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Analytical Method Guidance for EPA Method 1664A Implementation and Use (40 CFR part 136)

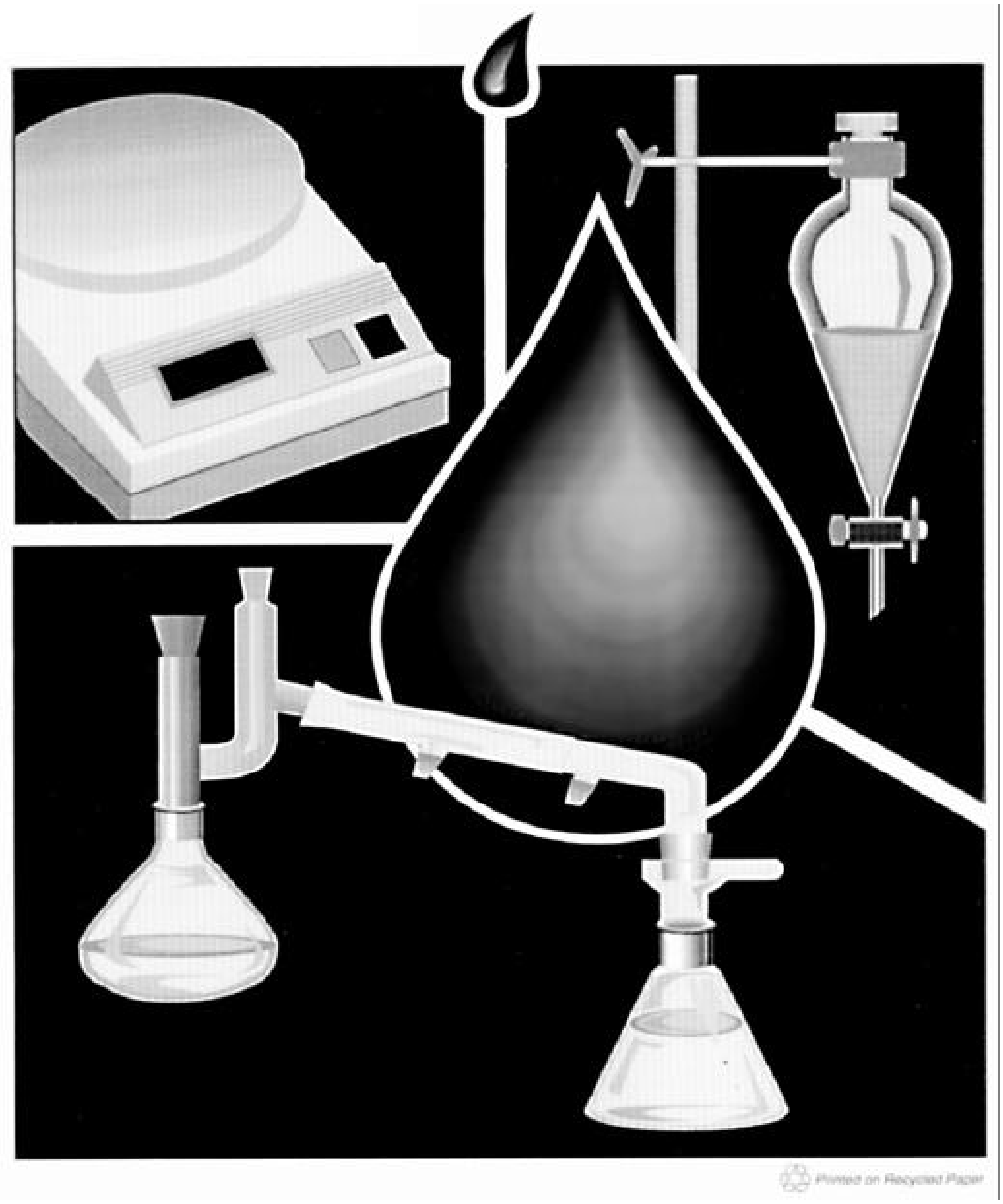

Table of Contents

Tables

Acknowledgements

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Disclaimer

This *Analytical Method Guidance for EPA Method 1664A Implementation and Use (40 CFR part 136)* (Guidance) is provided to help implement national policy on use of EPA Method 1664A. This Guidance does not, however, substitute for the Clean Water Act (CWA), the Resource Conservation and Recovery Act (RCRA), or EPA's regulations, nor is it a regulation itself. Thus, it cannot impose legally binding requirements on EPA, States, Tribes, or the regulated community and may not apply to a particular situation based upon case-specific circumstances. EPA and State decision makers retain the discretion to adopt approaches on a case-by-case basis that differ from this Guidance where appropriate. This Guidance may be changed in the future based on any future information made available to EPA. The material presented is intended solely for guidance and does not alter any statutory requirements.

Executive Summary

On May 14, 1999, the U.S. Environmental Protection Agency (EPA) promulgated Method 1664, Revision A: *N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry* (Method 1664A; the Method) at title 40, part 136 of the *Code of Federal Regulations* (40 CFR part 136) for use in EPA's CWA monitoring programs and at 40 CFR part 260 for use in EPA's RCRA monitoring programs. The purpose of this Guidance is to assist dischargers, generators, industrial users, and laboratories in the application of Method 1664A to wastewaters and wastes, to address potential differences between results obtained with Method 1664A and an approved method that employs CFC-113 (1,1,2-trichloro-1,2,2-trifluoroethane) as an extracting solvent, and to address questions regarding use and application of Method 1664A.

1 Introduction

On May 14, 1999, we promulgated Method 1664, Revision A: *N-Hexane Extractable Material (HEM; Oil and Grease) and Silica Gel Treated N-Hexane Extractable Material (SGT-HEM; Non-polar Material) by Extraction and Gravimetry* (Method 1664A; the Method) at 40 CFR part 136 for use in EPA's CWA monitoring programs and at 40 CFR part 260 for use in EPA's RCRA monitoring programs. The purpose of this Guidance is to assist you in the application of Method 1664A to wastewaters and wastes, and to address potential differences between results that could be obtained using Method 1664A and approved methods that employ CFC-113 as the extracting solvent. This Guidance also further explains the flexibility allowed within the scope of Method 1664A, particularly the use of solid-phase extraction (SPE), and answers frequently asked questions (FAQs) concerning Method 1664A.

This Guidance is specifically written to provide you with procedures for side-by-side testing of specific discharges (when necessary), and with clarification on the use of solid-phase extraction. To help in this process, the following topics are addressed:

- **Section 2** discusses differences in results produced by EPA Method 1664A and CFC-based methods and how to determine if results are equivalent or if determining a conversion factor is necessary;
- **Section 3** discusses use of solid-phase extraction (SPE) and how to determine if results produced with SPE are equivalent to those produced by liquid-liquid extraction (LLE) using CFC-113 (LLE/CFC-113) or Method 1664A (LLE/n-hexane);
- **Section 4** discusses flexibility in EPA Method 1664A;
- **Section 5** presents responses to specific questions raised by the regulated community regarding the use of Method 1664A.

Background:

The Clean Air Act Amendments of 1990 require the production phaseout and cessation of import of ozone-depleting substances (ODSs), including chlorofluorocarbons (CFCs), in order to protect Earth's ozone layer. The major reliance on CFC-113 in EPA's regulatory programs is in analytical methods for determination of the conventional pollutant "oil and grease." To address the phaseout, as applied to methods for determination of oil and grease, we began studying extraction solvent alternatives to CFC-113 in the early 1990s. We proposed Method 1664 on

January 23, 1996 (61 FR 1730). Method 1664 used normal hexane (*n*-hexane) in place of CFC-113. We promulgated Method 1664A on May 14, 1999 (64 FR 26316). Method 1664A also uses *n*-hexane as the extraction solvent.

Subjects Addressed in this Guidance:

Phase-out of production and cessation of import of ozone-depleting substances (ODSs), including CFCs.

The Montreal Protocol allows limited production of CFCs for certain uses that are considered to be essential. Under the Montreal Protocol these essential uses include laboratory and analytical use. In the preamble to the final rule promulgating EPA Method 1664A, we stated that since the laboratory use exemption for CFC-113 under the Montreal Protocol had been extended to 2005, EPA had decided to allow continued use of methods that use CFC-113 as the extraction solvent until that time.

However, the Clean Air Act Amendments of 1990 (CAAA) require the cessation of production and import of CFCs, including CFC-113 for laboratory uses, by January 1, 2000. Because we are governed by CAAA and the Montreal Protocol, we must enforce the more stringent of the two. Therefore, CFC-113 may not be available for continued use with analytical methods that use CFC-113 as the extraction solvent once current supplies are exhausted. You may continue to use existing supplies of CFC-113 after January 1, 2000 until existing supplies are depleted. However, we strongly recommend the switch to Method 1664A, and the discontinuation of use of CFC-113. (See the memo from Drusilla Hufford dated August 30, 1999 cited at the end of this Guidance, the *Federal Register* notice dated September 15, 1999 (64 FR 50083), and the *Federal Register* notice of the proposed rulemaking dated November 2, 1999 (64 FR 59141)).

Differences in amount of material extracted by CFC-113 and n-hexane.

We included in the administrative record at proposal studies comparing results obtained using CFC-113 and several other solvents, among them *n*-hexane. These studies showed that *n*-hexane produced results closest to results produced by CFC-113 but that, when applied to a given discharge, *n*-hexane could extract more or less material than the amount extracted by CFC-113. For details of the results of the studies, see the administrative record for Method 1664A in the Water Docket. (Chapter 7, *Where to Get Additional Help*, provides contact information for the Water Docket.)

At proposal, and at the final rule, we addressed the differences in results produced by CFC-113 and *n*-hexane, and the preamble to the final rule provided a procedure for gathering data to support that a statistically significant difference in results could be produced. This Guidance details how the procedure in the preamble is to be applied to a specific discharge.

Solid-phase extraction

Method 1664A employs liquid-liquid extraction (LLE) with a separatory funnel as the means for extracting oil and grease from water. As a part of the studies conducted in the early 1990s, we studied solid-phase extraction (SPE), also known as liquid-solid extraction. SPE uses a cartridge or disk to adsorb the components of oil and grease from the water, with subsequent desorption by an organic solvent. SPE has advantages over LLE, in that less manipulation of the sample is required and the amount of solvent used is considerably less. In general, SPE and LLE will produce nearly identical results when applied to final effluents.

In early versions of EPA Method 1664, we required a side-by-side comparison of SPE and LLE to demonstrate that equivalent results would be produced. We solicited comment on the need for this requirement. Commenters stated that the comparison procedure was cumbersome and that SPE should be allowed without a side-by-side comparison. (See Section VI of the final rule and the administrative record in the Water Docket for comments and responses.) As a result of the comments, we allowed use of SPE in Method 1664A without a side-by-side comparison, but cautioned that you and your laboratory must take responsibility for the results produced. However, for some discharges, particularly untreated effluents and in-process wastewaters, and for some final effluents, SPE can produce results different from those produced by LLE. This Guidance expands the discussion on use of SPE in Method 1664A.

Other Subjects:

This Guidance also gives details concerning the flexibility inherent in Method 1664A and provides answers to frequently asked questions (FAQs).

We trust that this Guidance will assist you in the use of Method 1664A for determinations of oil and grease (HEM) and non-polar material (SGT-HEM) in wastewaters and wastes. While this Guidance attempts to address issues and situations pertinent to Method 1664A, this Guidance also identifies and references other sources that you may wish to consult concerning selection and use of analytical methods. Also included is a list of EPA and other authorities to contact for more guidance.

2 Side-By-Side Comparison of CFC-113 and *n*-Hexane

This section provides a discussion of a difference in results that could be produced by EPA Method 1664A and CFC-based methods, how to determine if the difference is statistically significant, and how to calculate a conversion factor if the difference is statistically significant. For more background information on method comparisons, refer to *Guidelines Establishing Test Procedures for the Analysis of Oil and Grease and Non-Polar Material Under the Clean Water Act and Resource Conservation and Recovery Act; Final Rule* at 40 CFR parts 136 and 260, published in the *Federal Register* (64 FR 26315; May 14, 1999).

Are there differences in results produced using EPA Method 1664A versus CFC-based methods?

Prior to the advent of EPA Method 1664, the most commonly used EPA methods for determination of oil and grease were EPA Method 413.1 in our CWA program and EPA Method 9070 in our RCRA program. These methods use CFC-113 as the extraction solvent. CFC-113 is a Class I ozone-depleting substance under Section 604 of CAAA.

In comments on the proposal of EPA Method 1664A, several of you expressed concerns about the impact of differences resulting from substitution of CFC-113 with *n*-hexane on determinations of compliance under the NPDES program and pretreatment programs. We discussed this issue at proposal (61 FR 1730; January 23, 1996), and discussed the issue in workshops, conferences, and seminars between proposal and development of the final rule.

After proposal, we received numerous requests from States and EPA Regions for guidance on implementation of Method 1664. On July 9, 1996, we issued guidance to Pretreatment Coordinators and Regional NPDES Contacts. A copy of the memorandum was included in the administrative record for the final rule. In part, this memorandum stated:

> "EPA acknowledges that, due to the diverse nature of discharges, there may be instances in which *n*-hexane will extract an amount of oil and grease greater or less than the amount extracted by Freon-113. If these instances affect compliance, the permitting authority may wish to consider establishing a conversion factor, multiplier, or divisor to account for these differences in the permit. EPA emphasizes that few, if any, instances will likely be found in which the differences affect compliance and, therefore, urges direct substitution of the presently approved methods with Method 1664 when the date of substitution is announced in the Federal Register."

We still believe that the approach outlined in the memorandum appropriately accommodates any significant discrepancies that could arise in determining compliance with limitations or standards for oil and grease using

Method 1664A. Based on results from the Freon Replacement Studies, we found that, on average, *n*-hexane extracted approximately 96% of the material extracted using CFC-113. Therefore, while there may be some effluent matrices from which *n*-hexane will extract more material than CFC-113, on the whole, most dischargers would have little risk of a determination of non-compliance with existing limits.

The slightly smaller average amount of oil and grease extracted by *n*-hexane (96% versus 100% by CFC-113) is not statistically significant because errors in oil and grease measurement are in the order of 10% relative standard deviation. A coarse estimate of 95% confidence limits around the 96% recovery by *n*-hexane is 96% plus or minus 20%, or the true difference lies somewhere between 76-116%. This range encompasses 100%, which indicates that there is no significant difference. Given the lack of significance of the 4% difference, the measurement error that would be encountered in the side-by-side comparison (estimated at 10% for each measurement), the potentially significant cost of a side-by-side comparison with each discharge, and the low anticipated likelihood that a significant difference would be found (based on our studies), we do not recommend a side-by-side comparison for each discharge. Instead, we continue to recommend a direct replacement of the approved CFC-based methods with Method 1664A.

When should I conduct a side-by-side comparison?

The Montreal Protocol on substances that deplete the ozone layer allows production and use of Class I substances for certain critical uses, whereas Section 604 of CAAA requires production phase-out and cessation of import of Class I substances, with certain exceptions, by January 1, 2000. Until 1999, we allowed production and import of Class I CFCs under the exemptions in the Montreal Protocol. One of these exemptions is production and import of CFCs for laboratory use. We had planned to extend the exemption of production and import for laboratory use until 2005. However, in 1999, our Office of General Counsel clarified requirements under CAAA and concluded that CAAA does not allow any exemption to the phase-out of production and cessation of import of CFC-113 and other Class I substances for which there is no exemption. Therefore, at the end of 1999, production and import of CFC-113 will cease, and new supplies of CFC-113 will not be available. You may continue to recycle and use existing supplies of CFC-113 until stocks are exhausted.

In the preamble to the proposed and final rules for Method 1664A, we recommended that laboratories switch to Method 1664A rather than wait until expiration of the production exemption for Class I substances, and that regulatory/control authorities authorize the switch. The re-interpretation of CAAA requirements will hasten the switch to Method 1664A and could, possibly, result in compliance difficulties for you, although our studies have indicated that this possibility is remote. If you wish to use Method 1664A and believe that the switch will cause a non-compliance, we suggest that you perform a side-by-side comparison with an approved method that uses LLE/CFC-113. We addressed this possibility in the final rule promulgating Method 1664A, and stated that although it is unlikely that a non-compliance situation may occur, in a few cases it may be necessary to perform side-by-side testing with Method 1664A and an approved method that employs CFC-113 to demonstrate a significant difference in results between the solvents and methods. The production phase-out and cessation of import of CFC-113 may preclude this side-by-side demonstration at some point in the future because CFC-113 may not be available. Therefore, if you believe that you could be adversely affected by the switch from CFC-113 to *n*-hexane, you should perform the side-by-side demonstration while supplies of CFC-113 are available, because this option may not be possible after stocks of CFC-113 are exhausted, unless Congress further amends the Clean Air Act.

The side-by-side demonstration is detailed below and examples are provided in Appendix A to this Guidance. To allow you to make the calculations detailed below and in Appendix A easily, we have produced an Excel spreadsheet that does all calculations automatically after you have entered the necessary data. This spreadsheet is available via an E-mail attachment from our Sample Control Center (SCC). Please E-mail your request to SCC@dyncorp.com, or you may phone your request to 703-461-2100. If you telephone, please ask for the "Method 1664A Comparison Spreadsheet" and provide your E-mail address. You must have Microsoft's Excel 97 to run the spreadsheet.

What constitutes a side-by-side comparison?

For the side-by-side comparison of Method 1664A to an approved method that uses LLE/CFC-113, we suggest, at a minimum, analysis of three replicates of each sample by each method on any seven days over a minimum 30-day period, for a total of 42 analyses (21 by the previously used method and 21 by Method 1664A). For this side-by-side comparison, you should use the separatory funnel liquid/liquid extraction (LLE) procedure, not the optional SPE procedure, in Method 1664A because of the possible confounding of results that could occur when two variables (SPE and the solvent) are changed simultaneously. If all six results associated with any sample are less than the minimum level (<ML), these results should not be used in the comparison because it is necessary to have actual measured values to test equivalency. In the event that a test result less than the ML is obtained, samples should be collected on an additional day (i.e., the number of tests should be increased to provide a minimum of seven paired triplicate results for the comparison). If all or nearly all results are less than the ML, we suggest that no further testing be done and that a direct substitution of Method 1664A for the CFC-based method be made because a reliable conversion factor cannot be derived. Further details are provided below in response to the questions: *"How do I derive a conversion factor?"* and, *"What are the detailed components of a side-by-side comparison?"*.

How do I derive a conversion factor?

Step 1: Test for statistical significance using procedures for development of the root-mean-square deviation (RMSD) detailed in our Freon Replacement Study reports, and shown by example in Appendix A to this Guidance, using results obtained with the CFC-based method as reference. If the RMSD is within the acceptance limit, the results obtained using the different methods are equivalent and a conversion factor is not warranted. If the RMSD is not within the acceptance limit, the difference is significant.

Step 2: If the difference is significant, a second step is necessary to test whether the bias between methods varies significantly from sample to sample (a significant method/sample interaction). If there is no significant interaction, a conversion factor can be developed for application to future results obtained with Method 1664A to convert these results to what they would have been had an alternate, approved, CFC-based method been used. If a significant interaction is present, a conversion factor would not be appropriate. Appendix A to this Guidance gives detailed example calculations for a side-by-side comparison and development of a conversion factor (if appropriate).

What are the detailed components of a side-by-side comparison?

Step 1: Collect eight samples on a total of seven days spaced over a minimum of a 1-month period. Observe the required preservation and holding time for oil and grease (per the methods and 40 CFR 136.3(e), Table II).

Step 2: For the eight samples collected on each day, analyze three by EPA Method 1664A and three by EPA Method 413.1 or another, approved, CFC-based method (for a total of 6 samples). Spike and analyze the remaining two samples and analyze one by the CFC-based method and the other by Method 1664A as a matrix spike sample with each method. For analyses by Method 413.1 or other, approved, method, the QC requirements in Method 1664A must be applied (including the demonstration of initial precision and recovery, on-going precision and recovery, blank, and matrix spike) to assure that the QC used with Method 413.1 or other, approved, method are equivalent to those used with Method 1664A.

Step 3: Tabulate the results of the analyses.

Step 4: Calculate the logarithms of the results to assure that a single result does not unduly influence the outcome.

Step 5: Calculate the means of the triplicates of the log-transformed results for each method on each day. Label each mean value M_{ij}, for sample j, ranging from 1 to 7, and method i, ranging from 1 to 2 (for example, let Method 1664A be method 1 and Method 413.1 be method 2).

Step 6: Calculate the standard deviations of the triplicates of the log-transformed results for each method on each day:

$$S_{ij} = \sqrt{\frac{1}{2}\sum_{(k\in 1,\ldots,3)}(Y_{ijk} - M_{ij})^2}$$

where Y_{ijk} is the k^{th} replicate for the j^{th} sample, analyzed using method i.

Step 7: Calculate the mean-square error (MSE):

$$MSE = \frac{1}{14}\sum_{i\in(1,\ldots,2)}\sum_{j\in(1,\ldots,7)} s^2_{ij}$$

Step 8: Calculate the method specific-means M_{M1} and M_{M2}, the sample-specific means M_{S1}, M_{S2}, M_{S3}, ..., M_{S7}, and the overall mean M_o.

$$\mathrm{M}_{\mathrm{Mi}} = \frac{1}{\mathrm{J}}\sum_{(j\in 1,..,7)} \mathrm{M}_{\mathrm{ij}},\ \textit{for method } i\ (i = 1,\ 2)$$

Step 9: Calculate the root-mean-square deviation (RMSD) for the results using Method 1664A and the alternate, approved method (e.g., EPA Method 413.1):

$$\mathrm{M}_{\mathrm{Sj}} = \frac{1}{2}\sum_{(i\in 1,..,2)} \mathrm{M}_{\mathrm{ij}},\ \textit{for sample } j\ (j\ \textit{in}\ 1,...,7)$$

$$\mathrm{M}_{\mathrm{o}} = \frac{1}{2}\sum_{(i\in 1,..,2)} \mathrm{M}_{\mathrm{Mi}} = \frac{1}{\mathrm{J}}\sum_{(j\in 1,..,J)} \mathrm{M}_{\mathrm{Sj}}$$

$$\mathrm{RMSD} = \sqrt{\frac{1}{7}\sum_{j\in(1,...,7)} (\mathrm{M}_{1\mathrm{j}} - \mathrm{M}_{2\mathrm{j}})^2}$$

Step 10: Calculate $\mathrm{RMSD}_{\mathrm{MAX}}$ as:

$$\mathrm{RMSD}_{\mathrm{MAX}} = \sqrt{\frac{2 * \mathrm{MSE}}{3} * 2.36}$$

where 2.36 is the 95th percentile F value with 7 degrees of freedom in the numerator, and 28 degrees of freedom in the denominator.

Step 11: Compare results. If $\mathrm{RMSD}_{\mathrm{MAX}} > \mathrm{RMSD}$, there is not a significant difference between methods, and therefore no conversion factor is necessary.
If $\mathrm{RMSD}_{\mathrm{MAX}} < \mathrm{RMSD}$, the difference between results produced by the two methods is significant. However, it is necessary to test whether this difference is constant for each sample. Therefore, continue to step 12 only if $\mathrm{RMSD}_{\mathrm{MAX}} < \mathrm{RMSD}$.

Step 12: Calculate the mean squares attributable to a method-by-sample interaction (MSINT):

$$\mathrm{MSINT} = \frac{1}{2}\sum_{(i\in 1,2)}\sum_{(j\in 1,...,7)} (\mathrm{M}_{\mathrm{ij}} - \mathrm{M}_{\mathrm{Mi}} - \mathrm{M}_{\mathrm{Sj}} + \mathrm{M}_{\mathrm{o}})^2$$

Step 13: Divide MSINT by the MSE from Step 7, and label this ratio F_{calc}. Compare this to 2.45 (a 95 percentile F value with 6 degrees of freedom in the numerator and 28 degrees of freedom in the denominator). If $F_{calc} > 2.45$, there is a significant interaction between method and sample (i.e., the bias between methods varies significantly from sample to sample) and a conversion factor is not appropriate. Stop here.

If $RMSD_{MAX} < RMSD$, and $F_{calc} < 2.45$, there is a consistent bias between methods, and a conversion factor should be calculated. Proceed to Step 14 for calculation of a conversion factor.

Step 14: Calculate the conversion factor

In order to calculate the conversion factor, calculate the ratio of the averages of the method means of the log-transformed results as shown below. The result for Method 1664A must be in the denominator.

$$CF_L = \frac{M_{M2}}{M_{M1}}$$

This mean is the log of the conversion factor that could be applied to all future values to transform a result for Method 1664A to the result that would have been produced had an alternate, approved method been used.

For a given log-transformed result from Method 1664A, the converted value is:

$$X_R = EXP[Y_N * CF_L]$$

where X_R is the converted value in the original scale, and Y_N is the log-transformed value obtained using 1664A.

See Appendix A for examples using the procedure above.

3

Solid-Phase Extraction (SPE)

This section discusses use of solid-phase extraction (SPE) and how to determine if results produced with SPE are equivalent to those produced by liquid-liquid extraction (LLE).

What is solid-phase extraction and under what conditions may I use it?

SPE uses a cartridge or disk for removal of the oil and grease from the sample. A detailed description of the SPE technique was provided when Method 1664 was proposed (61 FR 1730). Even prior to proposal of Method 1664, proponents of SPE devices had requested that SPE be an allowed technique in Method 1664. Proposed Method 1664 allowed use of SPE, but required a demonstration that SPE produced results equivalent to results produced by separatory funnel liquid-liquid extraction (LLE). Proponents objected to this requirement, claiming that SPE provided sufficient advantages in solvent reduction, reduced analysis time, reduced emulsion formation, and other advantages so that its use should be allowed without a prior demonstration of equivalency. We discussed the issue extensively at proposal and in public workshops and meetings, and specifically solicited data demonstrating equivalency of results produced by SPE and LLE.

Some data demonstrated that results produced by LLE and SPE are equivalent, whereas other data demonstrated that results produced could be significantly different. We reopened the comment period (61 FR 26149) to allow submission of further data, and provided a notice of availability (62 FR 51621) of those and other data so that we could consider those data for the final rule.

Discussions of the detailed issues on SPE were summarized in Section VI of the preamble to the final rule promulgating Method 1664A, and were given in the detailed comments and responses included in the Docket for the final rule. Based on comments received and supporting data, we allowed use of SPE in Method 1664A without a prior demonstration of equivalency. Therefore, if SPE in Method 1664A produces results equivalent to results by LLE/CFC-113 in a approved method or to LLE in Method 1664A, SPE can be used as a directly equivalent extraction technique. However, we added a note at the beginning of the extraction procedure (Section 11.3) in Method 1664A to indicate that it is your responsibility to assure that the results produced are equivalent. The note states:

> "The procedure detailed below is for separatory funnel liquid-liquid extraction. Solid-phase extraction (SPE) may be used at the discretion of the discharger/ generator and its laboratory. However, if SPE is used, it is the responsibility of the discharger/generator and laboratory to assure that results produced are

> equivalent to results produced by the procedure below." [*The procedure following the note is the LLE procedure.*]

We emphasize in this Guidance that SPE may be used at the discretion of you and your laboratory without a demonstration of equivalency, provided that you assure that the results produced by SPE are equivalent to results produced by LLE and that you take responsibility for the results. Such an assurance, for example, could be based on the fact that monitoring of a given discharge produces results that are always below the minimum level (ML) of Method 1664A. For this instance, a side-by-side comparison cannot be performed because there is, essentially, nothing to measure. In this case, you could assure that results produced by SPE are equivalent to results produced by LLE. Another example would be that your discharge is comprised almost exclusively of a pure substance and you know that SPE extracts this substance with the same efficiency as LLE.

If there is doubt about the equivalency of SPE and LLE, a test should be performed as described below in the section titled: *"How can I demonstrate equivalency of liquid-liquid and solid-phase extraction?"*. If the SPE/*n*-hexane results differ significantly from the LLE/CFC-113 results or results produced by Method 1664A, you may wish to consider performing the 42-sample study described in Section 2 of this Guidance to determine if a conversion factor is warranted. In the final rule, we also acknowledged that if a Region, State, or other permitting or control authority has concerns about the difference in results produced by SPE and LLE, that authority may specify the use of either technique in the permit.

What waste streams were tested to attempt to establish that liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are equivalent?

We evaluated LLE and SPE in the Phase I and Phase II Freon Replacement Studies to attempt to demonstrate that the two extraction techniques are equivalent. In the initial portion of the Phase I study, we collected and analyzed treated effluent samples from a variety of industrial facilities. These samples frequently did not contain detectable levels of oil and grease. Therefore, it was not possible to compare solvents or extraction procedures with these samples. As a result, we conducted further studies on untreated effluents, in-process wastes, or treated effluents spiked with treatment system influents, so that we would have something to measure. For many of these samples, results from LLE and SPE were significantly different; for others, results were not significantly different.

In addition to our data gathering, we shared samples with vendors of SPE devices. Some results provided by these vendors showed significant differences and others did not. For our data gathering and data gathering by vendors of SPE devices, multiple solvents were tested, including CFC-113 and *n*-hexane, with both disk and cartridge SPE devices.

In addition to our data gathering and data gathering by vendors of SPE devices, some of you took the initiative to perform additional comparison studies. As with our studies and vendor studies, some results showed significant differences and others did not. This conclusion was valid regardless of solvent (*n*-hexane or CFC-113) or technique (SPE or LLE).

Based on all of these results, it is likely that LLE and SPE would not produce results that are significantly different when final effluents are analyzed. However, there may be significant differences when untreated effluents and in-process wastes are analyzed. As a result, we stated in Method 1664A that you may use SPE without a demonstration of equivalency provided that you assure that results produced are equivalent to the LLE procedure. You may compare results produced by SPE in Method 1664A to results by LLE/CFC-113 in an approved method or to LLE/*n*-hexane in Method 1664A.

How can I demonstrate the applicability of SPE to compliance monitoring with my discharge or waste stream?

We allowed use of SPE in Method 1664A provided that you take responsibility to assure that results produced are equivalent to results produced by the liquid/liquid extraction (LLE) procedure in Method 1664A. (See the note in Section 11.3 of Method 1664A). Therefore, if you want to apply SPE as an integral part of Method 1664A to compliance monitoring, you may apply it directly so long as you meet the requirements in the Method, in the same way that you would apply the LLE procedure in Method 1664A. This demonstration may be done in three steps:

Step 1: If you have not performed the initial demonstration of laboratory capability required for use of Method 1664A, you must perform this demonstration to assure that your laboratory is capable of practicing Method 1664A. This demonstration includes the method detection limit (MDL) and initial precision and recovery (IPR) tests given in Sections 9.2.1 and 9.2.2 of Method 1664A, respectively. These tests are reproduced and annotated in Appendix B of this Guidance. For these tests, SPE is included as an integral part of the Method.

If you have performed the initial demonstration of laboratory capability using liquid-liquid extraction (LLE), you must repeat the IPR test using SPE as an integral part of Method 1664A. If the MDL will be affected by use of SPE, you must repeat the MDL test in Section 9.3.1. See Section 9.1.2.1 of Method 1664A. Unless the sample volume or another significant change is made to Method 1664A, it is unlikely that you would need to perform the MDL test as a consequence of using SPE.

Step 2: Measure the concentration of HEM or NPM in your discharge or waste stream using Method 1664A with SPE as an integral part, in the same way that you would apply Method 1664A directly. If the result is satisfactory; i.e., concentration of HEM or NPM meets your regulatory compliance limit in the same way in which the compliance limit was met using an approved CFC-based method, you may use Method 1664A with SPE as an integral part. If the result is unsatisfactory, you may wish to establish a conversion factor using the procedure in Section 2 of this Guidance.

Step 3: Perform the on-going QC tests (on-going precision and recovery, blank, and matrix spike) as a part of the routine practice of Method 1664A with SPE as an integral part of the Method and meet the QC acceptance criteria in Method 1664A.

How can I demonstrate the equivalency of liquid-liquid and solid-phase extraction?

One example means of assuring equivalence of LLE and SPE was given earlier in this guidance (that all results are <ML). Assurance could also be provided by (1) making SPE a modification to EPA Method 1664A, (2) performing the tests required for demonstrating equivalency that are given in Method 1664A, and (3) meeting the QC acceptance criteria for equivalency specified in Method 1664A. This testing would be conducted in three steps, as follows:

Step 1: If you have not performed the initial tests required for use of Method 1664A, you must first perform these tests to demonstrate that your laboratory is capable of practicing Method 1664A as written, including the liquid-liquid extraction procedure given in Section 11.3 of Method 1664A. These tests include the initial precision and recovery (IPR) and method detection limit (MDL) tests. See Section 9 of EPA Method 1664A.

Step 2: The second step is detailed in Section 9.2 of EPA Method 1664A. This test is a repeat of the initial precision and recovery (IPR) test on reagent water with SPE as an integral part of Method 1664A. Section 9.2 of Method 1664A is reproduced in Appendix B of this Guidance and annotated in italics and brackets [*text*] to provide further guidance. If the MDL will be affected by the change to SPE, you must repeat the MDL test in Section 9.3.1. See Section 9.1.2.1 of Method 1664A. Unless the sample volume or another significant change is made to Method 1664A, it is unlikely that you would need to perform the MDL test as a consequence of using SPE. Once the equivalence of SPE is demonstrated, proceed to Step 3.

Step 3: The third step test is a demonstration of equivalency on each sample matrix type, as detailed in Section 9.2.3 of EPA Method 1664A, with SPE as an integral part of Method 1664A and with the matrix type being the actual discharge or waste stream to which SPE will be applied. Section 9.2.3 of Method 1664A is reproduced in Appendix C of this Guidance and annotated in italics and brackets to provide further guidance. After you demonstrate the equivalence of SPE using the IPR test (Step 1) and on the sample matrix type (Step 2), SPE may be used on that sample matrix type (discharge or waste stream) thereafter. For application to another sample matrix type, the equivalency demonstration would need to be repeated using Step 3; i.e., so long as the method is not modified further, the IPR test in Steps 1 and 2 do not need to be repeated. The on-going QC tests (on-going precision and recovery, blank, and matrix spike) must be performed and the QC acceptance criteria requirements in Method 1664A must be met when you apply the modification routinely to a sample matrix type.

4 Flexibility in EPA Method 1664A

This section discusses flexibility inherent in EPA Method 1664A and discusses the process of demonstrating equivalent performance when the Method is modified. This discussion is summarized from *Guidance on Evaluation, Resolution, and Demonstration of Analytical Problems Associated with Compliance Monitoring* (EPA 821-B-93-001).

Is there flexibility in EPA Method 1664A?

Flexibility exists for making changes to EPA Method 1664A. However you must demonstrate that your modification achieves equivalent or superior performance to the performance of Method 1664A.

What types of modifications may I make?

The types of modifications that you may make to Method 1664A are the typical changes that would make it easier for you to practice the Method without compromising performance. For example, change of a beaker to an Erlenmeyer flask or change of a boiling flask to a Kuderna-Danish is allowed, after a demonstration of equivalency, because they would not be expected to adversely affect method performance. Certain changes, including change of the extraction solvent, are not allowed as modifications, because the Freon Replacement Study data demonstrated that significant changes in results occur when an alternate solvent is used. A change in the *n*-hexadecane and stearic acid standards is not allowed because the performance data for Method 1664A were developed using these standards. (Please refer to section 9.1.2 of EPA Method 1664A, excerpted in response to the question below).

How can I demonstrate equivalent or superior performance for a method modification?

You can demonstrate equivalent or superior performance by showing that results produced by your modification are equal to or superior to results produced by the unmodified Method. The performance of a modified method is measured by precision and recovery (bias), and can be extended to include detection limit as well as other measures of method performance. You must perform the initial precision and recovery (IPR) test prior to practicing Method 1664A. This test is described in detail in Section 9 of the Method. Results of the IPR test must meet the precision and quality control (QC) acceptance criteria in Method 1664A. After the requirements are met for the unmodified Method, you must repeat the IPR test with the modification as an integral part of the Method. Your modification is permitted if the QC acceptance criteria for precision and recovery of Method 1664A are met.

As stated in Section 9.1.2 of EPA Method 1664A, the purpose of allowing changes to Method 1664A is to improve Method performance or lower the cost of measurements. Section 9.1.2 of Method 1664A states:

9.1.2 In recognition of advances that are occurring in analytical technology, the laboratory is permitted certain options to improve separations or lower the costs of measurements, provided that all performance specifications are met. These options include alternate extraction and concentration devices and procedures such as solid-phase extraction, continuous liquid-liquid extraction, and Kuderna-Danish concentration. Alternate determinative techniques, such as infrared spectroscopy or immunoassay, and changes that degrade method performance, are not allowed. If an analytical technique other than the techniques specified in this method is used, that technique must have a specificity equal to or better than the specificity of the techniques in this method for HEM and/or SGT-HEM in the sample of interest. Specificity is defined as producing results equivalent to the results produced by this method for analytical standards (Section 9.2.2) and, where applicable, environmental samples (Section 9.2.3), and that meet all of the QC criteria stated in this method.

5

Frequently Asked Questions (FAQs) Concerning EPA Method 1664A

The questions below are those that we have been most frequently asked. In comments on proposal of Method 1664, and in comments on notices that EPA published, commenters raised more than 100 questions/issues concerning Method 1664. EPA responded to these questions/issues and placed the comments/responses in the Water Docket to support the final rule. We urge dischargers/generators/ industrial users, regulatory/control authorities, laboratories, and others that have questions concerning Method 1664A to review the comments/responses in the administrative record at the Water Docket. (Chapter 7, *Where to Get Additional Help*, provides contact information for the Water Docket).

NOTE: In the questions below, the pronouns "I" and "we" refer to the questioner whereas the pronoun "you" refers to EPA. In the answers, the pronouns "we," "us," and "our" refer to EPA whereas the pronouns "you" and "your" refer to the questioner and to other users of Method 1664A.

We are having difficulty in achieving the recoveries of HEM and SGT-HEM specified in the QC acceptance criteria in Method 1664A. Why?

This has been the most frequently asked question since proposal of Method 1664A. Low recoveries appear attributable to two main sources: (1) failure to adequately rinse glassware and other surfaces that the sample contacts and (2) use of a hot plate or Roto-vap for evaporation of the solvent.

Stearic acid sticks to nearly everything. Therefore, to adequately recover stearic acid, you must rinse every surface that stearic acid touches with a small amount of *n*-hexane to assure that the stearic acid is removed and recovered. This includes the inside surfaces of the sample bottle (and liner), the separatory funnel or SPE device used for extraction, the sodium sulfate used for drying the extract, and the surfaces of the flask used for evaporation of the solvent.

A technique that will aid in recovery of HEM and SGT-HEM is use of a small stream of *n*-hexane from a squeeze bottle to rinse glassware surfaces. For example, after the third extraction using the separatory funnel, use a squeeze bottle to allow a small amount of *n*-hexane to stream down the inside of the separatory funnel while rotating the funnel to assure that the stream will rinse all of the inside surface. In Method 1664A, this technique is termed "quantitative transfer." (See the definition in the Glossary at the end of Method 1664A).

Use of a hot plate or Roto-vap for evaporation of the *n*-hexane can result in loss of *n*-hexadecane if the solvent is allowed to go to dryness, because *n*-hexadecane will evaporate rapidly as the temperature rises above the boiling point of *n*-hexane.

Our laboratory is having difficulty achieving the MDL in Method 1664A. Are there any tips that you can give us?

Obtaining the MDL in Method 1664A is dependent on performing the analysis precisely; i.e., performing it the same way each time. To perform the analysis precisely requires analyst skill and technique. For example, and in response to another FAQ, all surfaces that the sample contacts must be rinsed carefully and in the same way with solvent to recover HEM and SGT-HEM. Certain devices that automate the extraction and/or solvent evaporation processes can improve method precision, and may allow the MDL to be met more readily.

How can we overcome emulsions formed in the determination of oil and grease?

We have allowed great flexibility in overcoming emulsions, as listed in Section 11.3.5 of Method 1664A. The optimum technique depends upon the sample, but may include stirring, filtration through glass wool, use of solvent phase separation paper, centrifugation, use of an ultrasonic bath with ice, addition of NaCl, or other physical methods. Alternatively, solid-phase extraction (SPE), continuous liquid-liquid extraction, or other extraction techniques may be used to prevent emulsion formation, provided that the requirements in Section 9.1.2 are met.

The most effective ways that we have found to overcome emulsions are use of solid-phase extraction (SPE), as described in EPA Method 1613 (40 CFR Part 136, Appendix A) and other methods, and continuous liquid-liquid extraction (CLLE), as described in EPA Methods 625 and 1625 (40 CFR Part 136, Appendix A) and in other methods. The advantage of SPE and CLLE is that the sample is not shaken with the extracting solvent, thereby preventing the incorporation of air into the mixture. Saturation of the sample with salt (NaCl) prior to extraction using SPE or CLLE may also aid in preventing emulsion formation.

Our discharge contains sulfur that is being converted to thiosulfate upon acidification. The thiosulfate is being extracted into *n*-hexane and is inflating results for HEM. How can we solve this problem?

For this particular instance, where it is known that acidification of the sample is causing a problem, we recommend that the sample not be acidified. However, it may be difficult to recover stearic acid from the matrix spike if the sample is not acidic. You should work with your regulatory/control authority to resolve the problem by gathering data to demonstrate that the problem exists with the particular discharge and by gathering data to demonstrate that the matrix spike can be recovered effectively if the sample is not acidified.

Is Non-Polar Material (NPM) another name for Total Petroleum Hydrocarbons (TPH)? Can the test for NPM be used to analyze for TPH?

Non-Polar Material, or NPM, is another name for Silica-Gel-Treated Hexane-Extractable Material (SGT-HEM), and is operationally defined (or Method-defined) by the SGT-HEM procedure specified in Method 1664A. In other words, NPM are the compounds that are extracted from a sample with hexane after that sample has been treated with silica gel to remove polar materials, as per Method 1664A.

Total petroleum hydrocarbons, or TPH, may or may not be equivalent to NPM. A number of different methods exist for the analysis of TPH, and many use analytical procedures that differ significantly from Method 1664A. For example, EPA Method 418.1 for TPH employs sample extraction without silica-gel-treatment, followed by quantitation of TPH content using infrared analysis. The materials captured by this and other TPH methods may include or exclude organic compounds that are part of NPM using Method 1664A, and vice versa. Therefore, we cannot say conclusively that TPH is equivalent to NPM.

How can the non-polar material contribution to a total oil and grease measurement be distinguished from the fatty acid contribution?

If an environmental sample is composed of non-polar material (such as petroleum hydrocarbons), plus polar materials (such as glycerides, detergents, and fats), then the hexane-extractable material procedure will measure all of these substances, whereas the silica-gel-treated-hexane extractable material (SGT-HEM) procedure will measure the non-polar material after the polar material is removed. The difference between the two measurements will give the amount of polar material present.

When should the silica-gel-treated, hexane-extractable material (SGT-HEM) procedure be used?

We provided the SGT-HEM procedure for those instances in which a regulatory/control authority believes that it is appropriate to exclude certain polar materials from a compliance determination.

When CFC-113 becomes unavailable, what analytical method will replace CFC-113-based procedure for the Coil Coating Point Source Category at 40 CFR 465.03(c)?

Commenters pointed out that we had not proposed revisions to the CFC-based procedure in the Coil Coating standards at 40 CFR 465.03(c), the Metal Molding and Casting standards at 40 CFR part 464, the Aluminum Forming standards at 40 CFR 467, and other sections of the CFR that specify use of Method 413.1 or "Freon or equivalent."

We responded in the administrative record for the final rule that we would not replace the procedure at 40 CFR 465.03(c) with Method 1664A because we were in the process of re-evaluating the Coil Coating standards. We also pointed out that the NPM procedure in Method 1664A was virtually identical to the procedure in section 465.03(c), with the exception of the use of *n*-hexane in place of CFC-113. We further pointed out that the Davison Grade 950 silica gel specified in section 465.03(c) was no longer commercially available, that Standard Methods

503A and 503E referenced in section 465.03(c) were outdated, and that Method 1664 contained QC and QC acceptance criteria for NPM that were not present in the procedure in section 465.03(c).

Our response was based on an interpretation that CFC-113 would be available until 2005 under the exemption in the Montreal Protocol. However, and as stated in Section 2 of this Guidance, a clarification of requirements in the Clean Air Act Amendments of 1990 (CAAA) by our Office of General Counsel is that the production and import of CFC-113 must cease on January 1 of 2000. Supplies of CFC-113 may continue to be recycled and used until the laboratory use exemption expires in 2005. However, CFC-113 may not be available because of the production phaseout and cessation of import required by CAAA.

When CFC-113 is no longer available, you will have no choice but to use the silica-gel-treated, hexane-extractable material (SGT-HEM; non-polar material; NPM) procedure in Method 1664A. As stated throughout this Guidance, we do not expect significant differences between results produced by CFC-113 and *n*-hexane. However, if you believe that a difference could be significant and could affect compliance, you may use the procedure described in Section 2 of this Guidance, as supported by the examples in Appendix A, to demonstrate to your regulatory/control authority that a conversion factor is warranted.

In order to adsorb a larger amount of polar material for the SGT-HEM measurement, can I use a larger amount of silica gel?

Yes.

Does Method 1664A allow use of composite versus grab sampling?

Section 8 of Method 1664A gives requirements for sample collection, preservation, and storage, as outlined below.

Section 8.3 of Method 1664A states that samples must be collected as grab samples because extractable material may adhere to sampling equipment and result in measurements that are biased low. This condition precludes collection of a composite sample in the field.

Section 8.3 also provides two approaches to obtaining a composite measurement. Option 1 consists of collecting individual grab samples at prescribed time intervals, analyzing each grab separately, and averaging the determined concentrations. Option 2 consists of collecting four individual 250-mL samples over the course of a day and compositing these grab samples at the laboratory. At the laboratory, the four 250-mL grab samples are poured into the separatory funnel, and each sample container and cap liner are rinsed with *n*-hexane to ensure that all materials adhering to the walls of the sample containers and to the cap liners are transferred to the separatory funnel. For more explicit details, please refer to Method 1664A.

In making its decision to switch from CFC-113, did EPA consider the additional hazards associated with *n*-hexane in comparison to CFC-113?

Yes. We searched for a non-flammable solvent capable of producing results equivalent to results produced by CFC-113. In Phase I of our Freon Replacement Study, we evaluated DuPont 123 (2,2-difluoro-1,1,1-trifluoroethane) and tetrachloroethylene. However, neither of these solvents produced results as close to results produced by CFC-113 as did *n*-hexane. As a result, we chose *n*-hexane. To more extensively address the safety issue, we expanded the section on safety in Method 1664A promulgated in the final rule.

The quality control (QC) in Method 1664A is more extensive than in predecessor oil and grease methods. Why do~~es~~ you believe that the additional QC is necessary?

We based the decision to add QC to Method 1664A based on concerns from the regulated industry and from a history that some laboratories were practicing inadequate QC. We have added similar QC to other methods and believe that this minimum QC is necessary to demonstrate that results are reliable.

Why didn't EPA make solid-phase extraction (SPE) the reference technique in EPA Method 1664A?

We desired to match, as closely as possible, results produced by EPA Method 413.1 and other methods approved for determination of oil and grease. All of these previously approved methods use liquid-liquid extraction, and the effluent guidelines were developed using these methods. Had we been starting from scratch, SPE would have been the reference technique chosen.

If there are such problems with *n*-hexadecane and stearic acid, why were these compounds selected as standards rather than Wesson oil or other substances?

In our Freon replacement studies, industries were segmented into two main categories: petroleum and non-petroleum. The major component of petroleum-based samples is diesel oil, and the main component of diesel oil is *n*-hexadecane. The major component of non-petroleum-based samples is animal fat, and the main component of animal fat is stearic acid. We chose *n*-hexadecane and stearic acid as the compounds to be used for QC tests in Method 1664A so that we can be sure that the major components of petroleum-based and non-petroleum based samples are recovered.

We have preliminary data indicating that some of the hexadecane/stearic acid standard may be lost by evaporation using the procedure in Section 11.4.4 for drying the boiling flask. Has EPA seen other evidence of this problem?

Not until you indicated that the problem may exist. The procedure for drying the boiling flask at 70 °C for 30 - 45 minutes followed by dessication for 30 minutes was suggested by the American Petroleum Institute as a means for assuring that residual water or *n*-hexane would not affect the measurement. If this problem is experienced, we suggest a lower temperature or a shorter drying time.

An SPE vendor has stated that we should spike the hexadecane/stearic acid into the SPE reservoir, and not into the sample container, so that we can recover the matrix spike more efficiently. Is this allowed?

No. You must spike into the sample container, as stated in Section 9.3.2.2 of Method 1664A, because you must demonstrate recovery of the matrix spike (MS) from the sample container.

You can improve HEM and NPM recovery when SPE is used by rinsing the sample bottle with small portions (e.g., 3 x 10 mL) of *n*-hexane and using these portions to elute the HEM or NPM from the SPE disk. The procedure in Section 11.3.3 of Method 1664A gives detail on how to rinse the sample container.

The weighing procedure in Section 11.4.4 requires drying and re-weighing until constant weight is achieved. Should the final weight be used or should the final two weights be averaged?

The final weight should be used as the value for HEM or NPM.

What is the status of a method to replace EPA Method 418.1? *(Method 418.1 uses CFC-113 and infra-red spectroscopy (IR) to measure IR-sensitive substances in the sample).*

We continue development work on a replacement for Method 418.1. The solvent being studied most intensely at the time of writing of this Guidance is tetrachloroethene (tetrachloroethylene; perchloroethylene; perc). The number of solvents available for the IR method is severely limited because any solvent that contains a carbon-hydrogen bond will interfere in the determination. Most of the remaining solvents are hazardous (e.g., carbon disulfide), and perc is not without hazard. The most significant problem encountered with perc is that a stabilizer is needed to prevent degradation. To date, stabilizers have had a carbon-hydrogen bond, thus compromising IR measurements. We are working with manufacturers of perc to attempt to overcome this problem.

Instead of dealing with the solvent issue, why didn't EPA simply abandon the oil and grease test and rely on measurements of specific organic compounds for pollution control?

The Clean Water Act (CWA) requires regulation of "conventional pollutants," and oil and grease has been designated as a conventional pollutant under CWA. In order to eliminate oil and grease as a conventional pollutant, either CWA would need to be changed or designation of oil and grease as a conventional pollutant by the EPA Administrator would need to be rescinded. Changing CWA would take an act of Congress, and such a change would likely be lengthy and contentious. Similarly, the rescission of designation by the EPA Administrator would need to be proposed and would likely be contentious. Rather than attempt to change the CWA or the designation, we decided to move forward with a change in solvent.

(1) Section 18.2.2 of Method 1664 defines an analytical batch as a group of up to 20 samples processed together in a 12-hour shift. It does not specify that the samples be of the same matrix type. It does specify that each analytical batch include a laboratory blank, an ongoing precision and recovery sample (OPR), and a matrix spike (MS); (2) Section 18.2.2 refers to Section 9.3

regarding a definition of the MS; (3) Section 9.3 requires "The laboratory must spike a minimum of 5 percent of all samples from a given sampling site or, if for compliance monitoring, from a given discharge/waste stream." The dilemma is that the requirements for MS in Sections 18.2.2 and 9.3 appear to be different with respect to both frequency and matrix type. Several interpretations seem possible. Our questions are:

1. **Is there a requirement for a separate analytical batch (blank, OPR, and MS) for each discharge/waste stream?**

Requirements for a batch and discharge/waste stream are different. (For a definition of discharge/waste stream, see the Glossary at the end of Method 1664A.) The requirement for an analytical batch is that it must include a blank, OPR, and MS. A discharge/waste stream must be spiked at a minimum frequency of 1 in 20 samples; i.e., the first sample must be spiked, the 21st sample must be spiked, etc.

2. **Or, is the requirement a blank and an OPR per 12 hour shift in the lab, with an MS per sample?**

The batch is comprised of the samples started through the extraction process during a given 12-hour shift, to a maximum of 20 samples. If only 1 sample is started through the extraction process, the batch size is 1; if 20 samples are started through the extraction process, the batch size is 20.

3. **Or, is there a requirement for a blank and an OPR per analytical batch (18.2.2), with a matrix specific MS per 20 sampling events per effluent stream (9.3) over time, i.e. across analytical batches?**

Both. The requirement for a batch is that it must include a blank, OPR, and MS. The requirement for the frequency of the MS per discharge/waste stream is that the sample from the discharge/waste stream must be spiked at a frequency of 5 percent (a minimum of 1 in 20 samples).

> NOTE: The requirement for an MS per batch could result in a spike of the matrix type at a frequency of greater than 20 percent. For example, if a discharge is monitored daily and is the only sample in the batch, it must be spiked every day.

4. **Or, is it acceptable to perform a blank, an OPR, and a randomly selected MS per analytical batch?**

The MS can be selected randomly, provided that each discharge/waste stream is spiked at a frequency no less than 5 percent. For example, if there are 20 samples in the batch, and all had been spiked during the previous ten times that they were analyzed, none are required to be spiked. However, because of the requirement for an MS with the batch, any one of the samples may be chosen for the MS.

So, for example, if 2 waste streams are in a 20 sample are run within a 12-hour shift, it is clear that a blank and an OPR are required, but must 2 matrix spikes (one for each waste stream) be

run to be certain of achieving the 5% spike requirements for both the discharge/waste stream and the analytical batch?

If the waste streams had not been spiked in the previous 20 samplings, an MS must be run on each. Thereafter, the MS can be staggered between the waste streams so that 2 MSs are not required with each batch.

Explanations:

Batch and discharge/waste-stream-specific quality control (QC)

Batch-specific QC is required to demonstrate that the analytical process is in control during the 12-hour shift that samples, blanks, and standards (OPRs) will be analyzed. Discharge/waste-stream-specific QC is required to assure that the method continues to be applicable to that specific discharge/waste stream.

Discharge/waste stream (matrix type)

Discharge/waste stream are synonymous with "matrix type." The term "matrix type" was created to address wastewater streams in a given industrial subcategory. Industrial subcategories are defined in the wastewater regulations at 40 CFR parts 400-699. "Matrix type" means a sample medium with common characteristics across a given industrial subcategory. Examples include: C-stage effluents from chlorine bleach mills in the Pulp, Paper, and Paperboard industrial category; effluents from the continuous casting subcategory of the Iron and Steel industrial category; publicly owned treatment work (POTW) sludges; and effluents being discharged to POTWs from plants in the Atlantic and Gulf Coast Hand-shucked Oyster Processing subcategory. "Sample medium" means the physical phase of a sample matrix. Air, water, soil, sediment, rock, and sludge are sample media.

Strictly speaking, the discharge/waste-stream-specific QC would be applicable on the basis of matrix type; i.e., if a commercial laboratory was analyzing C-stage effluents from several chlorine bleach mills in the Pulp, Paper, and Paperboard industrial category, it would be necessary to collect and analyze an MS from any one of the C-stage effluents, only, to satisfy the discharge/waste-stream-specific QC. The reason that a single sample can be used to represent a particular wastewater stream in a given industry is that the industry is subcategorized based on the product produced and the process used to produce that product. Wastewater streams from the same product/ process will have the same characteristics.

In practice, it is unlikely that a commercial laboratory would know the specific stream sampled or the specific industrial subcategory. Therefore, it would be prudent for the discharger/industrial user to provide an extra sample for the matrix spike to meet the frequency requirement of 5 percent (1 in 20 samples).

6 Sources of Information

This section provides sources of information related to the final guidelines establishing test procedures for the analysis of oil and grease. Specifically, this section provides a listing of documents pertaining to the regulatory background and data gathering for oil and grease.

Regulatory Background

Acts

Clean Water Act (CWA) - Public Law 92-500, et. seq.; 33 U.S.C. 1251 et. seq.
Resource Conservation and Recovery Act (RCRA) - Public Law 94-580, et. seq.; 42 U.S.C. 6901 et. seq.
Clean Air Act Amendments (CAAA) - Public Law 101-549, et. seq.

Analytical methods under CWA Section 301, 304, and 501

History: see *Federal Register*, February 7, 1991 (56 FR 5090)
Support for effluent guidelines: see *Federal Register*, October 18, 1995 (60 FR 53988).
Proposal of Method 1664: See Federal Register, January 23, 1996 (61 FR 1730).

Analytical methods under RCRA

History: see *Federal Register*, June 13, 1997 (62 FR 32452)
Applicability to methods under CAAA: see *Federal Register*, July 3, 1991 (56 FR 30519)

Data Gathering for Method 1664A

Proposal

See the administrative record in the Water Docket for the proposed rule (61 FR 1730) for the following study reports

- Phase I Freon Replacement Study (EPA-821-R-93-011)
- Phase II Freon Replacement Study (EPA-820-R-95-003)
- Method Validation Study (821-R-95-036)

Notice of availability

See *Federal Register*, October 2, 1997 (62 FR 51621)

Water Pollution performance evaluation (PE) data

See Table 1 in the preamble to the final rule (64 FR 26316) for pertinent data

Data received from commenters

See the administrative record in the Water Docket for the final rule

Interpretation of Requirements in Clean Air Act Amendments

Letter from Drusilla Hufford, Director, Stratospheric Protection Division (6205J), Office of Atmospheric Programs, Office of Air and Radiation, to Regional Quality Assurance Managers, August 30, 1999

"Request for Applications for Essential Use Exemptions to the Production and Import Phaseout of Ozone Depleting Substances Under the Montreal Protocol" (64 FR 50089, September 15, 1999)

7

Where to Get Additional Help

Provided in this section are additional sources of information and EPA contacts that may provide additional information related to the final guidelines establishing test procedures for the analysis of oil and grease. Specifically, this section presents a list of documents and websites relating to the final rule for the analysis of oil and grease. These lists also include information on how to reach EPA program personnel and how to access these information sources.

Questions specifically related to Method 1664A should be directed to:

Maria Gomez-Taylor
Engineering and Analysis Division (4303)
U.S. EPA
401 M Street, SW
Washington, DC 20460
Tel: (202) 260-1639
Fax: (202) 260-7185
E-Mail: gomez-taylor.maria@epa.gov

Questions specifically related to the use of Method 1664A in the Resource Conservation and Recovery Act program should be directed to the regional delisting coordinator in each Regional Office:

U.S. EPA Region I One Congress Street John F. Kennedy Federal Building Suite 1100 Boston, MA 02114-2023 Tel: (617) 918-1111 Fax: (617) 918-1112	U.S. EPA Region II 290 Broadway New York, NY 10007-1866 Tel: (212) 637-3000 Fax: (212) 637-3526
U.S. EPA Region III 1650 Arch Street Philadelphia , PA 19103-2029 Tel: (215) 814-5000 Fax: (215) 814-5103	U.S. EPA Region IV 61 Forsyth Street, S.W. Atlanta, GA 30303-3415 Tel: (404) 562-9900 Fax: (404) 562-8174

U.S. EPA Region V 77 West Jackson Boulevard Chicago, IL 60604-3507 Tel: (312) 353-2000 Fax: (312) 535-4135	U.S. EPA Region VI Fountain Place 12th Floor, Suite 1200 1445 Ross Avenue / 6PD Dallas, TX 75202-2733 Tel: (214) 665-6444 Fax: (214) 665-2146
U.S. EPA Region VII 726 Minnesota Avenue Kansas City, KS 66101 Tel: (913) 551-7000 Fax: (913) 551-7467	U.S. EPA Region VIII 999 18th Street, Suite 500 / 8P-HW Denver, CO 80202-2466 Tel: (303) 312-6312 Fax: (303) 312-6339
U.S. EPA Region IX 75 Hawthorne Street San Francisco, CA 94105 Tel: (415) 744-1702 Fax: (415) 744-1514	U.S. EPA Region X 1200 Sixth Avenue Seattle, WA 98101 Tel: (206) 553-1200 Fax: (206) 553-0149

The administrative record (public comments, EPA responses, and all supporting documents for Method 1664A) are available for review at the Water Docket. For access to docket materials, phone the Water Docket between 9:00 a.m. and 3:30 p.m. for an appointment:

Water Docket
U.S. EPA
401 M Street, SW
Washington, DC 20460
Tel: (202) 260-3027

Documents on Compliance Monitoring and Methods

- # **Guidance on Evaluation, Resolution, and Documentation of Analytical Problems Associated with Compliance Monitoring**, EPA-821-B-93-00" June 1993.

Websites

- # EPA's homepage on the World Wide Web:
  http://www.epa.gov
- # EPA's Monitoring Science in the RCRA Program (OSW methods Team Homepage):
  http://www.epa.gov/SW-846
- # EPA's Office of Science and Technology's analytical methods page on the World Wide Web:
  http://www.epa.gov/OST/Methods/ (water methods)
  http://www.epa.gov/ost/guide/ (water documents)
  http://www.epa.gov/ttn/oarpg (air documents)

Appendix A

Example Calculations for Side-by-Side Comparisons

To allow you to make the calculations detailed in this Appendix easily, we have produced an Excel spreadsheet that does all calculations automatically after you have entered the necessary results. This spreadsheet is available via an E-mail attachment from our Sample Control Center (SCC). Please E-mail your request to SCC@dyncorp.com, or you may phone your request to 703-461-2100. If you telephone, please ask for the "Method 1664A Comparison Spreadsheet" and provide your E-mail address. You must have Microsoft's Excel 97 to run the spreadsheet.

Examples of a side-by-side comparison to determine if a conversion factor is warranted and to calculate the conversion factor if it is.

Example 1:

Steps 1-3: Eight samples were collected on a total of seven days spaced over a minimum of a 1-month period. For the samples collected on each day, three were analyzed by EPA Method 1664A and three by EPA Method 413.1 (for a total of 6 samples per day). All QC tests were performed and the results of the QC tests (including the matrix spike test) met the QC acceptance criteria in Method 1664A. Results of the triplicate analyses by each method on each day are listed in Table 1.

Table 1. Example results for side-by-side study*

		Results (mg/L)					
		Method 1664A			Method 413.1		
Date	Sample	rep #1	rep #2	rep #3	rep #1	rep #2	rep #3
8/13	1	13	18	12	23	28	29
8/17	2	10	12	14	21	19	17
8/22	3	22	26	22	41	36	35
8/25	4	12	17	15	26	27	24
8/30	5	20	17	12	26	23	27
9/4	6	37	35	31	52	48	40
9/9	7	11	14	13	21	20	25

*Data in this data set are estimations of data that could be produced in a side-by-side study and are not "real-world" data. For application of the comparison of results produced by alternative solvents to results produced by CFC-113 using "real-world" samples, see the Freon Replacement Study reports.

Step 4: The (natural log) log-transformed results are listed in Table 2:

Table 2. Log-transformed results

		Results (log mg/L)					
		Method 1664A			Method 413.1		
Date	Sample	rep #1	rep #2	rep #3	rep #1	rep #2	rep #3
8/13	1	2.56	2.89	2.48	3.14	3.33	3.37
8/17	2	2.30	2.48	2.64	3.04	2.94	2.83
8/22	3	3.09	3.26	3.09	3.71	3.58	3.56
8/25	4	2.48	2.83	2.71	3.26	3.30	3.18
8/30	5	3.00	2.83	2.48	3.26	3.14	3.30
9/4	6	3.61	3.56	3.43	3.95	3.87	3.69
9/9	7	2.40	2.64	2.56	3.04	3.00	3.22

Step 5: The 14 triplicate means of the log-transformed results are listed in Table 3:

Table 3: Triplicate means (M_{ij})

Sample (j)	Method 1664A (i=1)	Method 413.1 (i=2)
1	2.65	3.28
2	2.48	2.94
3	3.15	3.62
4	2.68	3.24
5	2.77	3.23
6	3.53	3.84
7	2.53	3.09

Step 6: The 14 triplicate standard deviations of the log-transformed results are listed in Table 4:

Table 4: Triplicate standard deviations (s_{ij})

Sample (j)	Method 1664A (i=1)	Method 413.1 (i=2)
1	0.215	0.125
2	0.168	0.106
3	0.096	0.084
4	0.176	0.060
5	0.261	0.084
6	0.090	0.134
7	0.124	0.117

Step 7: The mean-square error is:

$$\mathrm{MSE} = \frac{1}{14}[(0.215)^2 + (0.168)^2 + (0.096)^2 + \ldots + (0.134)^2 + (0.117)^2] = 0.020$$

Step 8: The method-specific means are:

$$M_{M1} = \frac{1}{7}\sum_{(j\in 1,..,7)} M_{1j} = \frac{1}{7}[2.65 + 2.48 + 3.15 + 2.68 + 2.77 + 3.53 + 2.53] = 2.83$$

Similarly, $M_{M2} = 3.32$.

$$M_{S1} = \frac{1}{2}[2.65 + 3.28] = 2.97$$

Similarly, $M_{S2} = 2.71$, $M_{S3} = 3.38$, $M_{S4} = 2.96$, $M_{S5} = 3.00$, $M_{S6} = 3.69$, and $M_{S7} = 2.81$.

$$M_o = \frac{1}{2}[2.83 + 3.32] = \frac{1}{7}\sum_{(j\in 1,..,7)}[2.96 + 2.71 + 3.38 + 2.96 + 3.00 + 3.69 + 2.81] = 3.07$$

Step 9: The RMSD is:

$$\text{RMSD} = \sqrt{\frac{1}{7}[(2.65-3.28)^2+((2.48-2.94)^2+\ldots+(2.53-3.09)^2} = 0.503$$

Step 10: The RMSD_{MAX} is:

$$\text{RMSD}_{\text{MAX}} = \sqrt{\frac{2*0.020}{3}*2.36} = 0.177$$

Step 11: The compared result is:

Because 0.503 > 0.177, the difference between the two methods is significant. Therefore, move on to step 12

Step 12: The mean square attributable to method/sample interaction is:

$$\text{MSINT} = \frac{1}{2}[(2.65-2.83-2.97+3.07)^2+(2.48-2.83-2.71+3.07)^2+\ldots+$$
$$(3.09-3.32-2.81+3.07)^2] = 0.017$$

Step 13: F_{calc} is:

F_{calc} = (0.017 / 0.020) = 0.85. Because 0.85 < 2.45, it cannot be concluded that there is a significant interaction between method and sample.

Because the RMSD was significant, and there was not a significant interaction between method and sample, a conversion factor should be calculated.

Step 14: The log-transformed factor is:

CF_L = 3.32 / 2.83 = 1.17.

Concentration adjustment for a new result:

Suppose a new value of 23 mg/L is obtained using method 1664A. The log-transformed value of this result is = 3.14. The converted value is:

$$X_R = \mathrm{EXP}[3.14 * (1.17)] = 39\ \mathrm{mg/L}$$

where X_R is the converted value in the original scale, and Y_N is the log-transformed value obtained using 1664A. Therefore, the result that would have been obtained had Method 413.1 been used is 39 mg/L.

Example 2:

Eight samples were collected on a total of seven days spaced over a minimum of a 1-month period. For the samples collected on each day, three were analyzed by EPA Method 1664A and three by EPA Method 413.1. Results of the analyses are listed in Table 5.

Table 5. Example results for side-by-side study*

		Results (mg/L)					
		Method 1664A			Method 413.1		
Date	Sample	rep #1	rep #2	rep #3	rep #1	rep #2	rep #3
8/13	1	20	17	21	25	28	32
8/17	2	21	20	23	29	26	26
8/22	3	29	27	31	23	25	26
8/25	4	34	36	34	25	29	28
8/30	5	30	27	32	22	24	24
9/4	6	16	18	14	19	18	20
9/9	7	22	18	21	21	19	23

*Data in this data set are estimations of data that could be produced in a side-by-side study and are not "real-world" data. For application of the comparison of results produced by alternative solvents to results produce by CFC-113 using "real-world" samples, see the Freon Replacement Study reports.

Step 4: The log-transformed results are listed in Table 6:

Table 6: Log-transformed results

		Results (log mg/L)					
		Method 1664A			Method 413.1		
Date	j	rep #1	rep #2	rep #3	rep #1	rep #2	rep #3
8/13	1	3.00	2.83	3.04	3.22	3.33	3.47
8/17	2	3.04	3.00	3.14	3.37	3.26	3.26
8/22	3	3.37	3.30	3.43	3.14	3.22	3.26
8/25	4	3.53	3.58	3.53	3.22	3.37	3.33
8/30	5	3.40	3.30	3.47	3.09	3.18	3.18
9/4	6	2.77	2.89	2.64	2.94	2.89	3.00
9/9	7	3.09	2.89	3.04	3.04	2.94	3.14

Step 5: The 14 triplicate means of the log-transformed results are listed in Table 7:

Table 7: Triplicate means (M_{ij})

Sample (j)	Method 1664A (i=1)	Method 413.1 (i=2)
1	2.96	3.34
2	3.06	3.29
3	3.37	3.20
4	3.55	3.31
5	3.39	3.15
6	2.77	2.94
7	3.01	3.04

Step 6: The 14 triplicate standard deviations of the log-transformed results are listed in Table 8.

Table 8: Triplicate deviations (s_{ij}) of the log-transformed results

j	Method 1664A (i=1)	Method 413.1 (i=2)
1	0.111	0.124
2	0.071	0.063
3	0.069	0.063
4	0.033	0.078
5	0.086	0.050
6	0.126	0.053
7	0.105	0.096

Step 7: The mean-square error is:

$$\text{MSE} = \frac{1}{14}[(0.111)^2 + (0.071)^2 + (0.069)^2 + \ldots + (0.053)^2 + (0.096)^2] = 0.0072$$

Step 8: The method-specific means are:

$$M_{M1} = \frac{1}{7}\sum_{(j\in 1,..,7)} M_{1j} = \frac{1}{7}[2.96 + 3.06 + 3.37 + 3.55 + 3.39 + 2.77 + 3.01] = 3.16$$

Similarly, $M_{M2} = 3.18$.

$$M_{S1} = \frac{1}{2}[2.96 + 3.34] = 3.15$$

Similarly, $M_{S2} = 3.18$, $M_{S3} = 3.28$, $M_{S4} = 3.43$, $M_{S5} = 3.27$, $M_{S6} = 2.86$, and $M_{S7} = 3.03$.

$$M_o = \frac{1}{2}[3.16 + 3.18] = \frac{1}{7}[3.15 + 3.18 + 3.28 + 3.43 + 3.27 + 2.86 + 3.03] = 3.17$$

Step 9: The RMSD is:

$$\mathrm{RMSD} = \sqrt{\frac{1}{6}[(2.96-3.34)^2+(3.06-3.29)^2+\ldots+(3.01-3.04)^2} = 0.231$$

Step 10: The RMSD$_{\mathrm{MAX}}$ is:

$$\mathrm{RMSD}_{\mathrm{MAX}} = \sqrt{\frac{2*0.0072}{3} \;*\; 2.36} \;=\; 0.106$$

Step 11: The compared result is:

Because 0.231 > 0.106, the difference between the two methods is significant. Therefore, move on to step 12.

Step 12: The mean square attributable to method/sample interaction is:

$$\mathrm{MSINT} \;=\; \frac{1}{2}[(2.96-3.18-3.15+3.19)^2+(3.06-3.18-3.18+3.19)^2+\ldots+ \\ (3.04-3.18-3.03+3.17)^2] = 0.092$$

Step 13: F$_{\mathrm{calc}}$ is:

F$_{\mathrm{calc}}$= (0.092 / 0.0072) = 12.77. Because 12.77 > 2.45, there is a significant interaction between method and sample. Therefore, a conversion factor is not warranted.

Appendix B

Annotated *Initial Demonstration of Laboratory Capability* for SPE

NOTE: The section numbers below refer to section numbers in EPA Method 1664A. Text in brackets and italics [*text*] is additional guidance and is not part of Method 1664A.

9.2 Initial demonstration of laboratory capability.

9.2.1 Method Detection Limit (MDL)—To establish the ability to detect HEM and SGT-HEM, the laboratory shall determine the MDL per the procedure in 40 CFR 136, Appendix B using the apparatus, reagents, and standards that will be used in the practice of this method. An MDL less than or equal to the MDL in Section 1.6 or less than 1/3 the regulatory compliance limit must be achieved prior to the practice of this method.

[*The MDL part of the demonstration with SPE does not need to be performed if the MDL was demonstrated previously with unmodified Method 1664A, and if the MDL is not expected to be affected by the measurement (see Section 9.1.2.1 of Method 1664A for this requirement). If the MDL is expected to be affected by use of SPE (or other modification), the MDL must be demonstrated per requirements in Sections 9.1.2.1 and 9.2.1 of Method 1664A.*]

9.2.2 Initial precision and recovery (IPR)—To establish the ability to generate acceptable precision and accuracy, the laboratory shall perform the following operations:

9.2.2.1 Determine the concentration of HEM and/or SGT-HEM in four samples of the PAR standard (Section 7.11) according to the procedure beginning in Section 11.

[*For this test, four 1-L aliquots of reagent water are spiked with hexadecane and stearic acid and processed through the entire analytical Method, including sample preservation, using SPE (or other modification) as an integral part of the Method.*]

9.2.2.2 Using the results of the set of four analyses, compute the average percent recovery (X) and the standard deviation of the percent recovery (s) for HEM and for SGT-HEM (if determined). When determining SGT-HEM, the true concentration (T) must be divided by 2 to reflect the concentration of hexadecane that remains after removal of stearic acid. Use the following equation for calculation of the standard deviation of the percent recovery:

Equation 1

$$s = \sqrt{\frac{\sum x^2 - \frac{(\sum x)^2}{n}}{n - 1}}$$

where:
n = *Number of samples*
x = *% Recovery in each sample*

9.2.2.3 Compare s and X with the corresponding limits for initial precision and recovery in Table 1. If s and X meet the acceptance criteria, system performance is acceptable and analysis of samples may begin. If, however, s exceeds the precision limit or X falls outside the range for recovery, system performance is unacceptable. In this event, correct the problem and repeat the test.

[*Table 1 of Method 1664A gives the QC acceptance criteria for the IPR test. These criteria must be met with SPE (or other modification) as an integral part of Method 1664A. If not, the modification must be improved and the test repeated. Only after the QC acceptance criteria have been met with SPE (or other modification) as an integral part of the test may the laboratory apply SPE (or other modification) to the sample matrix (see Appendix C).*]

Appendix C

Annotated *Equivalency Demonstration for Application of a Method Modification to Compliance Monitoring* for SPE

NOTE: The section numbers below refer to section numbers in EPA Method 1664A. Text in brackets and italics [*text*] is additional guidance and is not part of Method 1664A.

9.2.3 Equivalency demonstration for application of a method modification to compliance monitoring—To establish the ability of a modification of this method to recover an amount of HEM and/or SGT-HEM equivalent to the amount recovered by this method from a specific discharge/waste stream, proceed as follows:

9.2.3.1 Collect, extract, concentrate, and weigh the HEM or SGT-HEM in two sets of four aliquots of unspiked wastewater. One set of four wastewater aliquots is analyzed according to the protocol in Section 11 of this method and the other set of four aliquots is analyzed using the modified method.

[*For the equivalency demonstration with SPE, SPE constitutes the modification.*]

9.2.3.2 Calculate the average concentration of HEM and SGT-HEM for the set of results from this method and for the set of results from the modified method. The average concentration using the modified method must be 78 to 114 percent of the average concentration produced by this method for HEM and 64 to 132 percent of the average concentration produced by this method for SGT-HEM. If not, the modified method may not be used.

[*The QC acceptance criteria (78-114% for HEM and 64-132% for SGT-HEM) are identical to those for the IPR test (Section 9.2.2) but are applied to results obtained with LLE as the reference. This assures that if LLE recovers a lower amount of material from the sample matrix than recovered in the IPR test, the test will not be more stringent for SPE (or other modification).*]

NOTE: If the average concentration of the four results produced using this method and the average concentration of the four results produced using the modified method are below the minimum level (Section 1.6), and if the equivalency test of the modified method is passed for spikes of reference standards into reagent water (Section 9.2.2), the modified method is deemed to be equivalent to this method for determining HEM and or SGT-HEM on that specific discharge/waste stream.

[*This allowance for use of SPE (or other modification) when the concentration of HEM or SGT-HEM is below the ML addresses the issue that a reliable comparison between the LLE and SPE (or other modification) cannot be made at levels too low to be measured reliably.*]