incorporate activated carbon sorbent and a measured amount of soluble dye deployed into a groundwater monitoring well. When removed, the sorbent is analyzed for compounds of interest (e.g., PCE). The concentration of dye remaining provides a method to estimate Darcy groundwater velocity through the well screen. These data are combined to estimate the mass flux for compound of interest. The data can be variable across methods as identified in in USEPA from a field study that examined PFMs at a fractured bedrock site (USEPA, 2018). PFMs addressed in this QAPP addendum are manufactured by EnviroFlux LLC (EnviroFlux). The PFMs are five feet in length and can contain one to five sample collection regions. For example, five samples may be included to improve resolution on a vertical profile in a heterogenous or fractured bedrock environment. Multiple PFMs can be installed for analysis across a well screen or open borehole longer than five feet.

The objective of PFMs is to determine contaminant flux from a single monitoring point. In environments with tortuous flow paths, heterogeneous conditions, or other complicated hydrogeology, PFMs yield data that may not otherwise be collected or assessed.

2. Purpose of Addendum

The purpose of this Addendum is to define the approach of using PFMs and to provide the modifications of the PFM Standard Operating Procedure (SOP) (Appendix A) to accommodate monitoring wells with artesian conditions.

3. SOP Modifications

3.1 Installation Procedures

The PFMs are delivered in five-foot sections with the previously determined number of samplers installed. If multiple PFMs are to be deployed, they will be connected together. The PFM is pushed into the well to the desired depth. The desired depth may be the bottom of a well or boring. A retrieval cord is anchored by connection to a j-plug or other point to ensure the cord does not fall down the well.

3.2 Retrieval and Sampling Procedures

For each PFM, up to five total samples will be collected. The sorbent will be analyzed by EnviroFlux as described in the SOP. The data will be evaluated for PCE and dye concentrations.

Flowing groundwater collected during PFM deployment and retrieval procedures will be contained and hauled to the Chemplex treatment building. Water may be pumped to the Lyondell process wastewater treatment system for treatment and discharge to the Mississippi River under a National Pollutant Discharge Elimination System (NPDES) Permit.

3.3 Artesian Condition Considerations

With artesian wells, there is a concern regarding dye loss during deployment, particularly if there is a long water column which has been observed at certain monitoring wells at Chemplex. If dye loss is caused by vertical movement through the water column rather than by horizontal movement through the well screen, the groundwater velocity will be overestimated. EnviroFlux has collected data to represent dye loss in long water columns that will be incorporated into the evaluation.

If the artesian conditions require special assessment, an approach similar to an equipment blank may be used where a PFM is subjected to the deployment and removal process to test for loss of dye through these activities. For this blank test, a PFM or multiple PFMs would be deployed at the intended depth and immediately retrieved, and a second PFM or set of PFMs would be deployed at the intended depth for the planned amount of time (e.g., 2 weeks). Data from the rapidly removed PFM(s) would represent dye loss from the deployment and retrieval process and would be used to evaluate the amount of dye loss in the primary sample attributable to groundwater movement through the well screen.

For artesian wells with Margo plugs, a fitting will attached to the bottom of the Margo plug and at the top of the PFM, or another means will be employed to prevent flowing conditions (and thereby removing dye). If PFMs fill the entire well screen, they could rest on the bottom of the well and would not be suspended (which could create a downward stress on the Margo plug).

3.4 Data Validation

When a lab analysis is provided by EnviroFlux for the sorbent samples, GHD will verify the lab data to ensure the data is representative of the mass flux of PCE while deployed.

4. References

GHD, 2018. Quality Assurance Project Plan (QAPP) for the Performance Monitoring Evaluation Operable Unit No. 1, Chemplex Site, Clinton, Iowa. March 22, 2018.

USEPA, 2018. Comparative Evaluation of Contaminant Mass Flux and Groundwater Flux Measurements in Fractured Rock Using Passive Flux Meter. EPA/600/R-17/459. Accessed from: https://cfpub.epa.gov/si/si_public_file_download.cfm?p_download_id=537024&Lab=NRMRL.

Appendix A

Passive Flux Meters Standard Operating Procedure

ENVIROFLUX

PFM Standard Operation Procedure

EnviroFlux, LLC
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Gainesville, FL 32601
Work) 352-554-5296
E-mail: jay.cho@enviroflux.com

1.0. PFM Construction, Storage, and Transport

1.1. Description of PFM

The PFM is a self-contained permeable unit that is inserted into a well or boring such that it intercepts groundwater flow but does not retain it (See Figure 1-1).

The interior composition of the flux meter is a matrix of hydrophobic and hydrophilic permeable sorbents that retain dissolved organic and/or inorganic contaminants present in fluid intercepted by the unit. The sorbent matrix is also impregnated with known amounts of one or more fluid soluble 'resident tracers'. These tracers are leached from the sorbent at rates proportional to fluid flux.

After a specified period of exposure to groundwater flow, the flux meter is removed from the well or boring. Next, the sorbent is carefully extracted to quantify the mass of all contaminants intercepted by the flux meter and the residual masses of all resident tracers. The contaminants masses are used to calculate cumulative and time-averaged contaminant mass fluxes, while residual resident tracer masses are used to calculate cumulative or time- average fluid flux. Depth variations of both water and contaminant fluxes can be measured in an aquifer from a single flux meter by vertically segmenting the exposed sorbent packing, and analyzing for resident tracers and contaminants. Thus, at any specific well depth, an extraction from the locally exposed sorbent yields the mass of resident tracer remaining and the mass of contaminant intercepted. Note that multiple tracers with a range of partitioning coefficients are used to determine variability in groundwater flow with depth that could range over orders of magnitude. This data is used to estimate local cumulative water and contaminant fluxes.

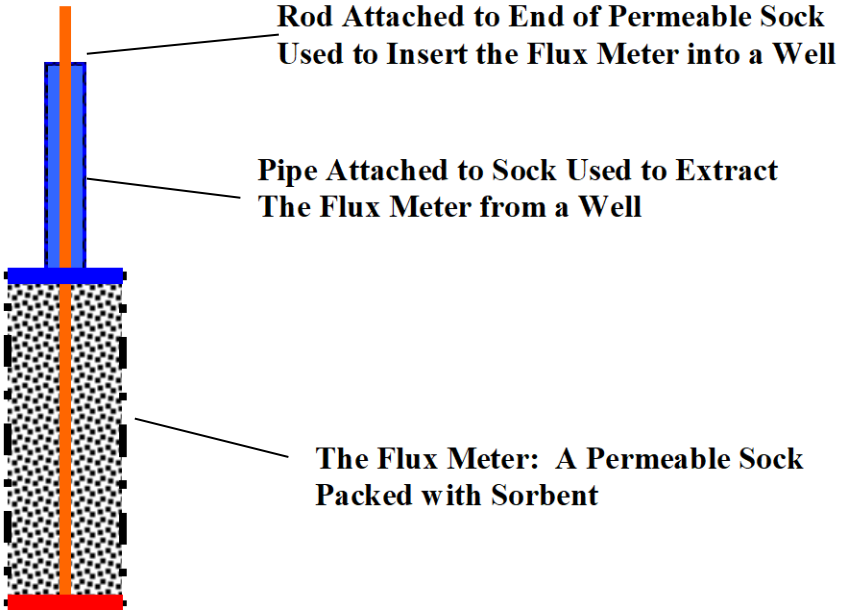

Figure 1-1. Schematic of a Flux meter comprised of a permeable sock filled with a selected sorbent.

1.2. Assembly of PFMs

The passive flux meters are constructed in a pipe having the same diameter as the well screen. The pipe used for construction should be slightly (0.1 inch) smaller diameter than the well screen. Prior to packing the PFMs with AC or AC with resin, the sock is attached to the center tube of the PFM. The center tube for 2-inch wells consists of 1/2 inch PVC. The bottom of the sock is clamped to the PVC pipe. AC is transferred into the PFM sock. After adding the required amount of AC up to the desired sampling interval, a thin viton washer is placed. This process is continued until completing. At the top of the PFM a thick viton washer is added followed by a sponge cut to the same size as the viton washer. The sponge is used to minimize AC loss from the top of the PFM. At this point the top of the sock is attached to the retrieval collar with a wire loop on which PFM retrieval rope is attached using a carabiner connector.

1.3. PFM Storage

If the PFMs are constructed for transport to the field site, the PFMs will be stored in tubes and a cooled area. PFM storage tubes are constructed using PVC pipe the same diameter as the packing tube. The PFM is then extruded from the packing tube into the storage tube. The storage tube is then sealed using gas tight mechanical plugs. The PFMs are then placed in cooled environment, under air conditioner until transport.

1.4. PFM Transport

The PFMs are transported in cardboard boxes to the site via. FedEx air express.

2.0. PFM Deployment and Retrieval/sampling

2.1. PFM Installation

At the field site the PFM in the transport tube is prepared for PFM installation into the well casing. A rope is attached to the top of the PFM using a safety carabineer connector. The tube is lined up with the top of the well casing and section of push rod (or by hand) is used to push the PFM from the tube into the top section of well casing.

Once the PFM is placed on the top of well and insert the tip of weight into the PVC center tube of PFM. Then lower the PFM with a weight to the bottom of the well or the desired depth. Another option could be pushing PFM into position in the well using Geoprobe rods while holding retrieval rope.

If multiple PFMs are deployed on a single line, short sections of cable (about 5.2ft long) are thread through the upper PFM to link the PFMs together well. When inserting the PFM some back

pressure may build since the water in the well casing must flow through the center tube as the PFM is inserted. Proceed slowly as pressure builds. The weight should be retrieved back when done and used for next PFM installation. The PFM retrieval rope is then secured to the well lid using cable ties or others to ensure that it will not be lost to the well head.

2.2. PFM Retrieval

PFMs are retrieved using the rope. The top PFM in the well is extracted first by gently pulling up on the rope (heavy work gloves should be worn when pull on rope). The PFM should be pulled to the top of the well casing. The PFM will occasionally catch on joints in the well screen. Simply apply more pressure to overcome. If the PFM will not move look at troubleshooting options below. When the PFM is at the top of the well casing untangle any rope (or wires) that are twisted at the well head. Thread the retrieval rope through a 5ft transport PVC pipe and place the pipe over the well to guide and contain the extruded PFM. Move the PFM to the sampling workstation.

2.3. PFM Sampling

A tarpaulin acts as a 'protective flooring' for the work zone. A portable table is used as a work zone for sampling the PFMs. Nitrile protective gloves and necessary other protective clothing will be worn by all samplers. A lined bucket (5gal) is placed under the work area to capture un-sampled residual activated carbon from the retrieved PFM. The sock is extruded from the PVC pipe to the sampling interval extent. The flexible mesh packing material is cut and the sorbent (activated carbon) captured in plastic or stainless steel mixing bowls for homogenization using a stainless steel spatula. A sub-sample is then transferred into 120 mL jars. It is very important to take a well homogenized sample. The jars are stored in a cooler for transport back to the laboratory for analysis. The center tube and viton washers are measured to obtain the sample interval lengths in the PFM. Sampling materials, spatula, scissors, mixing bowls are wiped clean to remove carbon (or resin) particles prior to retrieving the next PFM.

2.4. Transportation and Storage of PFM samples: Sorbent (GAC) samples are stored on-site in coolers then shipped via overnight air express (e.g., FedEx) to the EnviroFlux laboratory. Samples are stored in a cold storage room or refrigerator at 4^{o}C until analysis. Addition of preservatives is not necessary for PFM samples.

2.5. Troubleshooting PFM extraction

In the event that the PFM is difficult to remove from the well the following steps might be considered. If available, use metal rods or pvc pipes (1/2-inch for 2-inch PFM and 1-1/2-inch for 4-inch PFM), push down to move the PFM below the obstruction. Holding both the retrieval rope and the push rod, surge the PFM up and down to attempt to overcome the obstacle.

In the event that the rope breaks or becomes detached from the PFM, a corkscrew attachment can be added to the rod to attempt to "grab" the top of the PFM and advance it upwards. If this fails the corkscrew can be used to dig into the AC and viton washers again in an attempt to "grab" the PFM. Finally, a pump with tubing lowered to the top of the PFM can be used to extract the AC. This slow process obviously destroys the PFM, but can be successful in clearing the well.

3. Standard operating procedure for extraction and analysis of analytes from passive flux meter sorbents

3. 1. Scope and application

This SOP describes the sample procedures used by EnviroFlux LLC., for extraction and analysis of target analytes (including tracers) from sorbents used in Passive flux meter (PFM) inserted in monitoring wells.

The Passive flux meter (PFM) contains a permeable sorbent (AC and/or resin) which allows groundwater flow through the device. The sorbent matrix (AC) should be preloaded with five resident tracers. The tracers are displaced from the sorbent at rates proportional to groundwater flux. Simultaneously the sorbent (AC and/or resin) retains dissolved contaminants such as TCE, PFAS in the GW flowing through PFM. After a 2-3 weeks period of exposure to GW, the PFMs are removed from the well. The sorbent (AC and/or resin) samples from the PFM are sub-sampled into a 125ml of glass jars for AC and a 125ml of HDPE bottle for resin in the field and transferred to the Enviroflux lab for analysis. The sorbent is then extracted to quantify the residual masses of all resident tracers and/or contaminants. The extracted samples are analyzed for Darcy and contaminants fluxes.

The selected constituents should be target field contaminants and alcohol tracers:
The alcohol tracers are methanol, ethanol, iso-propanol, t-butanol, and 2,4-dimethyl-3-pentanol and the contaminants could be VOCs, CVOCs, semi-VOCs, PFAS, pesticides, PAHs, metals, nutrients, others.

3.2. Purpose

The purpose of this SOP is to: (1) insure reliable and reproducible results, and (2) track possible sources of error in the extraction of alcohol tracers and contaminants from the PFM sorbents and the subsequent analysis by analytical methodology.

3.3. Procedures

<u>Transportation and Sample Process</u>

Transportation and Storage: The field samples should be shipped to the Enviroflux laboratory packed in coolers containing "blue ice or ice" via overnight air express (e.g., FedEx) and stored in the refrigerator.

Analytical lab: PFM sample analysis should be conducted by certified laboratories or those accredited by DOD ELAP, other professional analytical labs, or Enviroflux lab. Our contract laboratories accredited by DOD ELAP handle most contaminants, including PFAS, semi-VOCs, metals, PAHs, and nutrients. However, for certain VOC samples, the analytical lab within the Chemistry Department at the University of Florida should be utilized. For PFM trace analysis and select CVOC analyses, the Enviroflux lab should be used to ensure optimal PFM results. While this lab is not accredited, it adheres to QA/QC procedures comparable to those of accredited labs.

Sample Process: As received the PFM samples from the field site should be extracted to quantify the residual masses of all resident tracers and contaminants. If not, the PFM samples should be stored in a refrigerator at 4^{o}C, until extraction/analysis, but no more than 1 month. 40 ml VOA vials are used for AC sampling. The vials are weighed empty (nearest 0.01 g) and recorded. A few grams of PFM sorbent samples from 125 ml sample jars should be subsampled into the pre-weighed 40-ml VOA vials. Following addition of AC, the vials are weighed. The vials weights are then recorded. The vials are then filled with extraction solvent using a fixed volume dispenser and sealed. Then the sample vials will be rotated, set at 20% rotation speed, for about 24 hours on a rotator (Glas-Col model RD 4512) and then refrigerated for several hours to allow suspended particulate matter to settle out.

Sub-sampling

When the suspended particle completely settled out, the supernatant should be taken into two separate 2-ml GC vials, one for alcohol tracer analysis and another for contaminants. Note that if the suspended particulate matter does not settle out, a syringe filter (0.22 micron) should be used to remove the suspended GAC or resin particles from the samples to protect analysis instruments. Then PFM samples will be sub-sampled into 2 ml GC vials. Pipets will be used to transfer samples from 40-mL sample vials to the 2-mL GC vials.

Chemicals and Laboratory Supplies and Materials

Certified ACS grade pure alcohols and solvent should be purchased from one or more of the following vendors; Fisher Scientific, VWR and/or Sigma-Aldrich and used as received. Alcohol tracers (methanol, ethanol, iso-propanol, tert-butanol, 2,4-dimethyl-3-pentanol) and extraction solvents are purchased from Sigma-Aldrich, all with purities >98%.

Volumetric class 'A' pipettes and volumetric class 'A' flasks for preparation of calibration standards and sample dilutions. Disposable Pasteur glass pipettes for sub-sampling. GC vials (2 mL) with Teflon-faced caps for GC analysis.

Calibration and Stock Standard Solutions

Contaminant stock standard solutions are purchased from Restek or Sigma Aldrich. If needed, individual alcohol tracer and some contaminant stock standard solutions are prepared in reagent solvent using volumetric glassware and stored in 20 or 40mL glass vials with Teflon-lined caps. Stock solutions should be kept in a refrigerator at 4^{o}C. Fresh stock standards should be prepared every month and follow protocols outlined in the Federal Register, Rules and Regulations, "Standard Stock Solutions".

Mixed calibration standards should be prepared by diluting stock standards in reagent solvent using volumetric glassware. A minimum of four standards should be prepared and should bracket the expected concentration range.

Analytical Instrumentation

A ThermoScientific Orbitrap Exploris GC/MS, ThermoScientific Trace 1610, and Perkin Elmer Clarus 590 Gas Chromatograph equipped with FID and ECD detectors, autosampler, a temperature-programmable oven, heated auto-injector and detector zones, a 60 meter or greater capillary separations column, nitrogen carrier gas, standard compressed air and hydrogen flame gases and controlled by a PC-based data acquisition/analysis software system.

Sample Analysis

All analyses should be performed consistent with the quality assurance program of Enviroflux. Individual alcohol tracer and contaminant identification should be based on absolute retention times compared to calibration standards. Alcohol tracer and contaminant concentrations should be calculated on chromatographic peak area response converted to units of concentration in ug/L or mg/L based on standard calibration curves.

Interferences

Contamination by carry-over may occur when high-level and low-level samples are sequentially analyzed. Subsequent dilution and reanalysis should be completed on samples identified as outside the standard concentration bracket. Samples analyzed immediately following a 'high-concentration sample' should be reanalyzed. In an attempt to minimize carryover, samples suspected of being in a higher concentration range should be isolated and bracketed by the analysis of reagent solvent samples.

Safety

Gloves and eye protection will be worn during all extraction activities. The Materials Safety Data Sheets (MSDS) will be kept in the lab for information on toxicity, flammability, and other hazard data.

4. Standard operating procedure for the sampling, collection, extraction and analysis of Alcohol Tracers utilized at EnviroFlux

The following described Standard Operating Procedures (SOP) are currently utilized by EnviroFlux.

4.1 Scope and application

This Standard Operating Procedure (SOP) describes the extraction and analytical procedures of alcohol tracers from a sorbent (Granular Activated Carbon) packed into passive flux meters. These alcohols are used as "resident" tracers that are pre-loaded on to the sorbent packed into the flux meter sock; loss of tracers via desorption and advective/diffusive/dispersive transport resulting from groundwater flow under natural hydraulic gradients is measured to estimate cumulative groundwater and contaminant fluxes. The alcohol tracers are methanol, ethanol, iso-propanol, t-butanol, and 2,4-dimethyl-3-pentanol.

4.2. Purpose

The purpose of this SOP is to: (1) insure reliable and reproducible results, and (2) track possible sources of error in the extraction of alcohols from a sorbent and the subsequent analysis by GC-FID analytical methodology.

4.3. Procedures

Sample Containers, Collection, Transportation and Storage

Sample Containers: Sorbent samples should be collected in 40mL VOA vials (Fisher Scientific Catalog # 05-719-106) sealed with Teflon-lined septa caps. Vials should contain 20mL of extraction solvent, prepared previously in the laboratory. All vials and caps are non-reusable.

Sample Collection: Sorbent aliquots collected over 1 to 5 foot increments from a Passive Flux meter should be transferred to a mixing bowl and homogenized well with a metal spatula. Approximately 10 to 20 grams of mixed sorbent should be placed into the 40 mL VOA vials containing extracting solvent.

Transportation and Storage: Field samples should be stored, on site, in coolers containing ice then shipped via overnight air express (e.g., FedEx) to the Enviroflux laboratory. Samples should be stored in a refrigerator at 4^{o}C until extraction and GC analysis.

Holing Time: Adhere to holding times specified in the relevant standard method, typically 30 days for PFM samples.

Laboratory Supplies and Materials

Volumetric class 'A' pipettes and volumetric class 'A' flasks for preparation of calibration standards and sample dilutions. Disposable Pasteur glass pipettes (Fisher Catalog # 13-678-6A) for sub-sampling. GC vials (2 mL) with Teflon-faced caps (Fisher Catalog # 03-375-16A) for GC analysis.

Reagents

Certified ACS grade pure alcohols and solvent purchased from one or more of the following vendors: Fisher Scientific, VWR and/or Sigma-Aldrich and used as received.

Calibration Solutions

Individual alcohol stock standard solutions should be prepared in certified ACS grade solvent, methylene chloride, using volumetric glassware and stored in 20 mL glass vials with Teflon-lined caps. Stock solutions should be kept in a refrigerator at 4^{o}C. Fresh stock standards should be prepared every.

Mixed calibration standards should be prepared by diluting stock standards in methylene chloride using volumetric glassware. A minimum of five standards should be prepared and should bracket the expected concentration range.

Instrument Calibration

Perform initial calibration using at least five concentration levels of calibration standards covering the expected range of analytes. Calculate calibration factors (CF) and establish the calibration curve.

Verify calibration daily before sample analysis with a mid-level calibration standard. Acceptable criteria for calibration verification are usually within ±10% of the expected value.

Sample Analysis

The established analytical method, a modified 8015C, for determining and quantifying alcohol concentrations in extracted samples involves the direct injection of the sample into a PerkinElmer Clarus 590 Gas Chromatograph (GC) equipped with a flame-ionization detector (FID). This method provides reliable and reproducible quantitation of alcohol at concentrations greater than or equal to 0.1 mg/L, which is the reportable minimum detection limit (MDL). The linear standard calibration range for the FID response is from the reported MDL up to a concentration of approximately 1500 mg/L per analyte of interest.

GC Procedure

Capillary GC; Rtx-624 Capillary Column (or J&W Scientific) ; 60m length; 0.53mm I.D.; 3.00microm df; Temp. Limits: -20 to 240 deg. C,

GC Analysis Method
Injection port temperature 200 C
FID detector temperature 230 C
Column Temperature Program:
Isothermal at 40C for 10 min; ramp to 110C at 5 C/min, hold 3min; ramp at 20C/min to 200C, hold 1 min.
Carrier gas Helium 99.9995% purity
Flame gases Air, 99.995% purity; Hydrogen, 99.995% purity

The temperature program can be changed dependent upon the sampling site (due to background baseline) and the target contaminants.

4.4 Quality Control

Method Blanks

Analyze method blanks to check for contamination during sample preparation and analysis. Ensure that blanks are free of target analytes or below the method detection limits (MDLs).

Laboratory Control Samples (LCS)

Analyze LCS to assess method accuracy. Prepare LCS by spiking a known quantity of target analytes into a clean matrix. Recovery should be within 70-130% of the expected value.

Matrix Spikes and Matrix Spike Duplicates (MS/MSD)

Analyze MS/MSD to evaluate matrix effects and method precision. Spike a known quantity of target analytes into a sample matrix and analyze in duplicate. Calculate the percent recovery and the relative percent difference (RPD). Acceptable recovery is typically 70-130%, and RPD should be $\leq$20%.

Duplicate Sample Analyses

Duplicate analyses are performed to evaluate the reproducibility of the method. Results of the duplicate analyses are used to determine the RPD between replicate samples. For each parameter analyzed, at least one duplicate sample is run per group of 20 samples.

Quality Control of GC System

GC injector septa should be changed every 100 to 150 injections, or sooner if instrument performance deteriorates. Injection port glass liner should be cleaned or changed after 100 to 150 injections or sooner if instrument performance deteriorates.

A method blank and matrix blank should be analyzed at the beginning of each sample set and after every 20 samples to monitor instrument background. A complete set of calibration standards (minimum 5) should be analyzed at the beginning of each day with a mid-range continuing calibration standard analyzed after every 20 samples.

4.5 Data Analysis:

Data Acquisition:

Acquire data ensuring adequate resolution and sensitivity to detect target analytes.

Integration and Quantification:

Integrate chromatographic peaks consistently. Manual integration should be minimized and justified. Quantify analytes using the calibration curve.

Quality Control Review:

Review QC sample results, including method blanks, LCS, duplicate, and MS/MSD. Ensure all QC criteria are met. Investigate and document any deviations.

Data Reporting:

Report concentrations of target analytes above the method detection limits (MDLs). Include any data qualifiers if QC criteria are not met.

Corrective Actions:

Investigate any QC failures to identify root causes. Implement corrective actions, such as reanalysis of samples, recalibration, or instrument maintenance.

4.6 Routine Maintenance:

Perform routine maintenance on the GC system to ensure optimal performance, including cleaning, column replacement, and leak checks. Conduct regular performance checks, such as checking for adequate resolution and sensitivity.

4.7 Training and Competency:

Ensure all personnel are adequately trained in GC operation and QA/QC procedures. Regularly assess the competency of personnel through proficiency testing and review of their analytical work. By following this QA/QC procedure, you can ensure the reliability and accuracy of alcohol analysis using GC FID, leading to confident and reproducible results.

5. Standard operating procedure for the sampling, collection, extraction and analysis of low range of CVOCs utilized at EnviroFlux

The following described Standard Operating Procedures (SOP) are currently utilized by EnviroFlux.

5.1. Scope and application

This Standard Operating Procedure (SOP) describes the extraction and analytical procedures of CVOCs from sorbent (Granular Activated Carbon or resin) packed into the passive flux meters. The mass of CVOCs accumulated by sorption on the sorbent from the groundwater passing through the passive flux meter is used to estimate the cumulative contaminant flux. The target analytes are CVOCs (e.g., TCE, PCE, EDB, etc).

5.2. Purpose

The purpose of this SOP is to: (1) insure reliable and reproducible results, and (2) track possible sources of error in the extraction of CVOCs from a sorbent and the subsequent analysis by analytical methodology.

5.3. Procedures

Sample Containers, Collection, Transportation and Storage

Sample Containers: Sorbent samples should be collected in 40mL VOA vials (Fisher Scientific Catalog # 05-719-106) sealed with Teflon-lined septa caps. Vials should contain 20mL of extraction solvent, prepared previously in the laboratory. All vials and caps are non-reusable.

Sample Collection: Sorbent aliquots collected over some increments from a Passive Flux meter should be transferred to a mixing bowl and homogenized well with a metal spatula. Approximately 10 grams of mixed sorbent should be placed into the 40 mL VOA vials containing extracting solvent.

Transportation and Storage: Field samples should be stored, on site, in coolers containing ice then shipped via overnight air express (e.g., FedEx) to the Enviroflux laboratory. Samples should be stored in a refrigerator at 4^{o}C until extraction and GC analysis.

Holing Time: Adhere to holding times specified in the relevant standard method, typically 30 days for PFM samples.

Laboratory Supplies and Materials

Volumetric class 'A' pipettes and volumetric class 'A' flasks for preparation of calibration standards and sample dilutions. Disposable Pasteur glass pipettes for sub-sampling. GC vials (2 mL) with Teflon-faced caps for GC analysis.

Reagents

Certified ACS grade pure alcohols and solvent purchased from one or more of the following vendors: Fisher Scientific, VWR, QEC, and/or Sigma-Aldrich and used as received.

Calibration Solutions

Individual alcohol stock standard solutions should be prepared in certified ACS grade solvent, methylene chloride, using volumetric glassware and stored in 20 mL glass vials with Teflon-lined caps. Stock solutions should be kept in a refrigerator at 4^{o}C. Fresh stock standards should be prepared every month.

Mixed calibration standards should be prepared by diluting stock standards in methylene chloride using volumetric glassware. A minimum of five standards should be prepared and should bracket the expected concentration range.

Instrument Calibration

Perform initial calibration using at least five concentration levels of calibration standard covering the expected range of analytes. Calculate calibration factors and establish the calibration curve.

Verify calibration daily before sample analysis with a mid-level calibration standard. Acceptable criteria for calibration verification are usually within ±10% of the expected value.

Sample Analysis

The established analytical method, a modified 551.1 with GC ECD for low level CVOCs, for determining and quantifying CVOCs concentrations in extracted samples is direct injection into a Perkin Elmer Clarus 590 Gas Chromatograph (GC) equipped with a Electron Capture detector (ECD). This method provides reliable and reproducible quantitation of CVOCs compounds at

concentrations greater than or equal to 1 ug/L, which is the reportable minimum detection limit (MDL).

GC Procedure
Capillary GC; Rtx-624 Capillary Column (or J&W Scientific); 60m length; 0.53mm I.D.; 3.00microm df; Temp. Limits: -20 to 240 deg. C,

GC Analysis Method
Injection port temperature 200-230 C
ECD detector temperature 300 C
Column Temperature Program:
Isothermal at 40C for 5 min; ramp to 100C at 5 C/min, hold 1min; ramp at 20C/min to 230C, hold 1 min.
Carrier gas Nitrogen 99.9995% purity
Make-up gases Nitrogen 99.9995% purity

The temperature program can be changed dependent upon the sampling site (due to background baseline) and the target contaminants.

5.4 Quality Control

Method Blanks

Analyze method blanks to check for contamination during sample preparation and analysis. Ensure that blanks are free of target analytes or below the method detection limits (MDLs).

Laboratory Control Samples (LCS)

Analyze LCS to assess method accuracy. Prepare LCS by spiking a known quantity of target analytes into a clean matrix. Recovery should be within 70-130% of the expected value.

Matrix Spikes and Matrix Spike Duplicates (MS/MSD)

Analyze MS/MSD to evaluate matrix effects and method precision. Spike a known quantity of target analytes into a sample matrix and analyze in duplicate. Calculate the percent recovery and the relative percent difference (RPD). Acceptable recovery is typically 70-130%, and RPD should be $\leq$20%.

Duplicate Sample Analyses

Duplicate analyses are performed to evaluate the reproducibility of the method. Results of the duplicate analyses are used to determine the RPD between replicate samples. For each parameter analyzed, at least one duplicate sample is run per group of 20 samples.

Quality Control of GC System

GC injector septa should be changed every 100 to 150 injections, or sooner if instrument performance deteriorates. Injection port glass liner should be cleaned or changed after 100 to 150 injections or sooner if instrument performance deteriorates.

A method blank and matrix blank should be analyzed at the beginning of each sample set and after every 20 samples to monitor instrument background. A complete set of calibration standards (minimum 5) should be analyzed at the beginning of each day with a mid-range continuing calibration standard analyzed after every 20 samples.

5.5 Data Analysis:

Data Acquisition:

Acquire data ensuring adequate resolution and sensitivity to detect target analytes.

Integration and Quantification:

Integrate chromatographic peaks consistently. Manual integration should be minimized and justified. Quantify analytes using the calibration curve.

Quality Control Review:

Review QC sample results, including method blanks, LCS, duplicate, and MS/MSD.
Ensure all QC criteria are met. Investigate and document any deviations.

Data Reporting:

Report concentrations of target analytes above the method detection limits (MDLs).
Include any data qualifiers if QC criteria are not met.

Corrective Actions:

Investigate any QC failures to identify root causes. Implement corrective actions, such as reanalysis of samples, recalibration, or instrument maintenance.

5.6 Routine Maintenance:

Perform routine maintenance on the GC system to ensure optimal performance, including cleaning, column replacement, and leak checks. Conduct regular performance checks, such as checking for adequate resolution and sensitivity.

5.7 Training and Competency:

Ensure all personnel are adequately trained in GC operation and QA/QC procedures. Regularly assess the competency of personnel through proficiency testing and review of their analytical work. By following this QA/QC procedure, you can ensure the reliability and accuracy of CVOC analysis using GC ECD, leading to confident and reproducible results.

6. This method involves the determination of VOCs and CVOCs in various matrices using Gas Chromatography/Mass Spectrometry (GC/MS) utilized at the University of Florida (Department of Chemistry)

6.1. Sample Collection:

Sample Collection:

Use appropriate, clean, and contaminant-free containers (e.g., 40 mL glass vials with Teflon-lined septa).

Sample Preservation:

Store samples at 4°C from the time of collection until analysis.

Holding Times:

Adhere to holding times specified in the relevant standard method, typically 30 days for PFM samples.

6.2. Instrument Calibration:

Initial Calibration:

Perform initial calibration using at least five concentration levels of calibration standards covering the expected range of analytes. Calculate calibration factors (CF) or response factors (RF) and establish the calibration curve.

Calibration Verification:

Verify calibration daily before sample analysis with a mid-level calibration standard.
Acceptable criteria for calibration verification are usually within ±20% of the expected value.

6.3. Quality Control Samples:

Method Blanks:

Analyze method blanks to check for contamination during sample preparation and analysis.
Ensure that blanks are free of target analytes or below the method detection limits (MDLs).

Laboratory Control Samples (LCS):

Analyze LCS to assess method accuracy. Prepare LCS by spiking a known quantity of target analytes into a clean matrix. Recovery should be within 70-130% of the expected value.

Matrix Spikes and Matrix Spike Duplicates (MS/MSD):

Analyze MS/MSD to evaluate matrix effects and method precision.
Spike a known quantity of target analytes into a sample matrix and analyze in duplicate.
Calculate the percent recovery and the relative percent difference (RPD). Acceptable recovery is typically 70-130%, and RPD should be $\leq$30%.

Internal Standards:

Add internal standards to all samples, standards, and QC samples to correct for variability in sample preparation and instrument response.
Ensure internal standard responses are consistent and within ±50% of the average response in the calibration standards.

6.4. Sample Analysis:

Sample Introduction:

Use appropriate sample introduction techniques, such as direct injection.

GC/MS Procedure:

Follow the specific GC/MS operating conditions including column type, temperature program, and MS settings.

Mass Spectrometry: ThermoScientific Orbitrap Exploris GC
Ionization: electron ionization (EI), 70 eV
Ion source temperature = 250 C
Resolution: 30000
MS: SIM

Gas Chromatograph:
ThermoScientific Trace 1610:
GC Injection port: 250 C
GC helium carrier gas: constant flow, 1 mL/min: vacuum compensated.
Injection mode: split, split flow rate =10 mL/min)
Temperature program: 30C(0-4 min) => 125C@90C/min => 200C@50C/min
GC Column: Restek Corp. Rxi-5ms (30 meter x 0.25 mm i.d. and 0.25 um df)
Autosampler: ThermoScientific AI/AS1610; Injection volume: 1 µL

6.5. Data Analysis:

Data Acquisition:

Acquire data in selected ion monitoring (SIM) mode or full scan mode as required.
Ensure adequate resolution and sensitivity to detect target analytes.

Integration and Quantification:

Integrate chromatographic peaks consistently. Manual integration should be minimized and justified. Quantify analytes using the calibration curve. Correct for any internal standard variations.

Quality Control Review:

Review QC sample results, including method blanks, LCS, MS/MSD, and internal standards. Ensure all QC criteria are met. Investigate and document any deviations.

Data Reporting:

Reporting Limits:

Report concentrations of target analytes above the method detection limits (MDLs).
Include any data qualifiers if QC criteria are not met.

Documentation:

Maintain detailed records of sample collection, analysis, and QC procedures.
Store data and records in a secure and organized manner for future reference.

6.6. Corrective Actions:

QC Failure Investigation:

Investigate any QC failures to identify root causes. Implement corrective actions, such as reanalysis of samples, recalibration, or instrument maintenance.

Documentation of Corrective Actions:

Document all corrective actions taken, including the rationale and results of any reanalysis.

6.7. Instrument Maintenance:

Routine Maintenance:

Perform routine maintenance on the GC/MS system to ensure optimal performance, including cleaning, column replacement, and leak checks.

Performance Checks:

Conduct regular performance checks, such as tuning the MS and checking for adequate resolution and sensitivity.

7.0. Quality Assurance Project Plan

7.1. Purpose and Scope of the Plan
This Quality Assurance plan focuses on field installation, sampling and processing of data from the Flux Meters.

7.2. Quality Assurance Responsibilities
The responsibility for QA should be by the Lab Manager/Project Manager of EnviroFlux.

7.3. Data Quality Parameters
This section discusses measures to be taken to ensure the representativeness, completeness, comparability, accuracy, and precision of the data.

Accuracy

Accuracy is defined as the closeness of the results to the true value.

The percent recoveries of surrogates, QC check standards, and matrix-spiked analytes are used to evaluate the accuracy of an analysis. The percent recovery represented by X can be calculated using the following equations:

For surrogates and QC check standards:

$$X = \frac{SSR}{SA} x\,100 \qquad 1$$

For matrix spikes:

$$X = \frac{SSR - SS}{SA} \times 100$$

where:

SSR = Spiked sample result
SS = Sample result
SA = Spike added from spiking mix

The mean percent recovery (X) is defined by:

$$\overline{X} = \frac{\sum_{i=1}^{N} X_i}{N} \qquad 2$$

where:

X_i = The percent recovery value of a spike replicate
N = Number of spikes

Precision

Precision is a measure of the mutual agreement among individual measurements of the same parameters under prescribed similar conditions.

The analytical precision is determined using results from duplicate or replicate analyses of samples and from matrix spike results for a given matrix. The Relative Percent Difference (RPD) is used to evaluate the precision of duplicate analyses. Relative Percent Difference is defined in the following equation:

$$\%RPD = \frac{2(X1 - X2)}{\bar{x}} \times 100 \qquad 3$$

X1 = First duplicate value
X2 = Second duplicate value

When replicate analyses are performed, precision is measured in terms of the Standard Deviation (SD) which is defined in the following equation:

$$S = \sum_{i=1}^{N} \left[\frac{(X_i - \bar{X})^2}{N - 1} \right]^{\%} \qquad 4$$

where:

X_i = The recovery value of a spike replicate
X = Arithmetic average of the replicate values
N = Number of spikes

Completeness

Completeness is defined as the percent of parameters falling within acceptance criteria and the results subsequently reported. Acceptable recovery is typically 70-130%, and RPD should be $\leq$ 20%.

The general requirement of this quality assurance program is to analyze a sufficient number of standards, replicates, blanks, and spike samples to evaluate results adequately against numerical QA objectives.

7.4. Calibration Procedures, Quality Control Checks, and Corrective Action

The focus of the following section is to describe initial and continuing calibration procedures for analytical instrumentation, duplicate and control testing and data reduction, validation, and reporting.

Supplies and Quality Control Materials

All supplies (i.e., glassware, chemicals, reagents) used will be of the best possible quality to ensure proper instrument calibration and avoid contamination. All reagents used are prepared from Analytical Reagent Grade (AR) chemicals or higher purity grades, unless such purity is not available. The preparation of all reagents will be documented, including source, mass, and dilutions. Each reagent will be clearly labeled with the composition, concentration, date prepared, initials of preparer, expiration date, and special storage requirements, if any.

Reagents

Reagent solutions are stored in appropriate glass, plastic, or metal containers. Reagents are stored under conditions designed to maintain their integrity (refrigerated, dark, etc.). Shelf life is listed on the label and the reagent is discarded after it has expired. Dry reagents such as sodium sulfate, silica gel, alumina, and glass wool are either muffled at 400°C or extracted with solvent before use for organic chemical analyses. Water used in the laboratory is glass distilled or deionized, and periodically checked for purity. In addition, water used in the organics area is carbon-filtered or purchased as certified grade. All organic solvents used are either glass-distilled or pesticide grade. Solvents and reagent solutions are checked for contamination by employing reagent blanks, before use in any analysis.

Quality Control Reference Materials

All Quality Control Reference Materials are acquired only from authorized vendors or sources commonly used by U.S. EPA Regional Laboratories.

Standards Traceability

When standard reference materials arrive at the laboratory, they are registered in a bound log book, "Standards Notebook for Neat Materials and Primary Solutions." An example of a logging sequence is used to illustrate this process.

(1-S-XXX-12-4) (label and log sequence)

where:

1 = Notebook log number
S = Standard Notebook--"Neat and Primary Standards"
XXX = Receiving analyst's initials
12 = Notebook page
4 = Entry number on notebook page

All working standards prepared at the site lab are logged in the "Standards Notebook for Intermediate and Working Standards." A similar labeling convention has been adopted for classifying these working standard materials. An example is given below.

1-W-XXX-6-5 (label and log)
Where:

1 = Number of notebook
W = Standards notebook - "Intermediate and Working" Standard
XXX = Analyst's initial
6 = Page Number

5 = Page entry number in sequence

Instrument Calibration

Every instrument used to analyze samples must pass the calibration criteria established in the appropriate SOP. Initial calibration criteria for instrument linearity, sensitivity, resolution, and deactivation must be met before samples can be analyzed. Sustained performance is monitored periodically during sample analyses by the use of continuing calibration check standards.

GC Section

Initial Calibration

The linear calibration range of the instrument must be determined before the analysis of any samples. Gas chromatographic conditions used for sample analyses are used during calibration.

The calibration is performed in accordance with the SOP derived from the methods used. For most GC analyses, a 5-level calibration is run. The concentrations of the standards must bracket the linear range of the instrument. Calibration using fewer than 5-levels is done only when specifically allowed by the method.

Relative Retention Times and Relative Response Factors

Instrument calibration and sample analysis must be performed using appropriate internal standards to establish relative retention times (RRT) and relative response factors (RRF) where required. Internal standards appearing in a chromatogram will establish primary search windows for those target compounds nearby in the chromatogram. RRT are calculated using this equation:

$$RRT = \frac{RT^{target}}{RT^{is}}$$ 5

The RRF may be calculated as follows:

$$\text{Absolute Response Factor} = RF = \frac{\text{Area}}{\text{Amount}}$$

Note: Amount in this equation refers to the mass (e.g. ug) of compound mixed into the solution injected.

Each calibration standard is analyzed and the RRF is calculated for each analyte according to the following equation:

$$RRF = \frac{A_s \, x \, C_{is}}{A_{is} \, x \, C_s} \qquad 6$$

A_s = Area of analyte
A_{is} = Area of internal standard
C_{is} = Concentration of internal standard
C_s = Concentration of analyte

Note: Certain data processors may calculate the RRF differently.

The standard deviation (SD) and the % coefficient of variation (CV) of RRFs for the compounds are calculated using the following equations:

$$S = \sum_{i=1}^{N} \left[\frac{(RRF_i - RRF_m)^2}{N - 1} \right]^{‰} \qquad 7$$

Where:

RRF_i = Individual RRF
RRF_m = Mean RRF
N = Number of RRFs

and

$$\%CV = \frac{S \, x \, 100}{RRF_m} \qquad 8$$

Coefficient of Variation

The %CV of each compound must be less than 30 percent. This criterion must be achieved for the calibration to be valid.

If the %CV is less than 20 percent, the RRF of the compound can be assumed to be invariant, and the average RRF can be used for calculations.

If the %CV is between 20 percent and 30 percent, calculations must be made from the calibration curve. Both the slope and the intercept of the curve must be used to perform calculations.

Initial Calibration Verification

The calibration curve must be validated further by analyzing a QC check sample. The QC check sample must be obtained from EPA, another vendor, or it must be from another lot number. The QC check sample verifies the validity of the concentrations of the standards used to obtain the initial calibration.

All analytes in the QC check standard must be recovered within 80 to 100 percent. If any analyte exceeds this criterion, then a new calibration curve must be established. All sample results for a target analyte can be reported only from valid initial calibrations.

Continuing Calibration

The working calibration curve or RRF for each analyte must be verified daily by the analysis of a continuing calibration standard. The ongoing daily continuing calibration must be compared to the initial calibration curve to verify that the operation of the measurement system is in control.

The continuing calibration check must be performed during each day of analysis to verify the continuing calibration of the instrument. A day is defined as 24 hours from the start run time of the last valid continuing calibration. Generally, a continuing calibration check sample is injected every 20 samples.

Verification of continuing calibration is performed by the analysis of a midpoint standard containing all of the analytes of interest. Verification of continuing calibration of the measurement system is done by calculating the percent difference (%D) of the continuing calibration RRF from the mean RRF from the initial calibration curve using the following equation:

$$\%D = \frac{(RRF_m - RRF) \times 100}{RRF_m} \qquad 9$$

where:

RRF_m = The mean relative response factor from the initial calibration curve

RRF = The relative response factor from the continuing calibration standard

The %D must meet the acceptance criteria established in the appropriate SOP. If these criteria are exceeded, a new calibration curve must be established.

Refrigerators

Refrigerators are maintained at 4°C, with control levels ranging from 1°C to 10°C. A temperature reading is taken each workday morning immediately after unlocking the refrigerator. The temperature reading is recorded and entered on the control chart posted on the door of the refrigerator. If a trend is apparent or if the temperature is outside the acceptable range, the Lab Manager is notified so that corrective action can be initiated if required.

Freezers

Freezers are maintained at -10°C, with control levels ranging from 0°C to -35°C. A temperature reading is taken each workday morning immediately after unlocking the freezer. The temperature reading is recorded and entered on the control chart posted on the door of the freezer. If a trend is apparent, or if the temperature is outside the acceptable range, the Lab Manager is notified so that corrective action can be initiated if required.

Calibration Standards

All calibration standards, including internal standards, are obtained from chemical suppliers with certificates of high purity and concentration.

Traceability

All standards are traceable to the National Institue of Standards and Testing (NITS) Standard Reference Materials (SRM) or to the U.S. EPA Reference Standards.

Working Standards

The commercial standards are used as stock standards. Working standards are made from the stock standards at appropriate concentrations to cover the linear range of the calibration curve. The working standards are used for initial calibration curves, continuing calibration checks, and preparation of analyte spiking solutions as appropriate for a particular analysis. All stock and working solutions are uniquely identified, dated, labeled, and initialed.

CORRECTIVE ACTIONS

Laboratory Imposed

Corrective actions will be initiated if the quality control criteria indicate an analysis is out of control.

- Check calculations for accuracy
- Check instrumentation to ensure it is operating properly. Recalibrate if necessary.
- Remake standards and reagents and reanalyze samples.
- Re-prep and re-analyze samples.

The analyst is responsible for initiating corrective actions for analytical problems encountered during analysis of samples. Most problems which occur and are corrected during the analytical run will be explained in the run log or analytical bench sheet for that run. A corrective action report (CAR) may be necessary for some problems encountered, such as complete system failure, chronic calibration failure, or severe matrix interferences.

During data review, the reviewer may initiate corrective actions based on problems or questions arising from the review. A CAR will be initiated.

The Laboratory Manager may initiate corrective actions if a problem is noticed during a QC review of data, a system audit, or a performance audit. A CAR will be initiated.

CARs are signed and dated by Project Manager, and by the Laboratory Manager. CARs will be filed in appropriate department files and in the Lab Manger's files.

Agency Imposed

Any actions deemed necessary by regulatory agencies, such as EPA, will be taken. These actions are most likely to arise from a systems or performance audit, or from data review conducted by the agency.

Corrective Action Reports

The laboratory will have a Corrective Action System that ensures the proper documentation and dispositions of conditions requiring corrective action. The system will also ensure that the proper corrective action is implemented to prevent recurrence of the condition.

Situations Requiring Corrective Action Reports

The Corrective Action System applies to all situations that affect data quality. These situations include, but are not limited to, quality control criteria being exceeded, statistically out-of-control events, deviations from normally expected results, suspect data, deviations from the standard operating procedure, and special sample handling requirements. Corrective actions may also be initiated as a result of other QA activities, such as performance audits, systems audits, laboratory/interfield comparison studies, and QA project-related requirements of certifying agencies such as EPA.

Corrective Action Procedures

The procedure requires documenting the condition requiring corrective action on a Corrective Action Report and implementing corrective action based on the results of the investigation performed to determine the cause of the condition (Table 4-1 and 4-2).

When a condition requiring corrective action arises, the Corrective Action Report is initiated. The initiator describes the condition requiring corrective action. An investigation, if necessary, is conducted to determine the cause of the condition. A corrective action is recommended based on the results of the investigation. The Corrective Action Report is reviewed by the Project Manager and the Lab Manager who either approve the recommended corrective action or indicate a different corrective action. The originator has the responsibility of following up to be

sure that the corrective action is implemented. Implementation of the corrective action is documented by the Corrective Action Report being signed and dated by the person who implemented the corrective action.

Table 7-1. Corrective Actions

QC Activity	Acceptance Criteria	Recommended Corrective Action
Initial instrument blank	Instrument response <MRL response	Prepare another blank, if same response, determine cause of contamination: reagents, environment, instrument equipment failure, etc.
Initial calibration standards	Coefficient of variation >0.995 or standard concentration value ± 10% of expected value	Reanalyze standards. If still unacceptable, then remake standards
QC Check Standard	± 10% of expected value	Reanalyze standard. if still unacceptable, then remake standards, or use new primary standards if necessary
Continuing calibration Standards	± of expected value	Reanalyze standard. If still unacceptable, then recalibrate and rerun samples from the last cc stnd. Check
Method blank	<MDL	Reanalyze blank. If still positive, determine source of contamination. If necessary, reprocess (i.e., digest or extract) sample set

Table 7-2. Corrective Action Report Criteria for Control Charts

Criteria	Corrective Action
A point outside ±3 standard deviations	Attempt to determine the source of the problem. Verbally report the deviation and results of preliminary investigation to the Field Site Manager, who will decide jointly what action to take. After implementing corrective action, complete the Corrective Action Report and submit it to the Project Manager and the Field Site Manager for approval.
Three consecutive points accuracy outside ± standard deviation	Conduct investigation. Check accuracy of data input, calculations, instrument, standards, etc., to locate the source of the problem. Document results in a Corrective Action Report. Have the report approved by the supervisor. No results can be reported until the Corrective Action Report

	has been approved. Send a copy of the Corrective Action Report and a copy of the QC chart to the Field Site Manager.
Obvious outlier.	Conduct investigation. Check accuracy of data input, calculations, dilutions, instrument, standard, etc.. present initial findings to the Field Site Manager. They will jointly decide what actions need to be taken. Document the results in a Corrective Action Report and have it approved by the Field Site Manager. No results can be reported until the Corrective Action Report is approved. Send a copy of the Corrective Action report and a copy of the control chart to the Field Site Manager.
Obvious shift in the mean.	Conduct investigation. Check calculations, data entry, standards, instrument, calibrations, etc. Document results in a Corrective Action Report. Have the Corrective Action Report approved by the Field Site Manager. No results can be reported until the report is approved. Send a copy of the Corrective Action Report and a copy of the QC chart to the Field Site Manager.

7.5. Demonstration Procedures

Maintenance Schedule

Preventive maintenance, such as lubrication, source cleaning, and detector cleaning, is performed according to the procedures delineated in the manufacturer's instrument manuals.

The frequency of preventive maintenance varies with different instruments. Routine maintenance performed includes cleaning and/or replacement of various instrument components. In general, the frequency recommended by the manufacturer is followed. In addition to the regular schedule, maintenance is performed as needed. Precision and accuracy data are examined for trends and excursions beyond control limits to determine evidence of instrument malfunction. Maintenance is performed when an instrument begins to degrade as evidenced by the degradation of peak resolution, shift in calibration curves, decreased ion sensitivity, or failure to meet one or another of the quality control criteria. GC injector septa is changed every 100 to 150 injections, or sooner if instrument performance deteriorates. Injection port glass liner is cleaned or changed after 100 to 150 injections or sooner if instrument performance deteriorated. A method blank is analyzed at the beginning of each sample set and after every 20 samples to monitor instrument background.

Instrument maintenance logbooks are maintained in the laboratory at all times. The logbook contains a complete history of past maintenance, both routine and nonroutine. The nature of work performed, the date, and the signature of the person who performed the work are recorded in the logbook. Preventive maintenance is scheduled according to each manufacturer's recommendation. Instrument downtime is minimized by keeping adequate supplies of all expendable items on hand. Expendable items are those with an expected lifetime of less than one year. Routine instrument preventive maintenance is handled by the instrument operator. Repair maintenance is performed by a full-time electronics technician, or by the manufacturer's service personnel.

7.6. Calculation of Data Quality Indicators

The focus of this section is to present methods of calculating data quality that will be used for this project.

Control Samples

The laboratory will employ control samples to assess the validity of the analytical results of the field samples. Determination of the validity of field sample results is based on the acceptance criteria being met by the control sample. The acceptance criteria for each type of control sample are delineated in the appropriate SOP. These acceptance criteria are based on the laboratory's statistical process capabilities determined from historical data, and meet the EPA CLP acceptance criteria as a minimum. Often, in-house criteria are more stringent than required by CLP. The control samples are analyzed in the same manner as the field samples. They are interspersed with the field samples at frequencies that are specified by the appropriate SOP.

Method Blank Analyses

A method blank is a "clean" sample (i.e., containing no analyte of concern), most often deionized water, to which all reagents are added and analytical procedures are performed. Method blanks are analyzed at a rate of one per sample lot or at least every 20 samples. The blank is analyzed in order to assess possible contamination from the laboratory or the procedure. If the analyte of interest is found in the blank at above reporting levels, inorganic analysis is suspended until the source of contamination is found and corrective action is taken. The Laboratory Manager is notified when blank results are unacceptably high, and may assist in the investigation.

Surrogate Spike Analyses

For certain analyses, each sample and blank is spiked with one or more surrogate compounds before preparatory operations such as purging or extraction. These surrogate standards are chosen for properties similar to sample analytes of interest, but are usually absent from the natural sample.

Surrogate spikes evaluate the efficiency of the analytical procedure in recovering the true amount of a known compound.

The results of surrogate standard determinations are compared with the true values spiked into the sample matrix prior to extraction and analysis, and the percent recoveries of the surrogate standards are determined. Recoveries should meet the upper and lower control limits as specified for each compound. If control limits are exceeded for surrogate standards, the following sequence of actions is taken:

a. The sample is re-injected.

b. Raw data and calculations are checked for errors.

c. Internal standards and surrogate spiking solutions are checked for degradation, contamination, or solvent evaporation.

d. Instrument performance is checked.

e. If a, b, and c fail to reveal the cause of the noncompliance surrogate recoveries, the sample is re-purged or re-extracted.

f. If all the measures listed above fail to correct the problem for laboratory blank surrogate analyses, the analytical system is considered out of control, and the instrument must be recalibrated and examined for mechanical faults.

g. If all the measures listed above fail to correct the problem for field sample surrogate analyses, the deficiency probably is due to sample interferences, and not due to any procedural or mechanical problems in the laboratory. The surrogate spike recovery data and the sample data from both extractions are reported and are flagged. The Laboratory Manager is notified with an exceptions report and the corrective actions taken.

Matrix Spike/Matrix Spike Duplicate Analyses

To evaluate the effect of the sample matrix on the analytical methodology, two separate aliquot samples may be spiked with a standard mix of compounds appropriate to a given analysis. The matrix spike and the matrix spike duplicate (MS/MSD) are analyzed at a frequency of one per lot or one per 20 samples, whichever is more frequent. The percent recovery for each of the spiking compounds is calculated. The relative percent difference (RPD) between the MS/MSD is also calculated.

The observed percent recoveries (%R) and relative percent differences (RPD) between the MS/MSD are used to determine the accuracy and the precision of the analytical method for the sample matrix. If the percent recovery and RPD results exceed the control limits as specified for each spiking compound, the sample is not reanalyzed. Poor recovery in matrix spiked samples

does not necessarily represent an analytical system out of control. It is possible that unavoidable interferences and matrix effects from the sample itself preclude efficient recoveries. The poor recovery is documented for the Lab Manager.

Internal Standards Analysis

Once an instrument has been calibrated, it is necessary to confirm periodically that the analytical system remains in calibration. The continuing calibration and precision of the organics analytical system are checked for each sample analysis by monitoring the instrument response to internal standards. When internal standard addition is not appropriate to a particular method, other means of accuracy checks, such as standard addition, are used. Results from internal standard analyses are compared to the mean calibrated value. Deviation from this mean beyond a predetermined magnitude, depending on the type of analysis, defines an out-of-control condition. The system must then be brought back into control by:

- Checking the quality of the internal standards and reanalyzing the sample
- Recalibrating the system
- Correcting the malfunctions causing the instrument to fall out of calibration

Duplicate Sample Analyses

Duplicate analyses are performed for cations analyses and upon special request for selected other parameters to evaluate the reproducibility of the method. Results of the duplicate analyses are used to determine the RPD between replicate samples. For each parameter analyzed, at least one duplicate sample is run per group of 20 samples.

The precision value, RPD, is reviewed by the section supervisor and the division manager. If the precision value exceeds the control limit or the established protocol criteria for the given parameter, the sample set is reanalyzed for the parameter in question unless it is determined that heterogeneity of the sample has caused the high RPD.

QC Check Standard Analyses

Analysis of QC check standards is used to verify the preparation process or the standard curve, and is performed with each group of samples. Results of these data are summarized, evaluated, and presented to the section supervisor and the division manager for review.

The results of the QC check standard analysis are compared with the true values, and the percent recovery of the check standard is calculated. If correction of a procedure or instrument repair is done, the check standard is reanalyzed to demonstrate that the corrective action has been successful.

At least twice a year, a QC check standard for each parameter group is analyzed as a double-blind sample. Samples are prepared, submitted, and evaluated by the Laboratory Manager.

Other Quality Control Samples

Under some sampling analysis, additional quality control samples may be required. These may include:

a. **Blank/Spike**--Analyte of interest or surrogate is spiked into blank water rather than into a sample. The blank/spike goes through the entire analytical procedure, and percent recovery is calculated with no likelihood of matrix effect. For many contracts, an externally provided LCS sample (EPA) serves as a blank/spike sample.

b. **Trip Blank**--A sample bottle filled with laboratory blank water travels with the sample kit to the sampling site, and is sent back to the laboratory packed in the same container as any volatile samples collected. Trip blank analyses check for possible volatile contamination during shipping or sampling.

c. **Field Blank**--A field blank can be a sample container filled with laboratory blank water and sent to the sampling site, or it may be filled at the site with purchased distilled water or decontamination water. The field blank analysis checks for possible contamination by the sampling team.

d. **Equipment Rinsates**--After equipment has been cleaned in the field, many contracts require that the equipment be rinsed and the rinsate analyzed for the same parameters requested on the samples. The rinsate analysis proves the equipment has been cleaned properly and will not contaminate the next samples taken.

Instrument Detection Limits, Method Detection Limits, and Reporting Limits

Instrument Detection Limits (IDL)

Instrument Detection Limit (IDL) studies are performed for inorganic parameters when an instrument is installed, when major maintenance or repair work has been done, and routinely once per calendar quarter.

To determine IDL, seven consecutive measurements per day are made on a prepared standard solution (in reagent water) of an analyte at a concentration 3 to 5 times the instrument manufacturer's suggested IDL. Each measurement is performed as though it were a separate analytical sample. This procedure is repeated on three nonconsecutive days. The standard deviation is calculated for each set of seven replicates and the average of the standard deviations is obtained. This average is multiplied by 3 to give the instrument detection limit (IDL).

Method Detection Limits (MDL)

The Method Detection Limit (MDL) is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the value is above zero. The sample must be carried through the entire method under ideal conditions. MDL is determined according to the method outlined in 40 CFR 136, Appendix B. MDLs are determined at least annually for all parameters. MDL studies are also conducted for new methods introduced in the lab, after major maintenance or modification to an instrument, and as part of the training of new analysts.

To determine MDL, seven replicate analyses are made of analytes spiked into blank water at 1 to 5 times the estimated method detection limit. The spiked samples must be carried through the entire analytical procedure, including any extraction, digestion, or distillation process, for MDL calculation. The SD of these replicates is calculated. Where: t = The student t value for a 99% confidence interval

$$MDL = t \times S \qquad 10$$

S = Standard deviation of the replicate analyses

Reporting Limits

In most cases, final report forms list reporting limits rather than either IDL or MDL. Reporting limits are taken from EPA SW846 published limits or from historical data. Matrixes or analyte concentrations which require dilution will change the detection limits for that sample.

4.7. Performance and System Audits

In this section information is provided on performance audits.

Performance Evaluation Samples

Performance evaluation samples are analyzed throughout the project for all parameters, as a constant check on accuracy and precision for all analyses.

Audits

Internal audits of the laboratory are conducted in two phases. The first phase is conducted by the Laboratory Quality Assurance Coordinator during the fourth quarter of the year. This is usually a 2-day systems audit which covers all sections of the laboratory. An audit report is issued within 2 weeks of completion. The Lab Manager has the responsibility for coordinating all responses to the audit finding and for following up on the required corrective action. A followup audit is made when deemed necessary by the Lab Manager.

The second phase consists of quarterly audits performed by the Lab Manager. These are half-day or day-long audits, and are concentrated on specific areas that are deemed problem areas by the Lab Manager. An audit report is issued at the completion of the audit. Responses and followup corrective action to the audit findings are required, and are monitored by the Field Site Manager.

All audit reports are issued to management and circulated to all staff. Copies are filed with the Laboratory Manager.

7.8. Quality Assurance Reports

The performance of the laboratory as assessed by the quality monitoring systems in place is reported by the Lab Manager to management quarterly and as needed. Copies of all quality reports are maintained in the Laboratory Manager files.

Quality assurance reports to management include, but are not limited to, the following:

- Results of performance and systems audits
- Status of corrective actions
- Periodic assessment of data accuracy, precision, and completeness
- Significant QA problems and recommended solutions

In addition to the quarterly reports, a final report summarizing items covered in the quarterly reports is provided by the Lab Manager to the Project Manager.

7.9. Data Format

Introduction

In order to provide analytical data which is technically sound and defensible, a system of data management will be implemented in the laboratory. All activities which pertain to a sample are documented.

All data generated during the demonstration, except those that are generated by automated data collection systems, will be recorded directly, promptly, and legibly in ink. All data entries will be dated on the day of entry and signed or initialed by the person entering the data. Any change in entries will not obscure the original entry, will indicate the reason for such change, and will be dated and signed or identified at the time of the change.

In automated data collection systems, the individual responsible for direct data input will be identified at the time of data input. Any change in automated data entries will not obscure the original entry. Updated entries will indicate the reason for the change, the date, and the person responsible for making the change.

Data Tracking in the Laboratory

The Lab Manager is responsible for developing a system for tracking and maintaining sample identity between the collection point, analysis and reporting. This process will be periodically reviewed by the Project Manager.

Analyses and Data Reduction

The Lab Manager is responsible for the reduction of raw data when such steps are required to produce the correct data format for reporting. Data reduction may be done manually or through one of a number of computer programs used in the laboratory.

Chromatogram Identification

In the GC section computer software is used to identify chromatograms. A system-supplied file name (a hexadecimal date-time) and a user-supplied file name (related to an entry in the injection log) identify each acquisition.

Data Reduction Formulas

Linear regression formulas are used in a computer software system to calculate samples values for many general inorganic parameters and metals analyses. These programs use the general formula for linear regression:

$$Y' = a + bx \qquad 11$$

where:

Y'	=	The predicted value of y for a selected value of x
a	=	The value of y when x = 0
b	=	The slope of the straight line
x	=	Any value of x selected

Sample values for GC/MS parameters are calculated by systems software using the general formula:

$$\frac{Area_{Target} \; x \; Amount_{IS}}{Area_{IS} \; x \; Response \; Factor} \qquad 12$$

GC data is calculated using either an internal or an external standard. For internal standards:

$$Concentration = \left(\frac{A_x^{sample}}{A_x^{standard}} \right) \left(\frac{A_{IS}^{standard}}{A_{IS}^{sample}} \right) \left(amt_x^{standard} \right) \left(\frac{P}{T} \right) \left(\frac{amt_{IS}^{Sample}}{Amt_{IS}^{standard}} \right) \qquad 13$$

where: P = 1/fraction of extract to which IS is added

For calculations using an external standard:

$$Concentration = \left(\frac{A_x^{sample}}{A_x^{standard}} \right) \left(C_x^{standard} \right) \left(\frac{V}{T} \right) \qquad 14$$

where: C = concentration of x in standard
V = volume of final extract
T = total sample extracted

7.10. Data Storage and Archiving Procedures.

Data will be saved in the computers using for instrument operation. This data will be batch processed into an Excel .csv file that can be easily converted to an Excel Worksheet. These files will be backed-up and transferred to individuals responsible for calculating flux results. All data related to the project will be organized for rapid retrieval and transfer to other interested parties.