Writing an Analytical SOP for PA State (Chapter 252) Accreditation

Disclaimer: The information in this guidance document does not supplant the provisions of the Environmental Laboratory Accreditation Regulations, 25 Pa Code, Chapter 252. This document is a tool to help laboratories comply with Chapter 252. If there is any disagreement between the contents of this document and Chapter 252, 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 method or regulatory requirements.

Standard Operating Procedure (SOP): A SOP is a written document that provides detailed instructions for the performance of all aspects of test, analysis, operation, or action. For laboratories, there are two basic types of SOPs: General SOPs and Analytical SOPs. General SOPs are written for general laboratory procedures that are performed by all technical lab staff, such as performing an Initial Demonstration of Capability (IDC) or washing glassware. Analytical SOPs provide instructions for performing a specific test method conducted by the laboratory.

An Analytical SOP must describe an analytical method used in the laboratory in sufficient detail so that a competent analyst, who is unfamiliar with the method, can obtain acceptable results and/or conduct a reliable review. The Analytical SOPs must accurately reflect *all* phases of laboratory activity associated with the method. SOPs must comply with the requirements of the reference method the lab follows ***and*** the requirements of Chapter 252. SOPs must be available to and used by all laboratory personnel. Many labs have a separate SOP for each analytical method performed. However, a lab can choose to put all of their SOPs into a single document, include them in their Quality Manual, or group them into documents by analytical category. The intent of Chapter 252 is that labs have a SOP for each analytical method performed. A lab may choose to organize its SOPs in any manner that best suits its operations.

1. **Header:** The laboratory's SOP should contain a header that contains the following information:

   1.1. Name of lab

   1.2. Revision number: Most likely, it will be necessary to revise the contents of the SOPs over time. The laboratory should track the changes made to the SOPs and assign revision numbers. This ensures that all laboratory personnel are using the most recently updated revisions of the SOPs.

   1.3. Effective Date: An effective date is ***required*** on all SOPs **[§252.307(d)(1(ii)]**. This allows employees, clients, and regulators to see when a certain revision of the lab's SOP was put into use in the lab or will be put into use in the lab. **NOTE**: Laboratories must retain copies of past versions of SOPs for at least 5 years from the date of retire.

   1.4. Approving Signatures: SOPs should be reviewed by at least one supervisor in the lab. By signing the SOP, lab personnel know that it has been reviewed and is approved for use by laboratory management.

2. **Distribution List:** SOPs *should* contain a distribution list that identifies the individuals that have been given copies of the SOPs. Distribution lists help laboratory management keep track of how many copies of the SOPs are in circulation, and identify which members of the technical staff have been given a particular SOP. Therefore, laboratory management can easily recall all of the old documents when new revisions are made, and thereby ensure that all of the necessary personnel are using the most recently updated revisions of the SOPs.

3. **Identification of the test method [§252.307(d)(1)(i)]:** The lab must identify the reference method used for each analytical test.

   3.1. When choosing a reference method, remember that Chapter 252, §252.307(a), requires labs to select an analytical method for each test that meets the following criteria:

      3.1.1. The method must be appropriate for the analyte and sample matrix. Therefore, the reference method must indicate that it is suitable for determining the analyte of interest in the matrix for which the lab is testing (i.e., drinking water, groundwater, wastewater, sludges, etc.).

         3.1.1.1. **Example**: In *Standard Methods, 20th ed.* (SM), 4500-NH_3 D Ammonia-Selective Electrode Method, Section 1.b, under "Scope and Application", it states, "This method is applicable to the measurement of 0.03 to 1400 mg NH_3-N/L in potable and surface waters and domestic and industrial wastes." Therefore, according to the method, it is suitable for use on several types of aqueous samples but not suitable for samples of a solid matrix.

      3.1.2. The method is required by or considered appropriate for use under applicable State or Federal regulations, a permit, an order, or is an approved alternate test method. Therefore, if a test method is specifically required by a permit administered by the Department (i.e. NPDES permit), the lab must follow the analytical method required by the permit. If the permit does not specify the use of a specific method, the lab must refer to 40 CFR 136.3 Tables 1A -1F for non-potable water testing and 40 CFR 141 for drinking water testing to find an appropriate approved method for the testing. Alternate Test Procedures (ATP) are usually vendor-developed methods that have been formally approved by the USEPA for use with compliance samples. Labs wishing to use a vendor-developed method for compliance testing should obtain a copy of the USEPA ATP Approval letter from the vendor before using the method to test compliance samples.

      3.1.3. The method enables the laboratory to quantitate to required levels. If a facility is required by permit or other regulation to ensure that contaminants are below a certain level, the method chosen must allow the lab to quantitate at or below that regulatory level.

         3.1.3.1. **Example**: In the example given in section 3.1.1.1 above, if a facility's permit limit for NH_3 is 0.01 mg NH_3-N/L, then SM 4500-NH_3 D is **not** acceptable for use, since it only allows the lab to quantitate to 0.03 mg NH_3-N/L, which is above the facility's regulatory limit.

4. **Scope, including applicable matrix or matrices, quantitation range, and for drinking water testing MCL(s) or action levels as appropriate [§252.307(d)(1)(iii)]:** The lab must identify the analytes and matrices the method is used to test. In addition the quantitation range, or range of calibration standards used, must be identified. If the lab performs drinking water analysis, then the MCL and/or action level for each analyte must be in the SOP.

   4.1. **Example**: In section 3.1.1.1 above, SM 4500-NH_3 D is capable of testing potable and surface waters and domestic and industrial wastes. However, the laboratory only uses this method to test domestic and industrial wastewaters. Therefore, the lab's SOP must state that the method is used for testing domestic and industrial wastewaters.

   4.2. This section must also contain the laboratory's quantitation range. The quantitation range is the concentrations between which the lab reports samples results. The quantitation range is usually between the lowest and highest calibration standards. The quantitation range includes the lab's reporting limit, which is the lowest concentration, mass, or amount that is quantified by the laboratory using the procedure. The reporting limit **cannot** be below the lowest calibration standard analyzed in the initial calibration curve.

   4.3. If the laboratory performs drinking water testing, then the lab must identify the MCL or action level for each analyte in the SOP. For example, the SOP for drinking water nitrate analysis must include the MCL of 10 mg/L of nitrate as N and the SOP for drinking water lead analysis must include the action level for lead of 0.015 mg/L.

   4.4. This section of the SOP is also a good place to define the lab's detection limit for the method [§252.402(k)].

5. **Sample Handling and Preservation [§252.401(f)]:** The lab must establish procedures for handling samples.

   5.1. This subject is also addressed in the compliance assistance document *"Writing a Quality Manual"*. In general, Chapter 252 requires labs to address sampling protocol, sample containers, sample preservation and holding time requirements, sample labeling, Chain of Custody procedures, and acceptance/ rejection of samples. Some of this information is useful in the Analytical SOPs, while some is more useful in the lab's Quality Manual. Labs may find it easier, more convenient and more sensible to place the method-specific information regarding sample storage conditions, appropriate sample containers, sample preservation, and holding times in the method-specific SOP only, while leaving general lab procedures concerning sample handling in the Quality Manual.

   The lab is **not** required to have the same procedure written in multiple places. When duplicate procedures are written in multiple places or multiple documents, and the procedure is updated, each of the documents that contain that procedure must also be updated. Labs may find it difficult to keep each copy of the procedure consistent between documents. When the lab chooses to address all of this information in the individual Analytical SOPs, the Quality Manual should reference the Analytical SOPs for the information regarding sample handling. If the laboratory chooses to keep all this

information in the Quality Manual, then the SOPs should reference the appropriate sections of the Quality Manual for sample handling information. Most likely, there will be some of this information in both the Analytical SOPs and the Quality Manual. In this case, the Analytical SOPs should reference the Quality Manual for general sample handling procedures, and the Quality Manual should reference the Analytical SOPs for method-specific information.

5.2. Labs must ensure that the sample handling procedures outlined in SOPs are appropriate for the particular compliance requirement. The sample collection, preservation and holding time requirements outlined in 40 CFR, Part 136 (NPDES) and Part 141 (SDWA) or in other regulation (such as 25 Pa. Code Chapter 109 for drinking water) take precedence over any method requirement. If the CFR (Code of Federal Regulations) and DEP regulation are silent, then the lab would use the criteria specified in the analytical method.

5.2.1. **Example:** Ammonia for NPDES compliance

40 CFR, Part 136, Table II states that ammonia samples must be collected in polyethylene, Teflon, or glass, acid preserved to pH<2 with H_2SO_4 within 15 minutes of collection, cooled to ≤6°C, and analyzed within 28 days.

The introductory text in SM 4500-NH_3 A addresses sample handling for ammonia samples. The section indicates that the most reliable results are obtained on fresh samples. If samples are to be analyzed within 24 hours of collection, refrigerate the samples unacidified at 4ºC. For preservation of samples up to 28 days, freeze at -20ºC unacidified, or preserve samples by acidifying to pH <2 and storing at 4ºC.

The laboratory's sample handling procedures must match the requirements outlined by the US-EPA in the CFR. The ammonia sample handling requirements from Standard Methods are superseded by the CFR. It would be inappropriate for an SOP to include the ammonia sample handling information from Standard Methods because these directions would confuse laboratory personnel.

6. **Equipment and supplies [§252.307(d)(iv)]:** The lab must list the equipment and supplies needed to perform the test method.

6.1. The laboratory must be specific in regard to the equipment that it uses, and not simply duplicate the equipment list from the method. However, the equipment that the lab uses must also comply with the equipment specifications of the method.

6.1.1. **Example:** SM 4500-NH_3 D, Section 2.a-b, states that the following equipment is necessary to perform the test method:
"1. Electrometer: A pH meter with expanded millivolt scale capable of 0.1mV resolution between –700mV and +700mV or a specific ion meter.
*2. Ammonia-selective electrode**: Orion Model 95-12, EIL Model 8002-2, Beckman Model 39565, or equivalent."

A lab that copies this text from the reference method into its SOP is **not** describing the equipment used in ***its*** operations. This text describes the method requirements, but does not specify what the ***laboratory*** is using. Therefore, it is not adding useful information to the SOP and does not provide sufficient detail. The lab must list the type, manufacturer and model number of the equipment ***it*** uses to perform the testing. By doing so, the laboratory can evaluate whether or not the equipment it uses complies with the method requirements.

6.2. The same specificity must be used for supplies used by the lab to perform the testing.

6.2.1. **Example:** In *Standard Methods, 20th ed.*, SM 2540 D, Total Suspended Solids Method, it specifies the use of glass fiber filter disks that are "Whatman grade 934AH; Gelman type A/E; Millipore type AP40; E-D Scientific Specialties grade 161; Environmental Express Pro Weigh; or other products that give demonstrably equivalent results."

Again, the above text describes the method requirements, and does not address which filters the laboratory uses. The lab should list the filter type it uses, including the manufacturer and other information that uniquely identifies the filter used. If the lab routinely purchases filters from several different manufacturers to incur the lowest cost, the lab may indicate that several different filter brands are used by stating in the SOP, for example, "Whatman grade 934AH filters, or equivalent" are used.

7. **Reagents and standards [§252.307(d)(1)(v)]:** The laboratory must list the reagents and standards needed to perform the test method.

7.1. The laboratory must be specific in regard to the reagents and standards that it uses, and not simply duplicate the list from the method. However, the reagents and standards that the lab uses must also comply with the specifications of the method.

7.1.1. **Example:** SM 4500-NH_3 D, section 3.d, states that the following reagents are necessary to perform the method:
1. Stock ammonium chloride solution: Dissolve 3.819g anhydrous NH_4Cl (dried at 100ºC) in water, and dilute to 1000mL; 1.00mL = 1.00mg N = 1.22mg NH_3.

A lab should copy this text into its SOP only if this is actually how it prepares stock ammonium chloride solution. If the lab purchases this solution, then the SOP should provide information regarding the manufacturer of the solution, the concentration of the purchased solution, and the storage requirements. If the lab prepares its stock ammonium chloride solution differently from the instructions given in the reference method, then the lab's SOP must give the preparation instructions used by its technicians and state the final concentration of the solution.

7.2. A lab may also choose to reference the location of reagent and standard preparation instructions. For example, labs may wish to provide instructions for preparing standards and reagents in the standard and reagent log books. If so, labs are not required to have those instructions duplicated in the Analytical SOP. For instance, labs may simply state

in the SOP that the instructions for preparing the stock ammonium chloride solution are located in the "Ammonia Method Standard Prep Logbook".

7.3. The laboratory must also include instructions for diluting reagents and standards to working concentrations, if applicable, and include the final concentrations of the working solutions.

8. **Calibration and standardization [§252.307(d)(1)(vii)]:** The laboratory must describe its procedure for calibrating the instrumentation used to perform the test method.

8.1. The laboratory must provide, or reference the location of, instructions for preparing all calibration standards in the SOP. The "Calibration and Standardization" section of the SOP is a good place to include this information, if such instructions were not already addressed in the "Reagents & Standards" section of the SOP. The number of standards used for instrument calibration must also be provided in the SOP and comply with the method requirements and the applicable sections of Chapter 252 (i.e. §252.402(c)-(f) for Chemistry testing).

8.2. The lab must include instructions for the initial instrument calibrations (ICAL) and calibration verifications (CCV). The frequency that each procedure (ICAL vs. CCV) is performed, the number of standards used for each procedure, the concentration(s) of standards used for each procedure, and the location of these standards within the analytical batch must be clear from the instructions given in the SOP. The ICAL and CCV procedures must comply with the requirements of the reference method and the applicable sections of Chapter 252 (i.e. §252.402(c)-(f) for Chemistry testing).

8.2.1. **Example:** A lab is performing SM 4500-NH_3 D. Assume that the lab's SOP requires an initial instrument calibration to be performed weekly, and the calibration is verified daily or before each use. Instructions for performing a calibration verification may read:

"A 0.5 mg NH_3-N/L and a 10.0 mg NH_3-N/L calibration verification standard (CCV) are prepared and analyzed each day prior to the analysis of environmental samples. A percent recovery of ± 5% must be achieved for the CCVs to be considered acceptable and before the analysis of samples may begin. If the initial CCVs fail to meet the acceptance criteria, the CCVs are reanalyzed. If the CCVs fail to meet the acceptance criteria after re-analysis, new CCV solutions are prepared from fresh aliquots of standard and analyzed. If the third attempt fails to meet the acceptance criteria, the instrument must be recalibrated according to the procedure for initial calibration.

Both the 0.5 mg & 10.0 mg NH_3-N/L CCVs are analyzed at the beginning of the analytical batch, after every 10 samples, and at the end of the analytical batch. All sample results must be bracketed by acceptable CCVs. Samples associated with failed CCVs must be reanalyzed and bracketed by acceptable CCVs. If, upon reanalysis, the CCVs are still unacceptable, the instrument must be recalibrated according to the procedure for initial instrument calibration, and the samples reanalyzed."

8.3. The laboratory must include instructions for evaluating the success of the ICAL and CCVs (i.e. acceptance criteria), such as the ± 5% percent recovery requirement from the example above. The acceptance criteria for the ICAL and CCVs must comply with the requirements of the reference method and the applicable sections of Chapter 252 (i.e. §252.402(c)-(f) for Chemistry testing).

8.4. The laboratory must include instructions for handling initial calibrations or calibration verifications that do not meet the acceptance criteria.

8.4.1. **Example:** A lab is performing SM 4500-NH_3 D. The manufacturer of the meter/electrode combination gives a slope of 59mV ± 3mV for determining the success of initial calibrations. Instructions for handling a failed initial calibration may read:

"If the initial calibration curve does not generate a slope of 59mV ± 3mV, the instrument must be recalibrated with aliquots of the previously used calibration standards. If the second calibration fails to generate an acceptable slope, the meter is calibrated again using freshly prepared calibration standards. If the third calibration does not generate an acceptable slope, maintenance must be performed on the probe and meter according to the instructions in the "Ammonia Instrument logbook", and the instrument recalibrated with a freshly prepared set of calibration standards before samples may be analyzed. If general maintenance does not produce an acceptable calibration curve, then the instrument shall be taken out-of-service until repairs can be performed and an acceptable curve generated."

9. **Quality Control [§252.307(d)(1)(vi)]:** The laboratory must describe all of the quality control measures that are performed with the test method.

9.1. The lab must define what quality control (QC) samples are prepared with each batch of samples, and it must also define a "batch" of samples. These QC measures must comply with the method requirements and the applicable sections of Chapter 252 (i.e. §252.402.g-l for Chemistry testing). The lab must follow the more stringent requirements between the method and Chapter 252.

9.1.1. **Example:** For SM 4500-NH_3 D, QC requirements are located in Section 4020.3, "Batch Quality Control". Section 4020.3, refers the reader to Section 3020.3.a-d, where labs are required to prepare and analyze a method blank (MB), a laboratory fortified blank (LFB), a duplicate, and a laboratory-fortified matrix (LFM) with each set of 20 or fewer samples. Chapter 252, §§ 252.402(g)-(l), requires labs to prepare and analyze a MB, a LFB and a duplicate with each "preparation batch" of 20 or fewer samples of the same matrix processed within 24 hours. Therefore, in order to comply with the most stringent requirements, a lab performing this method must prepare and analyze a MB, LFB, duplicate, and LFM with every batch of 20 or fewer samples that were prepared within a 24-hour period.

9.2. The lab must also address QC that is performed at alternate or additional frequencies, if applicable. These QC measures must comply with the method requirements and the applicable sections of Chapter 252 (i.e. §252.402(g)-(l) for Chemistry testing). The

laboratory must follow the more stringent requirements between the method and Chapter 252.

9.2.1. **Example:** Chapter 252, §252.404(i), requires labs to perform some QC on a monthly basis for Microbiology test methods. Chapter 252 states that for test methods that specify colony counts, duplicate counts must be performed monthly on one positive sample for each month that the test is performed. Therefore, a laboratory determining fecal coliforms by membrane filtration, for example, must indicate in the SOP that duplicate counts on a positive sample are performed monthly.

9.3. The laboratory must describe the calculations used to evaluate the QC samples against the established acceptance criterion for each QC type.

9.3.1. **Example:** A lab is performing SM 4500-NH_3 D.

1. Method Blank: To evaluate the MB, the lab calculates the result exactly like a routine environmental sample. A MB is considered contaminated if the concentration of the target analyte in the MB is at or above the reporting limit established by the method, the laboratory, or by regulation (the reporting limit must be equal to or greater than the concentration of the lowest calibration standard) **and/or** if the contamination in the MB otherwise affects the sample results [§252.402(g)(4)]. The lab's lowest calibration standard for the method is 0.1 mg NH_3-N/L, and 0.1 mg NH_3-N/L is the reporting limit for NH_3. Therefore, the lab's SOP must state that a MB is considered contaminated if the concentration of NH_3 found in the MB is 0.1 mg NH_3-N/L or greater, or otherwise effects the sample results.

2. LFB: To evaluate the LFB, the lab must calculate the percent recovery [§252.402(h)(6)]. The equation the lab uses for this calculation must be given in the SOP. The percent recovery must be compared to the method criteria. However, no acceptance criterion for the LFB is given in SM 4500-NH_3 D. In this case, the lab must develop its own acceptance criterion and document the procedure it used to establish the limits. For example, perhaps the lab chose to establish acceptance criterion of ±20% recovery for the LFB based upon performance of PT studies or IDCs. The SOP or Quality Manual must indicate that the lab decided to use ±20% based upon previous PT and IDC data.

10. **Analytical Procedure [§252.307(d)(1)(viii)]:** Labs must describe the stepwise procedure used to prepare and analyze samples according to the test method.

10.1. The lab must describe its procedure for conducting the test method, which must follow that given in the reference method but also be specific to the lab's procedure to perform the method. Often times, the procedure given in the reference method is ambiguous or allows multiple options for performance of the test method. Therefore, the lab's SOP must provide additional detail or clarification where needed to supplement that given in the reference method.

10.1.1. **Example:** A lab is performing SM 4500-NH_3 D. The method states to "add a sufficient volume of 10N NaOH solution (usually 1mL is sufficient) to raise pH

above 11" (SM 4500-NH_3 D.4.b). The lab's SOP must describe how it accomplishes this. For example:

1. Add 1mL of 10N NaOH solution to each sample using a 1mL graduated pipette.
2. Check pH of sample with 7.0-14 close range pH paper to ensure that sample pH is above 11. If sample pH is above 11, then proceed to step #3. If sample pH is at or below 11, add additional 10N NaOH in 0.2mL increments using a 1mL graduated pipette. Recheck with pH paper and repeat, if necessary, until the pH is above 11.

11. **Calculations [§252.307(d)(1)(ix)]:** The lab must include the calculations used to generate the sample results in the same units used to report final results.

    11.1. The lab must provide the equations it uses to generate the final sample result used when reporting. If the lab uses the same equations, as given, in the reference method, then the laboratory may copy those equations into the SOP. If the lab uses different or slightly modified equations to calculate sample results, the equations that are used by the lab must be given the SOP. If the lab uses a spreadsheet to calculate the final result, the lab's SOP must state that the raw data are entered into a spreadsheet, where the final result is calculated.

12. **Corrective actions or contingencies for handling out-of-control or unacceptable quality control data [§252.307(d)(1)(x)]:** Labs must describe the course of action taken when QC samples fail to meet the required acceptance criteria.

    12.1. The lab must describe its procedures for investigating and documenting QC failures and corrective actions. The procedure in the SOP should be consistent with that written in the Quality Manual, or the SOP should reference the procedure in the Quality Manual. All corrective actions should be documented. See *"Writing a Quality Manual"* for more information.

    12.2. The lab is required by Chapter 252 to flag all sample results associated with failed QC "in an unambiguous manner" on the final analytical report [§252.401(l)]. Chapter 252 also states, "to the extent possible, results of testing or analysis of samples must be reported only if all QC measures are acceptable".

        12.2.1. **Example:** A lab's SOP may read:
        "When the MB, LFB, Duplicate and/or LFM fail to meet the acceptance criteria given above, the entire analytical batch shall be re-analyzed. Upon, re-analysis, if the MB, LFB, Duplicate, and/or LFM continue to fail the acceptance criteria, the data shall be flagged appropriately and reported with data qualifiers."

13. **Reporting of results [§252.307(d)(1)(xi)]:** The lab must describe how data is reported for each analysis.

    13.1. If data reporting for all types of analyses is already addressed in the lab's Quality Manual, the SOP may simply refer to the appropriate section of the Quality Manual for data reporting instructions. However, any necessary clarifications or exceptions to the established polices for a single test method must be clearly described in that method's SOP.

13.2. The laboratory should describe the units for reporting results and any special instructions for reporting results. If the results did not meet method criteria or were associated with failed quality control, then the results must be reported with a qualifier. If the laboratory uses standard qualifiers, the qualifiers associated with the analysis should be defined here. For example, the laboratory may qualify BOD sample results if the result did not meet the 2mg/L depletion requirements. **NOTE:** Qualification of data does not mean that the data is acceptable for compliance purposes. Labs must make every effort to obtain results associated with acceptable quality control.

13.3. Laboratories must ensure that samples are reported in accordance with the specific DEP Program area requirements. For example: Drinking water sample results must be reported to DWELR by the 10th of the next month after the monitoring period. NPDES sample results must be reported in accordance with the DMR reporting rules.

14. **Please note:** SOP sections may be required by Chapter 252, §252.307(d)(1), that are not applicable to a given test method. In such instances, the SOP may indicate "Not Applicable" or "N/A" for that section or that section may be omitted from the SOP entirely. For example, calibration and standardization is not applicable to the fecal coliform analysis. However, the lab may choose to have a heading "Calibration & Standardization" in the fecal coliform SOP in order to maintain consistent formatting between SOPs, but state "Not Applicable" under that heading for the fecal coliform test. The SOPs should be responsive to all of the requirements of Chapter 252, while remaining brief and easy to follow.