

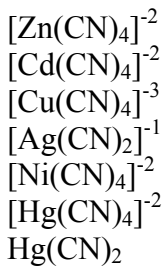
# Comparison of Cyanide Analytical Techniques used to Determine Weak Metal-Cyanide Complexes

## Introduction

Weak metal-cyanide complexes are those in which cyanide ions are weakly bound to a metal such that they can dissociate at  $\text{pH} < 6$  to form HCN. This is in contrast to strong metal-cyanide complexes that require additional energy, other than lowering of pH, to liberate Hydrogen Cyanide gas. There are three cyanide techniques designed to measure weak-metal complexes plus free cyanide.

## Discussion

Weak metal-cyanide complexes are:



The three techniques used to analyze for the cumulative sum of these cyanide species present in a sample are referred to a WAD (Weak Acid Dissociable), CATC (Cyanide Amenable to Chlorination, and Available Cyanide (Ligand Exchange, Gas Diffusion-Amperometry).

All three techniques recover most of these species quantitatively. The only technique that recovers every species quantitatively is ligand exchange gas diffusion amperometry.

A summary of each technique is as follows:

#### WAD

Hydrogen Cyanide (HCN) is liberated from a pH 4.5 buffered solution via a 1 – 2 hour distillation and purging with air. The HCN liberated is absorbed into a sodium hydroxide solution and any cyanide present is determined by titration, ion selective electrode, or colorimetry. Zinc acetate must be added to a buffered sample solution prior to distillation to increase selectivity by complexing with any iron cyanide complexes present. If iron cyanide represents more than half the cyanide complexes present the solution needs to be filtered prior to distillation or the results will be biased high.

#### CATC

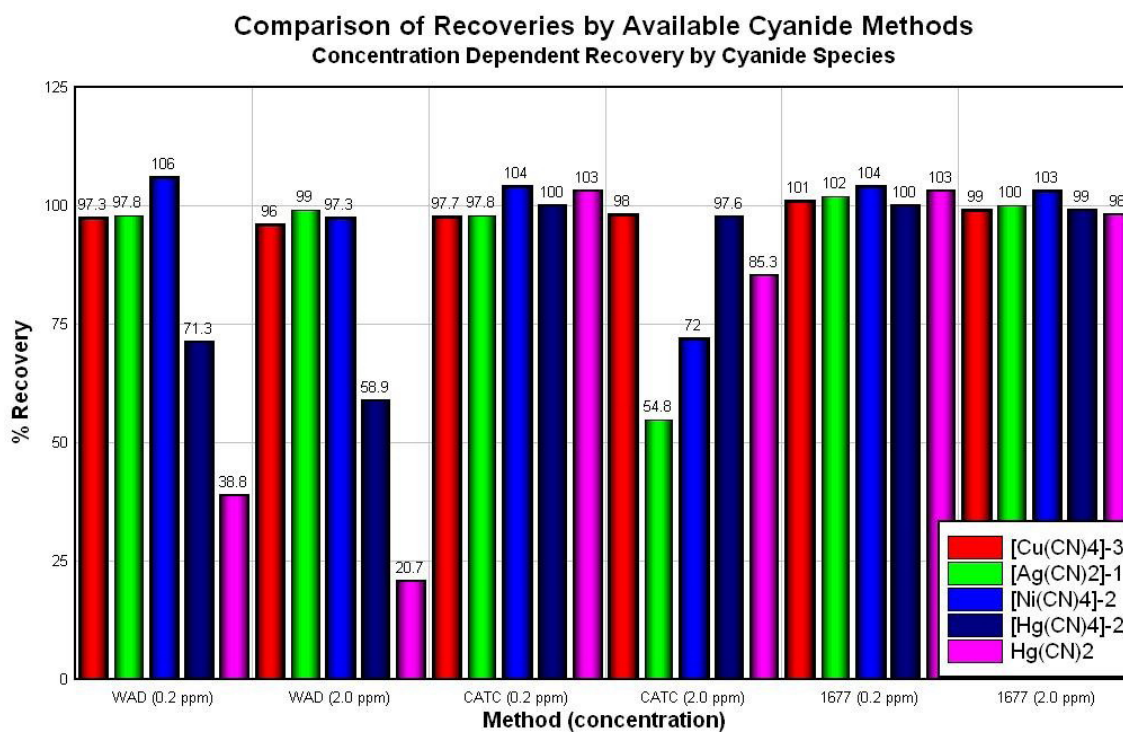
Upon chlorination certain cyanide complexes are dissociated and the cyanide liberated reacts with chlorine to form cyanate. In general, all weak metal-cyanide complexes dissociate whereas strong metal-cyanide complexes such as iron cyanide do not. CATC is measured by splitting the sample into two halves and reacting one half with basic chlorine solution. The two halves are then distilled by the total cyanide distillation and cyanide in each half is measured. The difference of the chlorinated portion subtracted from the unchlorinated portion equals CATC.

#### Available Cyanide

Ligands are added to an alkaline sample that is injected into an acidic stream containing a reagent that complexes up to 50-ppm sulfide. The HCN liberated passes through a membrane into a basic recipient stream where it is measured by a sensitive amperometric detector. The acid reagents combined with the ligands selectively react with only the weak metal-cyanide complexes and do not liberate cyanide from iron or any other strong metal-cyanide complexes. Since the method does not use heated distillation to separate HCN generated from the aqueous solution there are fewer interferences than found in distillation methods.

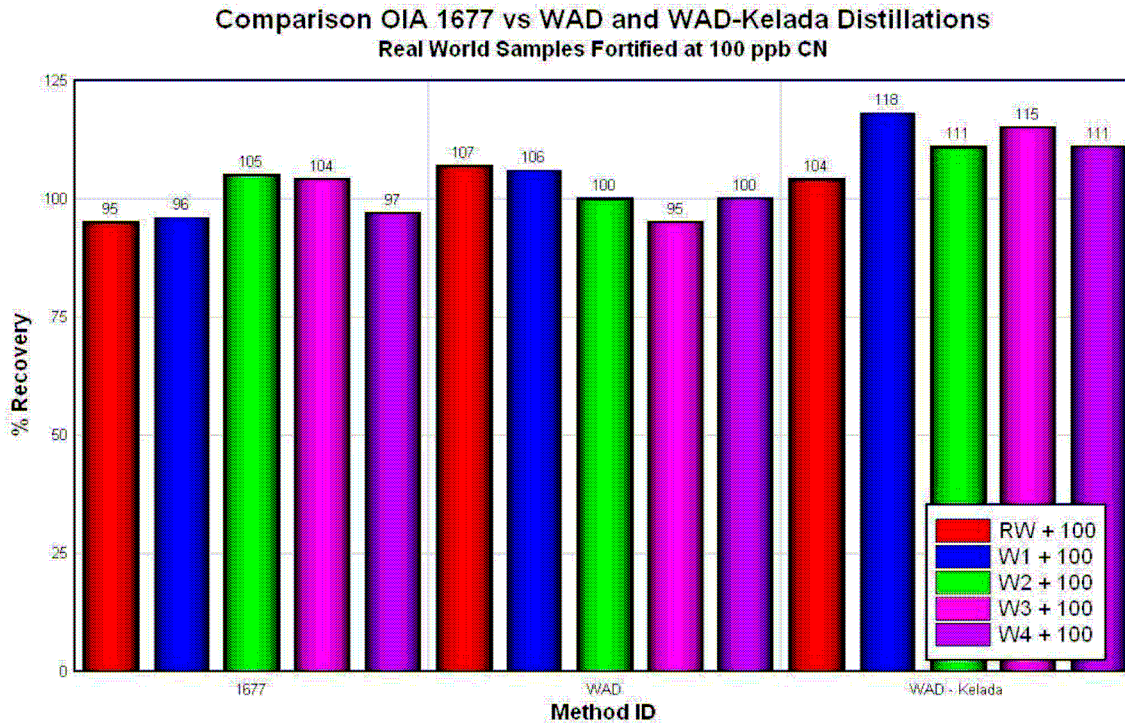
Comparison of Recoveries obtained:

The following chart compares the recoveries of selected weak metal-cyanide species by the three different techniques. The chart illustrates superior recovery of ligand exchange for mercury species.



Note that mercury complexes will be recovered in both WAD and CATC methods, however, the recovery is not quantitative and the incompleteness of recovery is concentration specific.

The following chart compares the recoveries of a weak metal-cyanide complex (nickel) when spiked at different levels into real world samples. The data demonstrates that WAD and OIA 1677 obtain almost identical results in real samples across a concentration range of 5 – 100 ppb CN.



### Conclusions:

Available cyanide methods recover the same metal-cyanide species as WAD and CATC methods except with greater accuracy. Available cyanide methods (OIA 1677 and ASTM D6888-04) are superior to traditional WAD and CATC methods for the following reasons:

1. Greater specificity for cyanide – Gas diffusion – amperometry when used with on-line sulfide abatement reagents makes the method specific for CN.
2. Flow Injection Analysis (FIA) improves the accuracy and precision by eliminating the variability introduced by manual distillations.
3. Amperometry measures cyanide reliably at very low concentrations.
4. The methods offer improved safety by eliminating high temperature distillations and the use of pyridine.
5. The methods shorten analysis time from 2 – 3 hours to 2 minutes per sample.
6. The methods reduce laboratory waste by using smaller amounts of sample and less reagent volume.