Chapter 2

Method Flexibility

2.1 Introduction

One of the primary goals of the streamlining initiative is to encourage the use of innovative technologies by increasing method flexibility so that laboratories can modify approved reference methods without formal EPA review. Under the streamlining program, it will no longer be necessary to apply for alternate test procedure (ATP) approval of modified methods. Rather, laboratories will be required to demonstrate and document that the modified method produces results equal or superior to results produced by the unmodified reference method. To ensure data quality, EPA is building in well-defined controls on this increased flexibility. These include designation of a reference method that contains quality control (QC) acceptance criteria for use in demonstrating equivalency, and specific requirements for validating modified methods and documenting equivalency. The purpose of this chapter is to describe the scope of the flexibility that will be offered under streamlining.

This chapter begins by describing the current flexibility in EPA's wastewater and drinking water programs, outlines the increased flexibility offered in the streamlining initiative, and defines the controls that will be used as the foundation for expanded flexibility. The key concepts presented and discussed in this chapter are: *limited flexibility, reference methods, other approved methods, flexibility in front-end and determinative techniques, new methods, method modifications, screening methods, method-defined analytes,* and *new target analytes*.

2.2 Existing Flexibility

Methods currently approved at 40 *CFR* parts 136 and 141 under EPA's wastewater and drinking water programs, respectively, allow two types of flexibility: (1) explicit flexibility, which does not require prior EPA approval, and (2) flexibility that requires prior EPA approval through the ATP process.

Method modifications currently are allowed without prior EPA approval only when the modification is explicitly allowed in the approved method. Explicit flexibility is termed **limited flexibility**. Some approved methods provide limited flexibility to substitute specific apparatus with apparatus demonstrated to be equivalent. The areas of currently allowed flexibility are indicated with the terms "should" or the phrase "or equivalent." Substitution of a 500-mL beaker for a 250-mL beaker or use of an "equivalent" chromatographic column are examples of such explicit flexibility. The EPA 600- and 1600- series wastewater methods approved at 40 *CFR* part 136, Appendix A provide limited flexibility to improve separations and reduce the cost of measurements as long as method performance is not sacrificed. Laboratories that choose to exercise explicit flexibility are required to meet the quality control (QC) acceptance criteria of the approved method for certain standardized QC tests. In the development of more recent methods (e.g., Method 1664 and Method 1613), EPA has expanded its definition of allowed flexibility to further encourage the use of new

techniques that provide equal or better performance at lower costs. However, no approved methods provide unlimited flexibility and few provide the extensive flexibility that EPA proposes in this initiative.

Currently, all modifications not explicitly allowed by the method require prior EPA approval. These modifications must be approved through EPA's alternated test procedure (ATP) program. Historically, the wastewater program has allowed some changes to front-end techniques but not to the determinative technique. The drinking water program has been somewhat less restrictive on changing the determinative technique and has allowed other changes to compliance methods, provided the chemistry of the method is not changed. Some modifications to a front-end technique, such as changing the extraction solvent, are not currently allowed in drinking water methods.

Procedures for requesting ATP approval are specified at 40 CFR 136.4 and 136.5 of the wastewater regulations and at 40 CFR 141.27 of the drinking water regulations. ATP approval requires concurrence by EPA (and sometimes the state) and in some cases, the method must be listed in the CFR via an Agency rulemaking. The current ATP process is described in Chapter 1, Section 1.1.2.

2.3 Scope of Flexibility Provided by Streamlining

The streamlining initiative will allow flexibility to modify approved reference methods without submission of ATPs, provided that a laboratory demonstrates and documents that the modified method produces results equal or superior to those produced by the EPA-designated reference method. Only new methods (or Tier 2 or Tier 3 modified methods for which developers specifically request EPA review) will be subject to the streamlined ATP process. The scope of method flexibility that will be allowed under streamlining is detailed in Sections 2.3.1 - 2.3.5.

It should be noted that the proposed flexibility does not extend to sample collection or preservation conditions. These conditions include, but are not limited to, containers, holding times, preservation procedures or reagents, shipping and storage procedures. Modifications to sample collection and preservation conditions continue to require a variance as specified at 40 CFR 136.3 (c) and 141.27.

2.3.1 Reference Method

The foundation of EPA's flexibility concept is based on the use of a **reference method** against which method modifications can be tested for equivalency. A reference method is a method that has been approved at 40 CFR part 136 or 141, and contains (or is supplemented with) standardized QC procedures and the required QC acceptance criteria for each of these procedures. Using QC acceptance criteria as the performance measure makes the reference methods performance-based without extensive method redevelopment.

Only one reference method will be designated for each combination of regulated analyte and determinative technique. The purpose of specifying a single reference method for a given combination of analyte and determinative technique is to avoid the possible confusion that could be created if two or more reference methods contained differing QC acceptance criteria. The QC acceptance criteria associated with the reference method will be the performance criteria against which method modifications are tested. Method equivalency is demonstrated when results produced by a modification meet or exceed the QC acceptance criteria in the reference method.

For the streamlining proposal, EPA selected reference methods primarily on the basis of existing QC acceptance criteria and/or the availability of data from which to develop QC acceptance criteria for each of the standardized QC elements described in Chapter 3 of this guide. An important additional consideration was whether or not the organization that developed the method would allow its methods to be subject to the flexibility proposed by the streamlined method approval process. Some external methods organizations, including Standard Methods, ASTM, and AOAC-International, have declined to allow unrestricted modifications to their methods. Their collective decision was based on the need to retain their methods as official "standards," which they have determined cannot be changed. Most of their methods have sufficient explicit flexibility to meet the objectives of streamlining or can be updated rapidly through their respective method approval processes. Because these methods cannot be modified, however, they cannot be designated as reference methods.

A reference method is needed to exercise the increased flexibility offered by the streamlining initiative. However, there are not reference methods for all listed combinations of analyte and determinative technique. In some of these cases (e.g., 40 *CFR* 136 Table ID), reference methods have not been cited because EPA has not yet developed QC acceptance criteria for the methods. In other cases, reference methods are not cited because the data are not yet available. In still others, it is not possible to cite a reference method since there are only Standard Methods, ASTM, or AOAC-International methods for that combination of analyte and determinative technique and these organizations do not allow modification of their methods. EPA has designated most of the reference methods and specified some of the QC acceptance criteria (in the Methods and Criteria document) for chemical analytes listed at 40 CFR parts 136 and 141. In a future rulemaking, EPA plans to designate additional reference methods and develop QC acceptance criteria for all wastewater and drinking water chemical methods, but EPA has not delayed proposal of the streamlining initiative while these activities take place.

Upon implementation of the streamlining initiative, EPA will retain all methods that are approved for use at 40 *CFR* parts 136 and 141, but will re-categorize each method as either a "Reference Method" or an "Other Approved Method". Regardless of whether a method has been designated as a "Reference Method" or as an "Other Approved Method", all approved methods cited at 40 *CFR* parts 136 and 141 will carry equal regulatory status. Reference methods will be cited by adding a column to the tables currently published at 40 *CFR* parts 136 and 141. A partial example of one table format is provided in **Table 2.1**.

Table 2.1: Example of Proposed 40 *CFR* part 136 Table IB with Reference Methods.

Table IB—List of Approved Inorganic Test Procedures

Parameter/ Methodology	Reference Method[1,35]	Other Approved Methods				
		Standard Methods 18th Ed.[39]	ASTM[39]	USGS[2,39]	AOAC-Intl.[39]	Other
1. Acidity, as $CaCO_3$, mg/L:						
Electrometric endpoint or phenolphthalein endpoint	305.1	2310 B(4a)	D1067-92			
2. Alkalinity, as $CaCO_3$, mg/L:						
Electrometric or Colorimetric titration to pH 4.5, manual or automated	310.1 310.2	2320 B	D1067-92	I-1030-85 I-2030-85	973.43[3]	
3. Aluminum–Total,[4] mg/L; Digestion[4] followed by:						
AA direct aspiration[36]	202.1	3111 D		I-3051-85		
AA furnace	202.2	3113 B				
Inductively Coupled Plasma/Atomic Emission Spectrometry (ICP/AES)[36]	[5]200.7	3120 B				
Direct Current Plasma (DCP)[36]			D4190-82(88)			AES0029[34]
Colorimetric (Eriochrome cyanine R)		3500-AI D				
4. Ammonia (as N), mg/L:						
Manual, distillation (at pH 9.5)[6] followed by	350.2	4500-NH_3 B			973.49[3]	
Nesslerization	350.2	4500-NH_3 C	D1426-93(A)	I-3520-85	973.49[3]	
Titration	350.2	4500-NH_3 E				
Electrode	350.3	4500-NH_3 F or G	D1426-93(B)			
Automated phenate	350.1	4500-NH_3 H		I-4523-85		
Automated electrode						379-75WE[7]
5. Antimony–Total,[4] mg/L; Digestion[4] followed by:						
AA direct aspiration[36]	204.1	3111 B				
AA furnace	204.2	3113 B				
ICP/AES36	[5]200.7	3120 B				

In the future, it is anticipated that new reference methods will be approved at 40 *CFR* parts 136 and 141 only if a new analyte becomes of concern to EPA or if a new determinative technique is developed for an existing analyte of concern. EPA intends to rely on outside organizations to develop most new methods for approval at 40 CFR parts 136 and 141. To be approved (promulgated) as a reference method, the method must meet the following requirements:

- The method submitter must be willing to allow the method to be modified as described in this streamlining initiative.

- The method must be for a combination of analyte of concern and determinative technique for which an approved method does not exist. (This requirement precludes non-unique combinations of analytes and determinative techniques.)

- The combination of analyte and determinative technique must, in EPA's judgement, be useful for determination of an analyte of concern in a matrix of concern to EPA. (This requirement precludes useless combinations of analytes and determinative techniques, e.g., use of a flame ionization detector with EPA Method 508 or 608.)

- The method must pass all criteria set forth in this initiative including requirements for format, QC, QC acceptance criteria, validation, and submittal of supporting documentation.

- The method must pass peer-review and the Agency rulemaking process of proposal, public comment, and final rule.

Based on suggestions and advice received to date, EPA believes that most organizations that modify methods will choose to document the validity of those modifications without seeking formal approval. Therefore, the streamlining initiative will eliminate multiple methods for the same combination of analyte and determinative technique.

After streamlining is implemented, EPA's role in developing methods may be limited to instances where a method is required for monitoring an unusual analyte and/or for monitoring in a specific sample matrix and/or on a schedule that cannot be met by an outside method developer. Regardless of the organization that develops a new method, all new methods considered for approval under 40 CFR part 136 and 141 would continue to be proposed in the *Federal Register* and subject to public comment prior to approval. Additional information concerning the method submission and approval process is provided in Chapter 5.

2.3.2 Modifications to Front-end and Determinative Techniques

Most method modifications allowed under the streamlining initiative fall into one of two categories: (1) modification of a "front-end" technique or (2) modification of the determinative technique. A third category, adding additional analytes, is discussed in Section 2.3.4.

A **front-end technique** is any technique in the analytical process conducted at the laboratory that precedes the determinative technique (see definition below). Front-end techniques include all procedures, equipment, solvents, etc., that are used in the preparation and cleanup of a sample for analysis. Under the streamlining initiative, EPA proposes to allow laboratories the flexibility to modify any and all front-end techniques without notifying EPA, provided the modification is not explicitly prohibited in the reference method and provided the modification can be demonstrated to

produce results equal or superior to results produced by the reference method. This flexibility includes the ability to modify the chemistry of the front-end of the method. For example, changing the extraction solvent and substituting liquid-liquid for solid-liquid extraction will be allowed. However, if changing the chemistry of the method might affect the extract holding times specified in the reference method, a new extract holding time study must be performed. For example, extracting the water sample with pentane rather than isooctane is not likely to affect extract holding times because the chemical properties of the solvents are very similar. However, replacing ethyl acetate with a chemically dissimilar solvent, acetone, would require a reverification of the holding times for the target analytes in acetone. The developer of a modified method always has the option of asking EPA or other regulatory authority for a technical opinion on the acceptability of the developer's validation data that supports the method modification. As noted in Appendix C (issue 26), changes in the sorbent trap in the purge-and-trap volatile organic compound (VOC) methods are allowed, but the methods specifically preclude changes to the purge and desorption times or gas flows. Although these are front-end procedures, the method explicitly disallows modifications because these conditions are independent of the sorbent used and have been optimized for full recovery of the target VOCs.

A **determinative technique** is the physical and/or chemical process by which the measurement of the identity and concentration of an analyte is made. For most methods, the determinative technique consists of an instrumental measurement (i.e., a detector). Examples of determinative techniques are provided in **Table 2-2** at the end of this chapter. Under the refined streamlining initiative, EPA proposes to allow use of an alternate determinative technique that is not explicitly prohibited in the reference method, provided that equivalency is demonstrated and documented as outlined above, and provided that four conditions are met: (1) the alternate determinative technique measures a property similar to the prescribed technique, (2) the alternate technique is demonstrated to be more specific (i.e., identifies the analyte in the presence of interferences) and/or more sensitive (i.e., produces a lower detection limit) for the analyte of concern than the determinative technique in the reference method, (3) there is not another approved method that uses the alternate determinative technique for the determination of that analyte, and (4) use of the alternate determinative technique will not result in a nonsensical combination of analyte, front-end technique, and determinative technique.

Examples of allowed changes to a determinative technique are substitution of a photoionization detector for a flame ionization detector for determination of polynuclear aromatic hydrocarbons, substitution of a nitrogen-phosphorous detector for an electron capture detector (ECD) for determination of analytes containing nitrogen or phosphorous, and substitution of a fluorescence detector for an ultraviolet or visible wavelength detector. Substitution of a mass spectrometer (MS) for an ECD would not be allowed if there is an approved MS method that measures the analyte of concern. Readers are referred to the Streamlining Guide for more guidance on this subject.

Substitution of a photoionization detector (PID) for the flame ionization detector (FID) specified in Method 610 is an excellent example of a useful and allowed modification to the determinative technique because (1) the PID will provide improved sensitivity and specificity for determination of the polynuclear aromatic hydrocarbons (PAHs) determined in Method 610, (2) there are no currently approved methods for PAHs that use the PID as the determinative technique, and (3) use of a PID does not create a nonsensical combination of analyte, front-end techniques, and determinative technique.

Conversely, substitution of a flame ionization detector (FID) for either an electron capture detector (ECD) or an electrolytic conductivity detector (ELCD) for determination of chlorinated pesticides in Method 508 or 608 would not be permitted because the FID is much less sensitive and

less selective than an ECD or ELCD, and would therefore be nearly useless for compliance determinations of pesticides in an environmental sample. In contrast, use of a high resolution mass spectrometer (HRMS) in place of an ECD or ELCD for determination of pesticides would represent a significant improvement in selectivity (specificity) and/or sensitivity. EPA would accept, and propose for approval, a fully developed method using HRGC/HRMS for determination of chlorinated pesticides.

EPA chose to limit changes to the determinative technique by the four conditions described above to preclude nonsensical combinations of analyte and determinative technique, to encourage a net benefit (increased sensitivity and/or specificity), and to preclude multiple reference methods with the same determinative technique but with different QC acceptance criteria for the same analyte(s) of concern. For example, if a mass spectrometer were substituted for the conventional detectors in EPA methods 601 - 612, all of these methods would become GC/MS methods, but all would contain different QC acceptance criteria. Further, they would all conflict with approved GC/MS Methods 625 and 1625. The proposed restriction on detector substitution also is consistent with EPA's decision in the December 5, 1994 drinking water methods final rule (59 *FR* 62456) not to allow substitution of MS in methods that specify conventional GC detectors. Another reason for limiting changes to the determinative technique is that there are techniques, such as immunoassay, for which EPA has no reference method and therefore no history to insure that the standardized QC proposed in today's rule are germane to, or adequate for, assurance of the quality of data produced by the novel determinative technique. EPA would prefer that a new method be written and submitted for approval when a novel determinative technique is developed. EPA invites public comment on the suitability of the conditions EPA proposes to place on the flexibility to modify determinative techniques in EPA reference methods. EPA would allow limited flexibility to change the determinative technique. An alternate determinative technique can be used provided that (1) the alternate technique is demonstrated to be more specific (i.e., identifies the analyte in the presence of interferences) and/or more sensitive (i.e., produces a lower detection limit) for the analyte(s) of interest than the determinative technique in the reference method, (2) there is not another approved method that uses the alternate determinative technique for determination of that analyte, and (3) use of the alternate determinative technique will not result in a nonsensical combination of analytes, front-end techniques, and determinative techniques.

2.3.3 Method-Defined Analytes

In its initial straw man, EPA expressed concern that some techniques may not produce results equivalent to results produced by techniques employed for "method-defined analytes". A **method-defined analyte** is an analyte that does not have a specific, known composition so that the analytical result depends totally on how the measurement is made. Therefore, a change to either the front-end steps or the determinative technique for a method-defined analyte has the potential of changing the numerical value of the result for a given sample. Examples of method-defined analytes include adsorbable organic halides (AOX), biochemical oxygen demand (BOD), total radioactivity and whole effluent toxicity (WET).

EPA believes that methods for some method-defined analytes will need to have less flexibility than methods for specific chemical substances. EPA believes, however, that some flexibility can and should be allowed in these methods. Therefore, EPA intends to restrict the allowable flexibility in methods for

Table 2-2
Examples of Determinative Techniques

The following is a partial list of determinative techniques. This list is not all-inclusive; it is merely intended to provide examples of the types of procedures that may be considered subject to modification as determinative techniques under the streamlining initiative.

Alkali Flame Detector (AFD)
Alpha Gas Proportional Counter
Alpha Scintillation Detection
Alpha Spectrometry
Amperometric Detection
Anodic Stripping Voltametry
Atomic Absorption Spectroscopy (AA)
Autoradiaography
Beta Gas Proportional Counter
Beta Scintillation Detection
Bioassay
Capillary Gas Chromatography/Electron Capture Detection (Capillary GC/ECD)
Capillary Gas Chromatography/Electrolytic Conductivity Detection (Capillary GC/ELCD)
Capillary Gas Chromatography/Flame Ionization Detection (Capillary GC/FID)
Capillary Gas Chromatography/Flame Photometric Detection (Capillary GC/FPD)
Capillary Gas Chromatography/High Resolution Mass Spectrometry (Capillary GC/HRMS)
Capillary Gas Chromatography/Low Resolution Mass Spectrometry (Capillary GC/LRMS)
Capillary Gas Chromatography/Nitrogen-Phosphorus Detection (Capillary GC/NPD)
Capillary Gas Chromatography/Photoionization Detection (Capillary GC/PID)
Cold Vapor Atomic Absorption (CVAA)
Cold Vapor Atomic Fluorescence (CVAF)
Conductivity Bridge (a.k.a. "Wheatstone Bridge")
Current Meter
Electret Ionization Chamber
Electrochemical Detector
Electrochemical Sensor
Electron Capture Detection (ECD)
Electrolytic Conductivity Detection (ELCD)
Electromagnetic Current Meter
Emission Spectroscopy
Filter Photometer
Flame Atomic Absorption (FLAA)
Flame Ionization Detection (FID)
Flame Photometric Detection (FPD)
Fluorometry
Fourier Transform Infrared Spectrometer (FTIR)
Gamma Ray Counter

Table 2-2 (Continued)
Examples of Determinative Techniques

Gamma Spectrometry
Gas Chromatography (GC)
GC/Alkali Flame Detector (GC/AFD)
GC/ECD
GC/ELCD
GC/FID
GC/FPD
GC/FTIR
GC/Halogen Specific Detector (HSD)
GC/Mass Spectrometry (GC/MS)
GC/Nitrogen Phosphorus Detector (GC/NPD)
GC/Photoionization Detector (GC/PID)
GC/Thermal Conductivity Detector (GC/TCD)
GC/Thermionic Detector
Graphite Furnace Atomic Absorption (GFAA)
High Resolution Gamma Spectrometry
High Resolution Gas Chromatography (HRGC)
High Resolution Mass Spectrometry (HRMS)
HPLC/Electrochemical Detector
HPLC/Fluorescence Detector
HPLC/FTIR
HPLC/Thermospray-Mass Spectrometry Detector
HPLC/Refractive Index Detector
HPLC/Ultraviolet Detector (HPLC/UV)
Human eye
Human nose
Human tongue
Hydrometer
Inductively Coupled Plasma/Atomic Emission spectroscopy (ICP/AES)
Inductively Coupled Plasma/Mass Spectrometry (ICP/MS)
Infrared Spectrophotometer (IR)
Ion-Selective Electrode
Laser Phosphorimeter
Liquid Scintillation Counter
Mass Spectrometer (MS)
Microscopy
Neutron Activation Analysis
Nitrogen-Phosphorus Detector (NPD)
Non-dispersive Infrared (NDIR)

Table 2-2 (Continued)
Examples of Determinative Techniques

Nephelometer
Particle Beam Mass Spectrometry
pH Meter
Photoacoustic Infrared Detector
Photoionization Detector
Photometer
Polarograph
Potentiometer
Pressure Meter
Quartz Furnace AA
Spectrophotometer
Stabilized Temperature Graphite Furnace AA (STGFAA)
Thermal Conductivity Detector
Thermal Chromatography/Mass Spectrometry
Transmission Electron Microscopy (TEM)
Tensiometer
Titration
Toxic Gas Vapor Detector Tube
Turbidimeter
X-Ray Diffraction
X-Ray Fluorescence

method-defined analytes and establish more stringent requirements for exercising this flexibility and for demonstrating equivalency. To implement this proposal, EPA would either not designate a reference method for a method-defined analyte or would footnote the tables in 40 *CFR* parts 136 and 141 for those analytes that are method-defined and either update or supplement these methods with explicit guidance concerning areas of allowed flexibility.

EPA will accept and review new or modified methods that produce results significantly different from results produced by approved methods for method-defined analytes. The Agency cannot guarantee, however, that such methods will ever be used in regulation development or monitoring. For example, methods currently approved at 40 *CFR* part 136 for determination of oil and grease are based on separatory funnel extraction using CFC-113 or hexane, drying, concentration, and weighing (gravimetry). Other methods based on GC, infrared spectroscopy (IR), or immunoassay techniques have been or are being developed for determination of oil and grease, but it is not expected that any of these other determinative techniques will produce results equivalent to results produced by gravimetry. EPA will accept application for approval of a new method that employs a different determinative technique from gravimetry, and will propose and attempt to approve such a method on request by the method developer; however, EPA will need to create a separate category within the tables in 40 *CFR* part 136 for such methods. This table will apply only to methods for method-defined analytes that produce results significantly different from results produced by the approved methods.

Given this limitation and the potential negative connotation that may be associated with methods in such a table, purveyors of new technology for determination of method-defined analytes may choose to avoid submitting a new method to EPA for approval and promulgation. Instead, they may find it preferable to exercise the flexibility provided in this initiative and demonstrate that the new technique produces results equivalent to the reference method on a matrix-by-matrix basis. EPA will work with method developers to determine that a combination of analyte and determinative technique is new and to assess whether a new method for a method-defined analyte is desirable.

2.3.4 Flexibility to Add New Target Analytes

In today's proposed rule, EPA has also given details for modifying the analytical scope of an approved method by adding additional analytes. This action is in response to public comment on previous rules (59 FR 62456, December 5, 1194; 58 FR 65622, December 15, 1993) to extend the scope of an approved method to the determination of other analytes. Method developers seek this approval when they want to adapt an existing method rather than develop a new one to obtain occurrence data for a new analyte. EPA believes these requests have merit when there is a potential for new regulatory requirements and historical monitoring data might be useful in making process, treatment, or regulatory decisions. Examples of monitoring for a new analyte include industrial or POTW monitoring for ethers in a discharge, PWS monitoring for unregulated pesticides or pesticide metabolites, and PWS monitoring for analytes on the drinking water priority list. EPA also believes these requests have merit when technological advances make the measurement of additional analytes feasible (e.g. adding lead to the scope of EPA Method 200.7). Under the proposed flexibility procedures for modified and new methods, developers can obtain approval for adding analytes to an approved method as an allowed method modification if the conditions below are met.

Laboratories may add a new target analyte to approved methods provided (1) it can be demonstrated that the analyte does not interfere with determination of the analytes of concern in that method, (2) QC acceptance criteria are developed and employed for determination of the target analyte, (3) there is not another approved method that uses the same determinative technique for that

analyte and (4) the that the reason for adding the analyte is not to avoid the sample preservation or sample (or extract) holding time conditions that are already required for that analyte in another approved method. The third and fourth criteria preclude method shopping whereby a user might add analytes to a reference method with less rigid QC acceptance, sample collection or holding time criteria. For example, if an approved method for an analyte of concern requires acidification of the sample, a user does not have the flexibility to modify a method that does not require sample acidification to include analysis of the analyte of concern. Modifications of this type require EPA approval as a new method.

If QC acceptance criteria do not exist for a new analyte, the guidelines contained in Chapter 3 should be followed to develop and obtain approval for these criteria. Alternatively, under conditions described in Chapters 4 and 5, QC acceptance criteria for the new analyte may be transferred from the criteria for an analyte with similar chemical characteristics. Other requirements for obtaining approval of QC acceptance criteria for additional target analytes are described in Chapters 4 and 5.

2.3.5 New Methods, Screening Methods, and Modified Methods

A critical aspect of the streamlining initiative is to provide flexibility to modify an existing approved method provided that results obtained using the modified method meet the QC acceptance criteria of the reference method. Following release of its initial straw man, EPA received several requests to clarify the differences between new and modified methods and the requirements that pertain to each. Many reviewers also asked EPA if the procedures for developing, proposing and approving methods for use in the wastewater and drinking water programs would be applicable to screening methods. Clarifications that address these issues are as follows.

A **new method** is a set of procedures that:

(1) Is documented in accordance with the requirements detailed in the *Guidelines and Format for Methods to be Proposed at 40 CFR Parts 136 or 141*,
(2) Contains the standardized QC elements detailed in Chapter 3,
(3) Contains QC acceptance criteria that have been developed in accordance with the requirements described in Chapter 3,
(4) Employs a determinative technique for an analyte of concern that differs from determinative techniques employed for that analyte in methods previously approved at 40 *CFR* part 136 or 141, and
(5) Employs a determinative technique that is more sensitive and/or selective (specific) than the determinative techniques in all methods previously approved for the analyte.

A method that meets all five of these characteristics is considered to be a **confirmatory method** if the method also is sufficiently selective and quantitative that <u>most</u> positive results do not have to be verified by analysis with another method. The term “confirmatory” is used to distinguish this type of method from a screening method (described below). All methods currently approved at 40 *CFR* parts 136 and 141 are confirmatory methods.

Methods with disparate characteristics have been developed and marketed as screening methods. Some are inexpensive and easy to use; others require expensive equipment and training to conduct complex procedures. Some screening methods are designed to be used at the sample collection site; others require a well-equipped laboratory. In this Guide, a **screening method** is defined as a method that meets the first four of the five conditions described above for new methods

and that has been demonstrated to produce a false negative probability of no more than one percent (1%) at the limit(s) of regulatory concern. Methods can fail the fifth condition for a new method, if they are non-selective or not quantitative for the target analyte. A non-selective method is a method in which the determinative (or other step) technique in the method may produce a result for any one of several analytes that share common physical or chemical characteristics with the target analyte. For example, an atrazine immunoassay might respond to any triazine (atrazine, simazine, cyanazine) pesticide in the sample.

Screening methods may be quantitative, but are often semi-quantitative or presence-absence. For example, if the same water sample containing a free chlorine residual of 1.3 mg/L were analyzed with several methods, a quantitative titrimetric method might provide a result such as 1.2 ± 0.2 mg/L. A semi-quantitative colorimetric method might indicate that the free chlorine residual concentration was in the range of 1.0 to 1.5 mg/L. Analysis with a presence-absence method that had a minimum sensitivity of 0.5 mg/L would produce a presence reading indicating that a free chlorine residual was present at 0.5 mg/l or more.

When using a screening method, <u>all</u> positive results must be verified by re-analysis with a confirmatory method because screening methods can be less selective and therefore more subject to false positives than confirmatory methods. Historically, EPA has not considered screening methods for approval at 40 *CFR* part 136 or part 141. Under the streamlining initiative, EPA proposes to consider the approval of these methods for compliance monitoring provided: (1) the method meets all the requirements described in the Streamlining Guide and in the regulations at 40 CFR 136.5 and 141.27, (2) all positive sample results obtained with the method are confirmed and reported using an approved confirmatory method, and (3) the probability of the method producing a false negative result at concentrations of regulatory interest is no more than one percent (1%). EPA notes that, for part 141 approval, these criteria may be when the Agency implements the requirements for screening methods that are in the August 2, 1996 amendments to the SDWA. When the streamlining initiative is promulgated, a separate table will be published at 40 *CFR* parts 136 and 141 to list screening methods that have been approved for compliance monitoring.

The definitions of confirmatory and screening methods in this section are deliberately narrow to preclude them from being considered as method modifications under the concept of method flexibility. A **modified method** is an approved method that has been modified to change a front-end technique or the determinative technique, either using explicit flexibility or expanded flexibility allowed under streamlining. Under the streamlining initiative, there will be two forms of method modifications:

- Modifications to approved methods may be made as specified within those methods. This explicit flexibility existed prior to the streamlining initiative and will continue to exist. Explicit flexibility exists for all approved methods including EPA, Standard Methods, ASTM, AOAC-International, and other methods approved at 40 *CFR* parts 136 and 141.

- Modifications to approved methods designated as reference methods. This flexibility does not exist prior to implementation of the streamlining initiative. After streamlining has been promulgated, modifications may be made to reference methods provided that the modification
  - Meets the requirements detailed in 40 *CFR* 136 or 141, and
  - Meets the requirements detailed in this Streamlining Guide which is being incorporated into the CFR by reference as part of the streamlining rule

These modifications may not be made to Standard Methods, ASTM, and AOAC-International methods, and none of these methods have been designated as a reference method under this initiative.

2.4 Controls on Flexibility

EPA has established a number of controls that provide the foundation for the increased flexibility allowed under streamlining. These controls are:

- A requirement to demonstrate and document equivalency when method modifications are used.
- Designation of a reference method that contains QC acceptance criteria for use in demonstrating equivalency.
- Standard procedures for validating new methods and demonstrating equivalency of method modifications, based on the intended use of the method.
- A requirement for all new methods to contain standardized QC and specify QC acceptance criteria.
- Detailed requirements for preparing the method validation package and supporting data when new or modified methods are validated.
- Guidance for regulatory authorities' use in assessing equivalency of method modifications.

These controls are described in the appropriate chapters of this guide, as described in Chapter 1, Section 1.4.