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CYANIDE ANALYSIS: INTERFERENCES, CHALLENGES, TROUBLESHOOTING & MAXIMISING DATA QUALITY

INTRODUCTION

Industry experts in the Environmental and Mining fields are all aware that both the chemistry of and analysis for Cyanide is a complex topic.

This Enviromail, the first of two, is designed to explain some of the technical issues and provide the Environmental Scientist or practitioner with some insight into factors which can potentially lead to data quality issues such as false positives or negatives. The impacts of false positives for Cyanide can be considerable and emotive for clients, just as the impacts of false negatives can be serious for the Environment.

METHOD CHANGES AND WHY?

With Cyanide analysis, various sample matrices present different quality challenges and therefore it is important to understand some chemistry and limitations. ALS has recently completed a year-long investigation and validation involving a thousand (plus) Cyanide tests on differing matrices. This will see ALS adopt new automated procedures which have been fine tuned to minimise false positives and negatives. ALS methods have also quantified the effects of some common interfering chemicals. The outcome has been a slight modification to methods and method references (see below). These methods have been rigorously tested for equivalence against current procedures, found to be superior and will automatically be adopted nationally starting with Melbourne (Springvale) effective immediately. This change has been made in the interests of data quality, low level precision and accuracy however includes ancillary benefits.

BENEFITS IN ADDITION TO QUALITY

ALS will move to 60mL containers which in turn will;

- Improve sampling efficiency for ground waters
- Increase the number of samples that can be sent via air under DG protocols (by 400%)
- Reduce the weight of eskies (manual handling)

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

CYANIDE USES & REGULATION

Cyanide is known for its use in the mining industry for extracting gold and silver from ore, however this use only accounts for ~13% of Cyanide. The remainder is used in other industrial processes such as steel hardening, electroplating, plastics production, and manufacture of adhesives, computer electronics, fire retardants, cosmetics, dyes, nylon, paints, pharmaceuticals, rocket propellant and the production of salts.

Cyanide is regulated because of potential significant impact not only on human health but also the environment. Guidelines including ADWG, ANZECC, NEPM and NAGD regulate Cyanide and it is a common test in many local waste classification and EPA screens.

CYANIDE ANALYSIS AND THE MANAGEMENT OF INTERFERENCES

There are several interferences for Cyanide analysis listed in methods such as APHA. These include:

- Sulfide
- Thiocyanate
- Nitrates/Nitrites
- Oxidising agents (e.g. Chlorine)

Sulfide Interferences

Enviromail 62 – June 2012, the second in this series provides full detail on field practices to eliminate Sulfide interferences. Sulfide can cause false negatives if not removed in the field.

Nutrient induced false positives:

Nitrate and Nitrite cause positive interferences for Cyanide during distillation by reacting with organic compounds. Nitrate may also be reduced to Nitrite compounding this interference. These interferences are removed at the laboratory prior to distillation by the addition of Sulfamic acid. For this reason, matrices with very high levels of nutrients may require special attention. In such cases a matrix study may become important in evaluating data quality.

UV induced false negatives

Iron-Cyanide complexes can break down in the presence of UV light. It is therefore important to store samples in the dark. Opaque sample containers are supplied to facilitate this.

Chlorine similarly can create false negatives.

Thiocyanate induced false positives

Thiocyanate can positively bias Cyanide analysis under distillation at a rate of 0.4% of the SCN concentration. 'Cyanide kill' (e.g. 'Inco' process) type samples can exhibit these effects.

CYANIDE ANALYSIS USING UV IRRADIATION AND MEMBRANE DIFFUSION

The analysis of Cyanide involves chemical reactions that break down complex Cyanides to give Free, measurable Cyanide ions. Traditionally these involve distillation/digestion incorporating heat and different strength acid solutions to determine various forms of Cyanide (i.e. Free, WAD and Total). The traditional ALS procedures for the analysis of Total, WAD and Free Cyanide have involved distillation/digestion followed by colorimetric determination.

The new NATA accredited procedure utilises Segmented Flow Analysis to determine Total, WAD and Free Cyanide in soil and water matrices. This fully automated system replaces manual distillation (using strong acids under heated conditions) with on-line UV irradiation for the break-down of tightly bound metal complexes in the determination of Total Cyanide. A diffusion membrane separates the Cyanide ions from the acidified sample stream (and potential interferences contained therein) replacing the need for manual distillation/digestion. The final colorimetric measurement follows the identical principles and chemistry to previous ALS methodology.

This analytical technique is widely used in the mining industry for the analysis of Cyanide and the physical preparation/digestion is based on recognised standards such as ISO 14403 and ASTM D7237. The significant improvements to Cyanide measurement to be gained through this technique are:

- Automation improves precision by eliminating variation inherent in manual techniques.
- Shorter analysis times increase service delivery.
- Reduction in the usage of chemicals and boiling acids (OH&S and Environmental benefits).
- Improvement in quality through reduction of certain interferences:
  - Under previous methods any thiosulfate present would react to form elemental Sulfur and Sulfur dioxide, leading to positive or negative interferences dependent on sample chemistry. With UV irradiation and membrane diffusion, strong acids and heat are eliminated reducing these interfering affects.
  - Under previous distillation conditions, Aldehydes could transform Cyanide to Nitrite (Nitrite having a positive interference). Thiocyanate can also be generated during the distillation process leading to positive bias. Distillation is not required under the segmented flow technique thus avoiding these types of interference.
- Facilitates sample volume reduction (i.e. 60mL versus 250mL sample volume) and associated benefits of waste reduction, transport cost and associated environmental impact reduction, manual handling improvements, etc.
- Improved management of sample-to-sample carryover.
- The ability to offer a trace level Cyanide method for certain water matrices.
- Significantly increased knowledge on Cyanide chemistry and interferences among ALS chemists and the client services team to facilitate increased trouble shooting ability for clients.

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. Refer to Enviromail 62.

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, Total Cyanide and Weak Acid Dissociable Cyanide by Flow Injection Analysis, in "Standard Methods for the Examination of Water and Wastewater", 22nd Ed.

Environment Australia (1998) – Cyanide Management: Best Practice 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