

Guide for the Assessment of EPA Method 1664A

Based on NELAC Chapter 5, Appendix D.1 – Chemical Testing Method Review

Reference Method Identifier:
 Laboratory SOP Identifier:
 Rev.:
 Effective Date:
 Personnel Records Evaluated (names):
 Data Records Evaluated:

No	NELAC Reference	Question	Method Reference	Comments
		Does the laboratory determine the required initial precision and recovery (IPR)?	9.2.1	Procedure requires four replicates of a blank spike at 20 mg/L each of hexadecane/stearic acid. Required precision limit is 11% for HEM and 28% for SGT-HEM.
		Does the laboratory meet the technical requirements for equivalency demonstration for application of a method modification to compliance monitoring?	9.2.3, Guide, pg 3-4	Requires a side by side comparison of the modified method with the liquid-liquid extraction (LLE) method. Four replicates by each method on a real-world sample of each industrial waste category to which the test will be applied . Average concentration of the modified method when compared to the LLE version must be 78 – 114% for HEM and 64-132 for SGT-HEM. Special criteria apply if the average concentration in the waste stream is less than 5.0 mg/L. Note: See Guide, pg 3-4 for detailed discussion of how to apply the equivalency demonstration
		Does the laboratory perform the required calibration at 2 mg and 1000 mg?	10.0	
		Does the laboratory perform the required calibration verification at 2 mg and 1000 mg before and after each analytical batch?	9.5	
		Does the laboratory observe the correct sample storage conditions, preservation techniques, and holding time?		Storage: 4° C Preservation : pH ≤ 2 Holding time: 28 days

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562	D.1.1.1.a	Is the method blank processed along with and under the same conditions as the associated samples including all steps of the analytical procedure?	9.4.1	
563	D.1.1.1.a	Are procedures in place to determine if a method blank is contaminated?	9.4.2	Method defined level for blank contamination is > Minimum Level (ML) of 5.0 mg/L; MDL is 1.4mg/L. -- Section 1.6.
564	D.1.1.1.a	Is any affected sample associated with a contaminated method blank reprocessed for analysis or the results reported with appropriate data qualifying codes?	9.4.2	<i>All samples must be associated with an uncontaminated method blank before the results may be reported for regulatory compliance purposes.</i> NOTE: Laboratory may provide results to the client if flagged with statement saying results can't be used for compliance reporting.
	NOTE	<i>Analytical Batch:</i> <i>The set of samples started through the extraction process in a 12 hour shift, to a maximum of 20 field samples. Each analytical batch of 20 or fewer samples must be accompanied by a laboratory blank (Section 9.4), an ongoing precision and recovery sample (OPR, Section 9.6), and a matrix spike, (Section 9.3), resulting in a minimum of four analyses (1 sample, 1 blank, 1 OPR, and 1 MS) and a maximum of 23 analyses (20 field samples, 1 blank, 1 OPR, and 1 MS) in the batch. If greater than 20 samples are to be extracted in a 12-hour shift, the samples must be separated into analytical batches of 20 or fewer samples. [Section 18.2.2]</i>		
565	D.1.1.1.b	Is the method blank analyzed at a minimum of 1 per preparation batch?	9.4.1	
567	D.1.1.1.c	Does the method blank consist of a matrix that is similar to the associated samples known to be free of the analytes of interest?	9.4.1	Laboratory reagent water is used for the blank.
568	D.1.1.1.d	Is each method blank critically evaluated as to the nature of the interference and the effect on the analysis of each sample within the batch?	NELAC	
570	D.1.1.1.d.1	Are samples affected by blank contamination reprocessed or is the data appropriately qualified if the concentration of a targeted analyte in the blank is at or above the reporting limit as established by the test method or by regulation, AND is greater than 1/10 of the amount measured in any sample?	9.4.2	The method makes no allowance for reporting samples associated with a contaminated blank regardless of the level of contamination.
571	D.1.1.1.d.2	Are samples affected by blank contamination reprocessed or is the data appropriately qualified if the blank contamination otherwise affects the sample results as per the test method requirements or the individual project data quality objectives?	9.3.4.1	<i>If the interference is attributable to sampling, the site or discharge/waste stream should be resampled. If the interference is attributable to a matrix problem, the laboratory must modify the method, repeat the tests required in Section 9.1.2, and repeat the analysis of the sample and the MS (and MSD, if performed).</i>
			9.4.2	<i>All samples must be associated with an uncontaminated method blank before the results may be reported for regulatory compliance purposes.</i> NOTE: Laboratory may provide results to the client if flagged with statement saying results can't be used for compliance reporting.

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572	D.1.1.1.d.3	When a blank is determined to be contaminated, does the laboratory investigate the cause and take measures taken to minimize or eliminate the problem?	9.4.2	
573	D.1.1.1.d.3	Does the laboratory evaluate samples associated with a contaminated blank as to the best corrective action for the samples (e.g. reprocessing or data qualifying codes) and is the corrective action documented?	NELAC	
574	D.1.1.2.1.b	Is the OPR analyzed at a minimum of 1 per analytical batch?	9.6.1	
575	D.1.1.2.1.b	In those instances for which no separate preparation method is used (example: volatiles in water) is the batch defined as environmental samples that are analyzed together with the same method and personnel, using the same lots of reagents, not to exceed the analysis of 20 environmental samples?	18.2.2	An additional requirement also applies; batches must be analyzed within one twelve-hour shift.
576	D.1.1.2.1.c	If the matrix spike is used in place of the OPR are the acceptance criteria as stringent as for the OPR?	18.2.2	Not Allowed; both samples are required.
577	D.1.1.2.1.a	Is the Ongoing Precision and Recovery Standard (OPR) used to evaluate the performance of the total analytical system, including all preparation and analysis steps? Note: The OPR is a controlled matrix, known to be free of analytes of interest, spiked with known and verified concentrations of analytes.	9.1.5, 18.2.17	
580	D.1.1.2.1.c	Are all the components spiked in the OPR as specified by the mandated test method or other regulatory requirement or as requested by the client?	7.10	OPR is a hexadecane/stearic acid 1:1 mixture in acetone at 2mg/L final concentration of each component.
			7.12	Expiration: 6 months after preparation or sooner.
			9.7:	Recommendation: Monthly QC check using 2nd source standard
586	D.1.1.2.1.a	Are results of the OPR compared to established criteria?	9.6.2 and Table 1	HEM Recovery 78–114 % SGT-HEM Recovery 64–132 %
587	D.1.1.2.1.d	Are the results of the individual batch OPR calculated in percent recovery or other appropriate statistical technique that allows comparison to established acceptance criteria?	9.6.3	
588	D.1.1.2.1.d	Does the laboratory document the statistical calculation for the OPR?	9.6.3	Requires that each passing OPR be added to the statistical evaluation of the OPR performance. Does not specify the frequency of the update.
589	D.1.1.2.1.d	Is the individual OPR compared to the acceptance criteria as published in the mandated test method?	9.6.2	

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591	D.1.1.2.1.a	If the OPR is found to be outside of these criteria, is the analytical system considered “out of control”?	9.6.2	An OPR failure determines the system is out-of-control. Results cannot be reported for compliance purposes.
593	D.1.1.2.1.d	Are samples analyzed along with an OPR determined to be “out of control” considered suspect and the samples reprocessed and re-analyzed or the data reported with appropriate data qualifying codes?	12.3.3	<i>Results from tests performed with an analytical system that is not in control (Section 9) must not be reported or otherwise used for permitting or regulatory compliance purposes but do not relieve a discharger or permittee of timely reporting.</i> NOTE: Laboratory may provide results to the client if flagged with statement saying results can’t be used for compliance reporting.
599	D.1.1.3	Does the laboratory have procedures in place for tracking, managing, and handling matrix specific QC criteria including spiking appropriate components at appropriate concentrations, calculating recoveries and relative percent difference, evaluating and reporting results based on performance of the QC samples?	9.3.2.2, Guide, pg 27	1. <i>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.</i>
			9.3.1.1	2. <i>If, as in compliance monitoring, the concentration of HEM or SGT-HEM in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit, at 1 to 5 times the background concentration of the sample (determined in Section 9.3.2), or at the concentration of the OPR (Section 9.4), whichever concentration is highest.</i>
600	D.1.1.3.1.b	Is the frequency of the analysis of matrix specific QC samples determined as part of a systematic planning process (e. g. Data Quality Objectives) or as specified by the required mandated test method?	9.3	The method requires two different types of matrix spikes: <ul style="list-style-type: none"> ➤ A BATCH MS is required at a frequency of once per batch of 20 samples, or once per twelve hour shift. ➤ DISCHARGE MS, defined by industrial waste subcategories (40CFR parts 403 to 500), is required 1/20 samples of the industrial waste category. [section 18.2.3]
601	D.1.1.3.1.c	Do the components in the matrix spike include those specified by the mandated test method?	9.3.1.1	<i>If, as in compliance monitoring, the concentration of HEM or SGT-HEM in the sample is being checked against a regulatory concentration limit, the spiking level shall be at that limit, at 1 to 5 times the background concentration of the sample (determined in Section 9.3.2), or at the concentration of the OPR (Section 9.4), whichever concentration is highest</i>
602	D.1.1.3.1.c	Are any permit specified analytes, as specified by regulation or client requested analytes also included in the matrix spike?	NELAC	
609	D.1.1.3.1.d	Are the results from matrix spike/matrix expressed as percent recovery (%R), relative percent difference (RPD) or other appropriate statistical technique that allows comparison to established acceptance criteria?	9.3.3	

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610	D.1.1.3.1.d	Does the laboratory document the calculation for %R, RPD or other statistical treatment used in the matrix spike?	NELAC	
611	D.1.1.3.1.d	Are the results of the matrix spike compared to the acceptance criteria as published in the mandated test method?	9.3.4	MS HEM Recovery 78-114% SGT-HEM Recovery 64-132% MS/MSD for HEM 18 % MS/MSD for SGT-HEM 34 %
612	D.1.1.3.1.d	Where there are no established criteria for the matrix spike, does the laboratory determine internal criteria and document the method used to establish the limits?		Not Allowed
613	D.1.1.3.1.d	Are matrix spike results outside established criteria corrective action documented or is the data reported with appropriate data qualifying codes?	9.3.4.1	<i>If the results of the spike fail the acceptance criteria, and the recovery of the QC standard in the ongoing precision and recovery test (Section 9.6) for the analytical batch is within the acceptance criteria in Table 1, an interference is present. In this case, the result may not be reported or used for purposes regulatory compliance purposes and the laboratory must assess the potential cause for the interference. NOTE: Laboratory may provide results to the client if flagged with statement saying results can't be used for compliance reporting.</i> <i>If the interference is attributable to sampling, the site or discharge/waste stream should be re-sampled. If the interference is attributable to a matrix problem, the laboratory must modify the method, repeat the tests required in Section 9.1.2, and repeat the analysis of the sample and the MS (and MSD, if performed).</i>
614	D.1.1.3.2.b	Is the frequency of the analysis of matrix duplicates determined as part of a systematic planning process (e. g. Data Quality Objectives) or as specified by the mandated test method?	9.3	MSDs are recommended but not required.
615	D.1.1.3.2.c	Are matrix duplicates performed on replicate aliquots of actual samples?	8.2	Aliquots must be used. MSDs are recommended, not required.
616	D.1.1.3.2.d	Does the laboratory document the calculation for relative percent difference or other statistical treatments for the matrix duplicate?	NELAC	Equation 3, Section 9.3.5
617	D.1.1.3.2.d	Are results of the matrix duplicate compared to the acceptance criteria as published in the mandated test method?	9.3.6	MSDs are recommended but not required.
618	D.1.1.3.2.d	Where there are no established criteria, does the laboratory determine internal criteria and document the method used to establish the limits for matrix duplicate?		Not Allowed

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619	D.1.1.3.2.d	For matrix duplicate results outside established criteria, is corrective action documented or the data reported with appropriate data qualifying codes?	9.3.6	<i>The relative percent difference for duplicates shall meet the acceptance criteria in Table 1. If the criteria are not met, the analytical system is judged to be out of control, and the problem must be immediately identified and corrected, and the analytical batch reanalyzed. Note that section 12.3.3 forbids reporting results from analytical systems deemed to be out of control.</i>
626	D.1.2	Are all procedures used to determine Limit of Detection documented, including the quality system matrix type and all supporting data?	NELAC	
627	D.1.2.1	Does the laboratory utilize test methods that provide a detection limit that is appropriate and relevant for the intended use of the data?	9.2.1	Allows the MDL to be 1/3 rd of the regulatory compliance limit.
628	D.1.2.1	Are LODs determined by the protocol in the mandated test method or applicable regulation?	9.2.1	Requires the use of 40CFR, Appendix B to establish the MDL
631	D.1.2.1.b	Are LODs determined each time there is a change in the test method that affects how the test is performed, or when a change in instrumentation occurs that affects the sensitivity of the analysis?	9.1.2, Guide, pg 20	Alterations to the method are tightly controlled and the modified method must meet stringent criteria for performance
632	D.1.2.1.c	Does the laboratory have established procedures to relate LOD with LOQ?	NELAC	
633	D.1.2.1.d	Is the LOD verified annually for each quality system matrix, method and analyte according to the procedure specified in C.3?	NELAC	
634	D.1.2.2.a	Are any established LOQ above the LOD?	1.6, 18.2.15	Method-specified Minimum Level (ML) = 5.0mg/L.
635	D.1.2.2.b	Is the LOQ verified annually for each quality matrix, method and analyte according to the procedure specified in C.3?	NELAC	
636	D.1.3	Are the procedures for data reduction, such as use of linear regression documented?	NELAC	
637	D.1.4.a	Do the source standards comply with 5.5.6.2.2.2?	NELAC	
638	D.1.4.b	In methods where the purity of reagents is not specified, is analytical reagent grade used?	7.0	
639	D.1.4.b.1	Are reagents of lesser purity than those specified by the test method never used?	7.5	Recommendation not to use powdered sodium sulfate.
640	D.1.4.b.1	Are the labels on the container checked to verify that the purity of the reagents meets the requirements of the particular test method? (Recommendation)	NELAC	

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641	D.1.4.b.1	Does the laboratory document the checks to verify that the purity of the reagents meets the requirements of the particular test method?	NELAC	
642	D.1.4.b.2	Is the quality of water sources monitored and documented?	NELAC	
643	D.1.4.b.2	Does the quality of water sources meet method specified requirements?	NELAC	
652	D.1.6.b	Is glassware cleaned to meet the sensitivity of the test method?	4.3	Specific requirements: 1. Detergent wash 2. Bake out OR solvent wash 3. Before use, dry boiling flask at 105-110° C, store in desiccator
653	D.1.6.b	Are any cleaning and storage procedures not specified by the test method documented in laboratory records and SOPs?	6.1.3	Bottles and liners must be lot-certified to be free of artifacts by running laboratory blanks according to this method (per Section 9.4). If blanks from bottles and/or liners without cleaning or with fewer cleaning steps than required above show no detectable materials, the bottle and liner cleaning steps that do not [<i>sic</i>] eliminate these artifacts may be omitted.
			6.1.2.1	Sample collection bottles must be solvent rinsed or baked at 200-250° C for 1 hour minimum prior to use.
			6.1.2.2	Bottle cap liners must be washed, solvent rinsed, AND baked at 110-200° C prior to use.

Procedural Details of EPA Method 1664A

Procedural Step, if not covered above	Method Reference	Comments
Sample size – 1 L	11.1.1	
Return sample to room temperature if necessary.	11.1.1	
Determine the pH of sample while in the original container. Use glass stirring rod to withdraw a drop of aqueous layer and test with pH paper. Wash glass rod into the separatory funnel [SF] with hexane.	11.2.1.3	DO NOT determine sample pH at the time of sample log-in.
If pH of sample is ≥ 2 , adjust with HCL or H ₂ SO ₄ solution to ≤ 2 in the original sample container	11.2.2	
Add equivalent amount of acid to both the MS and OPR samples that are being prepared in field sample containers	11.2.4	Must prepare QC samples in original sample containers containing 1 L reagent water.
Determine actual sample volume in the sample container and transferred to the SF	11.1.4	
If sample size is less than 950 mL, add sufficient reagent water to a final volume of 1 L	11.0 Note	
Rinse sample container and cap with hexane (30mL) and transfer to the SF.	11.3.3	
Shake for ~2 minutes, allow layers to separate, drain aqueous layer into original sample container along with small volume of hexane. Drain hexane from SF through small amount of Na ₂ SO ₄ into tared boiling flask. Repeat with 2 more volumes of hexane (30 mL)	11.3.4 to 11.3.12	
Remove solvent by distillation until temperature in the distillation head reaches 70°C or the flask appears almost dry. Sweep flask with air to remove solvent vapor.	11.4.2	
Dry the boiling flask for 30 -45 minutes at 70 ± 2° C. Cool to RT in a dessicator for a minimum of 30 minutes. Repeat the drying cycle as needed to reach constant weight.	11.4.4	
Calculate final sample weight, report results to three significant figures for results above 10 mg/L and two significant figures for results below 10 mg/L.	12.3	
Do not report results below MDL unless required by the permitting authority or permit.	12.3.2	