

and rejection notification to the National Alternate Test Procedure Coordinator.

[77 FR 29809, May 18, 2012, as amended at 82 FR 40875, Aug. 28, 2017]

§ 136.6 Method modifications and analytical requirements.

(a) *Definitions of terms used in this section*—(1) *Analyst* means the person or laboratory using a test procedure (analytical method) in this part.

(2) *Chemistry of the method* means the reagents and reactions used in a test procedure that allow determination of the analyte(s) of interest in an environmental sample.

(3) *Determinative technique* means the way in which an analyte is identified and quantified (e.g., colorimetry, mass spectrometry).

(4) *Equivalent performance* means that the modified method produces results that meet or exceed the QC acceptance criteria of the approved method.

(5) *Method-defined analyte* means an analyte defined solely by the method used to determine the analyte. Such an analyte may be a physical parameter, a parameter that is not a specific chemical, or a parameter that may be comprised of a number of substances. Examples of such analytes include temperature, oil and grease, total suspended solids, total phenolics, turbidity, chemical oxygen demand, and biochemical oxygen demand.

(6) *QC* means “quality control.”

(b) *Method modifications.* (1) If the underlying chemistry and determinative technique in a modified method are essentially the same as an approved Part 136 method, then the modified method is an equivalent and acceptable alternative to the approved method provided the requirements of this section are met. However, those who develop or use a modification to an approved (Part 136) method must document that the performance of the modified method, in the matrix to which the modified method will be applied, is equivalent to the performance of the approved method. If such a demonstration cannot be made and documented, then the modified method is not an acceptable alternative to the approved method. Supporting documentation must, if applicable, include the routine initial dem-

onstration of capability and ongoing QC including determination of precision and accuracy, detection limits, and matrix spike recoveries. Initial demonstration of capability typically includes analysis of four replicates of a mid-level standard and a method detection limit study. Ongoing quality control typically includes method blanks, mid-level laboratory control samples, and matrix spikes (QC is as specified in the method). The method is considered equivalent if the quality control requirements in the reference method are achieved. Where the laboratory is using a vendor-supplied method, it is the QC criteria in the reference method, not the vendor’s method, that must be met to show equivalency. Where a sample preparation step is required (*i.e.*, digestion, distillation), QC tests are to be run using standards treated in the same way as the samples. The method user’s Standard Operating Procedure (SOP) must clearly document the modifications made to the reference method. Examples of allowed method modifications are listed in this section. If the method user is uncertain whether a method modification is allowed, the Regional ATP Coordinator or Director should be contacted for approval *prior* to implementing the modification. The method user should also complete necessary performance checks to verify that acceptable performance is achieved with the method modification *prior* to analyses of compliance samples.

(2) *Requirements.* The modified method must meet or exceed performance of the approved method(s) for the analyte(s) of interest, as documented by meeting the initial and ongoing quality control requirements in the method.

(i) *Requirements for establishing equivalent performance.* If the approved method contains QC tests and QC acceptance criteria, the modified method must use these QC tests and the modified method must meet the QC acceptance criteria with the following conditions:

(A) The analyst may only rely on QC tests and QC acceptance criteria in a

method if it includes wastewater matrix QC tests and QC acceptance criteria (e.g., matrix spikes) and both initial (start-up) and ongoing QC tests and QC acceptance criteria.

(B) If the approved method does not contain QC tests and QC acceptance criteria or if the QC tests and QC acceptance criteria in the method do not meet the requirements of this section, then the analyst must employ QC tests published in the "equivalent" of a Part 136 method that has such QC, or the essential QC requirements specified at 136.7, as applicable. If the approved method is from a compendium or VCSB and the QA/QC requirements are published in other parts of that organization's compendium rather than within the Part 136 method then that part of the organization's compendium must be used for the QC tests.

(C) In addition, the analyst must perform ongoing QC tests, including assessment of performance of the modified method on the sample matrix (e.g., analysis of a matrix spike/matrix spike duplicate pair for every twenty samples), and analysis of an ongoing precision and recovery sample (e.g., laboratory fortified blank or blank spike) and a blank with each batch of 20 or fewer samples.

(D) If the performance of the modified method in the wastewater matrix or reagent water does not meet or exceed the QC acceptance criteria, the method modification may not be used.

(ii) *Requirements for documentation.* The modified method must be documented in a method write-up or an addendum that describes the modification(s) to the approved method prior to the use of the method for compliance purposes. The write-up or addendum must include a reference number (e.g., method number), revision number, and revision date so that it may be referenced accurately. In addition, the organization that uses the modified method must document the results of QC tests and keep these records, along with a copy of the method write-up or addendum, for review by an auditor.

(3) *Restrictions.* An analyst may not modify an approved Clean Water Act analytical method for a method-defined analyte. In addition, an analyst may not modify an approved method if

the modification would result in measurement of a different form or species of an analyte. Changes in method procedures are not allowed if such changes would alter the defined chemistry (*i.e.*, method principle) of the unmodified method. For example, phenol method 420.1 or 420.4 defines phenolics as ferric iron oxidized compounds that react with 4-aminoantipyrine (4-AAP) at pH 10 after being distilled from acid solution. Because total phenolics represents a group of compounds that all react at different efficiencies with 4-AAP, changing test conditions likely would change the behavior of these different phenolic compounds. An analyst may not modify any sample collection, preservation, or holding time requirements of an approved method. Such modifications to sample collection, preservation, and holding time requirements do not fall within the scope of the flexibility allowed at §136.6. Method flexibility refers to modifications of the analytical procedures used for identification and measurement of the analyte only and does not apply to sample collection, preservation, or holding time procedures, which may only be modified as specified in §136.3(e).

(4) *Allowable changes.* Except as noted under paragraph (b)(3) of this section, an analyst may modify an approved test procedure (analytical method) provided that the underlying reactions and principles used in the approved method remain essentially the same, and provided that the requirements of this section are met. If equal or better performance can be obtained with an alternative reagent, then it is allowed. A laboratory wishing to use these modifications must demonstrate acceptable method performance by performing and documenting all applicable initial demonstration of capability and ongoing QC tests and meeting all applicable QC acceptance criteria as described in §136.7. Some examples of the allowed types of changes, provided the requirements of this section are met include:

(i) Changes between manual method, flow analyzer, and discrete instrumentation.

(ii) Changes in chromatographic columns or temperature programs.

(iii) Changes between automated and manual sample preparation, such as digestions, distillations, and extractions; in-line sample preparation is an acceptable form of automated sample preparation for CWA methods.

(iv) In general, ICP-MS is a sensitive and selective detector for metal analysis; however isobaric interference can cause problems for quantitative determination, as well as identification based on the isotope pattern. Interference reduction technologies, such as collision cells or reaction cells, are designed to reduce the effect of spectroscopic interferences that may bias results for the element of interest. The use of interference reduction technologies is allowed, provided the method performance specifications relevant to ICP-MS measurements are met.

(v) The use of EPA Method 200.2 or the sample preparation steps from EPA Method 1638, including the use of closed-vessel digestion, is allowed for EPA Method 200.8, provided the method performance specifications relevant to the ICP-MS are met.

(vi) Changes in pH adjustment reagents. Changes in compounds used to adjust pH are acceptable as long as they do not produce interference. For example, using a different acid to adjust pH in colorimetric methods.

(vii) Changes in buffer reagents are acceptable provided that the changes do not produce interferences.

(viii) Changes in the order of reagent addition are acceptable provided that the change does not alter the chemistry and does not produce an interference. For example, using the same reagents, but adding them in different

order, or preparing them in combined or separate solutions (so they can be added separately), is allowed, provided reagent stability or method performance is equivalent or improved.

(ix) Changes in calibration range (provided that the modified range covers any relevant regulatory limit and the method performance specifications for calibration are met).

(x) Changes in calibration model. (A) Linear calibration models do not adequately fit calibration data with one or two inflection points. For example, vendor-supplied data acquisition and processing software on some instruments may provide quadratic fitting functions to handle such situations. If the calibration data for a particular analytical method routinely display quadratic character, using quadratic fitting functions may be acceptable. In such cases, the minimum number of calibrators for second order fits should be six, and in no case should concentrations be extrapolated for instrument responses that exceed that of the most concentrated calibrator. Examples of methods with nonlinear calibration functions include chloride by SM4500-Cl-E-1997, hardness by EPA Method 130.1, cyanide by ASTM D6888 or OIA1677, Kjeldahl nitrogen by PAI-DK03, and anions by EPA Method 300.0.

(B) As an alternative to using the average response factor, the quality of the calibration may be evaluated using the Relative Standard Error (RSE). The acceptance criterion for the RSE is the same as the acceptance criterion for Relative Standard Deviation (RSD), in the method. RSE is calculated as:

$$\% \text{ RSE} = 100 \times \sqrt{\frac{\sum_{i=1}^n \left[\frac{x'_i - x_i}{x_i} \right]^2}{(n-p)}}$$

Where:

x'_i = Calculated concentration at level i

x_i = Actual concentration of the calibration level i

n = Number of calibration points

p = Number of terms in the fitting equation
(average = 1, linear = 2, quadratic = 3)

(C) Using the RSE as a metric has the added advantage of allowing the same numerical standard to be applied to the calibration model, regardless of the form of the model. Thus, if a method states that the RSD should be $\leq 20\%$ for the traditional linear model through the origin, then the RSE acceptance limit can remain $\leq 20\%$ as well. Similarly, if a method provides an RSD acceptance limit of $\leq 15\%$, then that same figure can be used as the acceptance limit for the RSE. The RSE may be used as an alternative to correlation coefficients and coefficients of determination for evaluating calibration curves for any of the methods at part 136. If the method includes a numerical criterion for the RSD, then the same numerical value is used for the RSE. Some older methods do not include any criterion for the calibration curve—for these methods, if RSE is used the value should be $\leq 20\%$. Note that the use of the RSE is included as an alternative to the use of the correlation coefficient as a measure of the suitability of a calibration curve. It is not necessary to evaluate both the RSE and the correlation coefficient.

(xi) Changes in equipment such as equipment from a vendor different from the one specified in the method.

(xii) The use of micro or midi distillation apparatus in place of macro distillation apparatus.

(xiii) The use of prepackaged reagents.

(xiv) The use of digital titrators and methods where the underlying chemistry used for the determination is similar to that used in the approved method.

(xv) Use of selected ion monitoring (SIM) mode for analytes that cannot be effectively analyzed in full-scan mode and reach the required sensitivity. False positives are more of a concern when using SIM analysis, so at a minimum, one quantitation and two qualifying ions must be monitored for each analyte (unless fewer than three ions with intensity greater than 15% of the base peak are available). The ratio of each of the two qualifying ions to the quantitation ion must be evaluated and should agree with the ratio observed in an authentic standard within ± 20 percent. Analyst judgment must be ap-

plied to the evaluation of ion ratios because the ratios can be affected by co-eluting compounds present in the sample matrix. The signal-to-noise ratio of the least sensitive ion should be at least 3:1. Retention time in the sample should match within 0.05 minute of an authentic standard analyzed under identical conditions. Matrix interferences can cause minor shifts in retention time and may be evident as shifts in the retention times of the internal standards. The total scan time should be such that a minimum of eight scans are obtained per chromatographic peak.

(xvi) Changes are allowed in purge-and-trap sample volumes or operating conditions. Some examples are:

(A) Changes in purge time and purge-gas flow rate. A change in purge time and purge-gas flow rate is allowed provided that sufficient total purge volume is used to achieve the required minimum detectible concentration and calibration range for all compounds. In general, a purge rate in the range 20–200 mL/min and a total purge volume in the range 240–880 mL are recommended.

(B) Use of nitrogen or helium as a purge gas, provided that the required sensitivities for all compounds are met.

(C) Sample temperature during the purge state. Gentle heating of the sample during purging (e.g., 40 °C) increases purging efficiency of hydrophilic compounds and may improve sample-to-sample repeatability because all samples are purged under precisely the same conditions.

(D) Trap sorbent. Any trap design is acceptable, provided that the data acquired meet all QC criteria.

(E) Changes to the desorb time. Shortening the desorb time (e.g., from 4 minutes to 1 minute) may not affect compound recoveries, and can shorten overall cycle time and significantly reduce the amount of water introduced to the analytical system, thus improving the precision of analysis, especially for water-soluble analytes. A desorb time of four minutes is recommended, however a shorter desorb time may be used, provided that all QC specifications in the method are met.

(F) Use of water management techniques is allowed. Water is always collected on the trap along with the analytes and is a significant interference for analytical systems (GC and GC/MS). Modern water management techniques (e.g., dry purge or condensation points) can remove moisture from the sample stream and improve analytical performance.

(xvii) If the characteristics of a wastewater matrix prevent efficient recovery of organic pollutants and prevent the method from meeting QC requirements, the analyst may attempt to resolve the issue by adding salts to the sample, provided that such salts do not react with or introduce the target pollutant into the sample (as evidenced by the analysis of method blanks, laboratory control samples, and spiked samples that also contain such salts), and that all requirements of paragraph (b)(2) of this section are met. Samples having residual chlorine or other halogen must be dechlorinated prior to the addition of such salts.

(xviii) If the characteristics of a wastewater matrix result in poor sample dispersion or reagent deposition on equipment and prevent the analyst from meeting QC requirements, the analyst may attempt to resolve the issue by adding an inert surfactant that does not affect the chemistry of the method, such as Brij-35 or sodium dodecyl sulfate (SDS), provided that such surfactant does not react with or introduce the target pollutant into the sample (as evidenced by the analysis of method blanks, laboratory control samples, and spiked samples that also contain such surfactant) and that all requirements of paragraph (b)(1) and (b)(2) of this section are met. Samples having residual chlorine or other halogen must be dechlorinated prior to the addition of such surfactant.

(xix) The use of gas diffusion (using pH change to convert the analyte to gaseous form and/or heat to separate an analyte contained in steam from the sample matrix) across a hydrophobic semi-permeable membrane to separate the analyte of interest from the sample matrix may be used in place of manual or automated distillation in methods for analysis such as ammonia, total cyanide, total Kjeldahl nitrogen, and

total phenols. These procedures do not replace the digestion procedures specified in the approved methods and must be used in conjunction with those procedures.

(xx) Changes in equipment operating parameters such as the monitoring wavelength of a colorimeter or the reaction time and temperature as needed to achieve the chemical reactions defined in the unmodified CWA method. For example, molybdenum blue phosphate methods have two absorbance maxima, one at about 660 nm and another at about 880 nm. The former is about 2.5 times less sensitive than the latter. Wavelength choice provides a cost-effective, dilution-free means to increase sensitivity of molybdenum blue phosphate methods.

(xxi) Interchange of oxidants, such as the use of titanium oxide in UV-assisted automated digestion of TOC and total phosphorus, as long as complete oxidation can be demonstrated.

(xxii) Use of an axially viewed torch with Method 200.7.

(xxiii) When analyzing metals by inductively coupled plasma-atomic emission spectroscopy, inductively coupled plasma-mass spectrometry, and stabilized temperature graphite furnace atomic absorption, closed-vessel microwave digestion of wastewater samples is allowed as alternative heating source for Method 200.2—"Sample Preparation Procedure for Spectrochemical Determination of Total Recoverable Elements" for the following elements: Aluminum, antimony, arsenic, barium, beryllium, boron, cadmium, calcium, chromium, cobalt, copper, iron, lead, magnesium, manganese, molybdenum, nickel, potassium, selenium, silver, sodium, thallium, tin, titanium, vanadium, zinc, provided the performance specifications in the relevant determinative method are met. (Note that this list does not include Mercury.) Each laboratory determining total recoverable metals is required to operate a formal quality control (QC) program. The minimum requirements include initial demonstration of capability, method detection limit (MDL), analysis of reagent blanks, fortified blanks, matrix spike samples, and blind proficiency testing samples, as continuing quality control checks on performance.

The laboratory is required to maintain performance records on file that define the quality of the data generated.

(c) The permittee must notify their permitting authority of the intent to use a modified method. Such notification should be of the form "Method xxx has been modified within the flexibility allowed in 40 CFR 136.6." The permittee may indicate the specific paragraph of §136.6 allowing the method modification. Specific details of the modification need not be provided, but must be documented in the Standard Operating Procedure (SOP) and maintained by the analytical laboratory that performs the analysis.

[77 FR 29810, May 18, 2012, as amended at 82 FR 40875, Aug. 28, 2017; 86 FR 27260, May 19, 2021]

§136.7 Quality assurance and quality control.

The permittee/laboratory shall use suitable QA/QC procedures when conducting compliance analyses with any part 136 chemical method or an alternative method specified by the permitting authority. These QA/QC procedures are generally included in the analytical method or may be part of the methods compendium for approved Part 136 methods from a consensus organization. For example, Standard Methods contains QA/QC procedures in the Part 1000 section of the Standard Methods Compendium. The permittee/laboratory shall follow these QA/QC procedures, as described in the method or methods compendium. If the method lacks QA/QC procedures, the permittee/laboratory has the following options to comply with the QA/QC requirements:

(a) Refer to and follow the QA/QC published in the "equivalent" EPA method for that parameter that has such QA/QC procedures;

(b) Refer to the appropriate QA/QC section(s) of an approved part 136 method from a consensus organization compendium;

(c)(1) Incorporate the following twelve quality control elements, where applicable, into the laboratory's documented standard operating procedure (SOP) for performing compliance analyses when using an approved part 136 method when the method lacks such QA/QC procedures. One or more of the

twelve QC elements may not apply to a given method and may be omitted if a written rationale is provided indicating why the element(s) is/are inappropriate for a specific method.

(i) Demonstration of Capability (DOC);

(ii) Method Detection Limit (MDL);

(iii) Laboratory reagent blank (LRB), also referred to as method blank (MB);

(iv) Laboratory fortified blank (LFB), also referred to as a spiked blank, or laboratory control sample (LCS);

(v) Matrix spike (MS) and matrix spike duplicate (MSD), or laboratory fortified matrix (LFM) and LFM duplicate, may be used for suspected matrix interference problems to assess precision;

(vi) Internal standards (for GC/MS analyses), surrogate standards (for organic analysis) or tracers (for radiochemistry);

(vii) Calibration (initial and continuing), also referred to as initial calibration verification (ICV) and continuing calibration verification (CCV);

(viii) Control charts (or other trend analyses of quality control results);

(ix) Corrective action (root cause analysis);

(x) QC acceptance criteria;

(xi) Definitions of preparation and analytical batches that may drive QC frequencies; and

(xii) Minimum frequency for conducting all QC elements.

(2) These twelve quality control elements must be clearly documented in the written standard operating procedure for each analytical method not containing QA/QC procedures, where applicable.

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APPENDIX A TO PART 136—METHODS FOR ORGANIC CHEMICAL ANALYSIS OF MUNICIPAL AND INDUSTRIAL WASTEWATER

METHOD 601—PURGEABLE HALOCARBONS

1. Scope and Application

1.1 This method covers the determination of 29 purgeable halocarbons.

The following parameters may be determined by this method: