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Total Cyanide Test Interference

In the process of testing wastewater treatment plant effluent it is not uncommon to have effluent cyanide values higher than influent values. This often leaves plant operators or pretreatment coordinators struggling for answers about how the plant creates cyanide. There can be several reasons for this apparent increase in effluent cyanide including complex interferences or simply that the influent and effluent samples were not “paired.”

The common industrial pretreatment advice, to always retest, applies in these cases; but also, retest with full knowledge of times of sampling and the hydraulic detention time within the wastewater facility and of the many interferences to the Total Cyanide test.

“Standard Methods” lists eight possible types of interference which makes accurate testing complex. Three common ones are chlorine, sulfide, and nitrite. Chlorine will oxidize cyanide thereby lowering the test value. “Standard Methods” recommends the use of sodium thiosulfate if chlorine is ≥ 2.0 mg/L but also cautions against excessive sodium thiosulfate. Sulfide and fatty acids will distill over with the cyanide. This should not be an effluent test issue but could increase influent cyanide values. See “Standard Methods” for guidance.

Several Tennessee cities have experienced an increase in cyanide through the treatment plant. The process is reported to have three common characteristics, chlorinated effluent, nitrite is present and the addition of sodium hydroxide as a preservative in the sample container (Weinberg, et.al. 2005). Additionally, Weinberg reports that cyanide precursors are created in the chlorine contact chamber. The precursors react with nitrite in the sample vial when the pH is raised to the required >10 value. So the cyanide is really created within the sample vial. Increased values of 2.3 ug/L are reported in samples preserved with sodium hydroxide (Stanley, et. al. 2012).

To avoid this interference “Standard Methods” states; “Add at least 2g sulfamic acid at the time of **sample collection** and before dechlorination or basification [addition of sodium hydroxide] to avoid nitrite interference.” Sulfamic acid is a water soluble solid or powder. A more detailed dose of 4 g/L is specified in a WEF publication, *Cyanide Formation and Fate in Complex Effluents and its Relation to Water Quality Criteria*.

Stanley reported that samples maintained at ~ pH 7.0, kept chilled, and well-sealed maintained cyanide levels for approximately 48 hours, but should be analyzed immediately upon receipt by the lab.

Recommendations

If you are having elevated effluent cyanide, first retest taking into consideration the hydraulic detention time of the treatment facility. Where there is chlorination and especially dechlorination, discuss nitrite interference with your lab. They may be able to include the sulfamic acid as part of the test kit along with instructions. You may also want to sample before chlorination, and you may want to do parallel unpreserved samples as a test to demonstrate the interference. Do not use unpreserved samples for NPDES reporting without regulatory permission.

References

40 CFR 136, Guidelines Establishing Test Procedures for the Analysis of Pollutants under the Clean Water Act; Analysis and Sampling Procedures.

APHA/AWWA/WEF Standard Methods for the Examination of Water and Wastewater, 22 Edition.

Kavanaugh, Michael, et.al., Cyanide Formation and Fate in Complex Effluents and its Relationship to Water Quality Criteria. Water Environment Research Foundation, 2013.

Stanley, Brett J., Karen Antonio, Interlaboratory Study of Free Cyanide Methods Compared to Total Cyanide Measurements and the Effects of Preservation with Sodium Hydroxide for Secondary- and Tertiary-Treated Wastewater Samples, Water Environment Research, Volume 84, Number 11, November 2012.

Weinberg, Howard S., Steven J. Cook, Phillip C. Singer, Insights to False Positive Total Cyanide Measurements in Wastewater Plant Effluents, Water Environment Research, Volume 77, Number 5, Sept/Oct 2005.