Lab **Matters**

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Understanding Cyanide (CN^-)

Introduction – Cyanide and its toxic effects on life are fairly well known. Everyone knows the stereotype of the hidden cyanide pill that secret agents carry as a last resort. But cyanide isn't just for spy thrillers anymore. There are a variety of industries that use cyanide, most notably mining or metal processes. Don't try to rely on another stereotype of cyanide, the burnt almond odor, to warn you of danger. First off, you might miss out on enjoying some actual almonds and secondly, only those with a specific genetic trait are able to detect cyanide in this manner. The simple cyanide salts are most toxic in the environment due to their complete dissociation. Most of the transition metals form cyanide complexes having varying degrees of solubility, with iron cyanide complexes being the most stable. The iron-cyanide stability is what leads to its acute toxicity. The cyanide ions bind with certain iron containing proteins and inhibit the energy production in a cell. The nervous system and the heart are most susceptible to this type of disruption. Alkaline chlorination has historically been the most accepted means of treating cyanide in water streams.

Approved Methods – There are several different methods for analyzing cyanide. Each has its own set of advantages and disadvantages. Most cyanide analyses require distillation. This can be accomplished according to:

- EPA 335.4
- SM4500-CN-C
- ASTM D2036-98(A)
- Lachat Method 10-204-00-1-X

Following the distillation you can analyze via

- Titrimetric (detection limit 1.0 mg/L) – SM4500-CN-D
- Manual Spectrophotometric (detection limit 1-5 µg/L) –
  – SM4500-CN-E, ASTMD2036-98(A), or
  – USGS I-3300-85
- Automated Spectrophotometric (detection limit 1-5 µg/L) –
  – EPA 335.4 or
  – Lachat 10-204-00-1-X, or
  – USGS I-4302-85
- Ion Selective Electrode (detection range 0.05-10 mg/L) –
  – SM4500-CN-F or
  – ASTM D2036-98(A).

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There is an additional subset of cyanide analysis, cyanide amenable to chlorination. The approved methods are:

- Manually –
  - – SM4500-CN-G or
  - – ASTM D2036-98(B);
- Flow Injection Ligand Exchange –
  - – ASTM D6888-04 or
  - – OIA-1677 (OI Analytical)
  - – Automated Distillation and Colorimetry – Kelada-01.

Method Summary – The distillation is accomplished using high heat and a strong acid to convert all forms of CN^- into HCN gas. This gas is then bubbled through a NaOH scrubbing solution to convert back to CN^-. The scrubbing solution now contains all the cyanide that was present in the original sample aliquot and can be analyzed. The titration relies on the reaction of silver nitrate and cyanide with a rhodanine indicator. The ISE analysis utilizes a standard cyanide ISE to detect cyanide ions in solution. The colorimetric methods rely on the conversion of CN^- to CNCl and on the subsequent reaction with a pyridine-barbituric acid reagent.

What You Should Know – This particular analysis is one of the most interference prone tests you will find in the inorganic side of environmental analysis. There are several standard interferences that you must check for and address prior to beginning the distillation.

- Oxidizing agents will decompose most cyanide compounds and are a negative interferant.
- Sulfides will convert cyanide to thiocyanate at the pH required for preservation. Additionally, the sulfide can oxidize under the test conditions forming sulfite which will consume the chloramine-T in the colorimetric procedure. Sulfide will distill over with the cyanide and continue to present problems.

Both of these interferences can be mostly addressed by procedures outlined in the methods. There are numerous other interferences that can have an effect on your analysis.

- Fatty acids can distill and form soaps during the titration process.
- The presence of carbonate can cause a physical danger during distillation by foaming violently upon the addition of acid. Furthermore, lower concentrations may not foam over, but may still release enough carbon dioxide to change the pH value of the trapping solution. This will change the chemistry of the colorimetric analysis and alter the apparent concentrations.
- Most of the other interferences are related to nitrate or nitrite reacting with organic compounds to create cyanide where none was present. This is especially common when using ascorbic acid to dechlorinate. The addition of sulfamic acid will alleviate many of the problems associated with nitrate/nitrite.
- Aldehyde or sugars present in the sample will cause a formation of cyanohydrin from cyanide.
- Finally, for cyanides amenable to chlorination, *Standard Methods for the Examination of Water and Wastewater* contains the following statement, *"Some unidentified organic chemicals may oxidize*

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or form breakdown products during chlorination, giving higher results for cyanide after chlorination than before chlorination. This may lead to a negative value for cyanides amenable to chlorination after distillation for wastes from, for example, the steel industry, petroleum refining, and pulp and paper processing."

Unlike the distillation of ammonia or phenol, the distillation of cyanide does not carry over any of the liquid from the original sample aliquot. The distillation gases are bubbled through a predetermined volume of scrubbing solution. This means that careful measuring and dispensing of the sample aliquot and trapping solution are crucial to producing accurate results. This also means that a time limit must be specified to ensure adequate time for the complete transfer of the cyanide. Recent advances in distillation technology use hydrophobic frits in the assembly. In the distillation of cyanides this has several implications. The first thing is a reduction in the number of pieces that must be cleaned in between distillations. Some systems, such as the SimpleDist system from Environmental Express, also are able to eliminate the need for cooling water. The SimpleDist system also gives the user control over initial sample volumes of up to 50 mL while reducing the volume of the trapping solution. This effectively concentrates the sample and lowers detection limits.

Be advised that, due to pyridine, the waste from all colorimetric cyanide analyses will be considered hazardous. Also, levels of cyanide above certain action limits will cause your sample and all subsequent portions of that sample to be hazardous. Consult your local regulations for these limits.

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Method Procedure

Note – This is not intended to be a standalone method and does not address all safety or quality control aspects that may be required. Please consult your local regulations to comply with all requirements.

1. Collect your sample in a HDPE 500 mL or 250 mL container and preserve with the appropriate volume of sodium hydroxide.
2. Check your sample for the presence of chlorine (oxidizers) and sulfide using potassium iodide and lead acetate test papers. If positive treat as instructed in your regulatory method.
3. Set up the SimpleDist system with enough sample tubes. (A midi-distillation system, Microblock, is also available) Pour samples (treated when necessary) into the sample tubes and connect caps and vacuum tubes according to instructions.
4. Turn on the vacuum and adjust bubbling rates to the proper flow.
5. Add sulfamic acid, sulfuric acid, and magnesium chloride in that order to samples through the reagent addition tube. Allow for proper mixing between each reagent addition. If necessary, small amounts of reagent water may be used to wash the sulfamic acid crystals down the tube.
6. Distill according to instructions for the system of use. SimpleDist Instructions or Microblock Instructions.
7. Collect the distillate and store in a properly labeled sample collection container.
8. Analyze according to your preferred method:
    a. Ion Selective Electrode
    b. Colorimetric – Reagents
        i. Automated through your favorite discrete analyzer, flow-injection, or segmented flow analyzer. Contact your Sales Rep for autosampler supplies.
        ii. Manual on a spectrophotometer.

Find your calibration and second source verification standards here.

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Have something to add? Contact me at DavidS@envexp.com to let me know what you think.