UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

MEMORANDUM

SUBJECT: **Flexibility to Modify CWA Methods**

FROM: Richard Reding, Chief
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OFFICE OF WATER

TO: Quality Assurance Managers
ATP Coordinators
NPDES Coordinators

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The CWA methods team has conducted conference calls and other outreach with our regional and state colleagues about administering the CWA methods program. We have received many questions and suggestion about interpreting a user's current flexibility to modify a CWA, i.e. a Part 136 or 304(h), chemical analytical method without prior review or rulemaking by EPA. This flexibility is embodied in the quality assurance/control (QA/QC) section of many 1600-series methods, and more recently (March 12, 2007) in CWA regulations at 40 CFR 136.6. We appreciate your collaborative and cooperative approach in helping us implement this flexibility, and thereby get sound technical solutions to analytical problems in use more quickly than in the past. This memorandum is our current thinking about this flexibility. You may use it when auditing a laboratory, or fielding inquiries about allowed modifications to Part 136 chemical methods. As we gain experience with this flexibility we will update, as needed, via memoranda or updates to the Q&As at our CWA methods website http://www.epa.gov/waterscience/methods/.

You asked for examples of allowed flexibility. Lem Walker has prepared the following descriptions of developer and user responsibilities to document modifications they make to CWA methods. Developer responsibilities are germane to those, for example, who automate manual methods and often market these solutions for nationwide use for CWA compliance monitoring. User responsibilities are germane to those who modify existing CWA methods to solve matrix problems, or to speed or otherwise improve the analysis. Laboratories that modify Part 136 methods may be private, public or commercial and may conduct analyses for one or more clients or facilities.

Examples of Allowed Method Modification

In the past and often on a case-by-case basis, EAD wrote letters to co-regulators, developers, and others about modifications to Part 136 methods. If the underlying chemistry and determinative technique were essentially the same as the unmodified Part 136 method, we agreed that these modified methods were equivalent and acceptable alternatives. The current state is that those who develop or use a modification to an

approved (Part 136) method and document the modification as described at 136.6 will no longer receive or require a letter from us. The March 12th Methods Update Rule promulgated 136.6 which allows the regulated community more flexibility that includes:

- Changes between manual method, flow analyzer and discrete instrumentation
- Changes between automated and manual sample preparation such as digestions, distillations, and extractions; in-line sample prep is an acceptable form of automated sample preparation for CWA methods
- Changes in calibration range (provided that the modified range covers any relevant regulatory limit)
- Changes in equipment such as using similar equipment from a different vendor than that mentioned in the method
- Changes in equipment operating parameters such as minor changes in the monitoring wavelength of a colorimeter or modifying temperature program for a specific GC column, or sensible changes in reaction time and temperature as needed to achieve the chemical reactions defined in the unmodified CWA method
- Changes to chromatographic columns, including the use of capillary GC columns
- Changes in purge-and-trap sample volumes or operating conditions
- Adjusting sample sizes or changing extraction solvents to optimize method performance in meeting regulatory requirements (except for parameters that are defined by the method, such as oil and grease
- Minor changes in reagents used where the underlying reaction and principles remain virtually the same. Some examples are:

A. Changes in pH. A change in pH is allowed if the pH improves performance specifications. One example would be prevention of the formation of a precipitate as used by Rhine et al. Their article, "Improving the Berthelot Reaction for Determining Ammonium in Soil Extracts and Water" *(Soil Sci. Soc. Am. J. 62:473-480 (1198))* is attached. Another example is lowering the pH from 8.5 to 7.5 using an imidazole buffer for the nitrate nitrogen by cadmium reduction test.

B. 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 HCL in place of H_3PO_4.

C. Changes in buffer reagents provided that the change does not produce an interference. The purpose of a buffer is to maintain or adjust the sample to a certain optimized pH. If one buffer is found to work better than another in a certain matrix, or is found to improve performance, or is at a different pH, the buffer is allowed.

D. Changes in complexing reagent provided that the change does not produce interferences. The ammonia paper cited in section A provides an example of using a different complex reagent (citrate) other than either reagent specified in the EPA method

(sodium potassium tartrate and EDTA) because it was found to be more effective and not interfere.

E. Changes in reactants provided that the change does not produce interference. The ammonia paper cited in section A gives an example and references other examples of changing the precursor to a final product that still results in the same reaction (Berthelot reaction and formation of indophenol).

F. Changes in the order of reagent addition provided that the change does not produce interference. 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 improved.

The underlying philosophy of reagent modification should always include safety along with method performance. If equal or better performance can be obtained with an alternative reagent, then it is allowed.

NOTE: Changes in method parameters are not allowed, if such changes would alter the defined methodology (i.e. method principle) of the unmodified CWA 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.

Technologies allowed as alternatives under Part 136.6 include the following:

- discrete analyzers
- segmented flow analyzers
- flow injection analyzers
- micro distillation apparatus
- midi distillation apparatus
- prepackaged reagents
- colorimetric methods
- digital titrators and methods where the underlying chemistry used for the determination is similar as that used in the approved method
- ion chromatography
- TOC analyzers (oxidative method and detection)
- UV digestion

Changes are only allowed, if the modified method produces equivalent performance for the analyte(s) of interest, and the equivalent performance is documented.

EPA encourages regulatory authorities to allow flexibility in the spirit of method improvement. For example, because it is impossible to address all matrix interference in all wastewaters, it may be necessary to tailor a method modification to a specific matrix interference problem. The reason for allowing a method modification is to improve

method performance such as accuracy (e.g. recovery), lower detection limits, and better precision.

Evaluating Method Modifications

Regions and states periodically audit laboratories. When they do so, we recommend using the following items to evaluate the suitability of a modified Part 136 method:

Developer Responsibilities

- Provide the laboratory with a side-by side method comparison table The developer should provide to its customers an in-depth comparison of the modified method with the EPA approved method, and document the comparison in a two-column method comparison table. The two-column method comparison table shall include the number and title of each method, the latest revision date of the modified method and a detailed discussion of each of the 17 topics required by the standard EPA method format. Each topic should be discussed on a separate row in the method comparison table. The developer should highlight any differences between the modified method and EPA approved method. If the modified method is an automation of a previously approved manual method, any difference in kinetics and interferences should be presented and a comparison of final ratios of the concentrations of the reactants in the proposed and approved methods included.

- The developer should provide to their clients the modified method written in the standard EPA format: http://www.epa.gov/waterscience/methods

- Provide a copy of the data comparing the modified method performance to the approved method to demonstrate that the method is capable of yielding reliable data for compliance monitoring purposes. Test results from validation of a modified method are used to demonstrate that the modified method produces results are equivalent to results produced by the EPA-designated approved method. Equivalency is established by demonstrating that the modified method produces results meet or exceed the QC acceptance criteria of the EPA-designated approved method.

Verify that all items of the "Equivalency Checklist" are met:

Equivalency checklists:

1) Concentrations of calibration standards. Document the range of the concentrations of material used to establish the relationship between response of the measurement system and analyte concentration.

2) %RSD or correlation coefficient of calibration regression.

3) Performance range tested with units.

4) Sample(s) used in initial demonstration have the recommended preservative, where applicable.

5) Sample(s) used in initial demonstration met recommended holding times, where applicable.

6) Interferences.

7) Document the qualitative identification criteria used.

8) Performance evaluation studies performed for analytes of interest, where available.
   Latest study sponsor or title
   Latest study number.

9) Analysis of external reference material
   Results of analyses on reference material from a source different from that used to prepare the calibration standards, if applicable.

10) Sources of external reference material, if applicable.

11) Surrogates used, if applicable.

12) Concentrations of surrogates, if applicable.

13) Recoveries of surrogates appropriate to the proposed use, if applicable.

14) Sample preparation.

15) Clean-up procedures.

16) Method blank result.

17) Matrix (reagent water, drinking water, effluent)
    Matrix spikes.

18) Spiking system, appropriate to the method and application.

19) Spike concentrations (with units corresponding to the final sample concentration) and recoveries.

20) Source of spiking material.

21) Number of replicate spikes
Initial demonstration of capability.

22) Precision (analyte by analyte)
Duplicates.

23) Bias (analyte by analyte).

24) Detection limit (with units; analyte by analyte).

25) Confirmation of detection limit, if applicable.

26) Quantitation limit (with units; analyte by analyte)
Minimum level (ML), practical quantitation level (PQL) or limit of quantitation (LOQ).

27) Qualitative confirmation.

User Responsibilities

Although no comparative data between methodologies need to be provided to EPA prior to use, the user or laboratory should have a data package available for review that demonstrates proficiency by:

- making a detailed Standard Operating Procedure (SOP) available
- performing and documenting an initial demonstration of capability
    - Verify the modified method by analyzing and documenting 3-7 representative effluents (performed on different days of the week). The facility/lab is to show they can get the modified method to work and that it gets comparable results for their effluent.
- a demonstration of calibration linearity or use of a calibration curve
- periodic calibration verification
- an ongoing demonstration of performance (ongoing precision and recovery (OPR) and a blank with each sample batch)
- a demonstration of the method detection limit (MDL)
- matrix spike and matrix spike duplicate for each discharge the first time that the sample of the discharge is analyzed and at a frequency of 5% thereafter
- meeting the quality control (QC) specifications of the method
    - If the reference method does not provide sufficient QC specifications, the targets listed in the December 1996 Streamlining Guide *(applies only to CWA methods)* may be used (http://www.epa.gov/waterscience/methods/guide/flex.html).
- having the modified method manufacturer's supporting data available for review – when the manufacturer has developed the method modification.