



# Extraction and Analysis of Cyanide in Soil and Sediment Samples

## Introduction

The toxicity and mobility of cyanide in soil is governed by its chemical form. Simple cyanide, or the cyanide ion ( $\text{CN}^-$ ), can be weakly adsorbed onto soil particles at  $\text{pH} > 9.2$ . Weak metal-cyanide complexes ( $[\text{M}(\text{CN}_4)]^{2-}$ ) and strong metal – cyanide complexes ( $[\text{M}(\text{CN})_6]^{3-}$  or  $[\text{M}(\text{CN})_6]^{4-}$ ) have an affinity for metal oxides and organic matter that decreases with increasing pH, however, other salts in solution tend to inhibit adsorption<sup>1</sup>. Simple cyanide, weak metal-cyanide complexes, and strong-metal cyanide complexes are readily soluble in water. Metal – Metal cyanide complexes, such as Prussian Blue ( $\text{Fe}_4[\text{Fe}(\text{CN})_6]_3$ ), are insoluble in water and are the most common forms of cyanide found in sediment and soil<sup>2</sup>. 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<sup>3</sup>. This approach is valid for all cyanide forms except the metal-metal cyanide complexes that are most likely to be present. The quality control practice of spiking a soil sample with simple cyanides, or strong metal-cyanide complexes to validate acid distillation is misleading because these cyanide complexes are readily soluble. Acid distillation of cyanide in soil results in low and irreproducible recoveries for the metal-metal cyanide complexes most likely to be present. Acid distillation of cyanide in soil is ineffective and does not accurately measure “total” cyanide nor does it estimate cyanide toxicity.

## Regulatory Status of RCRA SW-846 Cyanide Analysis Methods

The U.S. EPA has issued a comprehensive set of cyanide analysis methods based on gas-diffusion amperometry for Safe Water Drinking Act and Clean Water Act compliance testing and reporting.<sup>4,5,6,7,8,9</sup> These employ ligand exchange or UV-digestion under acidic conditions to dissociate metal-cyanide complexes and form hydrogen cyanide gas which diffuses across a membrane into a base receptor solution where it converts back to  $\text{CN}^-$  and is measured amperometrically.

The situation is not so clear cut for cyanide analysis of soil and sediment samples. There are currently no U.S. EPA approved total cyanide analysis methods written specifically for soil. SW-846 9013A Extraction Procedure for Solids and Oils (Appendix to Method 9010)<sup>10</sup> is the closest to a total cyanide procedure for solid and soil samples.

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However, the method implies that it only analyzes “soluble cyanide” without defining what soluble cyanide is. While the method is an extraction procedure, it also allows acid distillation under certain conditions. Appendix X1.9.5 of ASTM D 2036<sup>11</sup> suggests that insoluble cyanides can be determined by placing a solid sample directly into a distillation flask, adding water, and following the total cyanide distillation procedure. It is our experience that most laboratories directly distill soil samples without considering that insoluble cyanide complexes, such as Prussian Blue, are not quantitatively recovered.

The Methods Team in the Waste Characterization Branch (WCB) of the U.S. EPA Office of Resource Conservation and Recovery (ORCR) is working on Update V of the SW-846 method manual. One method under consideration (9016 – Free Cyanide in Water, Soils and Solid Wastes by Microdiffusion) is under technical review to determine if the method is suitable for its intended purpose because of the relatively high pH at which release of free cyanide is measured. ORCR is evaluating information from experts within and outside the U.S. EPA to decide whether to keep or withdraw Method 9016.

### **Cyanide Chemistry and Recovery from Soil Samples**

Cyanide is a polyatomic anion consisting of covalently bonded carbon and nitrogen atoms. A single electron available for bonding gives the molecule a negative charge. The cyanide ion forms readily dissociable ionic bonds with alkali and alkali earth (group 1 and group 2) metals, such as sodium, potassium, and calcium. The cyanide ion acts as a ligand and forms weak to strong covalent bonds with group 8 through group 12 transition metals. The strength of the bonds tends to increase with coordination number. Complexes of copper, zinc, cadmium, silver, nickel, and mercury form moderate to moderately strong metal-cyanide bonds, and complexes of iron, cobalt, gold, and the platinum group metals form strong to very strong metal-cyanide bonds<sup>12</sup>. These metal-cyanide complexes are coordination complexes with a negative charge and the entire complex behaves as an anion in solution or within a crystal lattice.

The coordination compounds of cyanide may form ionic bonds with alkali or alkaline earth metals resulting in water soluble cyanide compounds that readily dissociate into the cation and its corresponding complex. For instance, a crystal of potassium ferrocyanide ( $K_4[Fe(CN)_6]$ ) dissociates into 4 potassium ions ( $4K^+$ ) and one ferrous iron cyanide complex ( $[Fe(CN)_6]^{4-}$ ). The cyanide coordination complex remains intact in the aqueous solution and does not release cyanide.

Transition metals may also bond with coordination compounds of cyanide. For example, Prussian Blue ( $(Fe_4[Fe(CN)_6])_3$ ) is crystal of  $Fe^{+3}$  with the ferrocyanide complex. The strongly covalent bond between the  $Fe^{+3}$  cation and the ferrocyanide complex make the molecule insoluble in aqueous solution. Extraction with solutions high in  $OH^-$  (sodium hydroxide solutions at pH 12 or higher) react with the  $Fe^{+3}$  cation to form  $Fe(OH)_3$  releasing the ferrocyanide complex anion into solution. Thus, metal-metal - cyanide complexes are insoluble in water but are soluble in strongly alkaline solutions.<sup>13</sup>

Available cyanide includes the cyanide ion and metal-cyanide complexes that liberate 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 acid distillation or UV irradiation to dissociate the cyanide into a measurable form.

## Extraction and Analysis of Cyanide Species from Soil Samples

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 total cyanide analysis using ASTM D 7511, completely recovers all cyanides as demonstrated by the following experiment.

A commercial cyanide in soil quality control (QC) sample<sup>14</sup> 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. This 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.

Recovery is dependent upon pH and makes it possible to selectively extract and analyze the different forms of cyanide complexes. An extraction solution of pH  $\leq 11$  can be analyzed for available cyanide by ASTM D 6888 and “water soluble total” cyanide by ASTM D 7511 simultaneously as described previously<sup>15</sup>. The pH 11 extraction recovers readily water soluble cyanide species but only partially recovers the insoluble cyanide complexes. “True total” cyanide is recovered by extraction at pH 14 and analysis by ASTM D 7511. Available cyanide and “true total” cyanide may be determined simultaneously after extraction at pH 14 as depicted in Figure 2.

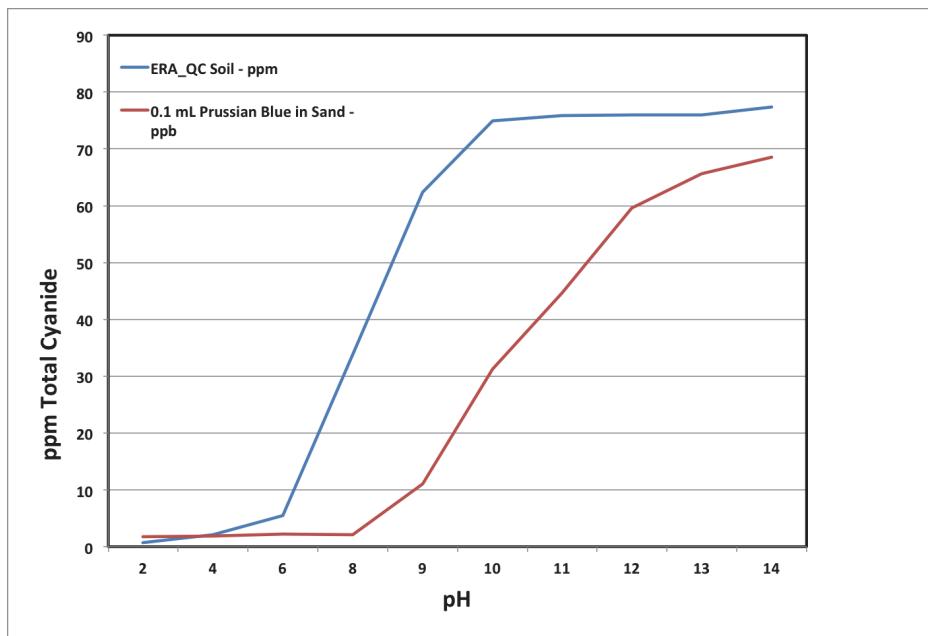


Figure 1. Total Cyanide Recovery from Extraction Solutions (pH 2 to 14) of Soil QC Samples and Prussian Blue Fortified Sand Samples

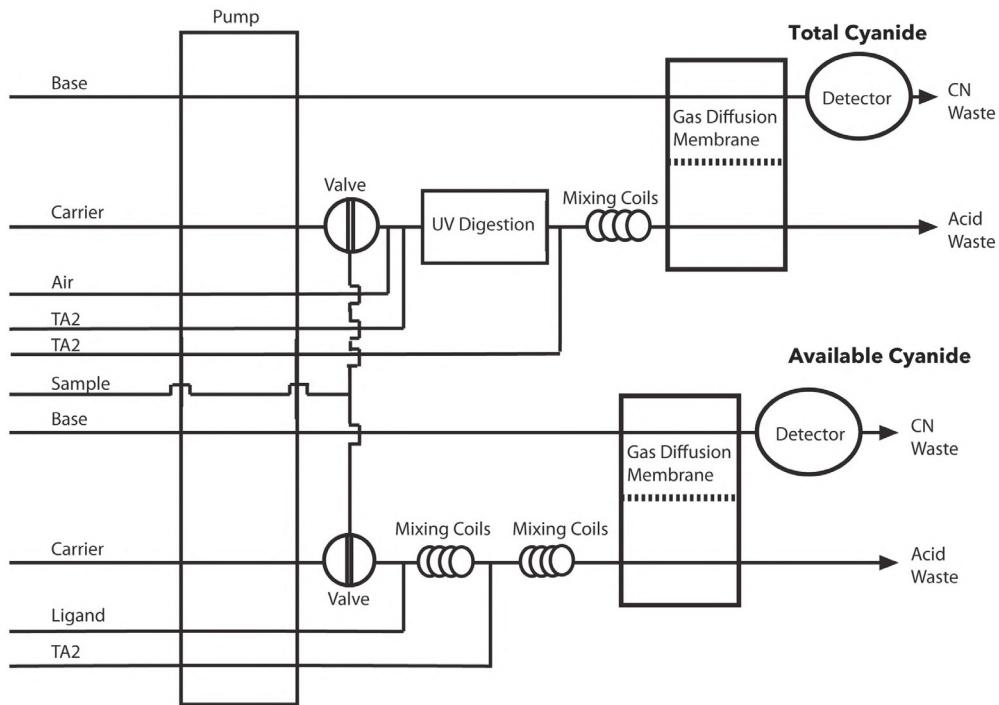


Figure 2. Flow Diagram of Dual Channel CNSolution 3100 System for Simultaneous Analysis of Available and Total Cyanide by ASTM Methods D 6888 and D 7511

Based on this information we developed the following extraction protocol for analysis of available and total cyanide in soil and solid waste. These simple extractions followed by analysis using gas diffusion amperometric methods on the CNSolution 3100™ cyanide analyzer 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 “Water Soluble Total” Cyanide***

1. Weigh 1.00 gram sample into a 25 mL centrifuge vial and add 10 mL of pH 11 buffer.
2. Shake for 10 minutes, centrifuge, and immediately filter into a 200 mL volumetric flask.
3. Dilute to the mark with pH 11 buffer and mix. Protect from light.
4. Determine available and total cyanide by ASTM D 6888 and ASTM D 7511.

### ***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.

Cyanide in ERA soil quality control samples are fortified with  $K_4[Fe(CN)_6]$ <sup>16</sup>. We extracted them with reagent water followed by total cyanide analysis by ASTM D 7511 to assess differences in recoveries obtained with different extraction solutions. Reagent water extraction recovered slightly more cyanide than direct acid distillation (Figure 3).

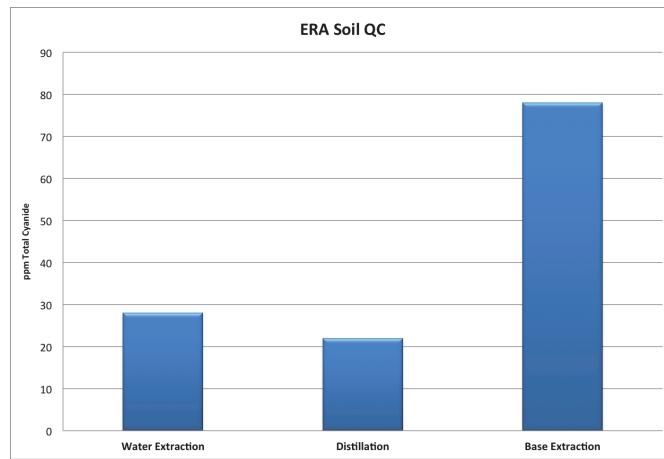


Figure 3. Water Extraction Compared to Acid Distillation and Base Extraction

As observed with the soil quality control sample, extraction with sodium hydroxide recovered significantly more cyanide from the silica sand fortified with Prussian Blue. Because extraction with base recovers more cyanide than acid distillation, direct distillation of a solid sample cannot be considered a valid measure of total cyanide.

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

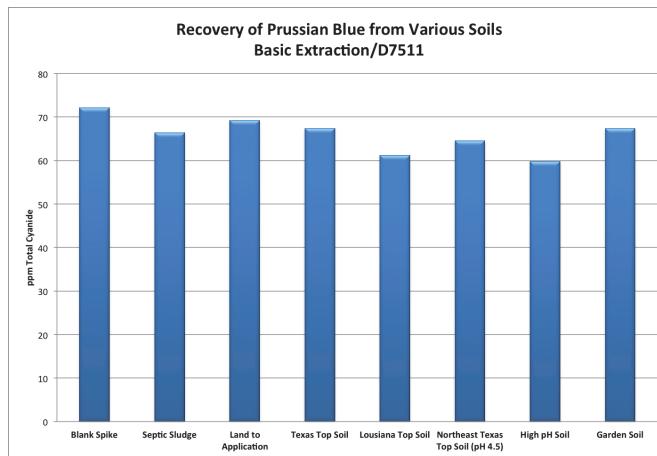


Figure 4. Recovery of Prussian Blue Cyanide in Various Soil Matrices by Extraction at pH 14

Available cyanide complexes in the sodium hydroxide extract can also be analyzed by ASTM D 6888 enabling speciation of the more toxic available cyanide and relatively non-toxic water soluble iron cyanide complexes. Figure 5 shows the recovery of available cyanide species extracted at pH 14 and analyzed by ASTM D 6888.

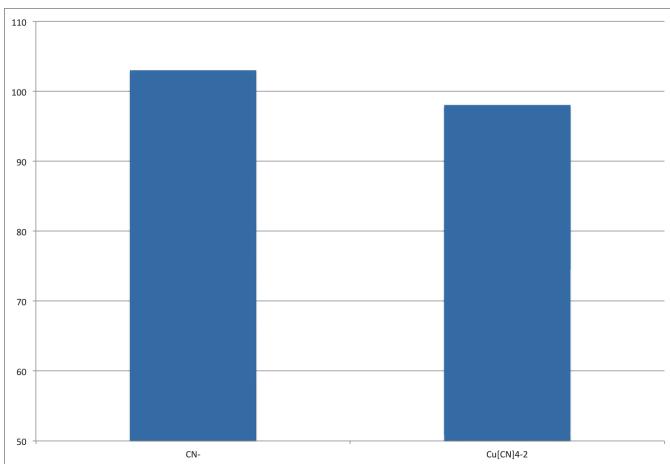


Figure 5. Recovery of Free and Available Cyanide by pH 14 Extraction

## Summary and 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. Simply extracting a soil sample with reagent water recovered more cyanide in a commercially available quality control sample than was recovered by distillation. Extraction with basic solution quantitatively recovers cyanide. Extraction at high pH followed by analysis with gas diffusion amperometric methods quantitatively recovers all cyanide and enables “speciation” of the various cyanide forms present in a soil or solid waste sample.

## References

1. Sorption of Iron-Cyanide Complexes in Soil, T. Reenert and T. Mansfeldt, Journal of the American Soil Science Society, Vol. 66, 437-444, 2002.
2. Extraction of Cyanide from Soil Using Alkaline Phosphate Solutions, Y. W. Choi, J. W. Lee, J. G. Kim, 19<sup>th</sup> World Congress of Soil Science, August 1-6, 2010, Brisbane, Australia.
3. Cyanide in Water and Soil-Chemistry, Risk and Management, D. A. Dzombak, R. S. Ghosh, G. M. Wong-Chong, CRC Press, 2006.
4. Federal Register, Vol. 64, No. 250, December 30, 1999.
5. U.S. EPA Method OIA-1677 Available Cyanide by Flow Injection, Ligand Exchange, and Amperometry, EPA-821-R-99-013, August 1999.
6. Federal Register, Vol. 72, No 47, March 12, 2007.
7. Federal Register, Vol. 77, No. 97, May 18, 2012.

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- 8. ASTM D 7511-09e2 Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-line Ultraviolet Digestion and Amperometric Detection, ASTM International.
  - 9. 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, ASTM International.
  - 10. U. S. EPA Method 9013A Cyanide Extraction Procedure for Solids and Oils, U.S. EPA Office of Solid Waste SW-846 Manual, Nov. 2004.
  - 11. ASTM D 2036-09 Standard Test Methods for Cyanides in Water, ASTM International.
  - 12. ASTM D 6696-10 Standard Guide for Understanding Cyanide Species, ASTM International.
  - 13. Dissolution Behavior of Iron Cyanide (Prussian Blue) in Contaminated Soils, J. C. L Meeussen, M. G. Keizer, W. H. van Riemsdijk, and F. A. M. deHaan, Environmental Science and Technology, Vol. 26, No. 9, 1832-1838, 1992.
  - 14. Environmental Resource Associates, Cyanide in Soil, Catalog No. 541, Lot # D077-541, [www.eraqc.com](http://www.eraqc.com).
  - 15. 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, 2012.
  - 16. E-mail Communication, S. Lynn, Environmental Resource Associates.



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