PROTOCOL FOR NATIONWIDE APPROVAL OF NEW OR REVISED METHODS FOR INORGANIC AND ORGANIC ANALYTES IN NATIONAL PRIMARY DRINKING WATER REGULATIONS MONITORING

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U.S. Environmental Protection Agency
Office of Research and Development
National Exposure Research Laboratory
Cincinnati, Ohio 45268

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INTRODUCTION

The Administrator, U.S. Environmental Protection Agency (EPA), approves analytical methods for all contaminants regulated under the Safe Drinking Water Act (SDWA). When EPA publishes a regulation under the SDWA that sets a maximum contaminant level, the regulation generally provides for at least one analytical method for detection and/or quantification of that contaminant. After any regulation is published, EPA may approve additional methods or modification to currently approved methods, following a set chemical method or microbiological method protocol of the ATP program.

This protocol describes the information and data EPA needs to evaluate an ATP for CHEMISTRY. The protocol is flexible in that EPA's National Exposure Research Laboratory (NERL) may tailor the criteria to a particular analyte, method, and/or sample matrix. For this reason, before beginning the required testing, the applicant is encouraged to discuss the application with EPA/NERL - Cincinnati, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268, to assure agreement on the testing design.

If the data evaluation demonstrates that the applicant's method performs at least as well as the currently approved method, EPA will recommend its approval to the Office of Ground Water and Drinking Water, which begins the regulation development process. Regulation development includes a Federal Register notice proposing to approve an ATP, public comment on the proposed method, and (depending on public comment) a final rule published in the Federal Register approving the method. The regulation development process may take about one year or more.

APPLICATION REQUIREMENTS

Any person may apply for nationwide approval of the use of either a new method or an optional minor modification of a previously promulgated method for a specific constituent in NPDWR monitoring. Before submitting an application, however, the applicant must provide a detailed write-up of the proposed method. If the proposed method is very similar to an approved and promulgated method, and/or represents a minor optional change of an approved method, the applicant should simply prepare a two-column side-by-side listing of the sections of the approved and proposed

methods. This document should include the title, identification number and date of each method and all the topics in the EMMC format provided in the Section, Method Description Requirements beginning on page 2 of this document. The applicant should highlight differences between the proposed and approved methods. If the method is an automation of a previously approved manual method, any differences in kinetics and interferences should be presented and a comparison of the final ratios of the reactants in the proposed and approved methods should be included. This information should then be forwarded to NERL-Cincinnati for review. NERL-Cincinnati will recommend nationwide approval/disapproval of the proposed method as: 1) identical to EPA's reference method, 2) an optional minor modification of a previously promulgated method or 3) significantly different method requiring an application for an ATP as a new or revised method.

Every application for approval of a new method or optional minor modification of a previously promulgated method shall be made by letter in triplicate and forwarded to the Director, Ecological Exposure Research Division - Cincinnati (NERL-Cincinnati), U.S. Environmental Protection Agency, Cincinnati, Ohio 45268.

The general requirements for an application for nationwide approval of any new or modified method include the name and address of the applicant and/or authorized representative; the contaminant for which the new or modified procedure is proposed; justification for the proposed new or modified method; the title of the method, company identification number and date of preparation of the proposed method; and, a complete description of the proposed method and of the approved method if used in a comparison. All information provided to the Government is subject to the requirements of the Freedom of Information Act. Any proprietary information in the proposed method should be marked as "Confidential". USEPA staff will handle all proprietary information according to the regulations in subparts A and B of Part 2 of Title 40 CFR.

Initially, an applicant should forward the above information, except the comparability data, to NERL-Cincinnati. Upon receipt of the application, the NERL-Cincinnati staff will assign an identification number for the application, which should be used in all future communications. The NERL-Cincinnati staff will also evaluate the submitted information and advise the applicant of the specific comparability data requirements, if applicable.

Method Description Requirements

The method write-up must address the following topics listed in the recently formulated Environmental Monitoring Management

Council (EMMC) method format:[1]

1.0 Scope and Application

Include analyte identification; CAS number; sample type; method sensitivity, expressed as mass; and, concentration range.

The range of the proposed method should be equal to or greater than that of the approved method. If the range is smaller than that of the approved method (particularly, if the detection limit is larger), NERL-Cincinnati may advise that the method is inapplicable or the method may require a declaration of method limitations.

2.0 Summary of Method

Describe scientific basis, e.g., chemical principles, reactions, and kinetics.

3.0 Definitions

4.0 Interferences

As a separate document, include data observed by applicant (during method development) using typical samples containing a specific quantity of an interfering substance).

5.0 Safety

Refer to good laboratory practice, appropriate material safety data sheets, and use of a hood, goggles, and/or protective clothing. Emphasize any special procedure.

6.0 Equipment and Supplies

As separate documents, include applicable manuals.

7.0 Reagents and Standards

Describe reagent formulations and shelf life of packaged materials.

8.0 Collection, Preservation, Shipment, and Storage

See general guidance in laboratory certification manual[2].

9.0 Quality Control (QC)

Indicate need for a formal laboratory quality assurance/quality control program; initial and periodic documentation of performance by reporting results of analyses of reagent blanks, check standards, and/or fortified samples; and, maintenance of records, QC charts, etc. The periodic checking of performance should preferably occur at a minimum frequency of 10% of the total samples.

10.0 Calibration and Standardization

This section should include the calibration steps that are not performed daily. Include the daily calibration step(s) in the procedural section.

11.0 Procedure

Include in the method write up the procedural steps and the daily calibration steps. As a separate document include a typical calibration graph or curve.

12.0 Data Analysis and Calculations

13.0 Method Performance

Indicate the percent recovery, precision, and bias of the method for typical samples, fortified with a known amount(s) of the analyte. Include the method detection limits (MDL), derived as outlined in Appendix B of section 136 of Title 40 of CFR, and expressed in weight/volume. The calculated MDL should be confirmed by analyzing a samples at the calculated MDL concentration. Note that the MDL should be equal to or smaller than that of the approved method. If the MDL is larger, NERL-Cincinnati may advise that the method is inapplicable or the method may require a declaration of the limited range of performance of the method.

14.0 Pollution Prevention

Cite good laboratory practices for pollution prevention.

15.0 Waste Management

Cite how waste and samples are to be disposed.

16.0 References

Include reference to documents and publications.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

Any proprietary information in the proposed method should be marked "Confidential". USEPA staff will handle all proprietary information according to the regulations in subparts A and B of Part 2 of Title 40 of CFR.

Comparability Data Requirements

A method comparability study will be required for each new or significantly revised method submitted for nationwide approval. Guidance for the comparability study is provided in the following text. Applicants are encouraged to have a brief consultation with the NERL-Cincinnati ATP staff regarding specific comparability study plans which may include the number of analyses, concentration levels, quality control (QC) activities, performance evaluation (PE) samples, etc. If a major area such as the concentration range of the proposed method differs from that of the approved method, the applicant must consult with the NERL-Cincinnati ATP staff to determine the appropriate modification of the comparability study design. The required comparability data shall include measurements of drinking water samples, QC samples and PE samples. Initially, each collected drinking water will be analyzed at least once by the approved method to determine the concentration of the constituents of interest and need for sample dilution and/or fortifying to achieve the 5 x MDL baseline concentration as detailed in the Subsample Preparation Requirements (pp. 6-7). After appropriate preparation, the subsamples of each drinking water will be analyzed by both the approved and proposed methods.

The QC samples and the PE samples are to be prepared in reagent water and used to determine if the laboratory is in control. PE samples of known analytes, but of concentration unknown to the analyst, will be provided by NERL-Cincinnati along with instructions for use. The analyst is responsible for preparing the final QC and PE sample solutions for analyses. The QC and PE solutions must be spaced every tenth sample among the drinking water samples which are to be analyzed by both methods.

As general guidance, the minimum number of analyses required are summarized in the following table. However, depending on the particulars of the method under review, the number of analyses may change. We strongly suggest consultation with the NERL-Cincinnati ATP staff prior to analyses.

Approval type	Applicant	Drinking water sample or subsample analyses per regulated constituent			QC\PE Samples	Total
		Initial screen	Adjusted to 5 MDL	Forti-fied		
Nationwide	Any	10	60	120-180	22-25	212-275

Drinking Water Sampling Requirements

For each constituent of interest, the applicant must collect a minimum of ten drinking water samples, ideally one from ten geographically-dispersed drinking water supplies. Six of these supplies should be from surface water sources and four from ground water sources. The supplies should contain variable water quality characteristics that may affect the analyses. These include pH, TOC, alkalinity, and TOX. We strongly suggest consultation with the NERL-Cincinnati ATP staff prior to sampling.

An applicant is required to diligently select a source and/or time of collection that will afford an analyte concentration as close as possible to 5 times the published MDL of the approved method. (If the MDL is unpublished, determine as directed in topic 13 on pp. 4). This sample selection will enable the preparation of the required subsamples by either dilution or fortifying with a minimum of alteration of sample matrix.

Most samples should be collected using the containers, preservation techniques, and holding times outlined in the approved methods. Samples for asbestos, barium, cadmium, chromium, fluoride, mercury, nitrate, nitrite, and selenium analyses should be handled as outlined in the Phase II regulations[2].

Subsample Preparation Requirements

The bias, precision, percent recovery and MDL of the proposed method will be compared to those of the approved method. Several levels of concentrations covering the performance range of the

proposed method will be used in the study. Ideally, the range of the concentrations for the proposed method will be the same as the approved method. The concentrations should include a level that is 5 X MDL, a level that is twice the maximum contaminant level and additional levels that take into account the method range. This issue must be addressed with the NERL-Cincinnati ATP staff prior to analyses.

The study experimental design initially requires a single analysis of each of the collected samples by the approved method to determine the concentration of the constituents of interest. If the initial concentration of constituents in any collected sample differs significantly from the 5 x MDL level, the sample must then be either diluted or fortified to achieve the 5 x MDL level. Dilution must be done using deionized distilled water. Sample fortifying must be accomplished using a substance whose character reflects the nature of the analyte in the drinking water and/or the calibration standards. For example, in an application for mercury, the fortifying substance should consist of a mixture of an inorganic and an organic mercury compound. All of the initial dilution or fortification (to achieve the desired 5 x MDL concentration) must be performed before splitting a sample into subsamples. Otherwise, the analytical error of each analysis may also include the error of the individual dilution or fortification of the subsamples and the data comparison may be inappropriate. Record and report the initial dilution or fortifying required to adjust each sample concentration to the 5 x MDL level.

The fortification of each subsample must also be performed before aliquoting for analysis. Otherwise, the analytical error will include any individual fortification error and the comparison data may be inappropriate. Record and report the amounts of the substance added to each fortified subsample and the theoretical total concentration in each subsample. The latter is calculated for subsample by adding the mean of the triplicate analyses of the subsample by the approved method to the amount of substance added to that subsample. The evaluation of the comparability of the proposed method is dependent upon the analyst's preparation and analysis of corresponding subsamples with very similar concentration.

Laboratory Requirements

It is highly desirable to have one laboratory analyze all of the samples required in the study design. This is to eliminate the effects of multiple laboratories on the comparison of data between methods. Analyses by an additional laboratory should be included as a QC check but these data are in addition to the required ATP comparative analyses by the primary laboratory. This option should

be discussed with the ATP staff. Preferably, the laboratory should be independent. NERL-Cincinnati will judge on the appropriateness of the suggested laboratory.

Approved Method Selection Requirements

Since the approval of a method depends upon the comparability of the bias and precision of the proposed method to that of an approved method, the applicants's analyses by the approved method must also be examined to determine their acceptability as a basis in the comparison. This acceptability will be determined by evaluating the applicant's analyses of QC and PE samples by both the approved method and the proposed method.

The criteria used in the evaluation will be derived from available regulations, text of the approved method, and/or various interlaboratory validation and/or PE studies. USEPA may, consequently, limit the applicant's choice of an approved method to insure that the approved method used in the study is one which has been evaluated with sufficient frequency in the interlaboratory studies to afford an appropriate data base with which to determine the acceptability of the applicant's analyses by the approved method.

Drinking Water Subsample Analysis Requirements

As general guidance, applicants for nationwide approval of a new or significantly revised method must perform six analyses of each subsample, three by the approved method and three by the proposed method. The drinking water sample, drinking water subsample, and analysis requirements are summarized in the following table:

Approval	Applicant	No.of collected samples	No.of subsamples per Collected Sample	Total No. samples for analysis	No.of repli-cate analyses per sub-sample per each of two methods	Total No. of analyses
Nationwide	Any	10	3-4	30-40	3	180-240

The aforementioned QC analyses should be performed along with the analyses of the drinking water subsamples (see Comparability Data Requirements, p. 5).

Data Reporting Requirements

Initial single observation of each collected sample by the approved method, the initial dilution and/or fortifying of each collected sample, the quantity of substance added to each subsample and the total theoretical concentrations of the subsamples, the replicate observations of all subsamples by both methods, and the quality control observations must be forwarded to USEPA. A suggested format for reporting the observations of each set of subsamples is attached. The quality assurance observations associated with each set of subsample observations should also be tabulated and identified. An evaluation of the application can be accomplished more quickly by the NERL-Cincinnati program and statistical staff, however, if the information is also forwarded on a floppy disc compatible with an IBM-PC computer. The text on the disc should be presented in the latest version of Wordperfect (currently, 6.0) and the data may be presented in Wordperfect or in ASCII.

DATA REVIEW AND METHOD RECOMMENDATION

Upon receipt of the applicant's data sets, NERL-Cincinnati staff will initiate its technical and statistical reviews. Appropriate criteria, derived either from published regulations or from interlaboratory studies, will be used to determine the acceptability of the approved method data as a basis in the evaluation of the analyses by the proposed method. If this evaluation is favorable, the evaluation of the comparability of the proposed method will follow. (If the results of the analyses by the approved method are not satisfactory, the applicant will be notified that the application has been defaulted.)

Since the sampling and analytical requirements for each application for approval of a new or significantly revised method are based on a factorial experimental design with three factors, namely, method, sample matrix, and constituent concentration, each comparability review will be conducted over the range of these three factors. Descriptive statistics, such as the mean, standard deviation, coefficient of variation (relative standard deviation), and percent recovery of each set of replicates will be calculated. The precision of the proposed method will be compared with that of the approved method by means of a nonparametric statistical procedure attributable to Scheffe. An analysis of variance (ANOVA) will be used to compare the recovery of the proposed method with that of the approved method.

Upon completion of the technical and statistical reviews, NERL-Cincinnati will prepare its recommendation for approval/disapproval of the new or significantly revised method, notify the applicant of its recommendation, and forward the recommendation to the Office of

Ground Water and Drinking Water (OGWDW), which has the responsibility of proposing the method in the Federal Register. After a three-month public comment period, OGWDW will review any submitted comments and prepare the final nationwide approval/disapproval decision and notice in the Federal Register.

If you have any questions regarding the requirements, especially the comparability study design and sample fortifying, please contact the NERL-Cincinnati ATP staff at 513-569-7307.

REFERENCES

1. Villa, O. and L. Reed, Co-Chairs, EMMC Methods Integration Panel. Final Version of Approved EMMC Format (Memorandum to Members of EMMC Steering Committee, Methods Integration Panel and Work Group, Tri-Chairs). U.S. Environmental Protection Agency, February 14, 1992, pp. 1-2.

2. Federal Register, Vol. 56 (20), part 141.23(1c)(4), pp. 3582-3583. Wednesday, January 30, 1991.

ATTACHMENT

Application No:_____ (EPA Assigned)*

NPDWR COMPARABILITY STUDY DATA

Source or Water Supply Identity:_____

Drinking Water Source Type: Ground _____ Surface_____

Constituent Identity: _____

Concentration Units (weight/volume): _____

Initial Sample Constituent Conc. (Before Adjustment)_____

Initial Sample Adjustment
by Dilution_____ or by Fortifying_____
(specify) (specify weight/volume)

	Theoretical Conc.		Approved Method Observations			Proposed Method Observations		
Sub-samp	Amount Added+	Total Conc +	Replicate 1	Replicate 2	Replicate 3	Replicate 1	Replicate 2	Replicate 3
1	0							
2								
3								
4								

* Identify the applicant or source of data ONLY by the EPA-assigned application number.

+ See pp. 7-9 of the protocol for a discussion of how these concentrations are derived.