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December 12, 2000

Dr. Maria Gomez-Taylor
U.S. Environmental Protection Agency
Engineering and Analysis Division
Ariel Rios Building (MC 4303)
1200 Pennsylvania Ave., N.W.
Washington, DC 20460

Dear Maria,

The AMSA Mercury Workgroup would like to take this opportunity to provide comments on the *Guidance for Implementation and Use of EPA Method 1631 (40 CFR part 136)* document published October 2000 (EPA 821-B-00-xxx). The guidance document shows that improvements have been made in the method. These improvements provide the user clearer instruction on performance of certain tasks and remove the ambiguity from some issues.

Although the document contains useful information, some issues still need revision before this document becomes final. More specific information/instructions would provide further clarification on issues that are still vague and confusing. Issues of greatest concern are the statements made in this guidance document that directly conflict with information previously received from EPA, both orally and in writing.

Unfortunately, this guidance document still reflects that Method 1631 is a very sensitive research method not suitable for use as a rugged, production-type, routine monitoring method. Because of this lack of robustness, the number of laboratories proficient in using Method 1631 is severely limited.

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Primary concerns with the *Guidance for Implementation and Use of EPA Method 1631 (40 CFR part 136)*:

1. Use of calibration factors or weighted regression for calibration and calculation of data.

- a) Page 5-11 of the FAQ section discusses the use of unweighted regression, e.g., slope, intercept and correlation coefficient. It clearly states that unweighted regression is prohibited and only weighted regression or the calibration factor (CF) approach may be used.

The question of using unweighted regression with automated sample introduction and data acquisition systems was posed to EPA by HRSD staff on December 2, 1999. Maria Gomez-Taylor responded to HRSD as follows, by her memo dated December 15, 1999:

“Regarding the use of calibration factors versus a linear calibration curve, AMS recommends the use of calibration factors over the use of a linear calibration curve for calibration of the instrumentation specified in the method....AMS is aware that many instrument manufacturers employ software that allows for automated calculations based on a linear calibration curve. Accordingly, AMS does not wish to preclude the use of automated calculations, and therefore, will allow the use of automated calculations based on a linear calibration curve. However, AMS is encouraging instrument manufacturers to switch to weighted regressions instead of unweighted regressions in the future.”

Conflicting guidance and allowances have been issued from the same EPA office. As of December 8, 2000, a manufacturer of one of the first two automated systems capable of meeting the performance criteria in Method 1631, had not been contacted by EPA regarding the use of weighted regression calculations. This conflicting information is very confusing to the method users, instrument manufacturers, and permittees. Once an issue like this is raised, we believe that EPA should make every effort to communicate their expectations to *all* instrument manufacturers and encourage further development of the best available technology (BAT).

Since Method 1631 was drafted, instruments have become available that can fully automate analysis and data handling. However, certain requirements in the method are specific to manual analysis and either cannot be performed with automated systems, severely limit or even preclude their use

- b) Inconsistencies in calibration requirements for Method 1631 as compared with other metals methods also cause concern. Since 1994, EPA has included the development of linear dynamic ranges (LDR), as part of the initial demonstration of performance for metals methods. Sample concentrations greater than 90% of the LDR must be diluted and reanalyzed, regardless of the

calibration range. Initial demonstration of performance for Method 1631 does not require the determination of a LDR. Therefore, the assumption could be made that all instruments are capable of calibrating from the analytical ML (~0.5 ng/L) to 100 ng/L – the entire working range of the method. Due to the sensitive nature of this method, analytical capabilities at the upper end of the calibration curve, especially when using weighted linear regression, are of great concern.

- c) No consideration is given to sample concentration when developing the calibration curve range. Traditionally, good laboratory practices dictate calibration encompassing the expected range of sample concentrations. Since many new NPDES permits reflect limits at the WQS of 12 ng /L Hg, the samples are expected to be this level or less. However the upper end of the calibration curve is an order of magnitude higher than the WQS. We believe that calibrating in relation to sample concentration ranges is a more prudent practice than use of calibration factors, or weighted linear regression.

2. Treatment of matrix interferences.

- a) High concentrations of organic matter are referenced as an interferent for Method 1631. Steps such as additional aliquots of BrCl and photo-oxidation with ultra-violet light are suggested as means to overcome these interferences. However, specific information on implementation of these procedures is not included in either the method, or guidance document.
- b) There are two major concerns with increasing the amount of BrCl and using heat to increase oxidation capabilities. The additional amount of BrCl that can be added without significantly diluting the matrix is not addressed in either the method, or guidance document. A potential solution of increasing the concentration of the BrCl for increased organic matter oxidation is not explored in the guidance document. Acceptable concentrations and volumes of additional reagents should be addressed and be clear to the method users.
- c) Use of heat with increased amounts of BrCl is also suggested. Maximum temperatures and heating times should be clearly stated. Application of heat to samples being analyzed for low-level mercury should be used with extreme caution because of the volatile nature of mercury and the uncertain oxidation states of mercury at the time of heating
- d) A photo-oxidation procedure using ultra-violet light is not sufficiently explained. As currently written, use of this step is very nebulous and may result in incomplete oxidation of organic matter. The concentration ranges of organic matter (e.g., TOC) for which additional BrCl and/or photo-oxidation would be applicable should also be stated in the guidance document. There may be some instances when the organic matter concentration of the sample(s) may exceed the capability

of the method. Considering the scope and application of Method 1631, such cases may be relatively common.

- e) The nonhomogeneity of sample matrices caused by solids content is not addressed in either Method 1631 or in the guidance document. It is a well known and widely accepted fact the mercury is strongly associated with the solid content in sample matrices. Because of this inherent nonhomogeneity, precision for total mercury analysis may be very poor, resulting in failed QC (e.g., MS/MSD). None of the techniques outlined in the method and guidance document deal with this situation.
- f) Section 1.1 of Method 1631 describes the monitoring programs for which the method 1631 is applicable. Several of the programs listed, deal with samples that have significant solids contents. Although POTW effluents do not typically fall into the high solids category, several other sample types (e.g., Industrial Pretreatment Program, Groundwater Remediation, etc.) characteristically contain sufficient amounts of solids to affect the reproducibility of results. This further shows the over-sensitive nature of this method and its extremely limited application.

1. Allowance of matrix specific MDLs.

- a) An excessive amount of information is required for submittal to the regulatory authority to demonstrate that an effluent-specific MDL and ML is appropriate. Section 9.2.1 of Method 1631 states that 40 CFR Part 136 Appendix B shall be used for the determination of the MDL. Appendix B allows for the development of a MDL in the sample matrix, however the requirements listed in the guidance document exceed those addressed in Appendix B.
- b) Although the analyst should demonstrate the capability to successfully perform Method 1631, confirmation of the “out-of-specification” MS/MSD recovery by a second laboratory and identification of the potential interferent(s) are unreasonable and are not required for any other metals parameters. Only a few laboratories in the U.S. perform Method 1631. Although EPA states that the “experts” reside in laboratories that participated in EPA’s inter-laboratory validation study of Method 1631, approximately half of the participating laboratories were located outside of the U.S. This severely limits the availability of “experts”. Significant additional costs for obtaining the external confirmation would be incurred by the permittee.
- c) Identification of the potential interferent(s) is an additional, specific requirement not practiced with other parameters. Although the interferent list is small, studies to identify the interferent(s) may be costly. If known interferences cannot be overcome using the procedures found in the guidance document, the identity of the interferent may be of no real benefit. EPA should consider

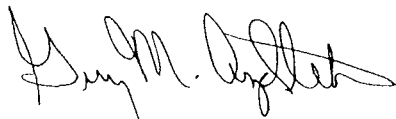
the additional costs (to the permittee) of performing such studies and balance them with the benefits that would be obtained.

2. Elimination of one or both of the gold traps requires balanced QC acceptance criteria.

- a) Our previous inquiries concerning the elimination of gold traps when using Method 1631 resulted in both EPA and state regulatory authorities stating that gold traps must be used with this method. Instrument manufactures have also been informed that the use of gold traps is mandatory for method 1631, regardless of the data quality objectives. Again, conflicting information from the same office in EPA.
- b) QC acceptance criteria can be readily met for the IPR and MS/MSD tests without the use of gold traps. Without the gold traps, the MDL and ML will increase but will still be capable of achieving the necessary detection/quantitation levels required for many projects. However, as the MDL/ML increases, the ability to differentiate analytical signals from background noise, such as reagent or bubbler blanks also increases therefore the allowable limits for these blank values should increase. There is no allowance made for this change in acceptance criteria when evaluating the reagent and bubbler blanks. For obtaining meaningful information, these acceptance criteria must be commensurate with the MDL/ML. As currently written the acceptance criteria for these blanks are set at or below the MDL published for the method, which is inappropriate for evaluation of potential contamination while using the method at the higher detection/quantitation level.

Thank you for the opportunity comment on this draft Method 1631 guidance document. If you have any questions concerning these comments, please contact me at 757/460-4243 or Mark Hoeke, AMSA at 202/833-9106.

Sincerely,



Guy Aydlett
Co-Chair, AMSA Mercury Workgroup
Director of Water Quality
Hampton Roads Sanitation District

cc: Steven Koorse, Hunton & Williams