Ozarks Environmental and Water Resources Institute (OEWRI)
Missouri State University (MSU)

Standard Operating Procedure for:

Total Suspended Solids

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Table of Contents

Identification of test method
Determination of Total Suspended Solids.

Applicable matrix or matrices
This method is suitable for determination of suspended material in potable, surface, and waste water samples yielding total suspended solids (TSS) of no more than 200 mg.

Detection limit
Desired detection limit for this method is 0.5 mg/L for a 1-L sample.

Scope of test method
This standard operating procedure provides OEWRI laboratory personnel with guidance on the procedure for determining TSS. This method is limited to determination of TSS in water samples yielding total suspended solids (TSS) of no more than 200 mg.

Summary of test method
The procedure described here follows published Standard Methods and U.S. Environmental Protection Agency (USEPA) protocols (USEPA 1971, Clesceri et al 1998). A well-mixed, measured volume of a water sample is filtered through a preweighed glass fiber filter (either 1.5 µm or .045 µm nominal pore size). The filter is heated to a constant mass at 104 ± 1º C and then weighed. The mass increase (mg) divided by the water volume filtered (L) is equal to the TSS in mg/L.

Definitions
1. Analytical batch: set of samples processed at the same time.
2. Laboratory reagent blank (LRB): An aliquot of deionized water treated as a sample in all aspects, except that it is not taken to the sampling site. The purpose is to determine if analytes or interferences are present in the laboratory environment, reagents, or apparatus.
3. Laboratory duplicate (LD): Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.
4. Method detection limit (MDL): The lowest level at which an analyte can be detected with 99 percent confidence that analyte concentration is greater than zero.

Interferences

It is recognized that TSS measurements may include both positive errors (occluded water and waters of crystallization) and negative errors (decomposition and volatilization of minerals such as carbonates, as well as loss of solids that are small enough to pass through the filter).

Health and safety

Analysis involves handling freshwater samples that may contain live microorganisms and therefore pose some threat of infection. Laboratory personnel who are routinely exposed to such water samples are encouraged to protect themselves from water-borne illnesses by wearing clean disposable gloves and washing their hands frequently. Additionally, the use of a vacuum pump during filtration carries a risk of implosion under certain circumstances. The lab analyst should ensure that the receiving flask is free from cracks or other imperfections.

Personnel qualifications

Laboratory and field personnel shall have a working knowledge of this analytical procedure and have received training from an MSU employee knowledgeable of the proper sample analysis procedures. Prior to their first batch of sample analyses, the lab analyst will complete a demonstration of capability exercise as described below in the Quality Control section.

Equipment and supplies

1. Filters, Glass microfiber
    a. A 47 mm diameter, 1.5 µm nominal pore size (such as Whatman 934AH, catalog number: 1827 047) or equivalent should be used for stormwater applications per Standard Method 2540 D (Clesceri et al. 1998).
    b. A 47 mm diameter, 0.45 µm nominal pore size (such as MilliporeSigma RMF, catalog number: RW0304700) may be used in conjunction with the total dissolved solids protocol following United States Geological Survey methods (Brown et al. 1970).
    c. Filter pore size used will be noted on bench sheet for reporting purposes.
2. Filtration apparatus
    a. Filter pump
    b. A 1-L or 4-L receiving flask
    c. Filter funnel manifold, 3 positions
    d. Magnetic filter funnels 300 mL
    e. Vacuum tubing, ¼” inside diameter
3. Drying oven (Room 125 of Blunt Hall, MSU), adjusted to 104 ± 1ºC.

4. Aluminum weighing dishes (or equivalent).
5. Analytical balance capable of reading to 0.0001 mg.

Reagents and standards

1. Deionized water (DI): water that has been passed through a purification system (e.g., Barnstead/Thermolyne system).
2. There are no standards available for this method.

Sample collection, preservation, shipment, and storage

1. See SOP for water sample collection procedures (OEWRI 2007).
2. Bottles are sealed and placed on ice in a cooler for transport to the laboratory, where samples are then placed in a laboratory refrigerator. The maximum holding time is seven days (SM, 2005), but analysis should begin as soon as possible upon delivery at the laboratory.

Quality control

1. Method detection limit and precision: initial demonstration of capability (for any new laboratory analyst)
    a) Carry out one round of samples through the procedure.
    b) Calculate the standard deviation of the results. The detection limit should be less than or equal to 0.5 mg/L.
2. Laboratory Duplicate (LD) reproducibility: Carry out with each analytical batch of filters.
    a) Carry out two replicates on same sample, using a sample volume sufficient to provide at least 5 mg solid (ideally, TSS > 10 mg/L).
    b) The relative percent difference (RPD) between two TSS values should be ≤ 20% of their average value.
    c) Use equation 1 to calculate RPD:

$$\text{Equation 1: RPD } (\%) = \frac{(A - B)}{(A + B)/2} \text{ X } 100$$

Where: A = mass of first aliquot (mg),
B = mass of duplicate aliquot (mg)

    d) Analyze one set of duplicates for every 10 samples analyzed.
3. Laboratory Reagent Blank (LRB): At least one blank should be measured with each analytical batch of filters and/or one blank for every 10 samples analyzed.
    a) For the blank measurement, filter 1L deionized water.
    b) The TSS value for the blank should be less than 0.5 mg/L. If it is not, evaluate procedure and correct sources of error.

Procedure

1. Perform a balance check prior to each batch of analyses:
    a. Balance should be level, clean and calibrated prior to use.
    b. Calibrate balance with 50 g weight.
    c. Check calibration with 5 g weight to ensure proper calibration. Scale should be within 0.0003 of the 5 g weight.
    d. Record values on bench sheet and in balance instrument logbook.
2. Preparation of filters:
    a. Place filter disks onto filtration apparatus with tweezers. Apply a small amount of deionized water to filter to ensure adhesion.
    b. Rinse cups 3 times with DI water to clean, then set magnetic cups on filter apparatus.
    c. Fill each cup with 300-mL volume of deionized water. Turn on vacuum and allow each cup to fully empty into waste container.
    d. Using tweezers place wet filter into small pans that are individually labeled and then place all smaller pans into larger aluminum pan (***do not allow the small pans to touch lab bench and don't touch with gloves).*** Using tongs, place larger pan in an oven set to 104 ± 1ºC. e. Heat for two hours to ensure that filters are dry.
    f. Remove filters from the oven with tongs and place them into a desiccator for 30-45 minutes until they have cooled to balance temperature.
    g. Record standard weight (obtained during balance calibration) before weighing filters to ensure scale accuracy.
    h. Weigh each filter in its aluminum pan, recording all measurements.
    i. Record mass of filter on bench sheet as Filter Tare Mass in mg.
    j. Store filters in a desiccator until needed again.
3. Selection of sample volume:
    a. Ideal mass increase for TSS measurement is between 2 and 200 mg. Volume of water sample needed to produce this mass change depends on TSS value.
    b. For water collected under base-flow conditions, the recommended starting volume is 150-300 mL. However, if suspended solids collected in filter are either too high or too low, or if filtration becomes slow due to clogging (total filtration time > 10 minutes), volume should be adjusted as indicated below. c. If mass of captured suspended solids is less than 1 mg, repeat analysis using a larger sample volume, up to 1 L.
    d. If filtration becomes slow because of clogging repeat procedure with a fresh filter, using a volume less than that needed to significantly reduce filtration rate.

e. Based on experience, lab analyst may adjust sample volume. If filtration of 500 mL produces little observable solids on filter, lab analyst may filter more of water sample.

f. If experience has shown that samples from a site normally have very high levels of TSS and/or frequently cause clogging, lab analyst may reduce sample volume, if mass of solid collected falls in range of 2 to 200 mg.

4. <u>For highly turbid samples or samples with expected high amounts of TSS:</u>
    a. Place a magnetic stir bar into sample bottle.
    b. Place the bottle onto a magnetic stirring unit. Stir at a sufficient speed to create a vortex.
    c. Use a 20 mL volumetric pipette to remove sample from bottle; choose a point that is mid-depth and midway between bottle wall and vortex to obtain a homogenous sample.
    d. Place measured sample onto filter and continue suction.
    e. Continue steps 3 & 4 until volume added starts to slow filtration rate.
    f. Record volume (in L) on bench sheet.
    g. Rinse filter pad with three 10 mL volumes of DI.
5. <u>Procedures for TSS:</u>
    a. Set up filtration apparatus and apply a filter.
    b. Wet filter with a small volume of deionized water to seat it.
    c. Shake sample vigorously and then measure out predetermined sample volume. Record volume filtered in L on bench sheet.
    d. Pour sample volume into filtration apparatus, allow full drainage into collect flask.
    e. Carefully transfer filter to an aluminum weighing dish, and place filter on a pie pan or similar device.
    f. Place filters on sheet into an oven set to 104 ± 1ºC and dry for 2 hours.
    g. Remove filters from oven and transfer them to a desiccator to cool to balance temperature 30-45 minutes.
    h. Record standard weight (obtained during balance calibration) before weighing filters to ensure scale accuracy.
    i. Record Oven Dry Mass (in mg) on bench sheet.
    j. Calculate TSS as described below.

Data acquisition, calculations, and reporting

1. For each sample analyzed, including quality control samples, record volume filtered and oven dry mass in the appropriate places on bench sheet (see below). Calculate TSS using equation 2.

$$\text{Equation 2.}\quad \text{TSS (mg/L)} = \frac{A - B}{V} \times 1000$$

Where: A = mass of filter + dried residue (g),
B = mass of filter (tare weight) (g), and
V = volume of sample filtered (L)

Conversion of grams to milligrams: grams X 1000 = milligrams

2. Results should be reported to 0.1 mg/L precision.
3. If multiple bottles were used to collect a composite sample across a stream channel, analyze each bottle separately and calculate the average of the values for final TSS concentration.

Method performance

1. Desired performance criteria for this measurement are:
   a. Detection limit: 0.5 mg/L
   b. Precision: ± 20% RPD
   c. Minimum Quantification Interval: 0.1 mg/L
2. Below are values of reproducibility at different TSS values for TSS process given in Standard Methods 2540 D (each for ten replicates by two different analysts; water volume not specified):

TSS mass (mg/L)	Standard deviation	Coefficient of Variation (%)
15	5.2	33
242	24	10
1707	13	0.76

Both Standard Methods 2540 D and EPA 160.2 indicate that residue should be weighed to a constant weight, defined as two consecutive weight measurements differing by less than 0.5 mg, or less than 4%, whichever is smaller. In addition, replicates should agree within 5% of their average (e.g. a percent difference between the values of 10%). Data noted here show that reproducibility is much poorer for samples with low TSS.

Data assessment and acceptable criteria for quality control measures

1. Lab analyst should review all data for correctness (e.g., calculations).
2. Precision values are calculated for pairs of duplicate analyses.
3. Record precision values as a percent on bench sheet.
4. Desired precision is ± 20% RPD.
5. Desired detection limit is 0.5 mg/L.
6. The completed bench sheet is reviewed by the lab manager and the OEWRI QA coordinator.

Corrective actions for out-of-control or unacceptable data

1. Quality control charts will be created for charting precision and blank values.
2. Results for precision and blank data are compared to acceptable values for this analysis; ± 20% and 0.5 mg/L, respectively.
3. If a precision value exceeds 20% RPD then lab analyst should write in the comments section of the bench sheet: “These data are associated with an out-of-control duplicate analysis. The UCL = 20%.” Note: “UCL” is Upper Control Limit
4. If a blank value exceeds 0.5 mg/L, then lab analyst should write in comments section of bench sheet: “These data are associated with a blank value that exceeds detection limit of 0.5 mg/L.”
5. Typically, there will be no more than 500 mL of sample available for filtration. Given limited sample volume, if the total 500 mL amount has been filtered and the resulting residue remains less than 2 mg or <0.5 mg/L, the sample will be recorded as below the detection limit.
6. Samples cannot be reanalyzed because sample volume will be depleted after initial analysis.
7. If data are unacceptable for any reason, lab analyst should review their analytical technique prior to conducting this analysis again.

Waste management

Wastes generated in this method are not hazardous. Both filtrate and raw sample can be discarded in laboratory sink and filter papers can be discarded with paper trash.

References

Brown, E., M. W. Skougstad, and M. J. Fishman (1970). Methods for Collection and Analysis of Water Samples for Dissolved Minerals and Gases, Book 5, Chapter A1. Techniques of Water-Resources Investigations of the United States Geological Survey.

Clesceri, L. S., A. E. Greenberg, and A. D. Eaton (1998). Standard Methods for the Examination of Water and Wastewater, 20th Edition. United Book Press, Inc., Baltimore Maryland.

OEWRI (2022) Standard Operating Procedure for: Operation of Analytical Balances. Ozarks Environmental and Water Resources Institute, Missouri State University.

OEWRI (2022) Standard Operating Procedure for: Water Sample Collection. Ozarks Environmental and Water Resources Institute, Missouri State University.

USEPA (1971). Method #: 160.2, Residue, Non-Filterable (Gravimetric, Dried at 103105°C). United States Environmental Protection Agency.

Tables, diagrams, flowcharts, and validation data

1. See the TSS Bench Sheet below. The analyst should make a copy of this sheet when processing samples for TSS.

Total Suspended Solids Bench Sheet

Missouri State University

Ozarks Environmental and Water Resources Institute

Data reviewed by:	

Analyst: _____

Date analyzed: _____

Calibrated mass 5.0000 +/- 0.0003 (g) _____ / _____

Filter size: ☐ 0.45 µm ☐ 1.5 µm

Sample Identification	**Date Collected**	**Weigh Pan Label**	**Filter Tare Mass (g)** *(B)*	**Volume Filtered (L)** *(V)*	**Oven Dry Mass (g)** *(A)*	**TSS (mg/L)** *[(A - B) / V] *1000*	**RPD %** [(V1-V2) / ((V1+V2) /2))] * 100

Comments:

_____

_____

TSS - Bench Procedures

Preparing filters:

1. Place filter disks onto filtration apparatus. Apply vacuum and rinse each with three successive 100-mL volumes of deionized water. Draw air through filters until it appears that all water has been drawn off.
2. Place filters (in individual labeled aluminum evaporating dishes) in an oven set to 104 ± 1ºC.
3. Heat filters for two hours to ensure that filters are dry.
4. Remove filters from oven and place them into a desiccator until they have cooled to balance temperature.
5. Weigh each filter, recording all measurements to 0.1 mg precision.
6. Record standard weight before every filter weight to ensure scale accuracy.
7. Record mass of filter on bench sheet as Filter Tare Mass (in g).
8. Store filters in a desiccator until use.

Sample Analysis:

1. Set up filtration apparatus, insert a filter, and apply vacuum.
2. Wet filter with a small volume of deionized water to seat it.
3. Shake sample vigorously and then measure out predetermined sample volume using a graduated cylinder. Record volume filtered in liters on bench sheet.
4. Continue suction until it appears that all water has been drawn off to ensure filtration is complete.
5. Carefully transfer filter to an aluminum weighing dish, and place filter on a cookie sheet or similar device.
6. Place filters on sheet into an oven set to 104 ± 1ºC and dry for two hours.
7. Remove filters from oven and transfer them to a desiccator to cool to room temperature.
8. Record standard weight before every filter weight to ensure scale accuracy.
9. Record Oven Dry Mass (in g) on bench sheet and calculate TSS.

Calculating TSS:

1. To calculate TSS, use the following equation:

$$\text{TSS (mg/L)} = \frac{A - B}{V} \times 1000$$

Where: A = mass of filter + dried residue (g),
B = mass of filter (tare weight) (g), and
V = volume of sample filtered (L)

Conversion of grams to milligrams: grams X 1000 = milligrams