Quantitative and Qualitative Extraction and Determination of Cyanide in Soils and Sediments

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Introduction

The toxicity and mobility of cyanide in soil is governed by its chemical form. Simple cyanide, or the cyanide ion (CN^-), can be weakly adsorbed onto soil particles at pH>9.2. Weak metal-cyanide complexes ($[M(CN_4)]^{-2}$) and strong metal – cyanide complexes ($[M(CN)_6]^{-3}$ or $[M(CN)_6]^{-3}$) have an affinity for metal oxides and organic matter that decreases with increasing pH, however, other salts in solution tend to inhibit adsorption. Simple cyanide, weak metal-cyanide complexes, and strong-metal cyanide complexes are readily soluble in water. Metal – Metal cyanide complexes, such as Prussian Blue ($Fe_4[Fe(CN)_6]^3$), are insoluble in water and are the most common forms of cyanide found in sediment and soil. Metal-metal cyanide complexes are insoluble in acid solution, and solubility increases with pH.

A common practice for the extraction of cyanide in soil and sediment is acid distillation. This approach is valid for all cyanide forms except the metal-metal cyanide complexes that are most likely to be present. Acid distillation of cyanide in soil does not accurately measure "total" cyanide, and it fails to estimate cyanide toxicity.

This poster presents an extraction and analysis protocol that selectively extracts and determines the various forms of cyanide that could be present in soil.

Experimental

There are currently no USEPA methods for total cyanide that were written specifically for soil. SW-846 9013 Extraction Procedure for Solids and Oils (Appendix to Method 9010)[1] is the closest to a total cyanide procedure for solid and soil samples. This method states it analyzes "soluble cyanide" without defining what soluble cyanide is.

An extraction and analysis scheme that selectively extracts and determines the various forms of cyanide present in a soil sample was developed. Analytical results demonstrate differentiation of potentially toxic simple and weak metal-cyanide complexes from relatively non toxic cyanides, strong metal-cyanide, and metal-metal cyanide complexes.

ASTM D 6888, ASTM D 7284, and ASTM D 7511 determine available and total cyanide respectively. Available cyanide includes the cyanide ion and metal-cyanide complexes that liberate cyanide as HCN upon acidification. Total cyanide includes available cyanide plus strong metal-cyanide complexes particularly those of iron. Iron cyanide complexes do not liberate cyanide upon acidification and require either boiling and reflux (acid distillation) or UV irradiation to dissociate the cyanide into a measurable form. ASTM D 7284[2], D 6888[3] and D 7511[4] are flow injection gas diffusion amperometric methods. An aqueous sample is injected into an acidic stream where cyanide in the sample converts to HCN. The HCN diffuses across a membrane into a basic stream and is converted back into the cyanide ion. The cyanide ion contacts a silver electrode oxidizing the silver and generating electrons. The electrons generated are proportional to the cyanide concentration. ASTM D 7284 and D 6888 employ acidification alone and measure available cyanide. ASTM D 7284 determines total cyanide following a preliminary manual acid distillation.

Experimental

ASTM D 7511 employs a UV irradiation step to dissociate cyanide from the strong metal-cyanide complexes, such as iron cyanides, eliminating the need for a preliminary distillation. After UV irradiation, the sample stream is treated identically to ASTM D 6888 and measures the iron complexes and all available cyanide.

ASTM D 6888 and D 7511 gas diffusion amperometry methods are unique in that they don't require acid distillation to separate cyanide from the sample matrix; un-distilled extracts can be determined by direct injection. These methods make it possible to "speciate" available from total cyanide by extraction, followed by direct injection into the analyzer.

Results and Discussion

Extraction and Analysis of Chemical Forms of Cyanide from Soil and Solid Waste

Insoluble cyanide complexes, such as Prussian Blue, are bound to particulate matter or soil particles and are not quantitatively recovered by distillation procedures. A sodium hydroxide extraction followed by a total cyanide analysis using ASTM D 7511, completely recovers all cyanides. A commercial cyanide in soil quality control (QC) sample[5] and laboratory prepared sand fortified with Prussian Blue were extracted in buffered extraction solutions ranging from pH 2 to pH 14. Once extracted, samples were immediately filtered and analyzed for total cyanide by ASTM D 7511 (data is presented in Figure 1). At pH 9.2 almost all of the cyanide from the QC sample is recovered but very little of the Prussian Blue. At pH 14, the Prussian Blue is completely recovered. Thus it is possible to extract and analyze the different forms of cyanide complexes. A pH 14 extraction solution can be analyzed for available cyanide by ASTM D 6888 and "true total" cyanide by ASTM D 7511 simultaneously as described previously[6].

The following extraction protocol was developed for analysis of available and total cyanide in soil and solid waste. This simple extraction followed by analysis by gas diffusion amperometry methods on the CNSolution™ 3100 provide a rapid and accurate assessment of cyanide species and relative concentrations in soil. With these data, cyanide mobility and toxicity can be estimated.

Extraction Procedure for Available and "True Total" Cyanide

1. Weigh 1.00 gram sample into a 25 mL centrifuge vial and add 10 mL of 1 N NaOH.
2. Shake for 10 minutes, centrifuge, and immediately filter into a 200 mL volumetric flask.
3. Dilute to the mark with reagent water and mix. Protect from light.
4. Determine available and "true total" cyanide by ASTM D 6888 and ASTM D 7511.

Figure 2 compares the total cyanide recovered from a commercially available quality control standard by distillation and analysis by ASTM D 7284 to the total cyanide recovered by pH 14 extraction and analysis by ASTM D 7511.

Figure 1. Total Cyanide Recovery from Extraction Solutions of (pH 2 to 14) Soil QC Samples and Prussian Blue Fortified Sand Samples

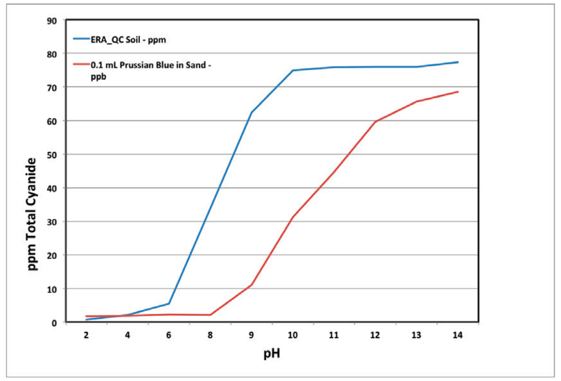
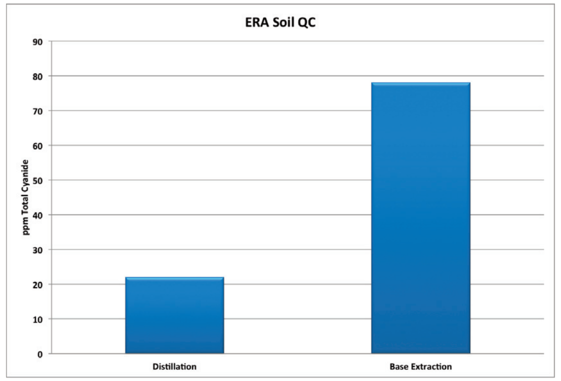


Figure 2. Comparison of Total Cyanide Recovered by Acid Distillation and Alkaline Extraction



Results and Discussion

Figure 3. Comparison of Total Cyanide Recoveries from Prussian Blue Spiked Sand Obtained by Acid Distillation and Alkaline Extraction

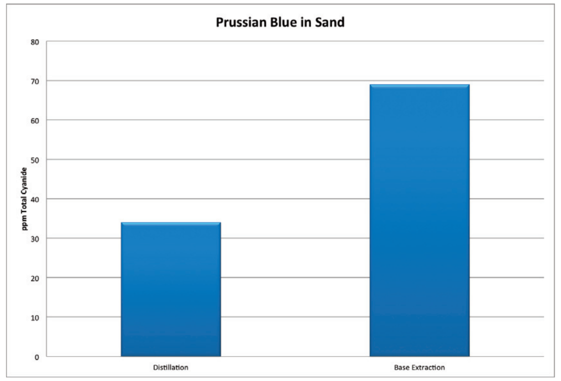


Figure 4. Recovery of Prussian Blue Cyanide in Various Soil Matrices by Extraction at pH 14

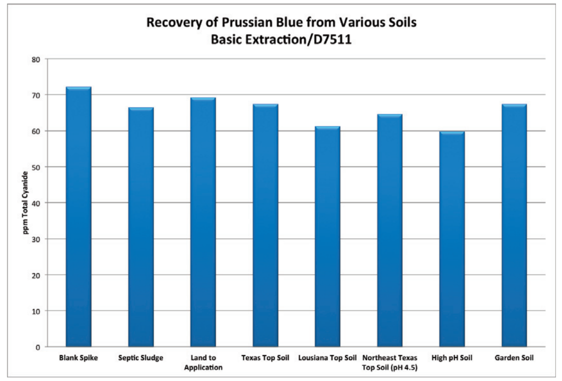


Figure 3 compares the recovery of a Prussian Blue fortified reagent sand by distillation and analysis by ASTM D 7284 to total cyanide recovered by a pH 14 extraction and analysis by ASTM D 7511. Approximately 3-4 times more cyanide was recovered from the soil using alkaline extraction versus acid distillation.

To demonstrate applicability of the pH 14 extraction, seven soils from various locations were characterized then fortified with a known concentration of Prussian Blue. The data is summarized in Figure 4.

Summary & Conclusions

Acid distillation procedures commonly used for determination of total cyanide in soil are inaccurate. Acid distillation only partially recovers insoluble metal-metal cyanide complexes. Extraction with a basic solution quantitatively recovers cyanide. Extraction at high pH followed by analysis with gas diffusion amperometry methods quantitatively recovers all cyanide and enables "speciation" of the various cyanide forms present in a soil or solid waste sample.

References

1. U.S. EPA Method 9013A Cyanide Extraction Procedure for Solids and Oils, U.S. EPA Office of Solid Waste SW-846 Manual, Nov. 2004.
2. ASTM D 7284-08 Standard Test Method for Total Cyanide in Water by Midi or Micro Distillation followed by Flow Injection Analysis with Gas Diffusion Separation and Amperometric Detection, ASTM International, West Conshohocken, PA, www.astm.org.
3. ASTM D 6888-09 Standard Test Method for Available Cyanide with Ligand Displacement and Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection, West Conshohocken, PA, www.astm.org.
4. ASTM D 7511-12 Determination of Total Cyanide by Segmented Flow Injection Analysis, In-Line Ultraviolet Digestion and Amperometric Detection, ASTM International, West Conshohocken, PA, www.astm.org.
5. Environmental Resource Associates, Cyanide in Soil lot# D077-541, ww.eraqc.com
6. OI Analytical Application Note #3793, Simultaneous Analysis of Available and Total Cyanide by Gas Diffusion Amperometry Methods USEPA OIA-1677 and ASTM D 7511-12.

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