

Appendix T

Total Residual Chlorine Study

November 2004

The total residual chlorine study was originally planned to look at chlorine residuals in representative wastewaters from facilities around the state. The study was modified following discussions with our Southwest Regional Office staff and members of the Kansas Department of Health and Environment. These discussions convinced us that the most appropriate way to arrive at an acceptable quantitation limit for incorporation into wastewater permits is to simply determine the method detection limit (MDL) for total residual chlorine under laboratory conditions. ESP chemists used standard techniques to determine the MDL of total residual chlorine in laboratory distilled water, using a widely available field colorimeter that is currently used by department inspectors. The techniques used are outlined below.

CLTRC Method Detection Level Determination

A method detection level (MDL) for Total Residual Chlorine was determined using a Hach colorimeter as follows:

Preliminary work was done by preparing standards at approximately 0.5 mg/L down to 0.01mg/L using a certified reference standard from NSI solutions and DI water. We used these to determine the linearity of the meter and to determine at what point the meter could differentiate a known spiked amount from a blank.

The meter was zeroed with DI water (without DPD reagent). We then measured each standard (with DPD reagent). We determined that the meter produced very accurate results when compared to the true values. The meter was also linear down to a concentration of approximately 0.025 mg/L.

Based on a previous MDL study performed in October 2003, we chose a standard concentration of 0.108 mg/L to use for our MDL study on 1/13/2004. This MDL standard was prepared using the NSI reference standard and DI water. We zeroed the meter with DI water (without DPD) and then measured the standard (with DPD) for seven times. We calculated a standard deviation using these measured values. To determine our MDL we multiplied the standard deviation by 3.14 (t value for 99% at 6 degrees of freedom). The calculated MDL value was 0.04 mg/L.

The standard concentration used to determine the MDL should fall between 1-5 times the calculated MDL, to show that a proper concentration was used for the study. Our concentration of 0.108 mg/L fell between 0.04 mg/L (calculated MDL) and 0.20 mg/L (5 times the calculated MDL).

Based on the results of the above work, we propose that at this point in time the MDL should be 0.04 mg/L.

On March 4, 2004, the CLTRC workgroup met and agreed to use 3 as the multiplier to calculate the practical quantification limit (PQL). This multiplier is based on Standard Methods (SM 1998), and EPA guidance (Federal Register 1995), as well as conventional ESP laboratory practices.

Some of the options available to the group are:

-Use the MDL (0.04 mg/L) as the enforceable limit; (Any reading above 0.04 is a violation). Kansas uses this approach. Their MDL was determined to be 0.05 mg/L. However, EPA does not recommend this approach.

-Use the PQL ($0.04 \times 3 = 0.12\text{mg/L}$) as the enforceable limit; (Any reading above 0.12 is a violation while any reading below 0.12 is in compliance).

-Use the MDL and PQL together (Any reading above the PQL is a violation with a high level of certainty. Any reading between the PQL and the MDL is a violation, but with a lower level of certainty, so use with caution. Any reading below the MDL is in compliance).

-Use the minimum level (ML) as defined by EPA. Since there is no promulgated ML for total residual chlorine, an interim ML could be calculated by multiplying the method detection limit by 3.18 ($0.04 \times 3.18 = 0.127$ or 0.13 mg/l); (Any reading above 0.13 is a violation while any reading below 0.13 is in compliance).

The work group originally recommended using the 0.12 mg/L PQL as the enforceable limit. However, further review of the ML indicates that it provides a method for determining compliance levels for any parameter, not just CLTRC, and therefore it is the preferable method. In addition, the ML method has the backing of EPA. The workgroup, therefore, recommended 0.13 mg/L as the enforceable limit. This limit was accepted by the Water Protection Program management.

References

Standard Methods for the Examination of Waters and Wastewater, 20th edition, Section 1030 C., published by the Water Environment Federation, 601 Wythe Street, Alexandria, VA 22314

Federal Register 1995, Determining Compliance With Water Quality Based Effluent Limits Below Quantitation in the Absences of Promulgated Minimum Levels (MLs).

<http://www.epa.gov/docs/fedrgstr/EPA-WATER/1995/May/Day-25/pr-121.html>