Suspended Solids: Unequal Results from Equal Methods

By John Stone

As of November 2003, 40 CFR, Part 136 lists five approved methods for determining Total Suspended Solids (Residue). Major differences between these methods can produce unequal results from similar samples. Currently approved methods are US EPA 160.2 (written in 1971), US Geological Survey Method I-3765-85 (1985), Standard Method 2540 D 18th Edition (1991), Standard Method 2540 D 19th Edition (1991), and Standard Method 2540 D 20th Edition (1997).

MDL's and Sample Volumes

Method Detection Limits vary between the approved methods; some are more plainly stated than others. EPA 160.2 is the clearest. It lists an MDL of 4mg/L to 20,000mg/L (Section 1.2). A minimum 1 mg residue must be collected on 47mm filters (Section 7.2), with no cap on the sample volume.

The 18th, 19th and 20th Editions of Standard Methods state the method MDL is "*up to 20,000mg/L*" (2540 A, Section 4). In addition to the "*up to 20,000mg/L*" common 2540 D statement, the 18th and 19th Editions require sample volumes selected "*yield a residue between 10 and 200 mg dried residue*", (with the interesting clause that when less than 10 mg of total suspended solids is collected "*compensate by using a high sensitivity balance, (0.002mg)")* (Section 3.b.). Because a minimum residue weight is required in the 18th and 19th, there is in fact a minimum MDL; but since no sample volume limit is established for these two methods, the lower MDL of the 18th and 19th Editions of 2540 D is indeterminable.

20th Edition followers are not required to own a secondary balance that will weigh to 0.002mg. They must however, use enough sample volume to "*yield 2.5 to 200 mg dried residue"* with total sample volume not to exceed 1 liter (Section 3.b). Although unstated, these parameters create a defacto lower MDL of 2.5mg/L. This lower MDL of 2.5mg/L is 60% less than EPA method 160.2 and much higher than the 18th and 19th Editions.

The 40 CFR, Part 136 approved USGS method stays above the MDL fray by not alluding to one.

Filter Prep Procedure

EPA 160.2 and the three approved versions of Standard Method 2540 D share a common filter prep procedure. This procedure requires filter rinsing with three successive 20mL aliquots of reagent-grade water under vacuum, then drying, desiccating and weighing the filter to 0.0001g. After recording the initial weight, a re-dry and re-weigh step is required until a constant weight is reached, ±0.5mg (EPA 160.2, Section 7.1; Standard Method 2540 D, Section 3.a).

The USGS method eliminates the drudgery of filter prep by not requiring any. To follow the USGS procedure, simply weigh the filter once before use (Section 6.2). The washing, drying, or obtaining of a constant weight before running the sample is not required to adhere to I-2765-85.

Eliminating the filter prep step produces erroneous data. In support of this claim stand two facts. First, washing the filter before use removes small fibers that would otherwise wash from the filter when a volume of water (i.e., sample) is vacuumed through the filter. This prep step precludes negative filter weights that would result from the loss of loose fibers.

Secondly, glass fiber filters in almost all environments hold a small amount of ambient water. This water-weight can only be removed by drying. The requirement to achieve a constant weight in 160.2 and 2540 D supports the claim that ambient moisture weight can adversely affect the final result, as does the USGS requirement to "*dry the residue and filter disk overnight at 105ºC*" (Section 6.4), then *"cool in dessicator and weigh"* (Section 6.5). Ambient water-weight of 0.2 to 0.4mg is usually measured in a 47mm filter, significantly more on larger filters.

Sample Storage and Holding Times

Sample Holding Times are congruent within the three approved Standard Method versions of 2540 D. Analysts reading these methods can decide to establish a holding time limit of *"begin analysis as soon as possible"* or *"24 hours"* or *"7 days"* (2540 A, Section 3). The 18th, 19th and 20th also require sample refrigeration (4°C) *"to minimize microbiological decomposition of solids"* (2540 A, Section 3).

EPA and USGS methods do not mention refrigeration and/or holding times.

Given the sample storage and holding time instruction set forth in the three approved Standard Method versions, it is evident that analysis results for suspended solids will vary depending on the quantity of "*microbiological decomposition of solids"* occurring during the period between sampling and analysis. Therefore, unequal results will occur due to differing parameters employed for Sample Storage and Holding Times.

Filter Selection

Suspended solids is a method defined parameter, defined in large part by the porosity of the filter used. As such, an assumption might be that approved methods prescribe similar filters. This would be incorrect.

The three Standard Method versions list filters equal to EPA Method 160.2 approved filters. These four methods each specify glass fiber, binder-free filters with a nominal

porosity of 1.5 m. However, USGS method I-3765-85 approves the use of any filter disk as long as it is *"glass fiber"* (Section 4.2).

A quick review of a major manufacturer's *"glass fiber"* disks – those filters acceptable under the USGS protocol – finds a wide variety available. Pore sizes range from 0.7 to >10 m. Manufacturers also commonly provide glass fiber filters with organic binders (glue), use of which would be disastrous in suspended solids testing because filter weight in the washing and oven-heating process would never achieve continuity.

Since Suspended Solids is, as the EPA Method states, *"those solids retained by a glass fiber filter"*, haphazard filter selection within the USGS method will produce results vastly dissimilar to the other four approved methods.

(Please note that in the past 12 years of assisting laboratories with suspended solids testing, I have never found one using a filter with binder; only occasionally do I find labs using glass fiber filters with pore sizes other than 1.5 m. Also, the USGS lab in Denver, CO, uses filters equal in all respects to the type designated in EPA 160.2 and Standard Methods 2540 D.)

Report

The USGS method includes a section entitled, "Report" (Section 8). Nothing like this is found in the other four approved methods. Section 8 of I-3765-85 requires the report of concentrations <1,000mg/L in "*whole numbers*" and ≥1,000mg/L to "*three significant figures*". Although sections 6.5 and 7.2 of I-3765-85 specifically indicate determinations to be made in 0.1mg increments, labs following this protocol are instructed to disregard the tenths increment for some sample results.

Precision and Accuracy

All five approved suspended solids methods include sections to delineate the Precision and Accuracy expected from the method.

Standard Methods 2540 D (18th, 19th and 20th Editions):

> "*The standard deviation was 5.2 mg/L (coefficient of 33%) at 15 mg/L, 24 mg/L (10%) at 242 mg/L, and 13 mg/L (0.76%) at 1707 mg/L in studies by two analysts of four sets of 10 determinations each." "Single-laboratory duplicate analyses of 50 samples of water and wastewater were made with a standard deviation of differences of 2.8 mg/L."* (Section 5)

EPA 160.2: "*Precision data are not available at this time."* (Section 9.1)

"*Accuracy data on actual samples cannot be obtained."* (Section 9.2)

USGS I-3765-85: "*Precision data are not available for this method*." (Section 9)

Interferences

In the 18th and 19th Editions of Standard Methods 2540 D, Section 1.b, titled "Interferences", the first sentence reads, "*Exclude large floating particles or submerged agglomerates of non-homogeneous materials from the sample if it is determined that their inclusion is not desired in the final result*." (underline added.)

Guidelines are not offered to establish how one defines what is or is not *"desired"*. Certainly two labs could run the same 18th or 19th 2540 D methods on the same sample and achieve vastly different results based on the desirability of the submerged agglomerate in Sample A. Also not addressed is the question of *who* determines desirability.

In discussing interferences the 20th Edition begins the same as the 18th and 19th in section 1.b., but ends with, "…. *if it is determined that their inclusion is not representative*." (underline added). Therefore, labs following the 20th Edition must first determine, "The submerged agglomerate in Sample A is (or is not) representative of *what*?" One lab might reasonably decide the submerged agglomerate in Sample A is representative of *the sample*; while the second might decide the agglomerate in Sample A is not representative of *the stream*, etc …

The 20th also includes the same reference found in the 18th and 19th methods that sends the reader to 2540 B.1 (Section 1.b). There 2540 B.1. in its discourse on interferences states, *"Exclude large floating particles or submerged agglomerates of non-homogeneous materials from the sample",* and concludes with, *" if it is determined that their inclusion is not desired in the final result"* (underline added).

So 20th Edition followers must tackle both *"not desired"* and *"not representative"* in deciding whether to leave the submerged agglomerate in, or take it out of, Sample A. (What happens if the agglomerate is *not desired*, but *representative*?)

Although this paper's focus is the differences between methods that can cause unequal results and not the variances within a particular method that can cause unequal results, herein lies the start point of the interference morass.

For the three approved versions of 2540 D to achieve equal results from Sample A with its submerged agglomerate, all labs following the 18th and 19th and 20th methods must agree on a definition of *"not desired in the final result"*. Then all labs following the 20th Edition must agree on a definition of *"not representative"* that in all circumstances does not conflict with the previously agreed upon definition of "*not desired*".

Moving on, EPA 160.2 addresses interferences in "Sample Handling", Section 4.1 stating, "*Non-representative particulates 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*." (underlines added). Here both limiting phrases appear in the same sentence, placing followers of the EPA method into the same boat as the followers of the 20th Edition 2540 D.

The Interferences section (Section 3) of the USGS method bears no resemblance to the other four methods. It states in totality, *"Precipitation in the sample during storage, such as iron, will produce erroneously high results."* This error-source is not mentioned in the other four methods.

Those who decide the submerged agglomerate of Sample A is an interference will remove it before analysis. Those who decide it a non-interference will include its solid weight in the sample results. Therefore, how one defines interferences becomes critical in determining the method-defined parameter: suspended solids. Finally, according to the USGS method, sample storage can create false positives, while according to Standard Methods (sic microbiological decomposition discussed in the Sample Storage and Holding Times section of this paper), false negatives.

Quality Control

The 18th and 19th Editions of Standard Method 2540 D require the analysis of all samples in duplicate (2540 A, Section 2). No other quality control samples are called for.

The 20th Edition not only requires 100% of samples be analyzed in duplicate (2540 A, Section 2), but includes the additional instruction to *"Analyze at least 10% of all samples in duplicate"* (2540 D, Section 3.c.). One might interpret 20th Edition duplicate statements as 90% non-redundant.

While blanks are not required in Standard Method versions of Suspended Solids, a blank is required *"with each set of samples"* in USGS Method I-3765-85 (Section 6.2), then blank correction is required per Section 7.2.

Within EPA 160.2, zero requirements for Quality Control are included.

Advancements in Suspended Solids

The 20th Edition of Standard Methods is the latest of all Methods, published in 1997. Section 3.c., "Procedure" therein begins with a sentence unlike any found in other method procedures. It states, *"If pre-prepared glass fiber filter disks are used, eliminate this step."* "*This step"* is the entire filter prep procedure: the washing with 3 X 20mL aliquots of DI water, drying at 103-105°C for an hour, desiccating to room temperature, and then weighing to 0.0001g and reweighing for stability. Environmental Express'

"pre-prepared glass fiber filter disks" – ProWeigh Filters – are listed by name as acceptable filters in 2540 C.2.a. of the 20th Edition.

Environmental Express' Universal Solids Standard can also improve quality control by allowing lab control samples (LCS) to be run along with blanks and duplicates. This standard comes in a pack of 10 small bottles. The entire contents of a bottle are added to a graduated cylinder. The LCS is created by filling the remainder of the graduated cylinder up to a working volume with lab water. The LCS is then treated as a normal sample for total suspended solids (TSS), volatile suspended solids (VSS), total dissolved solids (TDS), total solids (TS), and/or volatile solids (VS). The nominal result plus an acceptable range of 3 standard deviations is provided on each individual bottle for TSS, VSS, TDS, TS and VS.