



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

MEMORANDUM

OFFICE OF
WATER

SUBJECT: **Modifications to Method 1664A**

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TO: Quality Assurance Managers
ATP Coordinators
NPDES Coordinators

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As a follow up to my "Flexibility to Modify CWA Methods" memorandum of November 20, 2007, Lem Walker has participated in conference calls and other outreach with our regional and state colleagues regarding modifications to Part 136 methods, including EPA Method 1664A, which determines oil and grease, a method-defined parameter. We have received many questions and suggestions about interpreting a user's current flexibility to modify Part 136 chemical analytical method without prior review or rulemaking by the EPA. This flexibility is embodied in the quality assurance/control (QA/QC) section of 1664A and other 1600-series methods. This memorandum answers several questions about allowed modifications to Method 1664A. You may use it when auditing a laboratory or fielding inquiries about allowed modifications to Method 1664A.

Although analyst modifications to method-defined parameter methods are generally not allowed, some changes are acceptable. These modifications are described in general terms in the Scope and Application Section of 1664A:

- 1.7 *The laboratory is permitted to modify the method to overcome interferences or lower the cost of measurements, provided that all performance criteria in this method are met. The requirements for establishing method equivalency are given in Sections 9.1.2 and 9.2.3.*
- 1.8 *Any modification of this method, beyond those expressly permitted, shall be considered a major modification subject to application and approval of alternate test procedures under 40 CFR 136.4 and 136.5.*

Changes to the chemistry of the method, the determinative step (e.g., the detector), the quality control, or those not expressly permitted in 1664A are not allowed. This memo describes several modifications that are within the flexibility of 1664A, a solvent change that is not allowed, and a special modification approved only in one EPA region.

We appreciate your continued collaborative and cooperative approach to helping us implement the flexibility to modify Part 136 chemical methods. Please contact Lem Walker, if you have any questions or suggestions about the following examples. As we

gain more experience we will continue to update, as needed, via memoranda or updates to the Q&As at our CWA website <http://www.epa.gov/waterscience/methods/>.

Questions and Answers Concerning EPA Method 1664A

Allowable Modifications to EPA Method 1664A for Oil and Grease

1. PAR Standard

Question: May we spike samples at lower concentrations instead of 40 mg/L per the method?

Answer: It is allowable to use a lower PAR (Precision and Recovery) standard concentration such as 20 mg/L when spiking matrix samples provided the concentration of the spike is (a) greater than the background concentration, (b) less than or equal to the regulatory compliance level, and c) all quality control requirements of the test are achieved.

2. SPE Filters/Prefilters

Question: Our lab uses 47mm diameter SPE Filters to analyze blanks, QC tests and effluents and only uses 90mm diameter SPE Filters to analyze complex samples containing particulates and other substances. Is this OK?

Answer: All SPE (Solid Phase Extraction) filters used in the analytical batch should be of the same diameter and from the same manufacturer or brand (ideally the same lot number) as this may affect the chemistry and Quality Control of EPA Method 1664A. Use of optional prefilters for specific samples are allowed as described in §11.3.5 of *Method 1664A* which allows use of techniques to complete the phase separation when dealing with LLE emulsions.

3. Smaller Sample Size

Question: Please confirm that it is allowable to collect and analyze a smaller volume of sample as long as we express our final results as mg/L?

Answer: Per EPA Method 1664A Sections 1.7, 4.5, 6.1.1 Note, 8.1.2, 11.0 Note and 11.2.2, collection of a smaller sample is permitted and is an allowable change provided all the quality control requirements of sections 9.1.2, 9.2.3 are met as well as sections 9.3 and 9.4, matrix spikes and blanks respectively.

4. Alternate Concentration Techniques – Aluminum Pans – Beakers

Question: In the past with the old method, we concentrated our Oil and Grease extracts using beakers. Can we do the same with the new method?

Answer: Per EPA Method 1664A Section 9.1.2, alternate concentration techniques are permitted and include the use of aluminum pans or beakers with evaporation and/or distillation to aid concentration of the sample.

5. Acidification of Sample

Question: If analysis of the samples or QC tests will occur within 4 hours, do we still have to acidify them to pH < 2?

Answer: All samples must be acidified and/or verified in the lab to pH < 2 immediately prior to analysis. If analysis is to be delayed for more than four hours, it is acceptable to adjust the sample pH to less than 2.5 with HCl or H₂SO₄ solution (Section 7.2) at the time of collection and refrigerate to 0-6°C (40 CFR 136, Table II).

6. Matrix Spike Requirements

Question: The matrix spike requirements in the method seem complicated and appear as if they will be very burdensome for our lab. Can you please recommend simple, equally acceptable guideline that we can follow?

Answer: As a practical means of ensuring compliance with the matrix spike frequency requirement, perform the following steps for a given discharge/waste stream (See matrix type definitions – 40 CFR Parts 400-699):

1. Analyze at least one aliquot out of each analytical batch (up to 20 samples) from each site or discharge/waste stream per Method 1664A Section 9.3.2.
2. The laboratory should randomly choose and rotate through each site or discharge/waste stream for the matrix spike until every site or discharge/waste stream has been used as the matrix spike at least once.
3. Repeat and continue steps 1 and 2 above as needed.

7. Balance Calibration

Question: All of our other gravimetric methods specify use of a calibration weight greater than the expected value. Shouldn't this method be similar?

Answer: Use at least an additional upper limit (and possibly a lower) balance calibration weight to bracket the expected final weight values. This action should help improve data quality, but there is not any requirement for the laboratory to do it.

Unacceptable Modifications to EPA Method 1664A

Alternate Solvents

Question: I've been told to pre-rinse my emptied sample bottle with methanol to remove the residual water so the subsequent hexane extractions can more efficiently remove any oil and grease adhering to the walls. Is this allowed?

Answer: Based on the results of two Freon Replacement Studies, co-solvents and/or alternate solvents (including methanol) can significantly change the chemistry of Method 1664A. Thus, use of co-solvents or alternate solvents is not allowed because the chemistry of the method has been changed.

Limited Use Modifications to EPA Method 1664A – Region 8

Sulfur – Thiosulfate-Inflated HEM Results

Question: May we report results using modified Method 1664 “Cu” even though our lab is not in or regulated by EPA Region 8?

Answer: No. To address sulfur interference, a modified method (Method 1664 “Cu”) uses nitric acid-activated copper coils to remove sulfur from the hexane extract of produced water samples. This sulfur removal step occurs immediately prior to distillation of the solvent. EPA Region 8 has approved, only for use in Region 8, analysis of these “produced” water samples provided the discharger can initially demonstrate the presence of sulfur interference. Use of this modified method in other EPA Regions requires submitting a limited-use ATP application to the Region for approval.