VOLATILES GLASSWARE AND EQUIPMENT STANDARD CLEANING PROCEDURES

FLORIDA DEPARTMENT OF ENVIRONMENTAL PROTECTION

CHEMISTRY PROGRAM

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Volatiles Glassware and Equipment Standard Cleaning Procedures

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Volatiles Glassware and Equipment Standard Cleaning Procedures

1. SCOPE AND APPLICATION

1.1. The techniques described in this procedure are used to prepare glassware and other sample handling devices for volatile analysis. The objective is to remove all traces of the volatile compounds of interest and interferences from equipment surfaces that may come in contact with a sample. Criteria for acceptance of clean vials and jars for sample collection are established.

1.2. The cleaning procedures are designed for specific laboratory items that come into direct or indirect contact with the environmental or quality control samples. The procedures must be followed strictly in order to minimize contamination risks to the samples and instruments. The concepts and techniques contained within this Standard Operating Procedure (SOP) may also be applicable for cleaning other types of equipment for VOC analysis, but caution must be exercised. Verification of equipment cleanliness though the use of method blanks and quality control checks are also described.

1.3. The cleaning and maintanence schedule for the individual analytical instruments is not discussed in this SOP, but is described in the operator manual for each instrument. References for the analytical instruments are found in the analytical method SOPs.

1.4. The following analytical analysis and preparation methods apply:

1.4.1.	SOP **VO-002**	Analysis of VOCs in Water by EPA Method 624.1 and 8260D
1.4.2.	SOP **VO-003**	Analysis of VOCs in Sediment and Waste by EPA 8260D
1.4.3.	SOP **VO-004**	Analysis of Acrolein & Acrylonitrile in Sediment and Waste
1.4.4.	SOP **VO-005**	TCLP and SPLP Sample Preparation
1.4.5.	SOP **VO-006**	Analysis of Polar Organic Compounds in Water

1.5. Refer to the following Standard Operating Procedures for additional information:

These supporting SOPs contain critical details not fully described within this method SOP. The analyst must be completely familiar with all of these SOPs.

1.5.1. *Safety and Waste Management Practices in the Organic Analysis Groups* (SOP **OG-001**).

1.5.2. *Data Review/Authorization Procedures for the Volatile Organic Laboratory* (SOP **VO-010**).

1.5.3. *Quality Assurance/Quality Control Measurements in the Volatile Organics (VOC) Laboratory* (SOP **VO-001**).

2. CLEANING EQUIPMENT AND SUPPLIES

2.1. AquaSolution 2000 DI Water Purification System.

2.2. Fisher IsoTemp Forced-Air Oven.

2.3. Thermo Heratherm OMH400-SS Mechanical Convection Oven.

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2.4. Lancer Model 1400 Laboratory Dishwasher

2.5. Brushes:

2.5.1. Large Beaker Brush
2.5.2. Test Tube Brush
2.5.3. Nessler Tube Brush
2.5.4. Narrow Tube/Pipet Brush

2.6. Gloves:

2.6.1. Heavy Duty Latex Gloves
2.6.2. Neoprene Gloves
2.6.3. North Silver Shield Gloves(for handling methylene chloride)
2.6.4. Autoclave/Oven Gloves

2.7. Aluminum Foil, heavy-duty

2.8. Pressurized Air Cylinder and Regulator

2.9. Oil-Free Vacuum Pump and Traps

2.10. Fisher FS14 Ultrasonic Cleaner with basket

2.11. Kappler Tyvek Lab Coats – The Tyvek coats are used for cleaning since they are disposable, chemical resistant, and water resistant.

2.12. Technicloth Wipes or Kimwipes – lint-free cloth wipes

2.13. Standard Folded Paper Towels

2.14. Ziplock Bags, 4 mil, 9 x 13 inch

3. REAGENTS AND CHEMICALS

3.1. Organic Solvents

3.1.1. Methanol - HPLC Grade: CH_3OH - HPLC grade methanol is purchased in 4 L amber bottles from Fisher Scientific.

3.1.2. Methanol - P&T Grade: CH_3OH – Purge & Trap grade methanol is purchased in 500 mL amber bottles from Fisher Scientific

3.1.3. Methylene Chloride – HPLC Grade: CH_2Cl_2- HPLC grade methylene chloride is purchased in 4 L amber bottles from Fisher Scientific. This chemical is not to be used or stored in the volatiles laboratory, but must be used in the main laboratory bottle washing room. The use of methylene chloride for cleaning purposes must be approved by the supervisor.

3.2. Acids

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3.2.1. Hydrochloric Acid, HCl - Fisher Certified ACS Plus Grade. A dilute HCl solution is prepared by making a 1:2 dilution of the HCl acid into laboratory reagent water.

3.2.2. Nitric Acid, HNO_3 - Fisher Trace Metal Grade.

3.3. Detergents

3.3.1. Alconox Powder Detergent

3.3.2. NoChromix Reagent

3.3.3. LiquiNox Liquid Detergent

3.4. Laboratory Reagent Water

Laboratory reagent water prepared in the laboratory from the municipal water supply. The criteria for laboratory reagent water is that it must not contain any analytes of interest at a concentration greater than the minimum detection limit. Other non-target compounds may be detected in the laboratory reagent water, but must not interfere with the analysis of the target compounds. Examples of a non-target compounds commonly observed are methanol (used in glassware cleaning and standard preparation) and siloxanes (from surfactants, pump oils and column bleed).

3.4.1. Type 1 Laboratory Reagent Water: Municipal water is purified with a AquaSolution 2000 Water Purification System that uses activated carbon cartridges and multiple ion-exchange cartridges to remove impurities. Furthermore, the DI water within the hand dispensor is continuously passed through a secondary polishing ion-exchange filter. The Type 1 laboratory reagent water is evaluated every day, when sample data is collected, as a method blank sample.

4. LABWARE CLEANING AND TESTING PROCEDURES

4.1. VOA Vials, 40 mL or 20 mL

The standard 40 mL VOA vial is used in many applications including collection and analysis of water, soil and waste samples. The smaller 20 mL vial is used to prepare sample extractions with minimal headspace. New vials are more commonly used for most volatile sample collection and analysis applications, however the following cleaning instructions are available for situations where recyling of vials is warranted. The cleaning and testing procedure given here is sufficient for all of these vial applications.

4.1.1. Previously used vials must have all labels removed and contents disposed of properly in accordance with SOP **OG-001**. Vials heavily contaminated with oil, grease, paint or other waste product should be discarded, since the cost of cleaning exceeds the value of the vial. The remaining used vials may be cleaned in a detergent rinse (Alconox) until they are visually free of any solids and oily residues. The laboratory is equipped with a dishwasher for this purpose. The dishwasher is set to a 45 minute wash cycle at 170°F and includes a laboratory reagent water rinse. Any vial which does not clean easily or is damaged must be discarded. In most cases it is not cost effective to recycle vials.

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4.1.2. All vials, including new vials, must be visually inspected for cracks, chips or contamination. Discard damaged vials.

4.1.3. All cleaned vials, including new uncertified vials, must be baked at ≥105 °C for at least 24 hour prior to use. Certified vials may be used as received, provided the certification meeting the minimum vial requirements.

4.1.4. Vials may be stored in the oven or may be capped and stored in lots of 100 vials or more. In either case, the vials must be inclosed in a box, cabinet or covered with foil within a VOC-Free environment.

4.1.5. The Teflon/silicone septa for the VOA vials are placed into a stainless-steel tray and rinsed with HPLC grade methanol. The septa are then rinsed with laboratory reagent water three times. After the water on the spectra has been drained, they are baked for a minimum of 24 hours at 105 °C. The septa may be stored in the oven or in a sealed volatiles-free container until ready for use. Do not over-heat the septa since this may cause separation of the Teflon and silicone layers or cause silicone monomer bleed from the silicone layer.

4.1.6. The recycled screw caps for the VOA vials are cleaned in a detergent rinse until visually free of soil or oily residue. The laboratory is equipped with a dishwasher for this purpose. The dishwasher is set to a 45 minute wash cycle at 170 °F and includes a laboratory reagent water rinse. Any cap that is discolored, does not clean easily, or is damaged must be discarded.

4.1.7. If QC testing of vials is required, then submit at least 2 vials for each batch of cleaned vials for volatile analysis prior to use. The QC check vials are entered into the LIMS as samples. The vials are available for use once the data is reported in the LIMS and the vials are certified as clean for VOC applications. The criteria for the vials requires that no vial contain any analytes of interest at a concentration greater than half the minimum reporting limit. Other non-target compounds may be detected, but must not interfere with the analysis of the target compounds.

4.2. <u>General Glassware and Teflonware: sparge tubes, syringes, volumetric flasks, beakers, cylinders, jars and Teflon-coated stir bars</u>

4.2.1. Properly dispose of any removable sample material from the glassware. Soak the glassware in soapy water and scrub well with brushes. Rinse several times with laboratory reagent water and HPLC-grade methanol. Inspect the glassware for damage. Take care not to scratch the glassware with any metal components of the cleaning brushes. Remove damaged glassware from circulation until it can be repaired or disposed.

4.2.2. A Nochrome solution soak may be used to help clean heavily contaminated glassware.

4.2.3. For mineralized films, a 6 M HCL acid rinse may be used to aid in removal of the deposits. Acid waste must be neutralized before disposal.

4.2.4. Avoid prolonged use of strong alkaline cleaning reagents, since they can etch the glassware.

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4.2.5. The use of strong organic solvents such as methylene chloride should be used only as a last resort due to possible contamination of the VOC work environment. The organic solvents must be used in the bottle washing room in the main laboratory facility and must be properly disposed.

4.2.6. Bake all graduated glassware and Teflon items at ≤105 °C in the low-temperature glassware oven for at least 24 hours prior to use. A low-temperature bake cycle has not been observed to adversely affect the calibration of all-glass items used by our laboratory. However, take precautions if an item has plastic or glass/metal components that may be damaged by low-temperature heating. Any new graduated glassware should be carefully monitored and the calibration verified after the first few bake cycles.

4.2.7. All other non-calibrated glassware items may be baked at ≥105 ^{O}C for at least 24 hours prior to use. Do not put items containing plastics in the high-temperature ovens.

4.2.8. If the glassware has been stored on a shelf for an unknown time, assume it is contaminated. Clean and bake all glassware prior to use.

4.3. Metal Spatulas, Tongs, Knives and Needles

Needle and knife cleaning prodecures are described specifically because of the special concerns and risks associated with their handling and use. Handle and clean sharp items separately from other items.

4.3.1. Handle needles and knives with due care. Make sure that the needle points are always pointed away from you or others.

4.3.2. After use, rinse the outside of each part with HPLC-grade methanol. Use a methanol squirt bottle to force methanol through the inside of the needles and into a methanol waste collection beaker. Rinse the inside and outside of each part several times with methanol and laboratory reagent water.

4.3.3. If the needles or other metal parts are especially contaminated, soak the needles in methanol and then ultrasonicate them for 15 to 20 minutes. A dilute HCL rinse may also be used to remove tarnish, followed immedately by a soap wash. Acid will damage the metal surface if the exposure time is more than 5 to 10 seconds. Rinse well with laboratory reagent water and methanol.

4.3.4. If the needles are clogged, use a thin metal wire to clear the path and then clean as ussual.

4.3.5. Bake the metal parts at ≥105 ^{O}C for at least 24 hours prior to use. Keep in mind that volatile contaminates in needles come out very slowly due to the small internal surface area open to the outside.

4.3.6. Store the needles and other sharp items separately in an oven tray until ready for use.

4.4. Sample Cans (metal)

Metal cans are not used routinely as they were in the past. However, it is important to document special problems with metal cans just in case they are used to ship or receive

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samples in the future. It was observed that metal containers harbor VOCs in the metal seams that are extremely difficult to remove. The VOCs in the metal seams will frequently continue to be released from the can even after repeated bake cycles. For this reason we discontinued using metal cans routinely. If cans are used, a carbon sorbent pack should be added to capture VOCs released from the metal can.

4.4.1. Cans used for sample storage and transport must be cleaned and baked prior to each use. The used cans must first be inspected to make sure they are free of labels, sample, packing material, plastic bags, and oily residue. Clean any cans which are soiled with a detergent rinse followed by 3 or more laboratory reagent water rinses. Discard cans that are damaged, overly rusty, or soiled beyond cleaning.

4.4.2. Bake all cans (new or used) at ≥105 ^{O}C for at least 24 hours prior to use. Please be mindful of other ongoing laboratory work since baking of cans may generate odors in the lab. It is best to place the cans in the oven in the late afternoon before leaving for the day.

4.4.3. Allow cans to cool. Store the cans with the lids on tight within the VOC lab until ready for use.

4.5. Gas Tight Microsyringes Syringes (Class-A)

The Class-A gas tight microsyringes used for small volume measurements are expensive and fragile. All new Analysts must be trained to handle, use, and care for syringes per the manufacture instructions. In addition, a new Analyst should validate that they are able to measure out accurate volumes by gravimetric verification and are trained on the proper handling of these fragile measurement tools.

4.5.1. Visually inspect the syringe. Verify that the syringe plunger and needle are not bent or corroded. Check to make sure the syringe bore is not cracked, discolored, or worn.

4.5.2. Repair or dispose of any syringe that is not in good working order. Some effort should be made to repair syringes if possible.

4.5.3. Rinse the syringe at least 10 times with HPLC-grade methanol before every use.

4.5.4. Inspect the sample stream as you dispense the methanol. Clear the syringe needle if the needle appears to be clogged according to the manufacture directions.

4.5.5. The syringe must be inspected for gas tightness. The syringe must be discarded if air passes by the plunger while drawing up methanol or water.

4.5.6. If the syringe is equipped with a Chaney adapter, inspect the setting and condition of the adapter.

4.5.7. All syringes should be tested for calibration quarterly. While this is not a requirement for Class-A syringes, it is still a good practice. Any syringe that fails calibration must be repaired or discarded. The calibration test is the same procedure used for pipets in **SOP NU-039**.

4.5.8. The syringes must not be placed into ovens for drying. High heat can damage the syringes.

4.5.9. A syringe must be removed from inventory if it is damaged during use. Repair, set-aside, or discard any syringe that is damaged during use. Label any damaged

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syringe that is set-aside for later repair so that others will not accidently attempt to use it.

4.5.10. Notify the supervisor if you use the last new syringe in inventory so that additional units can be purchased.

5. ZHE APPARATUS CLEANING AND TESTING

The Zero Headspace Extractor (ZHE) used in Toxicity Characteristic Leaching Procedure (TCLP) or Synthetic Precipitation Leaching Procedure (SPLP) tests can be difficult to clean and can pose a high risk for contaminating future samples if the following cleaning procedures are not employed. Additionally, there are several test procedures that need to be performed after ZHE cleaning but before proceeding with the next extraction to insure the apparatus is functioning properly. See Reference 6.3 for more information.

5.1. If the ZHE has been previously used, then make sure all solids from the unit have been properly disposed. Always dispose of waste in accordance with the safety and hazardous waste disposal **SOP, OG-001**. The ZHE units must be cleaned thoroughly after every use.

5.2. Disassemble the ZHE with care so that the individual parts are not nicked or otherwise damaged. The inlet/outlet valve in each ZHE lid must also be disassembled, but do not remove the valve O-rings unless they show wear or damage. The inlet/outlet valve is a frequent source of contamination if not disassembled and cleaned.

5.3. Wipe all the ZHE parts with paper towels to remove excess oily waste and dispose of the towels with the sample waste. Use laboratory grade detergent to clean all the ZHE parts followed by methanol and laboratory reagent water rinses. Repeat this step until there is no visible contamination when the surface and crevices of the ZHE are wiped with a clean, white towel.

5.3.1. In cases where the ZHEs are contaminated with oily waste it may be necessary to first wipe or rinse all parts with methylene chloride, followed by methanol and water. Do not soak the O-rings or other polymer/plastic parts in the methylene chloride since this may result in damage. After using methylene chloride each part must be cleaned again thoroughly with detergent. Repeat these steps until there is nothing physically stuck or coated on the ZHEs and O-rings. **Cleaning a ZHE with methylene chloride should be used only as a last resort. Perform this activity away from VOC operations in the bottle washing room since methylene chloride is a target compound.**

5.3.2. The ZHE parts may be rinsed with a diluted HCL solution to remove tarnish or residue, but only a small amount of the acid solution must be used. Also, the acid must be rinsed off promptly to avoid damaging the metal components. Afterwards, use laboratory grade detergent to clean the ZHE parts followed by methanol and water rinses. The metal parts will be damaged or will rust if the acid is not immediately rinsed off and neutralized.

5.4. Soak the small stainless steel parts (i.e., screens, fittings, etc.) and O-rings in a beaker with methanol and sonicate for at least 20 minutes. Compressed air is very effective in removing particulates in crevices that are difficult to reach.

5.5. Bake the cleaned metal parts, except for the ZHE base, in the oven at > 150^{O}C overnight. The Viton® O-rings must also be baked at ≤ 105 ^{O}C overnight.

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5.6. Reassemble the ZHEs. All the primary ZHE components are marked with an identification number, so make sure the correct parts are used for each ZHE. Inspect the O-rings prior to installation for cracks or nicks. Discard any damaged O-rings.

5.7. ZHE Blank Check: Each ZHE unit must be verified in a blank check analysis at least once for every 20 uses. Add laboratory reagent water, tumble, and process the ZHE blank check as described in SOP **VO-005**. Check to make sure the unit is pressure tight. Collect the laboratory reagent water just as for a sample and analyze by GC/MS.

5.8. Any ZHE that was cleaned with methylene chloride or was used previously for a highly contaminated sample should be tested. A composite or batch blank test will suffice for the specially cleaned ZHEs in this case. The ZHEs must be re-cleaned and baked if a Clean Check sample contains more than the analytical method minimum detection limit (MDL) for any analyte of interest. Maintain the test results in the analytical batch records.

5.8. ZHE Storage: After a ZHE has been properly cleaned and checked, disassemble it and allow it to fully air dry. This will eliminate the possibility of corrosion or mold growth. After air-drying the ZHEs, store the ZHE components in the ZHE cabinet in the VOC laboratory. The O-ring and valve components should be covered with aluminum foil and labeled.

5.9. Since the ZHE cleaning procedures require a long processing time, it is suggested that cleaning be started as early as possible.

6. REFERENCES

6.1. *Test Methods for Evaluating Solid Wastes, Fourth Edition, SW-846,* Method 8260D, Revision 4, June 2018.

6.2. Test Methods for Evaluating Solid Wastes, Fourth Edition, SW-846, Method 8000D, March 2018.

6.3. Millipore Operation and Maintenance Instruction OM-149, Manual Number P-16764, OM-149, Manual Revision: November 1986.

6.4. Florida Department of Environmental Protection, Standard Operating Procedure **VO-001,** *Quality Assurance/Quality Control Measurements in the Volatile Organics (VOC) Laboratory*

6.5. Florida Department of Environmental Protection, Standard Operating Procedure **VO-010** *Data Review/Authorization Procedures for the Volatile Organic Laboratory*.

6.6. Florida Department of Environmental Protection, Standard Operating Procedure **VO-002** Measurement of VOCs in Water by Gas Chromatography/Mass Spectrometry.

6.7. Florida Department of Environmental Protection, Standard Operating Procedure **VO-003** Measurement of VOCs in Sediment and Waste by GC/MS.

6.8. Florida Department of Environmental Protection, Standard Operating Procedure **VO-004** Analysis of Acrolein and Acrylonitrile in Sediment and Waste by GC/MS.

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6.9. Florida Department of Environmental Protection, Standard Operating Procedure **VO-005** TCLP and SPLP Preparation Using Zero-Headspace Extraction.

6.10. Florida Department of Environmental Protection, Standard Operating Procedure **VO-006** Measurement of Polar Organic Compounds in Wastewater by GC/MS.

6.11. Florida Department of Environmental Protection, Standard Operating Procedure **LB-002** Non-Conformance Reporting System.

6.12. Florida Department of Environmental Protection, Standard Operating Procedure **LB-027** SOP for Reporting Qualified Data.

6.13. Florida Department of Environmental Protection, Standard Operating Procedure **OG-001** Safety and Waste Management Practices in the Organic Analysis Groups.

6.14. Florida Department of Environmental Protection, "Comprehensive Quality Assurance Plan" (2022).

7. APPENDIX - SIGNIFICANT CHANGES TO THIS SOP VERSION

1) Incremented version number.
2) Minor textual clarifications and typo corrections.
3) Updated equipment and references.

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