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Association of Metropolitan Sewerage Agencies

December 10, 2001

Method 1631 – Proposed Rule
Comment Clerk (W-01-05)
Water Docket (4101)
U.S. Environmental Protection Agency
Ariel Rios Building
1200 Pennsylvania Avenue, NW
Washington, DC 20460

Re: *Guidelines Establishing Test Procedures for the Analysis of Pollutants; Measurement of Mercury in Water; Revisions to EPA Method 1631; Proposed Rule, 66 Fed. Reg. 51518 (October 9, 2001)*

Dear Sir or Madam:

The Association of Metropolitan Sewerage Agencies (AMSA) is pleased to provide comments on the U.S. Environmental Protection Agency's (EPA's) *Guidelines Establishing Test Procedures for the Analysis of Pollutants; Measurement of Mercury in Water; Revisions to EPA Method 1631*. Founded in 1970, AMSA represents the interests of over 260 of the nation's publicly owned wastewater utilities (POTWs). AMSA members serve the majority of the sewered population in the United States and collectively treat and reclaim over 18 billion gallons of wastewater every day. Given EPA's new water quality criterion for methyl mercury, and the likelihood that POTWs soon will see increasingly stringent permit limits for mercury, AMSA believes a reliable, robust test method for measuring mercury must be available.

AMSA agrees with several of EPA's proposed changes that attempt to make Method 1631 results more reliable. However, AMSA continues to believe that Method 1631 is a very sensitive research method that may not be well suited for use as a routine monitoring method. AMSA supports the validation of Method 245.7, a method nearly as sensitive as Method 1631 but less burdensome and which can be preformed at a 30 to 40 percent cost savings. We encourage EPA to continue its efforts to approve Method 245.7 to ensure its availability to the regulated community.

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AMSA's specific comments on Method 1631 are outlined below. AMSA's comments include suggested changes to make the method more user-friendly, and sample analytical information demonstrating that the use of high-density polyethylene (HDPE) equipment and containers for sample collection does not compromise data quality.

Clean Techniques

EPA proposes to modify the text of Method 1631 to change "should" to "must" for a number of clean technique and quality control (QC) provisions, effectively making these previously optional steps mandatory procedures. At the same time, EPA proposes to add a provision to Method 1631 that would allow a permittee or industrial user to elect not to implement the required clean techniques and QC provisions "in its discretion and at its peril." Regulatory/control authorities, on the other hand, would be required to comply with these clean technique provisions in all instances. AMSA supports the proposed approach as the most appropriate option given the delicate balance that must be achieved between collecting data accurately, cost-effectively, and efficiently and the fact that such data later can assume significant evidentiary weight in an enforcement proceeding.

Under EPA's proposal, permittees would have the discretion to select the method procedures necessary to ensure sampling data are accurate. This proposal is appropriate, as permittees are familiar with the characteristics of their effluent and understand the level to which clean techniques must be followed to ensure accurate results. Permittees assume the liability associated with their sampling and recognize that poor data can have adverse consequences in the regulatory or enforcement context.

In contrast, EPA and state regulators do not have the same in-depth knowledge of a plant's effluent and are not directly liable for inaccurate sampling. In fact, under the current system permittees may be precluded from raising contamination as a defense in an enforcement action, or at a minimum bear the heavy burden of proving contamination of data generated by EPA or the states. It is imperative that EPA and the states be required to produce high quality data by using all of the necessary clean techniques in addition to the quality control requirements. These requirements will reduce the risk that enforcement decisions will be based in part on contaminated state or federal sample results.

Specific Technical Comments

Container Types

AMSA requests a revision of Method 1631 to allow collecting samples, especially composites, in high-density polyethylene (HDPE) containers, shipping them to the laboratory for preservation, and transferring to Teflon containers within 48 hours. The proposed changes to Method 1631 mandate the use of either Teflon or glass containers. While Teflon is the material of choice, depending on container size availability may be limited or cost-prohibitive. Glass is more economical and readily available, but impractical for shipping due to the high incidence of breakage.

AMSA laboratory data at Appendix A demonstrates that the use of HDPE equipment and containers for sample collection does not compromise data quality. These data include composite samples collected using discrete samplers and HDPE sampling materials.

Additional information at Appendix B shows that samples can be collected in HDPE containers and transported to the laboratory for preservation, then transferred to Teflon containers within 48 hours without sample compromise. Data show that samples can be maintained at room temperature in HDPE bottles for approximately 10 days before sample degradation begins.

Blank Acceptance Criteria
Most of the blank acceptance criteria referenced throughout the method are required to be less than or near the method detection limit (MDL) of 0.2 ng/L. An MDL of 0.2 ng/L is not required to meet performance specifications in this method. Section 9.2.1 states that *"...an MDL that is less than or equal to the MDL listed in Section 1.5 or one-third the regulatory compliance limit, whichever is greater"* is acceptable. For example, if the regulatory compliance level is 12 ng/L, the permittee is allowed up to 4 ng/L for a calculated MDL. If the calculated MDL were 4 ng/L, it would be impossible to measure the level of contamination at or near 0.2 ng/L since the laboratory has not demonstrated capability of measuring (or differentiating from zero) at this level. Therefore, AMSA instead recommends that reagent and method blank acceptance criteria be linked directly to the specific MDL achieved by an individual laboratory.

Section 12.5 directs the user to report reagent blanks to a level of 0.2 ng/L. This provision implies that the method is not capable of measuring to two decimal places. However, the reagent blank acceptance criterion in Section 9.4.3 is 0.25 ng/L. Since the method is not sensitive enough to measure at the 1/100th level, the blank acceptance criterion should be revised accordingly to ensure it is not beyond the capabilities of the method.

Blank Subtraction Criteria
Section 12.5.2 states "...the concentration of Hg in the method blanks or field blanks associated with the sample may be subtracted from the results for that sample...". While AMSA supports the concept of blank subtracting at extremely low concentrations, recognizing that some contamination may be inevitable, AMSA recommends that EPA develop criteria addressing the acceptable scenarios for which blank subtraction is appropriate. Specifically, AMSA requests that EPA clarify the concentration levels at which blank subtractions are appropriate.

Calibration Blanks
It is rarely practical to treat an automated system in the same way as a manual system, yet this is mandated by Section 9.4.2. Requiring three calibration blanks to be analyzed during each calibration precludes the use of automated data handling systems. In contrast, no other EPA method for low-level metals contains such a requirement. AMSA recommends this requirement be deleted to allow for the use of automated systems.

Calibration
The calibration requirements in section 10.3 of draft Method 1631D are inconsistent with other EPA metals methods, which allow the use of either a response factor approach or weighted linear regression

for calibration. Although the EPA guidance document for Method 1631 (page 5-16) allows for the use of weighted linear regression with automated systems, draft Method 1631D continues to require the use of calibration factors. This necessitates manual data manipulation when using automated systems. The reasons for using weighted linear calibration curves are the same regardless of the concentration range. Therefore, AMSA recommends that the weighted linear regression procedure be incorporated into Method 1631D.

Section 10.2.2 in the current method requires a minimum of five non-zero points for calibration. While this approach may be appropriate for a wide range of concentrations in the samples, it is meaningless when the sample concentration range is very narrow and often very low and close to the method MDL. In these cases, performing five-point calibration needlessly increases analytical labor and method costs. AMSA requests an approach that provides a range for the number of calibration standards (i.e., three to five) and specifies their concentration ranges based on actual sample concentrations.

Suggested Changes/Improvements

All-Inclusive QC Table
AMSA requests that all the Method 1631 QC acceptance criteria be included in one summary table to facilitate determinations by permittees of whether all criteria were met. Some of the pertinent criteria are currently found in Table 2. Having all QC acceptance criteria in one place will minimize potential omissions of specific QC requirements.

Standardization of EPA Methods
In the *Federal Register* preamble, EPA notes that one of the reasons for the rulemaking is to "...propose improvements and clarifications to EPA Method 1631 to make this test method more consistent with other approved methods and current practices and easier to use." Several metals methods have been revised recently and some are in the process of being validated. Great strides have been taken to standardize the format and content of these methods. Method 1631, however, remains an exception as it differs in a number of ways from other methods such as 245.7, 200.7, and 200.9. Some of the obvious differences include the requirements for automation sections and calibration requirements.

Conclusion

AMSA appreciates the opportunity to provide comments on the proposed revisions to Method 1631. While AMSA understands the importance of sensitive analytical tools like Method 1631, we again urge EPA to continue efforts to approve Method 245.7 to ensure its availability to the regulated community. If you have any questions about our comments, please contact me at 202/833-9106 or *chornback@amsa-cleanwater.org*.

Sincerely,

Chris Hornback
Manager, Government Affairs

APPENDIX A

Episode 4902 Clean vs. Ultra-Clean

Samples Collected: June 8, 1998

Sample ID	* ULTRA CLEAN Hg Concentrations (Ng/L)	# CLEAN Hg Concentrations (Ng/L)
Grab Samples		
Wastewater Process Samples		
PF-O	2.38	2.11
PF-Duplicate-0	2.92	2.31
PF-2	5.08	2.17
PF-4	2.64	2.00
PF-6	2.01	2.33
Field Blanks		
FB-0	0.240	0.210
FB-2	0.340	<0.200
FB-4	<0.200	<0.200
FB-6	<0.200	0.360
Manual Composite		
Wastewater Process Sample		
MC-PF-0-6	3.42	1.42
MC-PF-Duplicate	-----	2.68
Field Blank		
MC-FB-0-6	<0.200	<0.200
Automated Composite		
Wastewater Process Sample		
AC-PF	1.65	1.82
AC-PF-Duplicate	2.54	2.38
Field Blank		
AC-FB	0.270	<0.200
Trip Blank	<0.200	-----

* <u>ULTRA CLEAN</u>
Teflon sampling equipment construction. Equipment cleaning protocol is found in Method 1631.

\# <u>CLEAN</u>
HDPE sampling equipment construction. Cleaning protocol consists of washing the equipment with Contrad soap, rinse with water, 10% HNO3 soak for 24 hours, DI water and high purity water rinse.

Mean (x)	2.135	1.799
Number (n)	11	11
Std. Dev. (s)	1.482	0.817
Variance (s2)	2.196	0.667
S	4.722	
/t/	***0.070***	
/t/ of n-2=9 is 2.262		

Episode 4903 Clean vs. Ultra-Clean

Samples Collected: July 28, 1998

	* ULTRA CLEAN	# CLEAN
Sample ID	**Hg Concentrations (Ng/L)**	**Hg Concentrations (Ng/L)**
Grab Samples		
Wastewater Process Samples		
PF-O	2.35	2.71
PF-Duplicate-0	2.51	2.62
PF-2	2.74	3.40
PF-4	2.41	2.82
PF-6	4.36	14.9
Field Blanks		
FB-0	<0.200	<0.200
FB-2	<0.200	<0.200
FB-4	<0.200	<0.200
FB-6	<0.200	<0.200
Manual Composite		
Wastewater Process Sample		
MC-PF-0-6	2.04	2.83
MC-PF-Duplicate	-----	2.69
Field Blank		
MC-FB-0-6	<0.200	<0.200
Automated Composite		
Wastewater Process Sample		
AC-PF	2.17	1.81
AC-PF-Duplicate	2.29	3.10
Field Blank		
AC-FB	<0.200	<0.200
Trip Blank	<0.200	-----

* ULTRA CLEAN
Teflon sampling equipment construction. Equipment cleaning protocol is found in Method 1631.

CLEAN
HDPE sampling equipment construction. Cleaning protocol consists of washing the equipment with Contrad soap, rinse with water, 10% HNO_3 soak for 24 hours, DI water and high purity water rinse.

Mean (x)	2.609	4.098
Number (n)	8	9
Std. Dev. (s)	0.739	4.073
Variance (s2)	0.545	16.592
S	3.559	
/t/	***0.528***	
/t/ of n-2=9 is 2.447		

APPENDIX B

Mercury Preservation & Container Type Study

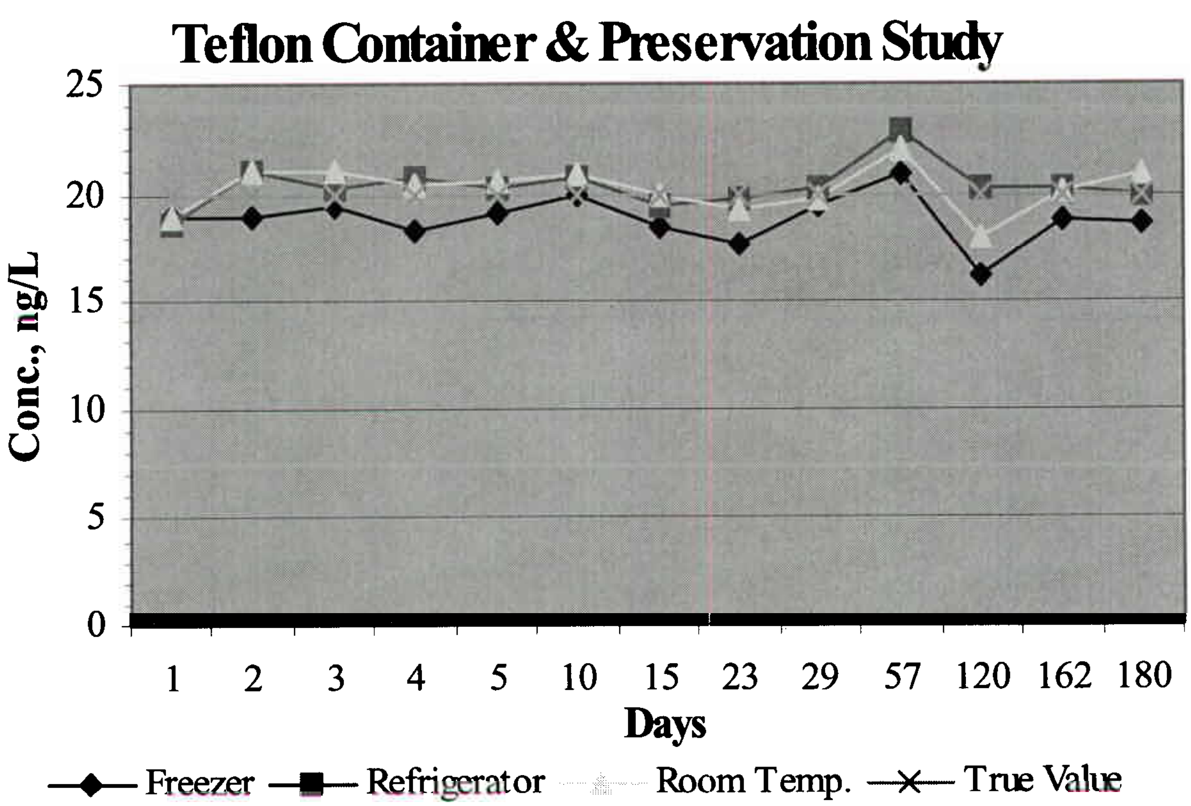
Teflon Containers

EPA Method 245.7
All Samples Spikes = 20 ng/L

TRS = Teflon Container; Refrigerated Sample
TRTS = Teflon Container; Room Temperature Sample
TFS = Teflon Container; Frozen Sample

	Day	TRS1	TRS2	TRS3	*Avg*	TRTS1	TRTS2	TRTS3	*Avg*
6/23/97	1	19.2	18.9	18.1	*18.7*	19.3	19.2	18.4	*19.0*
6/24/97	2	21.6	20.3	21.3	*21.1*	21.6	21.1	20.7	*21.1*
6/25/97	3	21.0	19.9	20.1	*20.3*	21.0	20.9	21.3	*21.1*
6/26/97	4	21.4	21.1	19.6	*20.7*	20.6	20.4	20.3	*20.4*
6/27/97	5	20.3	20.2	20.4	*20.3*	20.3	20.6	21.0	*20.6*
7/2/97	10	20.9	20.4	20.8	*20.7*	20.6	21.0	21.2	*20.9*
7/7/97	15	19.3	19.7	19.2	*19.4*	19.9	20.0	20.1	*20.0*
7/1597	23	20.0	20.0	19.3	*19.8*	18.8	19.4	19.7	*19.3*
7/21/97	29	19.8	20.4	20.9	*20.3*	19.5	20.5	19.3	*19.7*
8/18/97	57	22.9	22.5	23.0	*22.8*	22.2	22.0	22.1	*22.1*
10/20/97	120	18.8	22.0	19.9	*20.2*	17.3	17.7	18.6	*17.9*
12/1/97	162	20.1	19.5	21.3	*20.3*	19.5	20.6	20.3	*20.1*
12/19/97	180	19.3	20.0	20.2	*19.9*	20.4	21.3	21.1	*20.9*
Avg		20.3	20.4	20.3	*20.3*	20.1	20.3	20.3	*20.2*
Min		18.8	18.9	18.1	*18.6*	17.3	17.7	18.4	*17.8*
Max		22.9	22.5	23.0	*22.8*	22.2	22.0	22.1	*22.1*
Std. Dev.		1.2	1.0	1.2	*1.1*	1.2	1.1	1.1	*1.1*

	Day	TFS1	TFS2	TFS3	*Avg*
6/23/97	1	19.1	18.8	19.2	*19.0*
6/24/97	2	19.7	19.7	17.2	*18.9*
6/25/97	3	21.6	20.9	15.8	*19.4*
6/26/97	4	19.8	19.3	15.8	*18.3*
6/27/97	5	21.2	19.7	16.5	*19.1*
7/2/97	10	21.1	21.2	17.5	*19.9*
7/7/97	15	20.0	19.5	15.6	*18.4*
7/15/97	23	19.6	18.0	15.1	*17.6*
7/21/97	29	20.8	21.0	16.3	*19.4*
8/18/97	57	21.8	22.2	18.5	*20.9*
10/20/97	120	17.5	17.5	13.2	*16.1*
12/1/97	162	16.4	20.1	20.1	*18.8*
12/19/97	180	15.9	19.5	20.8	*18.7*
Avg		19.6	19.8	17.0	*18.8*
Min		15.9	17.5	13.2	*15.5*
Max		21.8	22.2	20.8	*21.6*
Std. Dev.		1.9	1.3	2.1	*1.8*

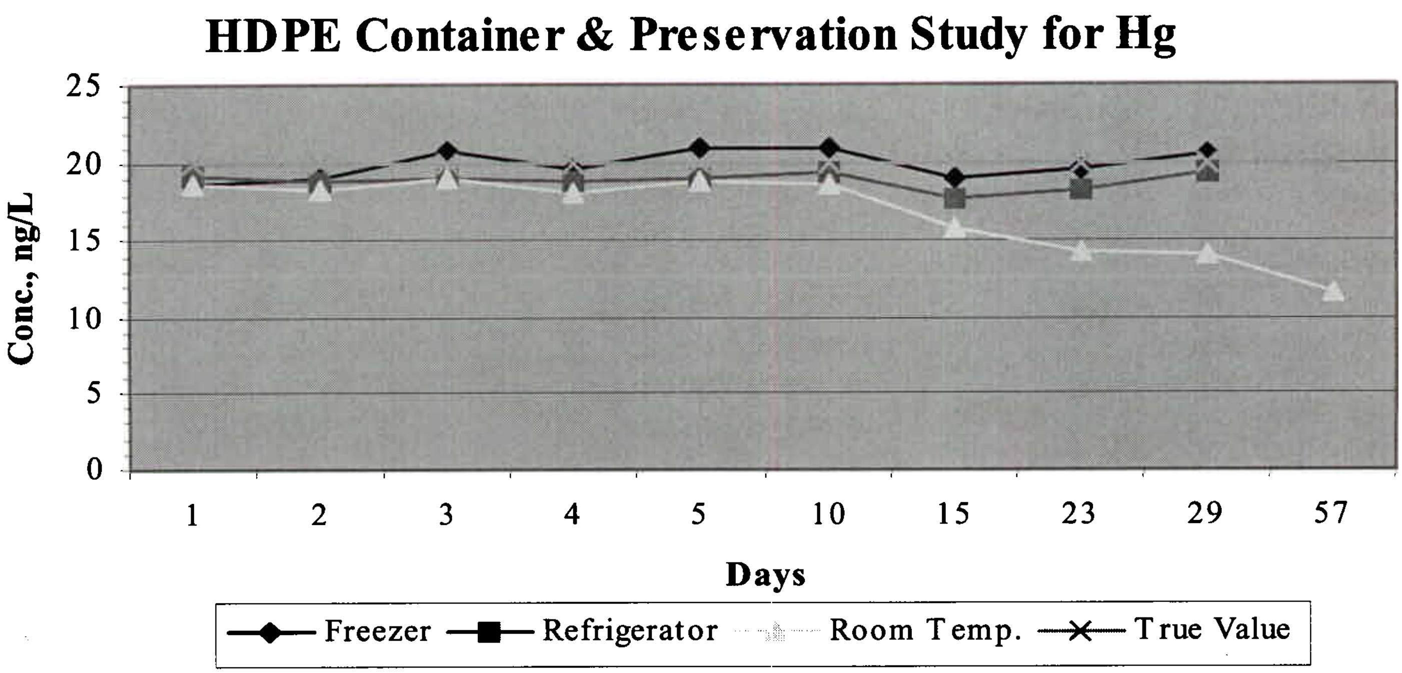


HDPE Containers
EPA Method 245.7
All Samples Spikes = 20 ng/L

HRS = HDPE Container; Refrigerated Sample
HRTS = HDPE Container; Room Temperature Sample
HFR = HDPE Container; Frozen Sample

	Day	HRS1	HRS2	HRS3	*Avg*	HRTS1	HRTS2	HRTS3	*Avg*
6/23/97	1	20.0	16.7	21.0	*19.2*	18.5	18.2	19.4	*18.7*
6/24/97	2	17.2	20.0	19.7	*19.0*	18.1	18.4	18.7	*18.4*
6/25/97	3	17.8	19.9	19.5	*19.1*	19.0	19.2	19.2	*19.1*
6/26/97	4	18.0	19.7	19.2	*19.0*	18.3	18.1	18.1	*18.2*
6/27/97	5	17.9	19.3	19.9	*19.0*	19.5	18.5	18.7	*18.9*
7/2/97	10	19.3	19.6	19.3	*19.4*	18.8	19.0	18.1	*18.6*
7/7/97	15	18.1	18.2	17.0	*17.8*	15.2	16.1	16.2	*15.8*
7/15/97	23	17.9	19.0	18.2	*18.4*	14.5	14.3	14.1	*14.3*
7/21/97	29	19.4	20.2	18.6	*19.4*	14.7	14.0	13.8	*14.2*
8/18/97	57					13.2	12.5	9.4	*11.7*
Avg		18.4	19.2	19.1	*18.9*	17.0	16.8	16.6	*16.8*
Min		17.2	16.7	17.0	*16.95*	13.2	12.5	9.4	*11.7*
Max		20.0	20.2	21.0	*20.38*	19.5	19.2	19.4	*19.4*
Std. Dev.		0.9	1.1	1.1	*1.1*	2.3	2.4	3.2	*2.7*

	Day	HFS1	HFS2	HFS3	*Avg*
6/23/97	1	18.9	19.2	18.0	*18.7*
6/24/97	2	18.3	20.2	18.9	*19.1*
6/25/97	3	22.5	20.3	19.7	*20.8*
6/26/97	4	19.0	20.7	19.1	*19.6*
6/27/97	5	22.0	19.9	20.8	*20.9*
7/2/97	10	20.8	20.6	21.5	*21.0*
7/7/97	15	19.7	18.8	18.8	*19.1*
7/15/97	23	18.6	21.0	19.3	*19.7*
7/21/97	29	21.5	20.7	19.7	*20.6*
Avg		20.1	20.2	19.5	*19.9*
Min		18.3	18.8	18.0	*18.4*
Max		22.5	21.0	21.5	*21.7*
Std. Dev.		1.6	0.7	1.1	*1.1*



HDPE Container & Preservation Study for Hg
Conc., ng/L
25
20
15
10
5
0
1
2
3
4
5
10
15
23
29
57
Days
Freezer
Refrigerator
Room Temp.
True Value