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

(Reference Method: EPA Method 160.2 and Standard Methods 208 E.)

Document #: NASLDoc-030

Revision 2019-1
Replaces Revision 2018-1
Effective May 1, 2019
I attest that I have reviewed this standard operating procedure and agree to comply with all procedures outlined within this document.

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Employee (Print)	Employee (Signature)	Date
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Revised by: ____________________ Date: __________

Reviewed by: ____________________ Date: __________

Laboratory Supervisor: ____________________ Date: __________

1.3 Changed the quantitation limit to 2.4 mg TSS/L and 0.9 mg TVS/L
2.1 Changed 550^{o}C to 500 ^{o}C
3.16 Changed 550^{o}C to 500 ^{o}C
3.21 Added “,or equal to the LOD”
6.4 Changed 550^{o}C to 500 ^{o}C
9.3.1 Added “Following initial analysis, place the chosen pad back into the drying oven for 1 hour and reweigh the pad. The results of the two numbers must be compared to each other. The difference between the two weights should be within 10% of each other.”
11.2.1 Changed 550^{o}C to 500 ^{o}C
11.2.9 Changed 550^{o}C to 500 ^{o}C

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 was set at 2.4 mg TSS/L and 0.9 mg TVS/L.

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 references 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. Once samples have cooled, they are individually weighed on a four place balance. 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 500° C for 1.5 hours. The samples are placed into a desiccator to cool. 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. 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 of 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 Method – A defined technical procedure for performing a calibration. (NELAC)

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

3.10 Deficiency – An unauthorized deviation from acceptable procedures or practices. (ASQC)

3.11 Demonstration of Capability – A procedure to establish the ability of the analyst to generate acceptable accuracy. (NELAC)

3.12 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.

3.13 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)

3.14 Field Duplicates (FD1 and FD2) – Two separate samples collected at the same time and place under identical circumstances and treated exactly the same throughout filed 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.

3.15 Field Reagent Blank (FRB) – A aliquot of reagent water or other blank matrix that is places 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.

3.16 Furnace – Combusts samples at 500°C.

3.17 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.

3.18 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.

3.19 Laboratory Reagent Blank (LRB) – A blank matrix (i.e., reagent 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.

3.20 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. Laboratory interchanges LOD and MDL. (ACS)

3.21 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, or equal to the LOD depending on the degree of confidence desired. Also referred to as quantitation limit.

3.22 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.

3.23 May – Denotes permitted action, but not required action. (NELAC)

3.24 Method Detection Limit (MDL) – The minimum concentration of an analyte that can be identified, measured, and reported with 99% confidence that the analyte concentration is greater than zero. (Standard Methods)

3.25 Must – Denotes a requirement that must be met. (Random House College Dictionary)

3.26 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)

3.27 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.
3.28 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.
3.29 Sample Volume – Amount of volume filtered.
3.30 Sensitivity – The capability of a test method or instrument to discriminate between measurement responses representing different levels (concentrations) of a variable of interest.
3.31 Shall – Denotes a requirement that is mandatory whenever the criterion for conformance with the specification requires that there be no deviation. (ANSI)
3.32 Should – Denotes a guideline or recommendation whenever noncompliance with the specification is permissible. (ANSI)

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. Protective clothing including lab coats, safety glasses and enclosed shoes may be worn. In certain situations, it may also be necessary to use gloves and goggles. Contact Solomons Rescue Squad (911) if emergency treatment is needed and also inform the Chesapeake Biological Laboratory (CBL) Associate Director of Administration and Facilities Maintenance of the incident. Contact the CBL Associate Director of Administration and Facilities Maintenance if additional treatment is required.
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 as anhydrous calcium sulfate or silica.
6.3 Drying oven capable of heating to 105° C
6.4 Muffle furnace capable of heating to 500° 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 μm), or equivalent.

8.2 Samples should be placed into an aluminum foil pouch and should be frozen at -20° 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 (iDOC) – 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 Method Detection Limits (MDLs) – MDLs should be established for TSS and TVS using a low level natural water sample. To determine the MDL values, analyzed seven replicate aliquots of water. Perform all calculations defined in the procedure (Section 11.3) and report the concentration values in the appropriate units. Calculate the MDL as follows:

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

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 annually or whenever there is a significant change in instrumental configuration or response.

9.3 Assessing Laboratory Performance

9.3.1 The laboratory performs duplicate analysis of 10% of samples, or at least 1 per batch, whichever is higher. Following initial analysis, place the chosen pad back into the drying oven for 1 hour and reweigh the pad. The results of the two numbers must be compared to each other. The difference between the two weights should be within 10% of each other.

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 29 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, staggering each pad, 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.

11.1.5 Turn on analytical balance and computer.
11.1.6 Perform a balance calibration. Check calibration by weighing a certified weight. Record weight on bench sheet.
11.1.7 Click on BalanceLink icon and be sure balance has been detected.
11.1.8 After pads have cooled, weigh pads individually on balance and enter data into respective spread sheets.
11.1.9 Store pads in their labeled boxes for future use.
11.1.10 When ready to sample, place pad **numbered side down** onto filtering apparatus.
11.1.11 Filter a known volume of sample through the filter pad.
11.1.12 Rinse pad very well with reagent water to rinse down filter tower and remove any salts from the pad.
11.1.13 Fold pad in half, sample side in and place pad into a labeled foil pouch. Place foil with sample 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.
11.1.14 When ready to analyze, place opened pouch with sample in 105° C drying oven overnight.
11.1.15 Repeat steps 11.1.4 – 11.1.8.
11.1.16 Reweigh certified weight and record on bench sheet.

11.2 Total Volatile Solids

11.2.1 Place pads straight from box into a crucible and combust at 500° 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 cooled, 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
11.2.7 Repeat steps 11.1.4 – 11.1.8 to determine the TSS value.
11.2.8 Once TSS value has been determined place pad into a numbered porcelain crucible. Record crucible number and sample ID.
11.2.9 Combust samples at 500° C in a muffle furnace for 1.5 hours.
11.2.10 Repeat steps 11.1.4 – 11.1.8.
11.2.11 Reweigh certified weight and record on bench sheet.

11.3 Calculations

11.3.1 Calculate TSS value:

$$\text{mgTSS / L} = \frac{(\text{Wpost}_{(\text{g})} - \text{Wpre}_{(\text{g})}) \text{ x } 1000}{\text{V (L)}}$$

11.3.2 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, 14th 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.