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MEMORANDUM

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Re: Cyanide Preservation by ASTM D7365-09a and Holding Time Determination by D4841

Introduction

Cyanide compliance issues were a topic of discussion at the February 8, 2011 EMG meeting. In this discussion, EPA's recent proposed rulemaking addressing changes to 40 CFR 136[1] were discussed, and in particular, adoption and formal codification of American Standard for Testing and Materials International (ASTM) Standard Practice D7365-09a, *Standard Practice for Sampling, Preservation and Mitigating Interferences in Water Samples for Analysis of Cyanide.* This memo aims to address the following key questions that were raised at the February EMG meeting:

1. How can the procedures detailed in ASTM D7365-09a be utilized to address cyanide compliance and analytical interference issues for wastewater dischargers in the Central Valley, and
2. Can the procedures detailed in ASTM D7365-09a be employed in a region-wide holding time study for all wastewater dischargers?

Background

As described in greater detail in the RBI white paper *Problems Associated with Using Current EPA Approved Total Cyanide Analytical Methods for Determining Municipal Wastewater Treatment Plant NPDES Permit Compliance* previously circulated to Regional Board staff on May 26, 2010, the currently

[1] Part 136 of Title 40 of the Code of Federal Regulations establishes guidelines for the testing and analysis of pollutants as required in the monitoring requirements of NPDES permits.

approved EPA methods used to measure cyanide in wastewater effluent are prone to numerous interferences that are unpredictable and difficult to mitigate. Substantial evidence indicates that these analytical problems have resulted in the reporting of false positives, rather than actual cyanide concentrations in the treated effluent that are above discharge limits. The preservative sodium hydroxide is required to be added to all samples that cannot be analyzed in less than 15 minutes, yet sodium hydroxide is itself a proven interference for which there is no specific mitigation technique. Substantial evidence suggests sodium hydroxide addition may be unnecessary to maintain sample integrity over typical hold-times prior to analysis. Based on this information, cyanide measurements made under the current 40 CFR 136 are likely inaccurate and produce unreliable information for determining NPDES permit compliance.

Historically, many of the interference problems associated with cyanide analysis have been addressed in footnote 6 of Table II found at 40 CFR 136.3(e). A need, however, arose to update the various measures of footnote 6, a task that ASTM bore in development of Standard Practice D7365-09a, an approved ASTM standard that is one of many modifications scheduled to be adopted in EPA's proposed rulemaking updates to 40 CFR 136. The various sample preservation and stabilization procedures represented in ASTM Standard Practice D7365-09a represent a significant positive step forward in resolving analytical interferences associated with cyanide analysis of treated wastewater effluent. Acknowledging the various analytical challenges related to cyanide, and the continuing developing science surrounding these challenges, EPA has proposed in recent rulemaking to amend footnote 6 of Table II of 40 CFR 136.3(e), approving of the various preservation and stabilization measures described in ASTM D7365-09a[2]. Specifically, EPA proposes to replace footnote 6 in its entirety with:

> Sampling, preservation and mitigating interferences in water samples for analysis of cyanide are described in ASTM D7365–09a. There may be interferences that are not mitigated by the analytical test methods or D7365–09a. Any technique for removal or suppression of interference may be employed, provided the laboratory demonstrates that it more accurately measures cyanide through quality control measures described in the analytical test method. Any removal or suppression technique not described in D7365–09a or the analytical test method must be documented along with supporting data.

As is the case under current regulations, guidance provided in footnote 6 of Table II would take precedence over any guidance or information provided in any specific analytical method. In summary, it is the expressed intent of EPA that ASTM D7365-09a be the source for procedures detailing how cyanide samples are to be collected and preserved, as well techniques for mitigating and suppressing related interferences.

In its proposed revisions of 40 CFR 136, EPA further acknowledges that: "…there may be interferences that are not mitigated by the analytical test methods or D7365-09a". In the proposed rulemaking, EPA revises part 136.3(e) in a manner delegating the approval authority of procedures outside the instruction provided by Table II to the local permitting authority. Specifically, EPA proposes:

[2] EPA. 2010. Guidelines Establishing Test Procedures for the Analysis of Pollutants Under the Clean Water Act; Analysis and Sampling Procedures; Proposed Rule. Federal Register, Vol 75, No. 184, 58024-58076. September 2010. Public comment closed on December 22, 2010.

> Information in this [Table II] takes precedence over information provided in specific methods or elsewhere unless a party documents the acceptability of an alternative to the Table II instructions. Such alternatives may include a change from the prescribed preservation techniques, container materials, and maximum holding times applicable to samples collected from a specific discharge. The nature and extent of the documentation of such changes (how to apply as well as supporting data) is left to the discretion of the permitting authority (state agency or EPA region) or other authority and may rely on instructions, such as those provided for method modifications at § 136.6.

In the introductory summary text of the proposed rulemaking, EPA explains the purpose of the proposed text revision, that new future methods of addressing analytical concerns may develop and conflict with the instructions of Table II, and in such cases alternatives to the instruction of Table II are to be encouraged, provided they improve or perform equally well to the procedures specified in Table II (Section F):

> EPA recognizes that there may be cases where new technologies or advancements in current technologies may produce approved methods with instructions for a specific parameter that differ from Table II instructions, and provide better results. Cyanide determinations and some automated methods may fall into this category. Therefore, EPA is proposing to revise the text at 136.3(e) to allow a party to submit documentation to their permitting or other authority that supports use of an alternative approach. EPA is proposing to revise the introductory text to the table to read as follows: [quoted text above] Thus, an alternate sample container, preservation and/or holding time may be considered at the discretion of the permitting authority or other authority.

By singling out cyanide analysis, EPA emphasizes the specific applicability of this text revision. Although ASTM D7365-09a represents a positive step forward, problems may still exist and additional solutions may still arise, with their consideration to be delegated to the permitting authority.

ASTM Standard Practice

ASTM D7365-09a acknowledges that in certain matrices, addition of sodium hydroxide as a preservative, when in the presence of other cofactors, may result in analytical interference (Section 8.3.5.1):

> Adding NaOH to samples containing formaldehyde (see Note 2 in Section 8.3.8) can possibly increase the cyanide concentration during storage. Conversely, adding NaOH to samples containing sulfite (see Note 3 in Section 8.4.2.2) can rapidly decrease the cyanide concentration. If the addition or lack of addition of NaOH would affect the holding time, hold the sample for a time no longer than the time necessary to maintain sample integrity (Section 8.3.2).

Further, ASTM D7365-09a suggests that an appropriate solution would be to omit sodium hydroxide (Section 8.3.5):

> Do not add NaOH if the cyanide concentration would change as a result of the addition.

As noted previously, interference in cyanide analysis is complex. ASTM D7365-09a recommends performing a holding time study in cases where interference is suspected (Section 8.3.2), and in cases

where changes to standard operating procedures are employed to mitigate or suppress these interferences. Such changes would include the omission of sodium hydroxide, as discussed in Section 8.3.5.1 (see excerpt above). ASTM D7365-09a states (Section 8.3.2 and Note 1):

> Unless otherwise specified, samples must be analyzed within 14 days. Certain sample matrices may require a shorter holding time or immediate analysis to avoid cyanide degradation due to interferences. Hold the sample no longer than the time necessary to preclude a change in cyanide concentration. A holding time study described in Practice D4841 is required if there is evidence that a change in cyanide occurs from interferences which would cause the holding time to be shorter than specified in this section, or within the time the sample would be held if shorter than the time specified in this section. Potential interferences and their corresponding analytical methods are shown in Table 1.
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> NOTE 1—It is recommended to investigate holding times for samples that meet any of the following conditions—disinfected by chloramination or ultraviolet irradiation, ammonia present and chlorinated, sulfur dioxide or sulfite used to dechlorinate, or if aldehydes are known or suspected to be present.

As stated by D7365-09a, sodium hydroxide should not be added in cases where its addition is suspected to contribute to measurement error (Section 8.3.5). Sodium hydroxide preservative, however, is specified in cyanide test methods as a means of extending the maximum holding time before analysis (14 days). Omission of sodium hydroxide effectively changes the maximum holding time.

A particular allowable holding time is often matrix specific; representing a complex interaction of an analyte's specific physical and chemical properties as they govern partitioning and stability in matrix (e.g., final effluent). Without elevating the pH with sodium hydroxide, there is the possibility that free cyanide may volatilize from the aqueous sample, thereby affecting the stability and integrity of the sample after collection. A properly conducted holding time study in matrix can determine the maximum holding time, a fact that is acknowledged in ASTM D7365-09a (see excerpts above). ASTM D7365-09a requires that a holding time study be conducted according to ASTM D4841, *Standard Practice for Estimation of Holding Time for Water Samples Containing Organic and Inorganic Constituents,* when there is evidence that an interference, or a measure suppressing an interference, would shorten the maximum allowable holding time of 14 days (Section 8.3.2 and 8.3.5.1). The standard practice represents the industry standard for performing such studies, and details the statistical procedures to be employed in determining holding time.

In summary, dischargers following the guidance of ASTM D7365-09a with regard to cyanide sampling, preservation, and mitigation of interferences would conduct a holding time study according to ASTM D4841 in order to document the allowable or maximum holding time for their effluent when samples are not preserved with sodium hydroxide. Conducting such a holding time study is desirable for two principal reasons, including: 1) a practical desire of wanting to ensure accurate measurement of cyanide, and 2) the practical solution to the logistical problems associated with analysis of unpreserved samples in less than 15 minutes, which is the only allowable practice in the case of unpreserved samples, in absence of a holding time study.

Facility Specific vs. Regional Holding Time Study

Holding time studies are logistically complex, requiring careful sampling and very precise analysis. As such, there are gains in efficiency when considering a regional holding time study relative to numerous facility specific studies. In such a regional holding time study, a selection of POTWs representing a range of treatment technologies and service area compositions would conduct individual holding time studies, with the shortest allowable holding time representing an acceptable holding time for those facilities that have no holding time determined. In other words, from a sample of POTW dischargers conducting matrix specific holding time studies, the shortest permissible holding time of the sample would become the maximum permissible holding time for all POTWs in the region that have not conducted their own matrix specific holding time study.

Although there are benefits in a regional holding time study, there are several practical limitations. First, holding time is matrix specific and there may be insufficient homogeneity among POTW effluents to reasonably allow an accurate subsampling of the whole POTW population. Secondly, there is little regulatory precedence for a regional holding time study. Current regulation requires submission of an alternate test procedure to the EPA Regional Authority (EPA Region 9). ASTM D7365-09a and ASTM D4841 do not provide specifications or guidance on performing holding time studies on a regional scale. However, under the proposed rulemaking, substantial authority on matters of instruction given in Table II of 40 CFR 136.3(e) would be delegated to the permitting authority, in this case the Regional Water Board. Because ASTM D7365-09a would effectively become Table II instruction (through cross reference), and because ASTM D7365-09a allows for the omission of sodium hydroxide provided an alternate holding time be verified, it is possible that a regional holding time study may fall under the discretion delegated to the permitting authority. Certainly, as individual facilities perform matrix specific holding time studies, such information could be shared with the Regional Water Board and used to make informed professional judgments on cyanide sampling as a whole.

Conclusion

Under existing regulation dischargers are permitted under the existing instruction of Table II of 40 CFR 136.3(e) to analyze unpreserved samples provided sample analysis can be initiated within 15 minutes of sample collection. Very few NPDES permit holders can initiate sample analysis within 15 minutes and, therefore, must preserve samples with sodium hydroxide or pursue approval for alternate test procedure with EPA. However, in those cases where samples are analyzed within 15 minutes, unpreserved samples routinely show lower cyanide concentrations when compared to samples preserved with sodium hydroxide, supportive of the conclusion that preservation is causing positive bias. Because existing regulation mandates the use of preservation, if a discharger suspects sodium hydroxide interference and wishes to omit sodium hydroxide from compliance monitoring samples, that discharger must demonstrate that sample integrity is maintained by means of a holding time study, and present this evidence to the EPA in application for an alternate test procedure. However, involvement of EPA through the alternate test procedure process is not necessary if the discharger wishes to continue to submit split preserved and unpreserved samples for permit compliance, as the preserved

sample would effectively comply with the preservation mandate of existing regulation. In such a case, the holding time study would provide evidence that: 1) the unpreserved split sample result is valid and not been subject to cyanide degradation due to sample storage before analysis, and 2) any difference between the preserved and unpreserved samples outside of normal method variability would be the cause of sodium hydroxide addition.

The potential for sodium hydroxide related interference has been acknowledged by EPA. In ASTM D7365-09a, instruction is given to omit sodium hydroxide if its use causes error in the measurement of cyanide. ASTM D7365-09a further instructs that a holding time study be conducted per the procedures of ASTM D4841 if attempts to mitigate or suppress an interference may affect the maximum holding time of 14 days. In recent proposed rulemaking, EPA intends to drop the historical instructions of Table II with that of a cross-reference to ASTM D7365-09a. Because there is a growing body of evidence suggesting sodium hydroxide related error in cyanide measurement, dischargers wishing to follow the latest instruction on cyanide sampling, preservation, and mitigation of interference will wish to perform holding time studies on unpreserved samples.

By following the instruction of ASTM D7365-09a, omitting sodium hydroxide when it is believed to be interfering with accurate cyanide analysis, and establishing an allowable holding time on unpreserved samples, dischargers will be taking proactive steps at improving cyanide analysis of their effluent. Improved, more accurate analysis, represents a first necessary step towards rectifying cyanide compliance issues, and may in fact provide substantive evidence supporting the assertion that facilities never had Reasonable Potential to exceed the Water Quality Objectives for cyanide. There are several practical limitations to conducting a regional holding time study. However, as the number of facilities performing holding time studies on unpreserved samples multiplies, an increasing body of evidence will build with regard to the likelihood that many facilities, if not most facilities, are experiencing similar analytical challenges, and an even stronger need for a regional solution may evolve.

Under the proposed changes to 40 CFR 136, dischargers that perform holding time studies will be able to submit unpreserved sample test results consistent with their holding time study results. As the body of evidence grows with each holding time study, the Regional Water Board may be able to use its discretion with other dischargers who have not performed holding time studies. For example, a discharger could submit both preserved and unpreserved results (unpreserved holding times consistent with the body of evidence) and the Regional Water Board could use its discretion to rely on data from the unpreserved samples for reasonable potential and compliance determination, and/or Mandatory Minimum Penalty (or other Administrative Civil Liability) determination.