

PA-DEP Laboratory Accreditation Program	SDWA Composite Analysis FAQ
Laboratory Compliance Assistance	Revision 0
	Date: 3/23/11

## SDWA Composite Analysis FAQ

### Inorganic Non-Metals Trace Metals Volatile Organic Compounds Synthetic Organic Compounds

**Disclaimer:** The information in this FAQ does not supplant the provisions of the Environmental Laboratory Accreditation Regulations, 25 Pa Code, Chapter 109, 25 Pa Code, Chapter 252, the 2003 NELAC Standard, EPA/600/R-04/003, effective July 2005, or 40 CFR, Part 141. This document is a tool to help laboratories understand and comply with the provisions of compositing SDWA compliance samples. If there is any disagreement between the contents of this document and any of the above regulations, the regulations shall prevail. The examples given in this document are for illustrative purposes only, meant to aide individuals in visualizing applications of the regulatory requirements. These examples do not represent all regulatory requirements.

#### **REGULATORY REQUIREMENTS:**

##### **§ 109.303—Sampling Requirements.**

§ 109.303(e) “Compliance monitoring samples for the contaminants listed under 40 CFR 141.40(n), 141.61(a) and (c), 141.62 and 141.88 may be composited in accordance with 40 CFR 141.23(a)(4), 141.24(f)(14), (g)(7) and (h)(10) and 141.88(a)(1)(iv) (relating to inorganic chemical sampling and analytical requirements; organic chemicals other than total trihalomethanes, sampling and analytical requirements; and monitoring requirements for lead and copper in source water) except:

- (1) Samples from groundwater entry points may not be composited with samples from surface water entry points.
- (2) Samples used in compositing shall be collected in duplicate.
- (3) If a contaminant listed under 40 CFR 141.61(a) or (c) is detected at an entry point, samples from that entry point may not be composited for subsequent or repeat monitoring requirements.
- (4) Samples obtained from an entry point which contains water treated by a community water supplier or a nontransient noncommunity water supplier to specifically meet an MCL for an organic contaminant listed under 40 CFR 141.61(a) or (c) or an MCL for an inorganic contaminant listed under 40 CFR 141.62 may not be composited with other entry point samples.”

##### **§ 109.1003—Monitoring Requirements.**

§ 109.1003(b)(5) “*Sampling Requirements.* Compliance monitoring samples required under subsection (a)(1)(iii) may be composited in accordance with 40 CFR 141.24(g)(7) (relating to organic chemicals other than total trihalomethanes, sampling and analytical requirements) except:

- (i) Samples from groundwater entry points may not be composited with samples from surface water entry points.
- (ii) Samples from one type of bottled water product or vended water product may not be composited with samples from another type of bottled water product or vended water product.
- (iii) Samples used in compositing shall be collected in duplicate.
- (iv) If a VOC listed under 40 CFR 141.61(a) is detected at an entry point, samples from that entry point may not be composited for subsequent compliance or repeat monitoring requirements.
- (v) Samples obtained from an entry point which contains water treated by a community water supplier or nontransient noncommunity water supplier to specifically meet an MCL for a VOC listed under 40 CFR 141.61(a) may not be composited with other entry point samples.”

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**§ 141.23—Inorganic Chemical Sampling and Analytical Requirements.**

§ 141.23 Community water systems shall conduct monitoring to determine compliance with the maximum contaminant levels specified in § 141.62 in accordance with this section.

§ 141.23(a)(4) “The State may reduce the total number of samples which must be analyzed by allowing the use of compositing. Composite samples from a maximum of five samples are allowed, provided that the detection limit of the method used for analysis is <1/5 of the MCL. Compositing of samples must be done in the laboratory.

- (i) If the concentration in the composite sample is greater than or equal to one-fifth of the MCL of any inorganic chemical, then a follow-up sample must be taken within 14 days at each sampling point included in the composite. These samples must be analyzed for the contaminants which exceeded 1/5 of the MCL in the composite sample.
- (ii) If the population served by the system is >3,300 persons, then compositing may only be permitted by the State at sampling points within a single system. In systems serving ≤3,300 persons, the State may permit compositing among different systems provided the 5-sample limit is maintained.
- (iii) If duplicates of the original sample taken from each sampling point used in the composite sample are available, the system may use these instead of resampling. The duplicates must be analyzed and the results reported to the State within 14 days after completing analysis of the composite sample, provided the holding time of the sample is not exceeded.

**§ 141.24—Organic Chemicals, Sampling and Analytical Requirements.**

§ 141.24(f) “Beginning with the initial compliance period, analysis of the contaminants listed in § 141.61(a) (1) through (21) [regulated VOCs] for the purpose of determining compliance with the maximum contaminant level shall be conducted as follows:

- (14) The State may reduce the total number of samples a system must analyze by allowing the use of compositing. Composite samples from a maximum of 5 sampling points are allowed, provided that the detection limit of the method used for analysis is <1/5 of the MCL. Compositing of samples must be done in the laboratory and analyzed within 14 days of sample collection.
  - (i) If the concentration in the composite sample is greater than or equal to 0.0005 mg/l for any contaminant listed in § 141.61(a), then a follow-up sample must be taken within 14 days at each sampling point included in the composite, and be analyzed for that contaminant.
  - (ii) If duplicates of the original sample taken from each sampling point used in the composite sample are available, the system may use these instead of resampling. The duplicates must be analyzed and the results reported to the State within 14 days after completing analysis of the composite sample, provided the holding time of the sample is not exceeded.
  - (iii) If the population served by the system is > 3,300 persons, then compositing may only be permitted by the State at sampling points within a single system. In systems serving ≤ 3,300 persons, the State may permit compositing among different systems provided the 5-sample limit is maintained.
  - (iv) Compositing samples prior to GC analysis:
    - (A) Add 5 mL or equal larger amounts of each sample (up to 5 samples are allowed) to a 25 mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe.
    - (B) The samples must be cooled at 4°C during this step to minimize volatilization losses.
    - (C) Mix well and draw out a 5-mL aliquot for analysis.
    - (D) Follow sample introduction, purging, and desorption steps described in the method.
    - (E) If less than 5 samples are used for compositing, a proportionately small syringe may be used.
  - (v) Compositing samples prior to GC-MS analysis:

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- (A) Inject 5-mL or equal larger amounts of each aqueous sample (up to 5 samples are allowed) into a 25-mL purging device using the sample introduction technique described in the method.
- (B) The total volume of the sample in the purging device must be 25 mL.
- (C) Purge and desorb as described in the method.”

§ 141.24(h) “Analysis of the contaminants listed in § 141.61(c) [synthetic organic compounds] for the purposes of determining compliance with the maximum contaminant level shall be conducted as follows, with the exception that no monitoring is required for aldicarb, aldicarb sulfoxide or aldicarb sulfone:”

(10) The State may reduce the total number of samples a system must analyze by allowing the use of compositing. Composite samples from a maximum of five sampling points are allowed, provided that the detection limit of the method used for analysis is less than one-fifth of the MCL. Compositing of samples must be done in the laboratory and analyzed within 14 days of sample collection.”

- (i) If the concentration in the composite sample detects one or more contaminants listed in § 141.61(c), then a follow-up sample must be taken within 14 days at each sampling point included in the composite, and be analyzed for that contaminant.
- (ii) If duplicates of the original sample taken from each sampling point used in the composite sample are available, the system may use these instead of resampling. The duplicates must be analyzed and the results reported to the State within 14 days after completion of the composite analysis or before the holding time for the initial sample is exceeded whichever is sooner.
- (iii) If the population served by the system is >3,300 persons, then compositing may only be permitted by the State at sampling points within a single system. In systems serving ≤ 3,300 persons, the State may permit compositing among different systems provided the 5-sample limit is maintained.
- (iv) Compliance with § 141.61(c) shall be determined based on the analytical results obtained at each sampling point.

**§ 141.88—Monitoring Requirements for Lead and Copper in Source Water.**

§ 141.88(a)(iv) “The State may reduce the total number of samples which must be analyzed by allowing the use of compositing. Compositing of samples must be done by certified laboratory personnel. Composite samples from a maximum of five samples are allowed, provided that if the lead concentration in the composite sample is greater than or equal to 0.001 mg/L or the copper concentration is greater than or equal to 0.160 mg/L, then either:

- (A) A follow-up sample shall be taken and analyzed within 14 days at each sampling point included in the composite; or
- (B) If duplicates of or sufficient quantities from the original samples from each sampling point used in the composite are available, the system may use these instead of resampling.”

**§ 141.89—Analytical Methods.**

§ 141.89(a)(iii) “Achieve the method detection limit for lead of 0.001 mg/L according to the procedures in appendix B of part 136 of this title. This need only be accomplished if the laboratory will be processing source water composite samples under § 141.88(a)(1)(iii).”

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## **Questions Relating to Terminology:**

**Question: What does the term “SDWA composite analysis” mean?**

Answer: “SDWA composite analysis” is a mechanism made available to Public Water Supplies that allows up to 5 separate samples to be combined and analyzed in a single analysis as a cost-saving measure. This “SDWA composite analysis” is a “new” sample that represents each of the up to 5 separate samples that were combined prior to analysis.

**Question: Is an “SDWA composite analysis” the same as an “NPDES composite sample”?**

Answer: No. “SDWA composite analysis” is a combination of up to 5 separate samples combined into one container. An “NPDES composite sample” is a single sample made up of multiple aliquots taken over a defined period of time.

**Question: What does “detection limit” mean in the 40 CFR references?**

Answer: “Detection limit” for the purposes of this section of 40 CFR is synonymous with “quantitation limit” as used in 25 Pa Code Chapter 252. Chapter 252 defines quantitation limit as “the minimum concentration or activity of the component, compound, element, or isotope that can be reported with a specified degree of confidence.” Range of Quantitation is defined as “the concentration range between which an environmental laboratory reports results quantitatively which is defined by a low concentration standard and a high concentration standard.”

**Question: What is the holding time for an “SDWA composite analysis”?**

Answer: The holding time for an “SDWA composite analysis” begins with the collection date and time of the first collected sample. For example: The following samples are to be composited for VOC analysis:

Sample #1	Collected 1/1/2011 at 12:05pm
Sample #2	Collected 1/2/2011 at 12:15pm
Sample #3	Collected 1/3/2011 at 4:07pm
Sample #4	Collected 1/4/2011 at 8:00am
Sample #5	Collected 1/5/2011 at 3:05pm

The calculation of the holding time for these samples would begin at 12:05pm on 1/1/2011. Since VOC samples must be analyzed within 14 days of collection, the “SDWA composite analysis” must be analyzed on or before January 15, 2011.

## **Questions Relating to Appropriate Techniques and Compositing Procedures:**

**Question: Who decides if analysis of an “SDWA composite analysis” is appropriate or allowed?**

Answer: The decision is based on the following factors:

1. Laboratory Accreditation: The accredited laboratory performing the testing must be able to meet the analytical requirements for “SDWA composite analysis” before the decision to composite can be made (see Questions Relating to Analytical Capability below).
2. Sample Type: Samples from groundwater entry points may not be composited with samples from surface water entry points.
3. Analysis Type: Disinfection byproduct (TTHM, HAA5, etc) samples may not be composited. Disinfection byproduct samples must be analyzed as a single source sample.
4. Population Served: If the population served by the system is > 3,300 persons, then compositing is only permitted at sampling points within a single system. If the population

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served by the system is  $\leq 3,300$  persons, then compositing among different systems is permitted provided the 5-sample limit is maintained.

5. **Historical Results:** If a contaminant listed under 40 CFR 141.61(a) or (c) is detected at an entry point, samples from that entry point may not be composited for subsequent or repeat monitoring requirements.
6. **Compliance with an MCL:** Samples obtained from an entry point which contains water treated by a community water supplier or a nontransient noncommunity water supplier to specifically meet an MCL for an organic contaminant listed under 40 CFR 141.61(a) or (c) or an MCL for an inorganic contaminant listed under 40 CFR 141.62 may not be composited with other entry point samples.”
7. **Bottled Water or Vended Water:** Samples from one type of bottled water product or vended water product may not be composited with samples from another type of bottled water product or vended water product.
8. **Approval from the PWS:** The Public Water Supply(ies) whose samples would be composited must be contacted and agree to allow their samples to be composited.

**Question: How should samples be collected if they are going to be combined into an “SDWA composite analysis”?**

Answer: Samples must be collected in duplicate. 25 Pa Code, Chapter 109 requires that all samples that will become “SDWA composite analysis” must be collected in duplicate. Even though 40 CFR, Part 141 states that duplicates are not required, Chapter 109 supersedes 40 CFR Part 141.

**Question: How many different samples can be combined into a single “SDWA composite analysis”?**

Answer: Up to 5 separate samples may be combined to yield a single “SDWA composite analysis.” Fewer than 5 samples may be composited, but the laboratory must use a proportionately larger aliquot of sample to obtain an acceptable sample size.

**Question: Who can composite the samples?**

Answer: The accredited laboratory that is going to perform the analytical testing of the “SDWA composite analysis” must composite the sample. A practical example would be: Laboratory ABC receives 5 samples from PWS #123456 and subcontracts the analysis of these samples to Laboratory XYZ. Laboratory ABC must ship all five original samples in their original containers (and duplicate samples) to Laboratory XYZ. Laboratory XYZ must composite the 5 separate samples into one container.

**Question: Where can the samples be composited?**

Answer: The samples must be composited at the accredited laboratory that is going to perform the actual testing of the sample. It is not acceptable for samples to be composited and then shipped to the location where the testing will be performed.

**Question: What are the requirements for laboratories that are going to ‘sub-contract’ part of the analytical testing for these samples?**

Answer: The laboratory that is sub-contracting any portion of the analytical testing must ensure that the sub-contract laboratory is accredited to perform the testing. Once an accredited laboratory is located and selected, all of the pertinent information relating to the samples must be provided to the sub-contract laboratory (along with the samples and duplicates) in order to ensure all notification and follow-up steps can be taken. This information would include: PWS ID# and contact information, Sampling Location, Sample Type, and Sampling Date and Time.

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**Question: How do I composite inorganic SDWA samples?**

Answer: The accredited laboratory must first ensure that all sample acceptance criteria are met, including holding time, sample preservation (both chemical and thermal), sample container, etc. If all sample collection criteria are acceptable, the accredited laboratory must measure equal aliquots of the individual samples and combine them into a single sample container meeting the sample container requirements for the analyte being tested. This new "SDWA composite analysis" sample must be mixed thoroughly. The accredited laboratory may then prepare and analyze this new "SDWA composite analysis" as it would any other SDWA compliance sample.

**Question: How do I composite VOC SDWA samples?**

Answer: The accredited laboratory must first ensure that all sample acceptance criteria are met, including holding time, sample container, etc. If all sample collection criteria are acceptable, the accredited laboratory must:

For analysis of "SDWA composite analysis" using GC analysis:

1. Add 5 mL or equal larger amounts of each sample (up to 5 samples are allowed) to a 25 mL glass syringe. Special precautions must be made to maintain zero headspace in the syringe.
2. The samples must be cooled at 4°C during this step to minimize volatilization losses.
3. Mix well and draw out a 5-mL aliquot for analysis.
4. Follow sample introduction, purging, and desorption steps described in the method.
5. If less than 5 samples are used for compositing, a proportionately small syringe may be used.

For analysis of "SDWA composite analysis" using GC-MS analysis:

1. Inject 5-mL or equal larger amounts of each aqueous sample (up to 5 samples are allowed) into a 25-mL purging device using the sample introduction technique described in the method.
2. The total volume of the sample in the purging device must be 25 mL.
3. Purge and desorb as described in the method.

The laboratory must ensure the integrity of the sample at all times. Since VOCs by nature are volatile, the laboratory must verify the sample preservation (acidification and dechlorination) using an aliquot of each uncombined individual SDWA sample after the "SDWA composite analysis" is prepared.

**Question : How do I composite SOC SDWA samples?**

Answer: The accredited laboratory must first ensure that all sample acceptance criteria are met, including holding time, sample preservation (both chemical and thermal), sample container, etc. If all sample collection criteria are acceptable:

1. The accredited laboratory must measure equal aliquots of the individual samples (up to 5 samples) using a measuring device that meets Class-A acceptance criteria (such as a graduated cylinder).
2. Each measured volume must be combined into a single sample container meeting the specific sample collection container requirements.
3. If the laboratory measures each aliquot using the same graduated cylinder, the laboratory must rinse the graduated cylinder with the appropriate extraction solvent after the final aliquot is added to the sample container.
4. If the laboratory uses multiple graduated cylinders to measure the aliquots, the laboratory must rinse each graduated cylinder with the appropriate extraction solvent.
5. Each rinse of the extraction solvent must be transferred to the separatory funnel (for liquid-liquid extractions) or held until extraction of the solid-phase disk (for SPE extractions).

The accredited laboratory may then extract and analyze this new "SDWA composite analysis" as a single sample.

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## **Questions Relating to Analytical Capability:**

**Question:** Are the analytical requirements for “SDWA composite analysis” different from the requirements for analysis of single location samples?

**Answer:** Yes.

- For analysis of “SDWA composite analysis” for inorganic compounds (except lead and copper) and SOCs, the accredited laboratory must be able to achieve a quantitation limit of at least 1/5 of the published MCL for each analyte of interest.
- For analysis of “SDWA composite analysis” for regulated VOC samples, the accredited laboratory must be able to achieve a quantitation limit of at least 0.0005 mg/L or 1/5 of the MCL, whichever is less. For analysis of “SDWA composite analysis” for vinyl chloride samples, the accredited laboratory must achieve a quantitation limit of at least 0.0004 mg/L, which is 1/5 of the MCL of 0.002 mg/L.
- For analysis of “SDWA composite analysis” for lead and copper, the accredited laboratory must be able to achieve a quantitation limit of at least 0.160 mg/L for copper and at least 0.001 mg/L for lead. Additionally, the accredited laboratory must achieve a calculated MDL of at least 0.001 mg/L for lead if analyzing “SDWA composite analysis” of source water samples.

**Question:** If I composite fewer than 5 separate samples, does this mean that I can have a proportionately higher quantitation limit?

**Answer:** No. The USEPA requires that if any samples are composited, the quantitation limit must be at least 1/5 of the MCL for each analyte of interest.

**Question:** If my instrumentation will not achieve a quantitation limit of 1/5 of the MCL, can I still perform testing if my MDL is at least 1/5 of the MCL?

**Answer:** No. 25 Pa Code Chapter 252, 252.402(d)(3) states, “If the results of testing or analysis of environmental samples that are below the initial calibration range are reported, the results shall be reported with appropriate data qualified flags.” In order for an SDWA compliance sample to be valid for compliance purposes, the analytical results must be associated with valid quality control. It is not possible to achieve valid sample results if the calibration range of the instrument does include the MCL.

**Question:** Why do I need to calibrate to 1/5 of the MCL?

**Answer:** Since the “SDWA composite analysis” consists of up to 5 samples, this means that approximately 1/5 of the “normal” sample volume is being analyzed. This would be similar to diluting a single sample with reagent water and analyzing the sample. If a single sample is diluted, the quantitation limit would be adjusted to account for the sample dilution. It would be impossible to determine if one of the 5 individual PWS samples were compliant if the laboratory’s quantitation limit was technically above the MCL.

## **Questions Relating to Reporting and Notification:**

**Question:** How should results of “SDWA composite analysis” samples be reported?

**Answer:** For “SDWA composite analysis” results that yield values below the quantitation limit (i.e.: <1/5 of the MCL), or sometimes referred to as “non-detect”, the accredited laboratory may report “<MCL” for each of the separate samples that were combined to yield the single “SDWA composite analysis” result. When the accredited laboratory reports these results to DWELR, they may be reported as “ZERO.”

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**Question: What should I do if the “SDWA composite analysis” result is a “detect”?**

**Answer:** For “SDWA composite analysis” results that yield values above the quantitation limit (i.e.: >1/5 of the MCL), the accredited laboratory must:

- Adhere to the reporting and notification requirements of 25 Pa Code Chapter 109.
- Analyze each individual sample that was combined to yield the “SDWA composite analysis” result. Since all samples that will be composited into an “SDWA composite analysis” must be collected in duplicate, the accredited laboratory must analyze the duplicate samples individually. The analysis of the individual duplicate samples must occur within 14 days of the analysis of the “SDWA composite analysis” or before the expiration of the holding time, whichever comes first.

**Question: What should I do if the holding time has expired for the duplicate sample before analysis of the duplicate sample can occur?**

**Answer:** The accredited laboratory must notify each affected PWS and the Department. Each PWS must ensure that another sample is collected within 14 days.