

Cyanide Analysis — Reducing Laboratory Operating Costs without Compromising Data Quality or Regulatory Compliance

Application Note 35150210

Keywords

ASTM D 7511-09
CNSolution™ Cyanide Analyzer
Gas-diffusion Amperometry
CNIRS—Cyanide Numerical
Interference Rating System

Introduction

The first generation of U.S. EPA cyanide analysis methods for Cyanides Amenable to Chlorination ([CATC] 335.1) and Total Cyanide (335.2) date back to the 1970s. The acid distillation step and colorimetric chemistries employed in these methods are susceptible to matrix interferences and are known to cause either negative or positive analytical biases. In fact, the U.S. EPA Solutions to Analytical Chemistry Problems with Clean Water Act Methods (“Pumpkin Guide”) states; “Next to oil and grease, cyanide is the pollutant for which the most matrix interferences have been reported to EPA.” The preliminary distillation step in these methods is also labor-intensive, increases the cost per analysis, and has a significantly lower sample throughput rate than non-distillation methods.

Newer U.S. EPA and ASTM methods (e.g., OIA-1677, D 6888-04, D 7237-06, D 7284-08, and D 7511-09), based on gas-diffusion amperometry, were specifically developed to mitigate the interferences associated with methods involving a distillation step. The Cyanide Numerical Interference Rating- System (CNIRS) allows direct comparison of the severity of interferences associated with different methods.

This application note compares and contrasts the analytical interferences, sample throughput, labor, equipment, and operating costs of distillation methods to more advanced U.S. EPA and ASTM methods for analysis of Available, CATC, Weak Acid Dissociable (WAD), and Total Cyanide.

Cyanide Analysis Methods

Cyanide methods are devised to measure groups of compounds (cyanide complexes) with similar characteristics and report them as a single value by performing sample pretreatment procedures such as acid distillation or addition of ligand exchange reagents. A summary of the most commonly used cyanide analysis methods including cyanide species measured and analytical technique employed is presented in Table 1.

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Table 1. Summary of Cyanide Analysis Methods

Description Name	Method	Description	Potential Interferences	Measurement
Free Cyanide	ASTM D 4282	Passive Diffusion at pH 6 and room temperature	<ul style="list-style-type: none"> Storage Measurement 	<ul style="list-style-type: none"> Manual chlorination of cyanide with chloramine-T and subsequent reaction with pyridine-barbituric acid. Maximum absorbance is determined by manual colorimetry.
	ASTM D 7237	Flow Injection Analysis (FIA) into a reagent at a pH of 6–8	<ul style="list-style-type: none"> Storage Measurement 	Gas-Diffusion Amperometry
Available Cyanide (CATC) (WAD)	SM 4500-CN G	<ul style="list-style-type: none"> Alkaline Chlorination to destroy all weak and dissociable metal-cyanide complexes and any free or simple cyanide. Two manual distillations (total-chlorinated)=CATC 	<ul style="list-style-type: none"> Excessive light, ammonia. Incomplete recovery on Ag-cyanide complexes. Storage Distillation Measurement 	<ul style="list-style-type: none"> Manual chlorination of cyanide with chloramine-T and subsequent reaction with pyridine-barbituric acid. Maximum absorbance is determined by manual colorimetry.
	ASTM D2036			
	ASTM D2036	Buffered (pH 4.5) manual distillation	<ul style="list-style-type: none"> Excess of Fe-cyanide complexes. Incomplete recovery on Hg-cyanide complexes. Storage Distillation Measurement 	<ul style="list-style-type: none"> Manual chlorination of cyanide with chloramine-T and subsequent reaction with pyridine-barbituric acid. Maximum absorbance is determined by manual colorimetry, manual Ion Selective Electrode (ISE), and Titration.
	ASTM D4374	Buffered (pH 4.5) automated flash distillation	<ul style="list-style-type: none"> Storage Distillation Measurement 	<ul style="list-style-type: none"> Automated chlorination of cyanide with chloramine-T and subsequent reaction with pyridine-barbituric acid. Automated colorimetry
	Kelada 01			
	OIA 1677 ASTM D6888	Pretreatment with ligand exchange reagents, room temperature automated gas diffusion.	<ul style="list-style-type: none"> Storage Measurement 	Gas-Diffusion Amperometry
Total Cyanide	SM 4500 CN D	<ul style="list-style-type: none"> Cyanide ion is released from cyanide complexes as HCN by means of macro manual reflux-distillation in the presence of a strong sulfuric acid solution and magnesium chloride. The HCN is swept into a dilute sodium hydroxide absorber solution. 	<ul style="list-style-type: none"> Storage Distillation Measurement Excessive Light 	Cyanide in the absorber solution is titrated with silver nitrate.
	SM 4500 CN E			<ul style="list-style-type: none"> Cyanide in the absorber solution is converted to cyanogen chloride by manual reaction with chloramine-T at pH <8. After reaction, the cyanogen chloride forms a red-blue color on addition of pyridine-barbituric acid reagent. Maximum color is determined by manual colorimetry.
	ASTM D2036	<ul style="list-style-type: none"> Cyanide ion is released from cyanide complexes as HCN by means of a macro, or scaled down manual reflux-distillation in the presence of a strong sulfuric acid solution and magnesium chloride. The HCN is swept into a dilute sodium hydroxide absorber solution. 	<ul style="list-style-type: none"> Storage Distillation Measurement Excessive Light 	<ul style="list-style-type: none"> Cyanide in the absorber solution is titrated with silver nitrate. Cyanide in the absorber solution is determined manually by Ion Selective Electrode (ISE). Cyanide in the absorber solution is converted to cyanogen chloride by manual reaction with chloramine-T at pH <8. After reaction, the cyanogen chloride forms a red-blue color on addition of a pyridine-barbituric acid reagent. Maximum color is determined by manual colorimetry.
	EPA 335.4	<ul style="list-style-type: none"> Cyanide ion is released from cyanide complexes by means of a scaled down (midi) manual reflux-distillation in the presence of a strong sulfuric acid solution and magnesium chloride. The HCN is swept into a dilute sodium hydroxide absorber solution. 	<ul style="list-style-type: none"> Storage Distillation Measurement Excessive Light 	<ul style="list-style-type: none"> Cyanide in the absorber solution is converted to cyanogen chloride by automated reaction with chloramine-T at pH <8. After reaction the cyanogen chloride forms a red-blue color on addition of a pyridine-barbituric acid reagent. Maximum color is determined by automated colorimetry.
	Kelada 01, ASTM D4374, EPA 335.3	<ul style="list-style-type: none"> Cyanide ion is released from cyanide complexes by means of UV irradiation and automated flash distillation in the presence of a strong sulfuric acid solution. The HCN generated is injected into an auto chemistry analyzer chemistry cartridge. 	<ul style="list-style-type: none"> Storage UV Irradiation Distillation Measurement 	<ul style="list-style-type: none"> Cyanide in the adsorber solution is converted to cyanogen chloride by automated reaction with chloramine-T at pH <8. After reaction, the cyanogen forms a red-blue color on addition of a pyridine-barbituric acid reagent. Maximum color is determined by automated colorimetry.
	ASTM D7284	<ul style="list-style-type: none"> Cyanide ion is released from cyanide complexes by means of a scaled down (midi) manual reflux-distillation in the presence of a strong sulfuric acid solution and magnesium chloride. The HCN is swept into a dilute sodium hydroxide absorber solution. 	<ul style="list-style-type: none"> Storage Distillation Measurement 	Cyanide in the absorber solution is determined by automated gas diffusion amperometry.
	OIA 1678/ASTM D7511-09	<ul style="list-style-type: none"> Cyanide ion is released from cyanide complexes by UV irradiation. The HCN generated diffuses across a membrane and is measured amperometrically. 	<ul style="list-style-type: none"> Storage UV Irradiation Measurement 	Cyanide is determined by automated gas-diffusion amperometry.

The sample pre-treatment and processing procedures used in cyanide analysis methods are known to cause negative or positive analytical biases. Analytical interferences that can be introduced by various sample processing techniques are summarized in Table 2. Methods that employ acid distillation procedures prior to colorimetric measurements are the most prone to interferences.

Table 2: Summary of Known Interferences from Sample Processing Procedures in Cyanide Analysis Methods

Compound	Process/Measurement Technique	Description of Interference
Oxidizers	Distillation	Reacts with cyanide decreasing its concentration.
Sulfide	Distillation	Distills into absorber solution and reacts with CN forming thiocyanate.
	Gas-diffusion	Passes through diffusion membrane.
Sulfite (or Sulfur Dioxide)	Distillation	Reacts with cyanide decreasing its concentration. Distills into absorber solution and reacts with cyanide decreasing its concentration.
Thiosulfate and other oxidized sulfur species (except sulfate)	Distillation	Decompose to form native sulfur and sulfur dioxide. React with cyanide decreasing its concentration. Sulfur Dioxide distills into absorber solution and reacts with cyanide decreasing its concentration.
Thiocyanate	Cyanide Amenable to Chlorination (CATC)	Reacts with chlorine during alkaline chlorination and generates cyanide. Causes negative CATC results.
	Distillation	Decomposes to sulfur dioxide and reacts with cyanide decreasing its concentration. Sulfur dioxide distills into absorber solution.
	UV Irradiation	Can react at < 280 nm to form cyanide
Thiocyanate + Nitrate or Nitrite	Distillation	Decompose to form cyanide
Misc. Organics + Nitrate or Nitrite	Distillation	Decompose to form cyanide
Carbonate	Distillation	Excessive foaming and possible violent release of carbon dioxide
	Gas diffusion	Passes through diffusion membrane

The Cyanide Numerical Interference Rating System (CNIRS) provides a systematic approach for comparing the severity of interferences associated with sample processing and measurement techniques and directly comparing cyanide analysis methods ⁽¹⁾. Under the CNIRS system, the score increases each time a technique is cited for a known interference. The higher the CNIRS score, the greater the number of interferences reported for the technique (Table 3).

Table 3: Cyanide Numerical Interference System (CNIRS)
for Estimating Method Interferences

CN Technique	Score
Sampling, Preservation, and Storage	
Automated Method	1
Semi-Automated Method	2
Manual Method	3
Sample Processing	
Distillation	8
Gas-Diffusion	2
UV-irradiation	1
Measurement	
Colorimetry	3
GD–Amperometry	2

Tallying a composite CNIRS score for each cyanide analysis method allows the severity of method interferences to be classified and used for direct comparisons (Table 4).

Table 4: Composite CNIRS Scoring Ranges for Classification of Cyanide Method Interferences

	Class I	Class II	Class III
Composite Interference Score	3–6	7–10	>10
Interference Severity Rating	Low	Moderate	High

When the CNIRS system is applied to U.S. EPA method 335.4 for total cyanide analysis by acid distillation/ colorimetry it results in a composite interference score of 13 and a Class III interference severity rating for high levels of interferences.

When the CNIRS system is applied to ASTM method D 7511-09 for total cyanide analysis by gas–diffusion amperometry, it results in a composite interference score of 6 and a Class I interference severity rating for low levels of interferences.

Acid Distillation of Cyanide Samples

Acid distillation, is a sample pretreatment used to dissociate cyanide from metal cyanide complexes and separate cyanide from the matrix. Classical distillation involves boiling 500 milliliters of the sample in acid solution, purging with air, and trapping the HCN generated in 250 milliliters of a basic absorber solution. This manual “distillation” is a low throughput, labor intensive and expensive procedure.

Smaller volume distillations, known as Midi Dist, use more compact distillation glassware that reduces laboratory space requirements as well as the volume of sample and reagents required to complete the tests. The reduced space requirement of the midi distillation apparatus enables laboratories to increase capacity and somewhat decrease human errors.

The MICRO DIST system is a 21-place block digester that distills samples in disposable polypropylene tubes. The MICRO DIST scales the Midi distillation down further so less than 10 milliliters of sample is used.

Once a sample is distilled by macro distillation, midi distillation, or MICRO DIST an aliquot of the absorber solution can be analyzed by any of the methods known to determine cyanide in dilute sodium hydroxide solution (EPA 335.4 ⁽²⁾, ASTM D 7284-08).

UV Digestion of Cyanide Complexes

The UV digestion gas diffusion amperometry method performed on the CNSolution™ Cyanide Analyzer (Figure 1) eliminates distillation. An aliquot of the sample is placed on an autosampler tray and the instrument automatically decomposes metal cyanides to HCN, separates the HCN from the matrix, and accurately measures the CN concentration. There are no time consuming preliminary steps required. This method (ASTM D 7511-09) ⁽³⁾ has been proven reliable in numerous peer-reviewed articles and is cited on the U.S. EPA website as a possible amendment to 40 CFR 136 Clean Water Act Methods. The U.S. EPA currently grants approval to use the method on a case-by-case basis ⁽⁴⁾.



Figure 1. CNSolution Cyanide Analyzer

Sample Throughput — Acid Distillation Techniques vs. Gas Diffusion Amperometry

Figure 2 illustrates the maximum capacity possible with manual distillation compared to automated gas-diffusion amperometry performed on the CNSolution, cyanide analyzer. The maximum capacity is based on the number of samples possible to distill in an 8 hour work day on one 10 place midi distillation block, one 21-place Micro Dist, or one CNSolution analyzer configured to run total cyanide or available cyanide. Data for the Midi and Micro distillations are from a supplier company web site, and probably overstate potential capacity by not taking into account factors such as operator fatigue, coffee breaks, etc. Data on the CNSolution is based on the number of samples it can run in an 8 hour period at 1 minute per injection. Not included is the amount of time for the actual analysis of the samples that were manually distilled. The manual distillation data is strictly the maximum number of samples possibly processed, but not necessarily analyzed. The CNSolution data, represents simultaneous UV-digestion and analysis of samples.

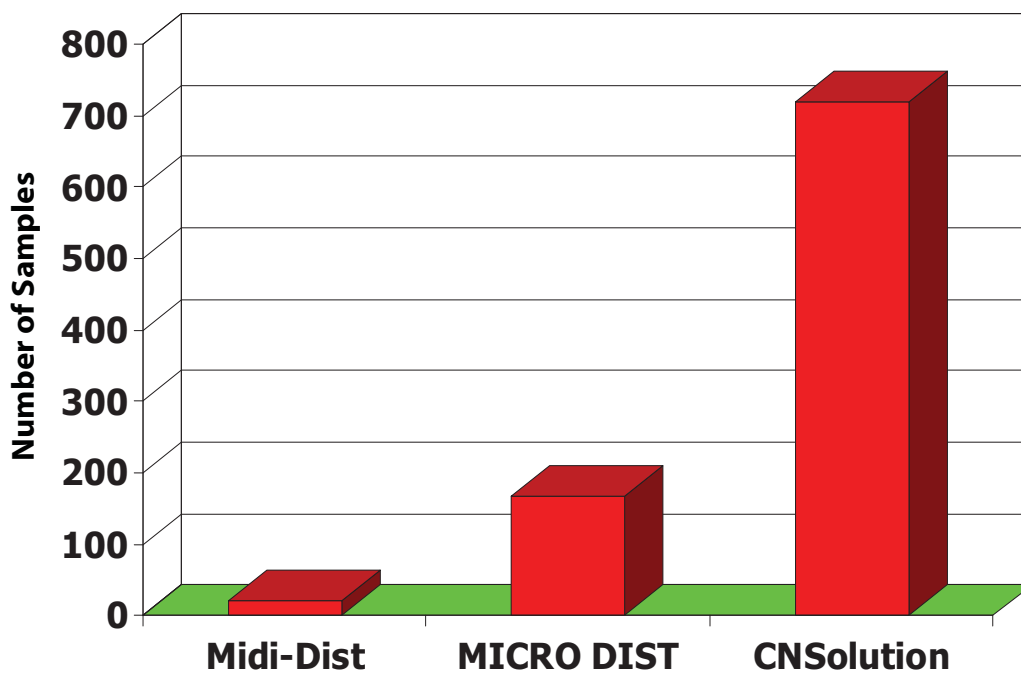


Figure 2. Analytical Sample Throughput in an 8-hour Shift

Reagent and Consumables Cost — Acid Distillation Techniques vs. Gas Diffusion Amperometry

Figure 3 summarizes the reagent and consumables cost for distillation and determination steps. The determinative step used in the calculation for the midi and micro distillations is a colorimetric measurement per EPA 335.4. The cost for gas-diffusion amperometry performed on a CNSolution analyzer is less than \$1.00 per test. While the cost of reagents for micro distillation is low, the consumable cost is high because of the disposable polypropylene distillation tubes. The midi distillation uses significantly more reagent per test than the MICRO DIST, increasing its cost.

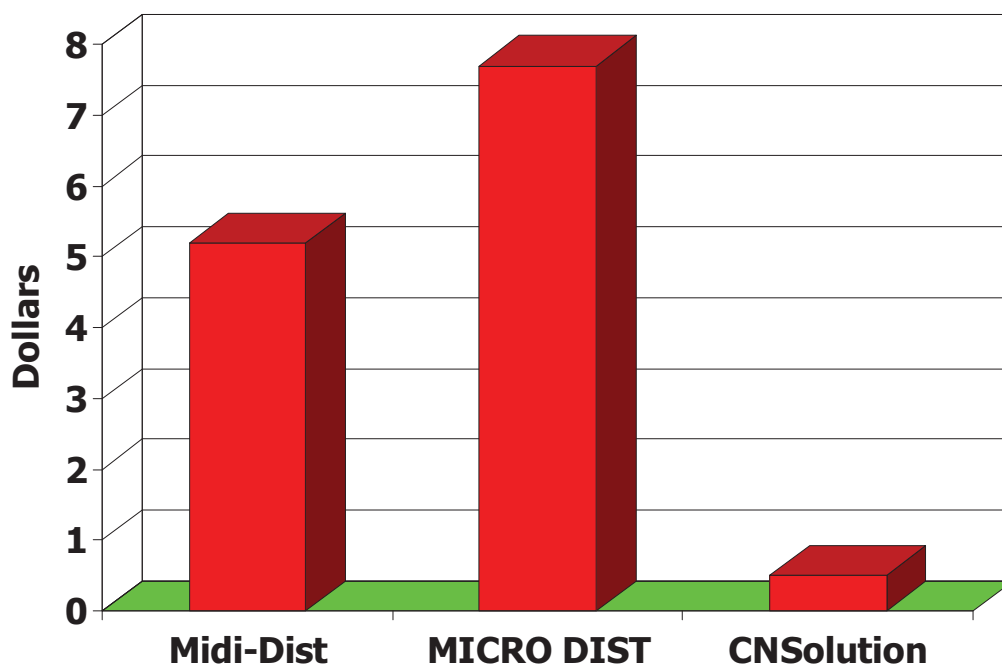


Figure 3. Estimated Reagent and Consumables Cost per Analysis Including Distillation and Final Determination Steps

Annual Operating Cost of Using Disposable Distillation Tubes

The MICRO DIST apparatus uses a disposable polypropylene distillation tube that has a fairly significant cost (~\$7.50) per test. Though glassware does break, the reusable glassware required for a midi distillation is not considered a consumable in this example (Figure 4). Because there is no distillation step required when gas diffusion amperometry methods are performed on the CNSolution there are no disposable costs associated with it.

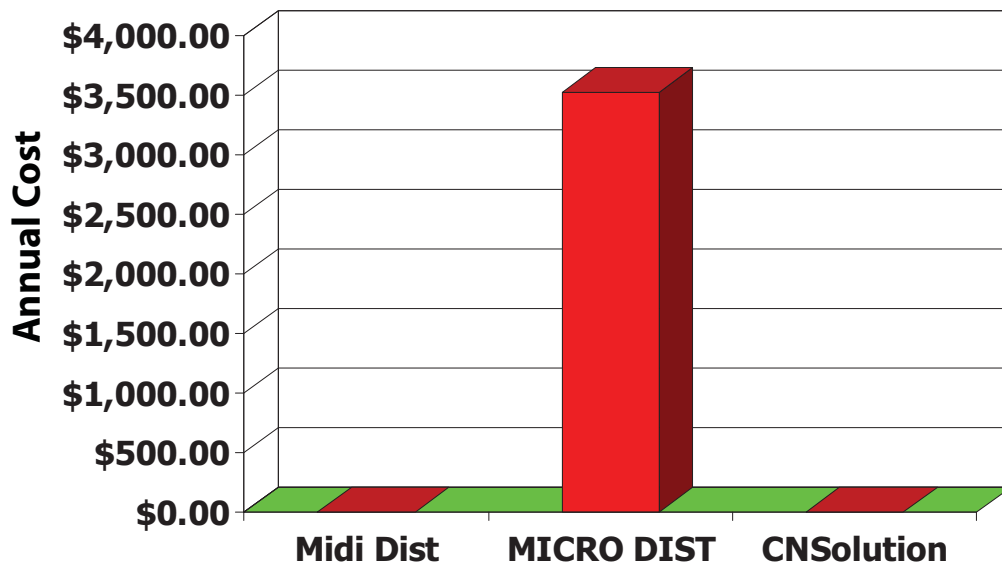


Figure 4. Estimated Annual Cost of Using Disposable Polypropylene Tubes to Distill and Analyze 40 Samples per Month

Labor Costs — Acid Distillation Techniques vs. Gas Diffusion Amperometry

The labor involved in the midi distillation includes estimated time spent on glassware setup, disassembly, and washing. Labor also includes the hands on labor of actually processing the samples (pipetting sample, acid, MgCl_2 , NaOH, etc). Because gas–diffusion amperometry methods performed on the CNSolution do not involve manual distillation of samples, there are no associated labor costs.

Figure 5 estimates the total cost of labor for a \$15.00 per hour technician to distill 40 samples per month. These estimates assume 100% efficiency and so they likely underestimate the actual cost.

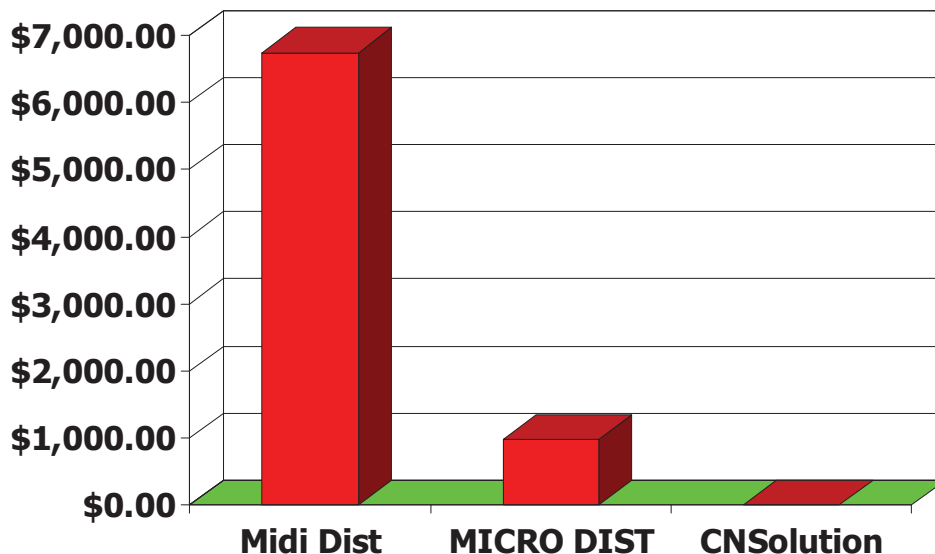


Figure 5. Estimated annual labor cost required for distilling and analyzing 40 samples per month

Total Annual Operating Costs — Acid Distillation Techniques vs. Gas Diffusion Amperometry

Total estimated annual operating cost for performing 40 and 100 cyanide analyses per month using MICRO DIST and midi distillations versus analyses performed using gas-diffusion amperometry are presented in Figure 6. The labor and materials costs increase with the number of distillations a lab must perform.

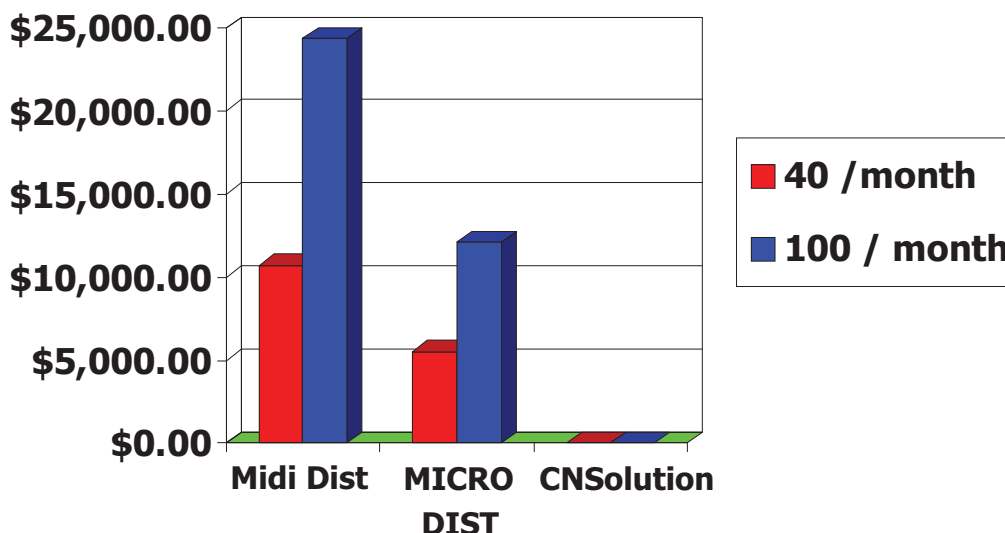


Figure 6. Estimated Total Annual Operating Costs for Acid Distillation versus Gas-diffusion Amperometry Cyanide Methods.

Summary & Conclusions

Newer U.S. EPA and ASTM cyanide analysis methods based upon gas-diffusion amperometry do not require a preliminary acid distillation step. These methods were specifically developed to mitigate interferences and analytical biases associated with acid distillation and provide more accurate results.

Moving away from cyanide methods with acid distillations sample pretreatment steps to gas-diffusion amperometry methods has the additional benefit of significantly reducing a laboratory's operating costs. The U.S. EPA currently grants case-by-case approval for laboratories to use ASTM D 7511-09 for total cyanide analysis in lieu of method 335.4 which requires acid distillation of samples. The U.S. EPA has cited ASTM D 7511-09 as one of the possible amendments to 40 CFR 136 Clean Water Act Methods on their website. Full regulatory approval will come with publication of next the Method Update Rules (MUR) in the Federal Register.

Laboratories adopting gas-diffusion amperometry cyanide analysis methods can reduce their operating costs, improve data quality, and meet regulatory compliance requirements.

References

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