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CYANIDE DETERMINATION: FIELD TECHNIQUES AND CONSIDERATIONS TO MAXIMISE DATA QUALITY

INTRODUCTION

This Enviromail is the second of a series of two designed to improve Cyanide data quality and reduce the risks of FALSE POSITIVES or NEGATIVES (see also EnviroMail 61). Enviromail 62 focuses on the field considerations (mainly Sulfide related) as opposed to analytical and matrix troubleshooting. False negatives (reporting results of 'Not Detect' or '<LOR') when Cyanide was really present or false positives (finding Cyanide in samples where none exists in the sample in its natural environment) both can have a very significant impact on clients and protection of the environment.

BACKGROUND

As the determination of Free, Total or Weak Acid Dissociable (WAD) Cyanide is prone to chemical interferences from Sulfide, it is important to select a sampling procedure that addresses this potential interference when it is likely to be present. ALS facilitates this through a 'two bottle Cyanide sampling option' which enables the pre-treatment of samples. The procedure uses one bottle to remove Sulfide interference, with a second (industry standard NaOH – caustic preserved) bottle to stabilise the resulting water samples for subsequent Cyanide analysis.

This procedure conforms to leading mining and environmental guidance (Minerals Council of Australia and the respective state Environmental Regulatory Authorities).

If matrices require the inclusion of significant solids in the water sample portion for analysis this must be clearly stated and alternate procedures utilised.

BENEFITS OF ALS METHODS

Enhanced ALS methods have facilitated a 75% reduction in sample volumes for the analysis of Total, WAD and Free Cyanide in water (i.e. All tests can be performed using 60mL instead of the previous 250ml).

REPORTING

Unchanged except for additional method references

METHOD INFORMATION

ALS METHOD CODE
EK025 (Free), EK026 (Total), EK028 (WAD)

LIMITS OF REPORTING (LOR)
EK025, EK026, EK028: 0.004 mg/L
Low level e.g. EK028-LL: 0.002 mg/L

Method References
ISO 14403 (2002), APHA 4500 CN-O, ASTM D7237

SULFIDE INTERFERENCE

Sulfide can exert either a positive or a negative interference in the determination of Cyanide species. Failure to remove the Sulfide before raising the pH may result in the formation of Thiocyanates that give a positive interference for Cyanide analysis. False negatives can occur when Cyanide reacts with Sulfide in the sample.

The procedure on page two of this Enviromail details how to overcome Sulfide interferences

Sulfide in Mining

Sulfide can be found in water from mine sites where Cyanide is used to extract metals bound in Sulfide minerals. Flotation process waters for example are almost certain to contain Sulfides. High levels of Sulfide can also be found in some mine tailings water, such as CIL or flotation return water and a range of other process or 'Cyanide kill' feed waters.

Sulfide in other waters

Sulfide may also be found in many ground waters and oxygen deficient waste waters (e.g. sewers) or water associated with in acid sulfate soil or mangrove environments.

Testing for Sulfide

If unsure of the presence of Sulfide this can be assessed with test strips in the field by placing a few drops of sample on moistened lead acetate test-paper. Darkening of the paper indicates the presence of Sulfide in the environment.

SAMPLE TREATMENT AND PRESERVATION TO REMOVE SULFIDE

To remove Sulfide the following steps need to be performed;

1. The sample first needs to be added to the Sulfide pre-treatment bottle. The pre-treatment bottle contains lead acetate which reacts with Sulfide in the sample to precipitate insoluble lead Sulfide.

   Please note:

   - *Lead acetate is toxic and a listed carcinogen so it is necessary to avoid contact and all appropriate safety precautions should be taken.*
   - *Care must be taken to avoid spilling this into the environment and extreme care should be exercised (possible change of gloves) before collecting and field filtering samples for Lead, as a single drop of the treated Cyanide sample water can cause a significant lead false positive).*

2. The bottle should then be capped and mixed by swirling for a few seconds followed by standing for 5-10 minutes to allow any precipitate to settle
3. After settling, decant the treated sample into the second (standard) ALS bottle which already contains Sodium Hydroxide. This will raise the pH to approximately 12 and maintain an alkaline pH to prevent the loss of Cyanide through the formation of hydrogen Cyanide gas.

   Please note: Sodium Hydroxide is corrosive. Avoid any direct contact especially with the eyes. Samples should then be packed in an esky and transported to the laboratory for analysis.

4. Please note that any used Sulfide pre-treatment bottles may be returned to the zip lock bag in which they were provided and returned to ALS for disposal.

OTHER CHALLENGES ASSOCIATED WITH CYANIDE MONITORING

Carryover induced quality issues – a key issue in mining:

High Cyanide concentration samples can contaminate equipment leading to carryover (positive bias) to subsequent samples and can delay results and significantly increase workloads. The key to addressing this is effective communication to the laboratory clearly identifying any such samples on the Chain-of-Custody.

Key steps in effective communication

High level samples = **any samples expected to exceed 1ppm** Cyanide in any form. Examples include:

- CIL dam water and CIL tank profiles;
- Cyanide Kill Feed samples,
- Metallurgical test solutions

GENERAL SAMPLING REQUIREMENTS

Bottle requirements for Cyanide sampling involve two options; either direct into bottle 'B' where Sulfide is not present, or using bottles 'A' and 'B' and the procedure where Sulfide is present

A. Sulfide pre-treatment 60ml HDPE bottle (containing lead acetate solution)

B. Standard Cyanide 60mL HDPE bottle for sample preservation (containing Sodium Hydroxide pellets)

HOLDING TIMES

The holding time for Free, WAD and Total Cyanide analysis in water samples is 14 days.

REFERENCES

APHA (2012) – Method 4500 CN O in Standard Methods for the Examination of Water and Wastewater.

Environment Australia (1998) – Cyanide Management: Best Practise Environmental Management in Mining.

USEPA (1996) – Method 9012 Total and Amenable Cyanide in Test Methods for Evaluating Solid Waste, Physical/Chemical Methods (3rd Edition).

ISO 14403 (2002) - Water quality — Determination of Total Cyanide and Free Cyanide by Continuous Flow Analysis.

ASTM D7237 - Standard Test Method for Free Cyanide with Flow Injection Analysis (FIA) Utilizing Gas Diffusion Separation and Amperometric Detection.