

November 9, 2009 Meeting with NACWA

Clarification or guidance from EPA Engineering Analysis Division: (NACWA comments/questions in bold)

1. In certain circumstances (for example cyanide samples, composite samples collected in individual bottles and then preserved and composited, preserving a sample to a specific pH, etc.) it is often physically impossible to complete testing for possible interferences and preserve the sample within 15 minutes.
 - a. Recommend preservation language be modified (for grabs and composites) to read “commence within 15 minutes and complete ASAP; must not exceed 30 minutes.”

Footnote 2 to Table II at 40 CFR Part 136.3(e) reads:

Except where noted in this Table II and the method for the parameter, preserve each grab sample within 15 minutes of collection. For a composite sample collected with an automated sampler (e.g., using a 24-hour composite sampler; see 40 CFR 122.21(g)(7)(i) or 40 CFR Part 403, Appendix E), refrigerate the sample at $\leq 6^{\circ}\text{C}$ during collection unless specified otherwise in this Table II or in the method(s). For a composite sample to be split into separate aliquots for preservation and/or analysis, maintain the sample at $\leq 6^{\circ}\text{C}$, unless specified otherwise in this Table II or in the method(s), until collection, splitting, and preservation is completed. Add the preservative to the sample container prior to sample collection when the preservative will not compromise the integrity of a grab sample, a composite sample, or an aliquot split from a composite sample ; otherwise, preserve the grab sample, composite sample, or aliquot split from a composite sample with in 15 minutes of collection. If a composite measurement is required but a composite sample would compromise sample integrity, individual grab samples must be collected at prescribed time intervals (e.g., 4 samples over the course of a day, at 6-hour intervals). Grab samples must be analyzed separately and the concentrations averaged. Alternatively, grab samples may be collected in the field and composited in the laboratory if the compositing procedure produces results equivalent to results produced by arithmetic averaging of the results of analysis of individual grab samples. For examples of laboratory compositing procedures, see EPA Method 1664A (oil and grease) and the procedures at 40 CFR 141.34(f)(14)(iv) and (v) (volatile organics).

Options:

The multiple variables listed in this footnote take into effect grabs and composites under a wide range conditions.

- A. If the sampler is an automated grab sampler, the sample bottle can have the preservative added in advance.
- B. Otherwise, 15 minutes within collection is interpreted as within 15 minutes of pouring the sample into sample bottle from a composite container or a grab collector. This time

requirement very easily met in the field and any variation of this time requirement is covered in the first statement in footnote 2, but must be supported by the method or Table II.

- C. Leave the requirement of 15 minutes and that the EPA recommends that the collection of two separate grab samples. The first sample should be used to determine what steps are necessary to collect the sample (such as filtration, pH adjustment, interference mitigation, etc. on the first sample and then collect the sample to be used for compliance purposes and perform the necessary steps. If they cannot complete the steps necessary to collect the sample correctly then you should document what is needed to do so and how long it takes; then request a variance and we would support that variance.

b. Recommend approval of ASTM Method D7365-07 for cyanide when detect positive sulfide.

Option:

- A. We are recommending that EPA propose current version of ASTM Standard practice D7365, which is D7365-09a, for use with current approved cyanide methods. D7365-09a, specifies that users should conduct a holding time study prior to eliminating the NaOH. All that is required is a holding time study with D4841, then NaOH may be omitted as a preservative to avoid positive interference so long as the samples are analyzed within the determined holding time. Excerpts from D7365 follow:

From D7365-09a regarding sulfide abatement-

8.3.6 Sulfide—During sample collection, test for the presence of sulfide by placing a drop of sample on a lead acetate test strip that has been previously moistened with acetate buffer. If the test strip turns black, sulfide is present (above approximately 50 mg/L S₂⁻) and treatment is necessary as described below.

8.3.6.1 If the sample contains sulfide as indicated with a lead acetate test strip or is known to contain sulfides that will interfere with the test method, dilute the sample with reagent water until the lead acetate test strip no longer indicates the presence of sulfide (<50 mg/L S₂⁻) or until the interference is no longer significant to the analytical test method. For example, add 50 mL of freshly collected sample into a bottle containing 200 mL of reagent water, then test for sulfide again with the lead acetate test strip. If the test for sulfide is still positive, further dilution is required; however, be careful not to over dilute the sample as the detection limit will be elevated by this factor. In the aforementioned example, the dilution factor

would be equal to 5 (total volume/sample volume). It is recommended to perform this dilution during sample collection to avoid cyanide degradation; if this is not feasible, dilute the sample upon receipt in the laboratory and qualify the data. Clearly indicate the dilution volumes on the sample and chain-of-custody form so that the laboratory can mathematically correct the result.

8.3.6.2 Some analytical methods specify the use of lead carbonate or lead acetate to precipitate sulfide; however, sulfide and cyanide can form thiocyanate in the presence of lead sulfide causing decreased cyanide recoveries; therefore, lead carbonate and lead acetate should be avoided unless there is no other means to mitigate the sulfide or if the sample cannot be diluted as described in 8.3.6.1. Sulfide is removed by treating the sample with small increments of powdered lead carbonate or with the dropwise addition of lead acetate solution. Black lead sulfide precipitates in samples containing sulfide. Repeat the operation until no more lead sulfide forms, as indicated by testing the supernatant liquid with lead acetate test paper as indicated in 8.3.6. Immediately (within 15 minutes) filter with coarse filter paper (5 μm), then stabilize the sample according to 8.3.5. If the sample contains colloids that may contribute to the total cyanide concentration, filter the sample prior to adding the lead, then recombine the solids with the filtrate prior to analysis. Samples that are known or suspected to contain sulfides should be analyzed as soon as possible to avoid cyanide degradation.

8.3.6.3 Precipitation of sulfide with cadmium chloride should be avoided since the formation of insoluble cadmium cyanide complexes can result in loss of cyanide. Sulfide volatilization techniques and methods that specify the addition of bismuth nitrate to treat sulfide during total cyanide distillations have been demonstrated by ASTM Subcommittee D19.06 to be ineffective.

8.3.6.4 Samples known or suspected to contain sulfide should be analyzed with an analytical test method that has been demonstrated to be free from sulfide interference. Test Method

D 6888 employs sulfide mitigation that can effectively remove up to 50 mg/L S²⁻ without prior treatment and has a lower method detection limit compared to colorimetric methods to compensate for any required dilutions specified in section 8.3.6.1. To reduce or eliminate the need for dilution, samples containing up to 200 mg/L S²⁻ can be analyzed for available cyanide within 24 hours using Test Method D 6888 if the sulfide abatement reagent is prepared with 4 g/L bismuth nitrate pentahydrate in 1 M H₂SO₄ instead of 1 g/L as described in the test method. Since sulfide competes with cyanide in the reaction with colorimetric methods, it is recommended to determine total cyanide with Test Methods D 7284, D 7511, or distill as described in Test Methods D 2036 Test Method A or equivalent method (for example, MIDI distillation described in EPA Method 335.4) then analyze the distillate by Test Method D 6888 with sulfide abatement. Alternatively, Test Method D 4374 specifies that up to 10 mg/L S²⁻ can be tolerated without significant interference. Samples and distillates known or suspected to contain sulfide should be processed as quickly as possible to avoid cyanide degradation.

- 2. Hexavalent chrome has a narrow pH adjustment range and it is hard to get stability within pH range within 15 minutes without compromising the sample.**
 - a. Recommend same preservation language recommended above: “commence within 15 minutes and complete ASAP; must not exceed 30 minutes.”**

Q&A from our webpage:

<http://www.epa.gov/waterscience/methods/update/questions-cr6.html>

Correct pH range

Question: What about the disparity in the pH range specified in footnote 20 in Table II at Part 136.3, and in EPA Method 218.6?

Response: The correct pH range is 9.3 - 9.7 as specified in footnote 20, and must be met when the holding time is extended by use of either sodium hydroxide (NaOH), or the buffer solution in Section 7.9 of the method. We suggest that you use the buffer described in Section 7 of EPA Method 218.6, if the pH range can be achieved with sample dilution by no more than 10%. If this pH range cannot be achieved without diluting the sample by more than 10%, use a minimum amount of NaOH solution, supplemented by buffer solution as necessary.

Footnote 20 states: "To achieve the 28-day holding time, use the ammonium sulfate buffer solution specified in EPA Method 218.6. The allowance in this footnote supersedes preservation and holding time requirements in the approved hexavalent chromium methods, unless this supersession would compromise the measurement, in which case requirements in the method must be followed."

Options:

- A. The pH requirements for hexavalent chromium apply only to the EPA method 218.6 as stated in Table II Endnote 20. To achieve the 28-day holding time, use the ammonium sulfate buffer solution specified in EPA Method 218.6. The allowance in this footnote supersedes preservation and holding time requirements in the approved hexavalent chromium methods, unless this supersession would compromise the measurement, in which case requirements in the method must be followed.
- B. Colorimetric methods such as those in Standard Methods only require refrigeration. The final sentence in Endnote 20 allows this mode of preservation.
- C. Starting the buffering process of pH preservation within 15 minutes not necessarily completing the process, if the method requires it.

Note: Endnotes 2 and 20 allow time to preserve the sample and do not require pH preservation, if the method is compromised by the final pH requirement. If analysts were allowed to begin, as suggested, within 15 minutes, complete ASAP, but not exceed 30 minutes most will read it as 30 minutes. We do not have data to support a 30-minute threshold.

3. What documentation is required or recommended to demonstrate samples (grabs and composites; portable samples using ice or permanent samplers with refrigerators) are maintained at ≤ 6 degrees between collection and delivery at the lab?

- a. Recommend for composite samples that are collected with automatic samplers that are iced - document presence of ice at sample pick-up and during transportation to the laboratory.
- b. Recommend recording temperature of sample at the lab by a non-immersion method of temperature measurement.
- c. Recommend for samples that are collected in refrigerated samplers - document refrigerator temperature at start and completion of composite sample.
- d. Recommend recording temperature of sample at the lab by a non-immersion method of temperature measurement.
- e. Recommend grab samples be transported on ice to the laboratory.

- f. Recommend recording temperature of sample at the lab by a non-immersion method of temperature measurement.

There are multiple ways to meet the temperature requirements for sample preservation.

1. Wet ice and blue ice both have their good points and bad points.
2. Refrigerated composite samplers need to be monitored during all of the collection cycle to make sure the refrigerated sample compartment always stayed within the allowed temperature range. This is accomplished with a solid-state temperature recorder.
3. Non immersion temperature recorders, such as IR, also have their good and bad points. Specifically, with clear glass bottles and low suspended solids water samples, you can measure the temperature in the bottle behind the bottle you are scanning. Sample temperature should be measured using a non-immersion method of temperature measurement if an immersion based method would compromise sample integrity (e.g., oil and grease measurement).

Note: These QC points are usually covered in each laboratory's QA/QC plan. Each auditing state will have a different variation on these requirements that do not lend themselves to prescriptive regulatory requirement.