Free and Simple Cyanide
Definition and Methods of Analysis

Definitions

ASTM D 6696 – 05 (section 5.1.2) defines free cyanide as "the form of cyanide that is bioavailable and known for its toxic effect on organisms. Free cyanide refers to the sum of molecular hydrogen cyanide (HCN) and the cyanide ion (CN-).

ASTM D6696 – 05 (section 5.1.3) defines simple cyanide as " a neutral compound comprised of an alkali metal, alkaline earth metal, or ammonium cation bound to cyanide. Simple cyanides are so named because of their structural simplicity and their ability to completely dissolve and dissociate in water to produce free cyanide.."

ASTM D 4282 defines free cyanide as "the cyanide that diffuses as cyanide at room temperature from a solution at pH 6."

ASTM D 7237 – 08 (section 1.1) defines free cyanide as "(HCN and CN-) and cyanide bound in the metal-cyanide complexes that are easily dissociable into free CN- ions at the pH of the aquatic environment ranging from pH 6 to pH 8." Section 1.3 further explains that the free cyanide measured should be similar to the actual levels of HCN that would be present at the pH of the actual aquatic environment.

EPA Ambient Water Criteria for Cyanide – 1984 defines free cyanide as "the sum of cyanide present as HCN and CN-, and the relative concentrations of these two forms depend mainly on pH and temperature. When pH is below 8 and temperature is below 25 C, at least 94 percent of the free cyanide exists as HCN."

Methods of Analysis for Free Cyanide

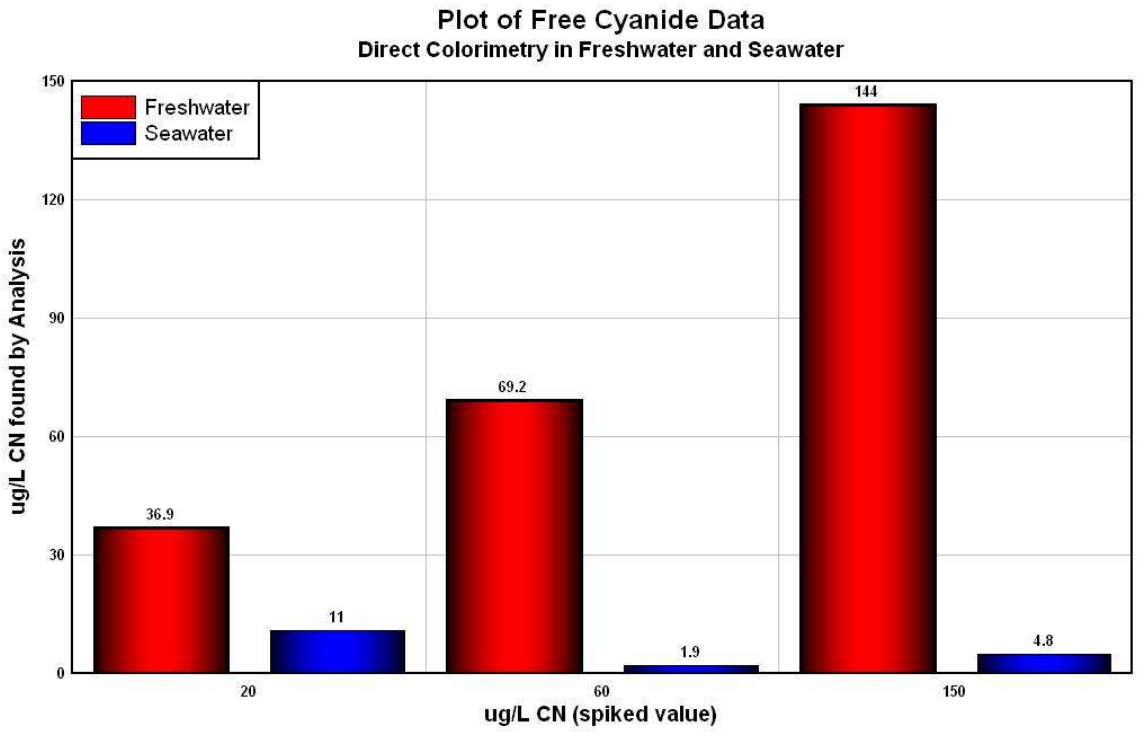
EPA believes that measuring free cyanide provides a more scientifically correct basis for establishing criteria for cyanide, however, in 1984 (when criteria was established) there were no EPA approved methods for free cyanide. Since no free cyanide methods were available, EPA recommended measurement of cyanide after a "total" distillation.[1]

Gensemer, Dzombak, and Santore[2] analyzed free cyanide by colorimetry without preliminary distillation. The methods, they explain, normally include a key distillation step to remove any interference, however, that distillation can be omitted if the sample contains only simple cyanides in a matrix that is free of interferences. Interferences include sulfide, metals, thiocyanate, a varying pH, and a varying salt content. To accurately measure " free cyanide" by colorimetry without distillation requires that samples and standards be carefully matched in salinity.

Dzombak, Ghosh, and Wong-Chong[3] explicitly discourage the analysis of "free" cyanide by direct colorimetry. They reported grossly inaccurate results for "free" cyanide by direct colorimetry in the analysis of freshwater and seawater samples (Figure 1). The failure of the analysis on both freshwater and seawater samples illustrates that varying salinity produces inaccurate results. Dzombak, Ghosh and Wong-Chong also mention that, though it is feasible to measure free cyanide by Ion Selective Electrode (ISE), it is only accurate in relatively simple, low ionic strength matrices.

[1] EPA 440/5-84-028, "*Ambient Water Criteria for Cyanide – 1984",* January 1985
[2] Gensemer, Dzombak, and Santore, *Scientific Review of Cyanide Ecotoxicology and Evaluation of Ambient Water Quality Criteria,* Water Environment Research Federation 01-ECO-1, 2007
[3] Dzombak, Ghosh, and Wong-Chong, *Cyanide in Water and Soil, Chemistry, Risk, and Management,* Taylor and Francis, 2006, pp 137 - 141

Figure 1 Direct Colorimetric Analysis of Cyanide in Freshwater and Seawater



The USEPA Environmental Technology Verification (ETV) Program evaluated direct colorimetry and Ion Selective Electrode (ISE) methods against EPA 335.1 Cyanide Amenable to Chlorination (CATC) to determine "free" cyanide in drinking water and source waters. Data presented on the EPA's own website[4] demonstrates that while direct colorimetry and ISE are adequate in determining "free" cyanide in standard solutions (Figures 2 & 3), they are grossly inadequate in determining "free" cyanide in real world samples (Figures 4 & 5).

[4] http://www.epa.gov/etv/vt-ams.html#pca, accessed December 8, 2008

Figure 2

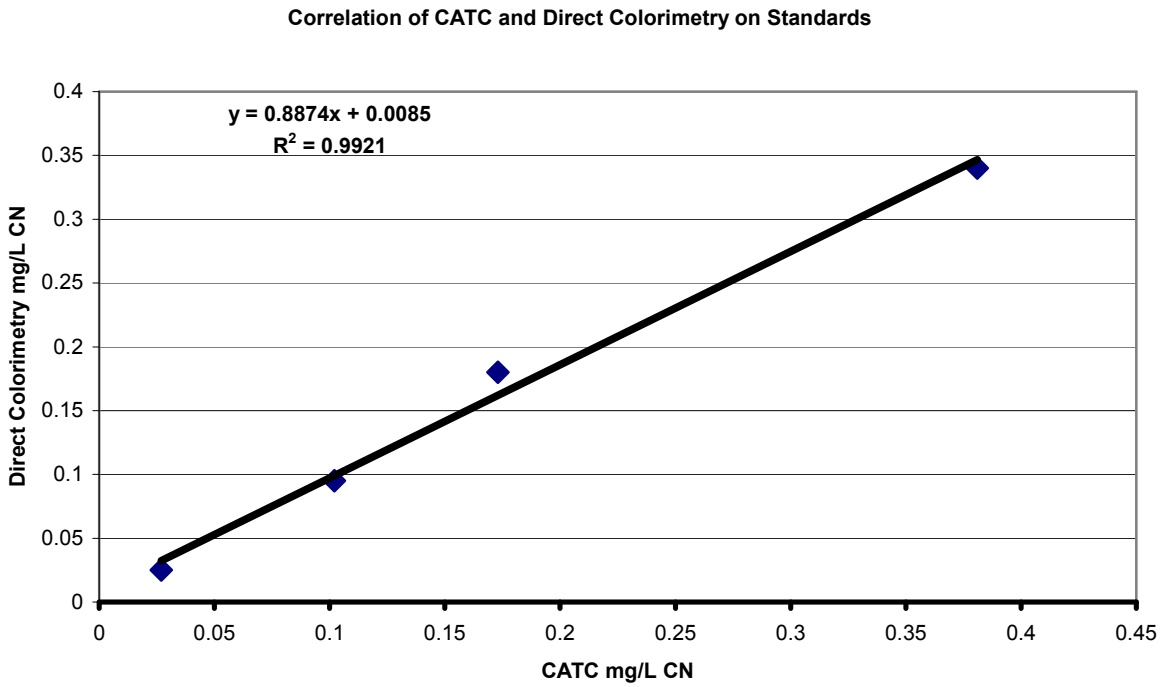


Figure 3

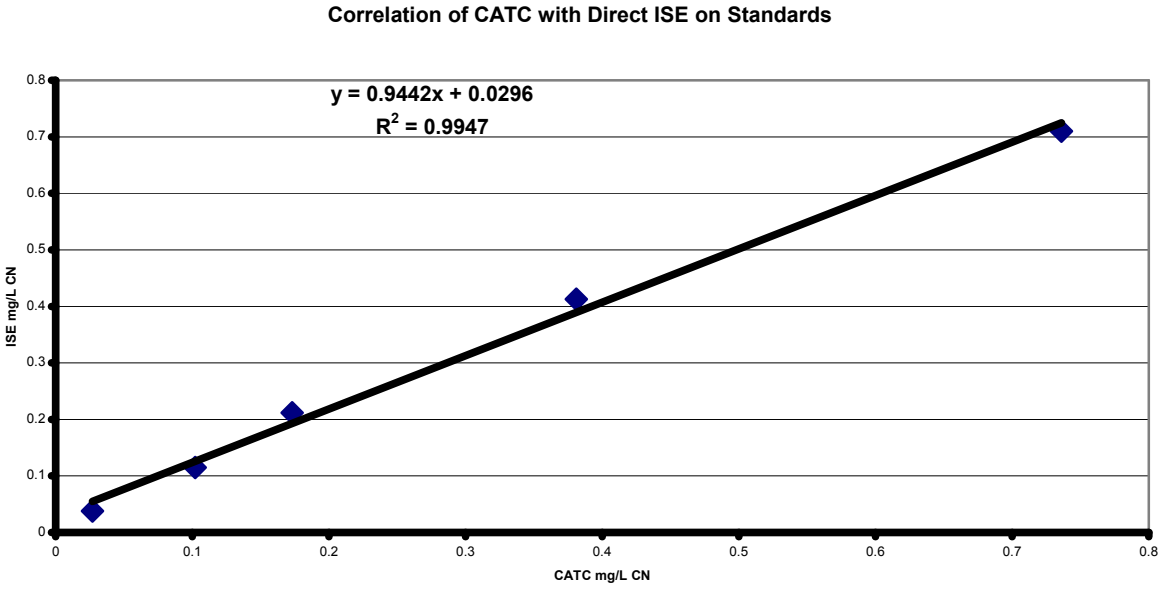


Figure 4

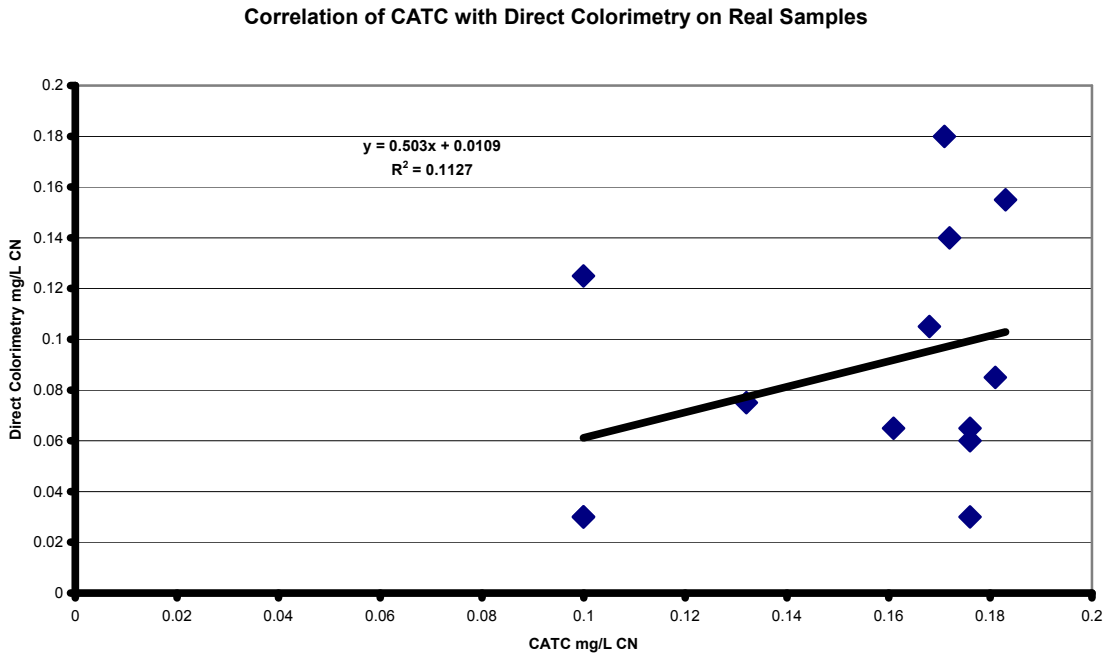
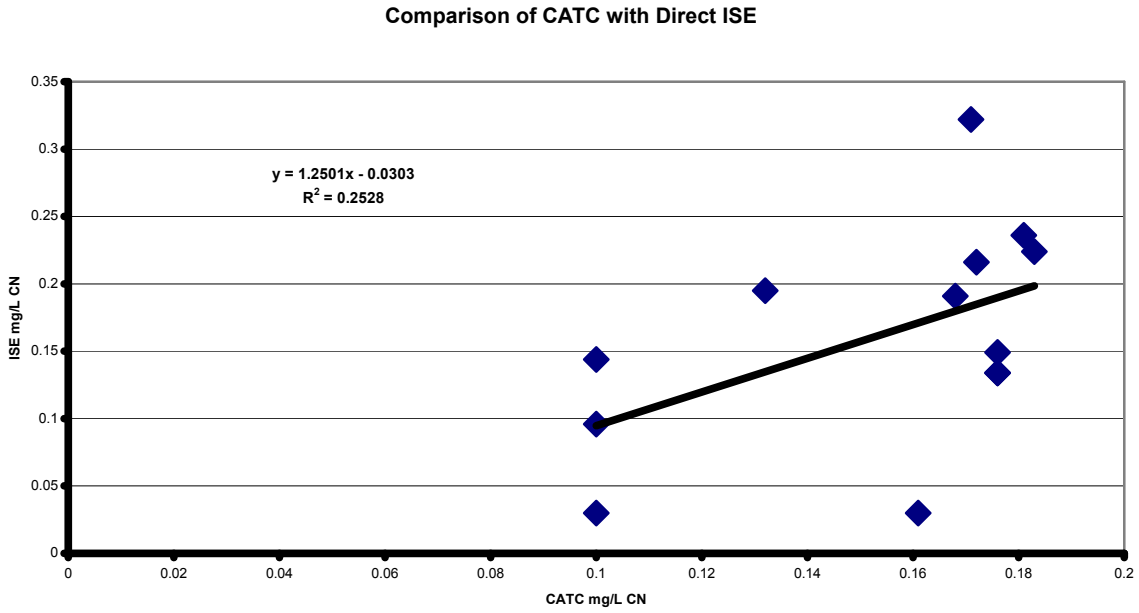


Figure 5



It is important to note that while CATC (EPA 335.1) does not measure “free” cyanide it does measure the same cyanide species that is measured by OIA 1677 and / or ASTM D6888-04. Also, the EPA March 12, 2007 MUR approves OIA 1677 – DW and ASTM D6888-04 for the analysis of “free” cyanide in SDWA compliance samples.

Conclusion

Free cyanide cannot be accurately measured by direct colorimetry or ISE because sample matrices interfere with the determination step. The only methods that can measure free cyanide are ASTM D 4282 or ASTM D 7237. The EPA considers CATC to be equivalent to “free” cyanide and has approved OIA 1677 and ASTM D 6888-04 for the analysis of “free” cyanide in SDWA compliance samples.