SOP-C-108

Determination of Nonfilterable Volatile and Fixed Residue (Volatile and Nonvolatile Suspended and Total Solids)

Revision 13

Approval:

Laboratory Manager ~~3/14/22~~ 3.14.22 Date

Concurrence 03-14-2022 Date

Effective date: 3.16.22

Renewal date: _____ Initials: _____

i. Identification of the method

a. EPA 160.4 (1971), Standard Methods 2540E and G, latest online edition (approved 2017) when used for other solids.

ii. Applicable matrix or matrices

a. Waters, solids

iii. Limits of detection and quantitation

a. LOQ of 10 mg/L up to 20,000 mg/L for waters. Samples may be concentrated or reduced in volume to extend the ranges. LOQ of 0.01% up to 100% for solids.

iv. Scope and application, including parameters to be analyzed;

a. This SOP may be used to determine volatile suspended solids (VSS), total volatile solids (TVS), or volatile dissolved solids (VDS). This SOP may also be used to determine nonvolatile (fixed) suspended solids (NVSS), total fixed solids (TFS), or fixed dissolved solids (FDS).

b. Volatile and Nonvolatile suspended and fixed solids with the following relationships to other solids**:**

   i. TS=TSS + TDS in water samples
   ii. TSS=VSS + NVSS in water samples
   iii. TDS=VDS + FDS in water samples
   iv. TS=TVS + TFS in water samples
   v. % Solids=TVS + TFS in solid samples

v. Summary of the method

a. A well-mixed water sample is tested gravimetrically based on weights before and after drying to constant weight at 103-105°C (TS,TSS), 180°C (TDS) and ashing to constant weight at 540-555°C (range is a modification from the method, which gives only 550°C with no variation).

b. The storage temperature of >0-≤6° C is a modification of the original method which calls for 4°C and no variation.

c. Solid samples may also be measured, but TIAER Lab is not accredited for these at the time of this revision.

d. This SOP may be used in conjunction with SOP-C-107, “Determination of Total Suspended Solids,” SOP-C-109, “Determination of Total Dissolved Solids,” and SOP-C-130, “Determination of Total and Percent Solids,” to

determine other types of solids. This method has been enhanced by TIAER to include a check standard (LCS/LCSD).

vi. Definitions

a. NVSS are those solids that remain on the filter after ignition in a muffle furnace at 540-555ºC.
b. TVS, or organic material, are the solids that are removed from a sample by ignition in a muffle furnace at 540-555ºC.
c. TFS, also known as total fixed solids or ash, are the solids that remain after ignition of the sample in a muffle furnace at 540-555ºC.
d. VDS are those solids dissolved in a sample that pass through a glass fiber filter, are dried to a constant weight at 180°C, and are then lost through ignition in a muffle furnace at 540-555°C.
e. FDS are those dissolved solids that remain after ignition in a muffle furnace at 540-555°C.
f. Refer to QAM-Q-101, "Laboratory Quality Control," for standard QC definitions.

vii. Interferences

a. Non-representative particulates; floating oil and grease, if present should be included in the sample and dispersed by a blender device before aliquot division, if the inclusion is desired in the final result by the client.
b. For solids samples, the container should remain closed to prevent moisture loss. Negative errors in the volatile solids may be produced by loss of organic matter during drying.
c. Determination of low concentrations of volatile matter in the presence of high fixed solids concentrations may be subject of considerable error. Additionally errors may arise from loss of water of crystallization, incomplete oxidation of certain complex organics and decomposition of mineral salts during combustion.
d. Highly alkaline residues may react with silica in the samples or silica containing containers.

viii. Safety

a. Routine laboratory safety precautions

b. Use the oven mitts to remove the sample trays from the oven.
c. Allow containers in the furnace to cool significantly before attempting to remove with tongs and place in the desiccator.

ix. Equipment and supplies

a. Glass fiber filter discs without organic binder (Millipore AP40, Reeves Angel 934-AH, Gelman type A/E or equivalent)
b. Ceramic dishes or crucibles
c. Filtering apparatus with 40-60 micron fritted disc filter support
d. Side-arm suction flask with vacuum attachment
e. Class A graduated cylinder calibrated “to contain”
f. Drying oven set at 180 ± 2°C (lower to 104 ± 1°C for initial evaporation)
g. Muffle furnace set at 540-555°C
h. Desiccator
i. Analytical balance capable of weighing increments of 0.1mg.
j. ISCO™ plastic sample bottles, or equivalent (1liter) with cap
k. Sample tray
l. Aluminum weighing pans (also see SOP-C-107)
m. Forceps and tongs
n. Evaporating dishes/crucibles
o. Wide bore pipettes, beakers, stirrers, general lab equipment

x. Reagents and standards

a. Reagents:
    i. Deionized water, ASTM Type II
    ii. Hydrochloric acid, 0.1 N: Carefully mix 8.3 mL of conc. HCL into about 800 mL of DI water in a 1 L volumetric flask. Dilute to volume
b. Standards
    i. Sodium Chloride, 100 mg/L, LCS/LCSD. Weigh 0.1000 g of NaCl (dried at 180°C and cooled in a desiccator) and dissolve into DI water in a 1L volumetric flask. Shelf life is 7 days.

ii. Celite™ standard, 100 mg/L, LCS/LCSD for NVSS
   1. Rinse about 500 g of Celite™ 545, or equivalent, with three 250mL portions of 0.1 N HCL by mixing in a large beaker, allowing to settle and decanting each time.
   2. Rinse the Celite™ with three portions of DI water in the same manner and decant.
   3. Dry the rinsed Celite™ overnight at 180°C
   4. Stir the solid with a glass rod to ensure homogeneity of drying and place in a dessicator
   5. Weigh 0.1000 g of prepared Celite™ and mix with about 800 mL DI water in a 1 L volumetric flask. Dilute to volume. Standard is ready for analysis. Mix well each time prior to use.

iii. TS/TVS/TFS standard, 300/134/166 mg/L (LCS/LCSD)
   1. Ignite about 0.5 grams of NaCl at 540-550°C in a muffle furnace for 20 minutes, cool and store in a dessicator until needed.
   2. Dry 1 gram of KHP at 104±1 °C in an oven for one hour, cool and store in a dessicator until needed.
   3. Weigh 0.1000 g of dried NaCl and 0.2000 g of prepared KHP and dissolve in about 800 mL DI water in a 1L volumetric flask. Dilute to volume. Standard is ready for analysis.

xi. Sample collection, preservation, shipment and storage

a. Holding Time: 7 days for waters, begin analysis as soon as possible; 6 months for solid matrix samples.
b. Preservation: Refrigerate sample to >0-≤6° C until analysis
c. Refer to field procedures for sampling

xii. Quality control

a. Refer to QAM-Q-101, “Laboratory Quality Control.”
b. For every 10 samples, analyze at least one sample duplicate (QCB).
c. Method blanks and LCS/LCSD pair are analyzed for every set of 20 samples or less (PB).

d. No CCV, CCB, AWRL or LOQ standard is required for this procedure.
e. The analytical balance should be calibrated with the 0.1 g class 1 weight before the initial and final weights of the filters or crucible are taken. Calibrate in accordance with QAM-I-101, "Operation and Calibration of the Analytical Balance".

xiii. Calibration and standardization

a. None

xiv. Procedure

a. Sample Handling and Preservation
    i. Sample containers should be plastic or glass.
    ii. Non-representative particulate, such as leaves, sticks, fish and lumps of fecal matter, should be excluded from the sample if it is determined that their inclusion is not desired in the final result.
    iii. Analysis should begin as soon as possible. Samples should be placed on ice or refrigerated to maintain a temperature of >0-≤6° C, and thereby minimize microbiological decomposition of solids. Bring samples to room temperature before analysis.
    iv. Approximately 100 mL of sample is needed for water analysis. About 100 g is needed for solids analysis. This may be adjusted due to amounts required for other analyses or for the presence of more suspended matter that precludes larger volumes passing through the filter for waters, and amount of liquid in solid samples
b. Preparation of filter (dissolved/suspended solids) or evaporating dish/crucible (total or filtered solids).
    i. Prepare filter or dish according to SOP-C-107, SOP-C-130, or SOP-C-109. Filters require additional preparation, while crucible/dishes do not.
    ii. Ignite evaporating dish/crucible/beaker at 540-555°C in a muffle furnace for at least 1 hour. Ignite filters for at least 20 minutes. Cool and store in a desiccator until needed.
c. Analysis of Samples

i. Weigh filter or dish/crucible to nearest 0.1 mg and record in personal logbook or E-log.
ii. Visually inspect the sample. For apparently low suspended solid samples, shake the container vigorously at least 25 times and pour a measured volume into a calibrated graduated cylinder (To Contain type). For higher apparent suspended solids, stir sample with a magnetic stirrer in a beaker. While stirring, pipet from a point mid-depth and midway between the container wall and vortex.
iii. Analyze samples according to SOP-C-107, SOP-C-130, or SOP-C-109, filtering or pouring samples as directed. For solid samples, obtain a weighed, representative sample from a well-mixed portion of the original.
iv. Transfer dish/crucible to the cool muffle furnace and turn on, set to 540-555°C.
v. If igniting filters place them on an aluminum or ceramic pan.
vi. Ignite filters with samples in muffle furnace for at least 20 minutes.
vii. Ignite dishes/crucibles with samples for at least 1 hour. Residues above 200 mg may require longer ignition times to fully ash the sample. If it is apparent that the residue contains a large amount of organic matter, first ignite the dried sample over a gas burner under an exhaust hood. Adequate air should be present to lessen losses due to reducing conditions. Be careful to not allow sample to be blown out of the container.
viii. Remove filters or dishes/crucibles from the muffle furnace and cool in desiccator to room temperature.
ix. Weigh filters or dishes/crucibles to nearest 0.1 mg and record in personal logbook.
x. The cycle of ignition, cooling, desiccation, and weighing should be repeated until a constant weight is seen or until weight change is less than 4% or 0.5 mg, whichever is less. Analyst may ignite sample for

2 hours prior to cooling and weighing instead of repeating the cycle (modification to method).

xv. Data analysis and calculations;

a. Approved spreadsheets or Elog on laboratory computer to calculate solids and QC may be used or required.

b. Calculations:

mg volatile solids/L

(VSS, VDS, & TVS in water) = $\frac{(A - B) \times 1000}{\text{sample volume (mL)}}$

mg fixed solids/L

(NVSS, FDS & TFS in water)= $\frac{(B - C) \times 1000}{\text{sample volume (mL)}}$

percent volatile solids (TVS in solids)= $\frac{(A - B) \times 100}{\text{sample weight (mg)}}$

percent fixed solids (TFS in solids) = $\frac{(B - C) \times 100}{\text{sample weight (mg)}}$

Where:

A = weight of residue + filter or dish/crucible before ignition,
B = weight of residue + filter or dish/crucible after ignition, and
C = weight of filter or dish/crucible

xvi. Method performance

a. Duplicate determinations should agree within 5% of their average weight.

b. Analyze the LCS/LCSD standards in the same manner as any sample.

xvii. Pollution prevention

a. Not applicable

xviii. Data assessment and acceptance criteria for quality control measures

a. Refer to QAM-Q-101, “Laboratory Quality Control.”

b. If any QC samples do not pass the acceptance criteria as described in QAM-Q-101, “Laboratory Quality Control,” reanalyze immediately if possible (holding time and sample volume are sufficient) and complete a Corrective

Action Report in accordance with QAM-Q-105, "Corrective Actions".

c. Duplicate acceptance limits are ±10% RPD for sample duplicates, ±20% RPD for LCS/LCSD and ±30% RPD for field splits. At present there is no standard or LCS for VSS.
d. QC Samples for TFS (NaCl), TVS (KHP), and NVSS (Celite™): For every 10 samples, analyze at least one sample duplicate. Method blanks and LCS/LCSD pair (with no sample duplicate) are analyzed for every set of 20 samples or less.

xix. Corrective actions for out-of-control data

a. Refer to QAM-Q-105, "Corrective Actions."

xx. Contingencies for handling out-of-control or unacceptable data

a. Refer to QAM-Q-105, "Corrective Actions," and QAM-Q-101, "Laboratory Quality Control."

xxi. Waste management

a. Not applicable; for general waste management and pollution prevention, refer to QAM-W-101, "Disposal of Laboratory Waste".

xxii. References

a. EPA 160.4 (1971), Residue, Volatile (Gravimetric, Ignition at 550°C) by Muffle Furnace
b. Standard Methods for the Examination of Water and Wastewater, latest online edition approved 2017, ed. by Arnold E. Greenberg, et al., APHA, AWWA, Washington D.C., Method 2540 E.
c. National Environmental Laboratory Accreditation Conference (The NELAC Institute) standard, 2016.
d. Code of Federal Regulations, 40 CFR 136, July 2012

xxiii. Any tables, diagrams, flowcharts and validation data

a. Example Total Volatile and Fixed Solids Template
b. Example Total Volatile and Fixed Solids Template showing formulas

Attachment 1: Example Total Volatile and Fixed Solids Template

Total Solids / Total Volatile and Fixed Solids

Revised 10/1/21 jrh | QA: jrh 11/21/19 | **PAN** | | | oven O-8 103-105C | M-1 540-555C

ANALYST jrh | **Start Date/time** | **End Date/time** | balance: S-2

beaker prep 540-555C | after 103-105 | cylinders: | **after 540-555C** | Furnace ID: M-1

Container ID	SAMPLE NUMBER	INITIAL Weight (g)	Second Weight	% difference	difference	% check	VOLUME (L)	Final TS Weight 1	Final TS Weight 2	mg/L TS	QC Check	% difference	difference	% check	Comments	Final TVS Weight 1	Final TVS Weight 2	mg/L TFS	QC Check	% difference	difference	% check	Comments	mg/L TVS
A1	mb-			#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A2	LCS-			#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A3	LCSd-			#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A4				#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A5	dup-			#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A6				#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A7				#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A8				#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A9				#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A10				#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A11				#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A12				#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A13				#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A14				#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A15				#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
A16				#DIV/0!	0.0000	#DIV/0!	0.100			0.0	Too little residue	#DIV/0!	0.0000	#####	na			0.0	too little residue	#DIV/0!	0.0000	#####	na	0.0
		In O-6 or M-1					in O-6@	back in O-6@	In M-1 @							back in M-1@	end							

Attachment 2: Example Total Volatile and Fixed Solids Template showing formulas