

Cyanide in Soils by Sodium Hydroxide Extraction - Prescriptive

Parameter	Weak Acid Dissociable (WAD) Cyanide, NaOH Extractable Strong Acid Dissociable (SAD) Cyanide, NaOH Extractable Free Cyanide, NaOH Extractable		
Analytical Method	10:1 aqueous sodium hydroxide extraction followed by appropriate analytical technique.		
Introduction	<p>Cyanide and cyanide compounds are present in soil and sediment due to both natural and anthropogenic sources. Soils represent the major potential pathway for cyanide contamination of groundwater. High concentrations of cyanide in landfill waste or industrial effluents present a hazard to both soil and groundwater.</p> <p>Strong Acid Dissociable Cyanide is also commonly referred to as Total Cyanide.</p>		
Method Summary	<p>As-received (wet) soils are tumbled a minimum of 6 hours (maximum 24 hours) with 0.05 N sodium hydroxide at a ratio of 10 parts NaOH solution to one part soil (v/w). Following extraction, pH must be ≥ 10. If pH falls below 10, NaOH concentration is increased and the extraction procedure is repeated (as described in the procedure).</p> <p>This method is prescriptive. It must be followed exactly as described. Where minor deviations are permitted, this is indicated in the text.</p>		
MDL and EMS Codes	<u>Analyte</u>	<u>Approx. MDL (units)</u>	<u>EMS Code</u>
	Cyanide, Free	0.050 mg/kg	n/a
	Cyanide, WAD	0.050 mg/kg	n/a
	Cyanide, SAD	0.050 mg/kg	n/a
Matrix	Soil and sediment		
Interferences	Refer to appropriate analytical methods.		
Sample Handling and Preservation	Collect samples in HDPE or glass jars with Teflon®-lined lids. Protect from light. No preservation is required.		
Stability	Holding Time: 14 days as-received (Ref: US EPA SW846 Ch3 Feb 2007).		
Storage	Store moist soils at $\leq 6^{\circ}\text{C}$. Extracts may be stored at $\leq 6^{\circ}\text{C}$ for up to 14 days.		
Procedure	<p>Homogenize the as-received sample prior to weighing to obtain a representative aliquot. Accurately weigh a minimum of 4.0 ± 0.1 grams (wet weight). Transfer sample to a suitable extraction vessel and add 40 mL 0.05N sodium hydroxide. <i>Note: Larger sample sizes may be used provided a 10:1 volume to sample weight is maintained.</i> Cap and shake the extraction vessel.</p> <p>Extract the soil for a minimum of 6 hours (to a maximum of 24 hours) by end-over-end tumbling in a rotary extraction apparatus or by shaker table or a comparable means of mechanical extraction (rolling on-axis not permitted).</p> <p>Following extraction, check the pH. Optionally, the pH may also be checked mid-way through the extraction process. If the pH is found to have dropped to < 10 at any time during the extraction, increase the NaOH concentration by adding 6N NaOH in 1.0 mL increments until the pH increases to above 12 and remains above 12 for at least one minute (with shaking), then repeat the extraction process described above (i.e. continue the extraction with the same portion of sample for an additional 6-24 hours, and verify pH is ≥ 10 at completion).</p>		

Centrifuge and decant or filter the extract. Analyze the extract by a Ministry-approved analytical technique for cyanide (WAD, SAD, or Free).

Convert the results back to mg/kg cyanide on a dry weight basis based on moisture correction of the original soil.

Quality Control

Summary of QC Requirements		
QC Component	Minimum Frequency	Minimum Data Quality Objectives*
Method Blank	One per 20 samples, minimum one per batch	Less than reported DL
Laboratory Control Sample	One per 20 samples, minimum one per batch	80 - 120%
Matrix Spike or Reference Material	One per 20 samples, minimum one per batch	70 - 130%
Sample Duplicate	One per 20 samples, minimum one per batch	≤35% RPD
* Minimum DQOs apply at levels above 10x MDL. Report qualified data if DQOs are exceeded.		

Method Blank. Required. One per batch or every 20 samples, whichever is more frequent, to evaluate laboratory contamination. Should be matrix-matched (same concentration of reagents as calibration and QC standards) and distilled with samples in batch.

Laboratory Control Sample. Required. One per batch or every 20 samples, whichever is more frequent, to evaluate laboratory method accuracy without matrix effects. A separate-source standard is spiked pre-extraction with a 50/50 mixture of KCN and FeCN spiking materials onto an inert solid matrix (e.g. clean sand). KCN should be detected as Free CN, WAD CN, and SAD CN. FeCN should only be detected as SAD CN.

Matrix Spike or Reference Material. Required. One per batch or every 20 samples, whichever is more frequent, to evaluate laboratory method accuracy including matrix effects. Sample Matrix Spikes are spiked post-extraction with a 50/50 mixture of KCN and FeCN spiking materials. KCN should be detected as Free CN, WAD CN, and SAD CN. FeCN should only be detected as SAD CN.

Sample Duplicate. Required. One per batch or every 20 samples, whichever is more frequent, to evaluate sample homogeneity and laboratory method precision. Sample duplicates should replicate both the extraction procedure and the analysis.

References

1. Canadian Council of Ministers of the Environment (CCME), Guidance Manual on Sampling, Analysis and Data Management for Contaminated Sites, Volume IV: Compendium of Analytical Methods for Contaminated Sites (currently draft).
2. EPA SW846 Method 9013A "Cyanide Extraction Procedure for Solids and Oils", Revision 1, November 2004.
3. Ontario MOE-LaSB Method E3015.

Revision History

Aug 15, 2014 New prescriptive method added to BC Lab Manual to improve inter-laboratory consistency. Effective date of this method is Nov 1, 2014.