

# Determination of Total Suspended Solids (TSS) and Total Volatile Solids (TVS) in Waters of Fresh/Estuarine/Coastal Waters

## 1. SCOPE and APPLICATION

- 1.1 Gravimetric analysis is used to determine total suspended solids (TSS) and total volatile solids (TVS), also known as volatile suspended solids (VSS) using a four place analytical balance.
- 1.2 A Method Detection Limit (MDL) of 2.4 mg TSS/L and 0.9 mg TVS/L were determined using the Student's *t* value (3.14) times the standard deviation of seven replicates. If more than seven replicates are used to determine the MDL, refer to the Student's *t* test table for the appropriate *n*-1 value.
- 1.3 The quantitation limit for TSS was set at 0.0005 mg/L TSS.
- 1.4 This procedure should be used by analysts experienced in the theory and application of TSS. 1 month experience with an experienced analyst, certified in the analysis using the four place balance, is required.
- 1.5 This method can be used for all programs that require analysis of total suspended and volatile solids.
- 1.6 This procedure conforms to EPA Method 160.2 and Standard Methods 208 E.

## 2. SUMMARY

- 2.1 Measured aliquots of a water sample are filtered through a pre-weighed glass fiber filter pad. These pads are placed into a 105° C drying oven overnight to remove any remaining water. The pads are removed from the oven and placed into a desiccator to cool to room temperature. Once samples have reached room temperature, they are individually weighed on a four place balance and their respective weights are recorded in a spreadsheet and the concentration is reported as mg/L total suspended solids. If samples are to be used to determine total volatile solids they are placed into a numbered porcelain crucible and dried in a muffle furnace at 550° C for 1.5 hours. The samples are placed into a desiccator to cool to room temperature. Once they have cooled, they are weighed on the four place balance and their weights are recorded into the spreadsheet.

## 3. DEFINITIONS

- 3.1 Acceptance Criteria – Specified limits placed on characteristics of an item, process, or service defined in a requirement document. (ASQC)
- 3.2 Accuracy – The degree of agreement between an observed value and an accepted reference value. Accuracy includes a combination of random error (precision) and systematic error (bias) components which are due to sampling and analytical operations; a data quality indicator. (QAMS)
- 3.3 Aliquot – A discrete, measured, representative portion of a sample taken for analysis. (EPA QAD Glossary)

- 3.4 Batch – Environmental samples, which are prepared and /or analyzed together with the same process and personnel, using the same lot(s) of reagents. A **preparation batch** is composed of one to 20 environmental samples of the same matrix, meeting the above mentioned criteria and with a maximum time between the start of processing of the first and last sample in the batch to be 24 hours. An **analytical batch** is composed of prepared environmental samples (extracts, digestates, or concentrates) and/or those samples not requiring preparation, which are analyzed together as a group using the same calibration curve or factor. An analytical batch can include samples originating from various environmental matrices and can exceed 20 samples. (NELAC/EPA)
- 3.5 Blank- A sample that has not been exposed to the analyzed sample stream in order to monitor contamination during sampling, transport, storage or analysis. The blank is subjected to the usual analytical and measurement process to establish a zero baseline or background value and is sometimes used to adjust or correct routine analytical results. (ASQC)
- 3.6 Calibrate- To determine, by measurement or comparison with a standard, the correct value of each scale reading on a meter or other device, or the correct value for each setting of a control knob. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements. (NELAC)
- 3.7 Calibration – The set if operations which establish, under specified conditions, the relationship between values indicated by a measuring device. The levels of the applied calibration standard should bracket the range of planned or expected sample measurements. (NELAC)
- 3.8 Calibration Curve – The graphical relationship between known values, such as concentrations, or a series of calibration standards and their analytical response. (NELAC)
- 3.9 Calibration Method – A defined technical procedure for performing a calibration. (NELAC)
- 3.10 Calibration Standard – A substance or reference material used to calibrate an instrument. (QAMS)
  - 3.10.1 Initial Calibration Standard (STD) – A series of standard solutions used to initially establish instrument calibration responses and develop calibration curves for individual target analytes.
  - 3.10.2 Initial Calibration Verification (ICV) – An individual standard, analyzed initially, prior to any sample analysis, which verifies acceptability of the calibration curve or previously established calibration curve.
  - 3.10.3 Continuing Calibration Verification (CCV) – An individual standard which is analyzed after every 10-15 field sample analysis.

Corrective Action – Action taken to eliminate the causes of an existing nonconformity, defect or other undesirable situation in order to prevent recurrence. (ISO 8402)

- 3.11 Deficiency – An unauthorized deviation from acceptable procedures or practices. (ASQC)
- 3.12 Demonstration of Capability – A procedure to establish the ability of the analyst to generate acceptable accuracy. (NELAC)
- 3.13 Detection Limit – The lowest concentration or amount of the target analyte that can be determined to be different from zero by a single measurement at a stated degree of confidence.
- 3.14 Duplicate Analysis – The analyses of measurements of the variable of interest performed identically on two sub samples (aliquots) of the same sample. The results from duplicate analyses are used to evaluate analytical or measurement precision but not the precision of sampling, preservation or storage internal to the laboratory. (EPA-QAD)
- 3.15 Field Duplicates (FD1 and FD2) – Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 provide a measure of the precision associated with sample collection, preservation and storage, as well as with laboratory procedures.
- 3.16 Field Reagent Blank (FRB) – A aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to the sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.
- 3.17 Furnace – Combusts samples at 550°C.
- 3.18 Holding time – The maximum time that samples may be held prior to analysis and still be considered valid (40 CFR Part 136). The time elapsed from the time of sampling to the time of extraction or analysis, as appropriate.
- 3.19 Instrument Detection Limit (IDL) – The minimum quantity of analyte of the concentration equivalent which gives an analyte signal equal to three times the standard deviation of the background signal at the selected wavelength, mass, retention time absorbance line, etc.
- 3.20 Laboratory Duplicates (LD1 and LD2) – Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.
- 3.21 Laboratory Reagent Blank (LRB) – A blank matrix (i.e., DI water) that is treated exactly as a sample including exposure to all glassware, equipment, solvents, and reagents that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the instrument.
- 3.22 Laboratory Control Sample (LCS) – A sample matrix, free from the analytes of interest, spiked with verified known amounts of analytes from a source independent of the calibration standard or a material

containing known and verified amounts of analytes. The LCS is generally used to establish intra-laboratory or analyst-specific precision and bias or to assess the performance of all or a portion of the measurement system. (NELAC)

- 3.23 Limit of Detection (LOD) – The lowest concentration level that can be determined by a single analysis and with a defined level of confidence to be statistically different from a blank. (ACS)
- 3.24 Limit of Quantitation (LOQ) – The minimum levels, concentrations, or quantities of a target variable (target analyte) that can be reported with a specified degree of confidence. The LOQ is set at 3 to 10 times the LOD, depending on the degree of confidence desired.
- 3.25 Linear Dynamic Range (LDR) – The absolute quantity over which the instrument response to an analyte is linear. This specification is also referred to as the Linear Calibration Range (LCR).
- 3.26 Material Safety Data Sheets (MSDS) – Written information provided by vendors concerning a chemical's toxicity, health hazards, physical properties, fire, and reactivity data including storage, spill, and handling precautions.
- 3.27 May – Denotes permitted action, but not required action. (NELAC)
- 3.28 Method Detection Limit (MDL) – The minimum concentration of an analyte that can be identified, measured, and reported with 98% confidence that the analyte concentration is greater than zero.
- 3.29 Must – Denotes a requirement that must be met. (Random House College Dictionary)
- 3.30 Precision – The degree to which a set of observations or measurements of the same property, obtained under similar conditions, conform to themselves; a data quality indicator. Precision is usually expressed as standard deviation, variance or range, in either absolute or relative terms. (NELAC)
- 3.31 Preservation – Refrigeration, freezing, and/or reagents added at the time of sample collection (or later) to maintain the chemical and or biological integrity of the sample.
- 3.32 Quality Control Sample (QCS) – A sample of analytes of known and certified concentrations. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.
- 3.33 Run – One sample analysis from start to finish, including printout.
- 3.34 Run Cycle – Typically a day of operation – the entire analytical sequence of runs from the first run to the last run and including the transfer of run cycle data to the disc.
- 3.35 Sample Volume – Amount of volume filtered.
- 3.36 Sensitivity – The capability of a test method or instrument to discriminate between measurement responses representing different levels (concentrations) of a variable of interest.

- 3.37 Shall – Denotes a requirement that is mandatory whenever the criterion for conformance with the specification requires that there be no deviation. (ANSI)
- 3.38 Should – Denotes a guideline or recommendation whenever noncompliance with the specification is permissible. (ANSI)
- 3.39 Standard Reference Material (SRM) – Material which has been certified for specific analytes by a variety of analytical techniques and/or by numerous laboratories using similar analytical techniques. These may consist of pure chemicals, buffers, or compositional standards. The materials are used as an indication of the accuracy of a specific analytical technique.

#### **4. INTERFERENCES**

- 4.1 Excessive residue may form a water trapping crust. Sample size should be limited to yield < 200 mg of residue.
- 4.2 Samples from saline waters will not weigh to a constant weight. Therefore they must be rinsed with copious amounts of distilled water.

#### **5. SAFETY**

- 5.1 Safety precautions must be taken when handling reagents, samples and equipment in the laboratory.
- 5.2 The muffle furnace becomes extremely hot. Use care when removing crucibles from the furnace. Be sure they have cooled to the touch. Use gloves or tongs if necessary.

#### **6. EQUIPMENT AND SUPPLIES**

- 6.1 A four place analytical balance.
- 6.2 Desiccator with drying agents such anhydrous calcium sulfate or silica.
- 6.3 Drying oven capable of heating to 105° C
- 6.4 Muffle furnace capable of heating to 550° C.
- 6.5 Freezer, capable of maintaining -20° ± 5° C.

#### **7. REAGENTS AND STANDARDS**

- 7.1 Purity of Water – Unless otherwise indicated, references to water shall be understood to mean reagent water conforming to ASTM Specification D 1193, Type I. Freshly prepared water should be used for making the standards intended for calibration. The detection limits of this method will be limited by the purity of the water and reagents used to make the standards.
- 7.2 Blanks – ASTM D1193, Type I water is used for the LRB.
- 7.3 Quality Control Sample (QCS) – For this procedure, the QCS can be any

certified dissolved sample which is obtained from an external source. If a certified sample is not available, then use the standard material.

## **8. SAMPLE COLLECTION, PRESERVATION, AND STORAGE**

- 8.1 Water collected for TSS and/or TVS should be filtered through a Whatman GF/F glass fiber filter (nominal pore size 0.7  $\mu\text{m}$ ), or equivalent.
- 8.2 Samples should be placed into an aluminum foil pouch and should be frozen at  $-20^{\circ}\text{C}$ .
- 8.3 Frozen TSS/TVS samples may be stored longer than 28 days.

## **9. QUALITY CONTROL**

- 9.1 The laboratory is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the continued analysis of laboratory instrument blanks and calibration standard material, analyzed as samples, as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of data generated.
- 9.2 Initial Demonstration of Capability
  - 9.2.1 The initial demonstration of capability (DOC) – is used to characterize instrument performance (MDLs) and laboratory performance (analysis of QC samples) prior to the analyses conducted by this procedure.
  - 9.2.2 Quality Control Sample (QCS/SRM) – When using this procedure, a quality control sample is required to be analyzed at the beginning and end of the run, to verify data quality and acceptable instrument performance. If the determined concentrations are not within  $\pm 10\%$  of the certified values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with analyses.
  - 9.2.3 Method Detection Limits (MDLs) – MDLs should be established for TSS and TVS using a low level ambient water sample. To determine the MDL values, analyzed seven replicate aliquots of water. Perform all calculations defined in the procedure (Section xx) and report the concentration values in the appropriate units. Calculate the MDL as follows:

$$\text{MDL} = S t_{(n-1, 1-\alpha=0.99)}$$

Where, S = Standard deviation of the replicate analyses.  
n=number of replicates  
 $t_{(n-1, 1-\alpha=0.99)}$  = Student's *t* value for the 99% confidence level with n-1 degrees of freedom ( $t=3.14$  for 7 replicates.)  
MDLs should be determined yearly.

### 9.3 Assessing Laboratory Performance

- 9.3.1 Laboratory Reagent Blank (LRB) – The laboratory must analyze at least one LRB with each batch of samples. The LRB consists of Nanopure water treated the same as the samples. LRB data are used to assess contamination from the laboratory environment.
- 9.3.2 Quality Control Sample (QCS)/ Standard Reference Material (SRM) – when using this procedure, a quality control sample is required to be analyzed at the beginning of the run and end of the run, to verify data quality and acceptable instrument performance. If the determined concentrations are not within  $\pm 3\sigma$  of the certified values, performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before either proceeding with the initial determination of MDLs or continuing with the analyses. The results of these samples shall be used to determine batch acceptance.
- 9.3.3 The QCS will be obtained from a source external to the laboratory and different from the source of calibration standards.

### 9.4 Data Assessment and Acceptance Criteria for Quality Control Measures

- 9.4.1 If a Total Volatile Solid (TVS) result is more than the Total suspended Solid (TSS) result, an error code 9 is assigned to the sample.
- 9.4.2 If duplicates have been provided for a sample, the results of the two numbers must be compared to each other. If the difference between the two numbers is equal to or more than 50% of the lower number then an error code 14 is assigned.

### 9.5 Corrective Actions for Out of Control Data

- 9.5.1 Out of control data is not reported. Generally portions of the pad are missing and therefore the measurement is considered useless. An error code is assigned.

## 10. CALIBRATION AND STANDARDIZATION

10.1 Calibration – Daily checks of calibration of balance using a certified weight must be performed before sample analysis may begin. The balance is professionally calibrated annually.

## 11. PROCEDURE

### 11.1 Total Suspended Solids

- 11.1.1 On a clean piece of paper lay out filter pads for numbering
- 11.1.2 Use a Sharpie permanent ultra fine or very fine point black marker, sequentially number outside edge of each pad with a unique label.
- 11.1.3 After pads have been labeled, place in a Pyrex dish and dry overnight in a 105° C oven.
- 11.1.4 When ready to weigh, remove pads from oven and place into a desiccator to cool to room temperature.
- 11.1.5 Turn on analytical balance and computer.
- 11.1.6 Check calibration.
- 11.1.7 Click on BalanceLink icon and be sure balance has been detected.
- 11.1.8 After pads have come to room temperature, weigh pads individually on balance and enter data into respective spread sheets and store in their labeled boxes for future use.
- 11.1.9 When ready to sample, place pad **numbered side down** onto filtering apparatus.
- 11.1.10 Filter a known volume of sample through the filter pad.
- 11.1.11 Rinse pad very well with deionized water to rinse down filter tower and remove any salts from the pad.
- 11.1.12 Fold pad in half, sample side in and place pad into a labeled foil pouch and place in labeled storage bag and store in -20° C freezer. Place replicate pads side by side in pouch and not on top of each other.
- 11.1.13 When ready to analyze, place opened pouch with sample in 105° C drying oven overnight.
- 11.1.14 Repeat steps 11.1.4 – 11.1.7.
- 11.1.15 Calculate TSS value:

$$\text{mgTSS / L} = \frac{(\text{W}_{\text{post}(\text{g})} - \text{W}_{\text{pre}(\text{g})}) \times 1000}{\text{V (L)}}$$



## 11.2 Total Volatile Solids

- 11.2.1 Place pads straight from box into a nickel crucible and combust at 550° C in a muffle furnace for 1.5 hours.
- 11.2.2 Move pads to a 105° C oven for storage until ready to use.
- 11.2.3 Repeat steps 11.1.4 – 11.1.7.
- 11.2.4 After pads have come to room temperature, weigh pads individually on balance and enter data into respective spread sheets and store into individually labeled Petri dishes for future use.
- 11.2.5 When ready to sample, place pad onto filtering apparatus.
- 11.2.6 Repeat steps 11.1.10 – 11.1.13 to calculate TSS value.
- 11.2.7 Once TSS value has been determined place pad into a numbered porcelain crucible and record crucible number and sample id.
- 11.2.8 Combust samples at 550° C in a muffle furnace for 1.5 hours.
- 11.2.9 Repeat steps 11.1.4 – 11.1.7
- 11.2.10 Calculate TVS:

$$mgTVS / L = \frac{(W_{post(g)} - W_{combust(g)}) \times 1000}{V(L)}$$

## 12 REFERENCES

- 12.1. APHA. 1975. Method 208D. Total Nonfilterable Residue Dried at 103-105 C (Total Suspended Matter) *in* Standard Methods for the Examination of Water and Wastewater, 14<sup>th</sup> Edition. American Public health Association. Washington, D.C. 460pp.
- 12.2. USEPA 1979 Method No. 160.2 (with slight modification) *in* Methods for chemical analysis of water and wastes. United States Environmental Protection Agency, Office of Research and Development. Cincinnati, Ohio. Report No. EPA-600/4-79-020 March 1979. 1193 pp.

