ROI Analysis of Total Cyanide Testing by ASTM Method D 7511-09e2

Introduction

The first generation of U.S. EPA cyanide analysis methods from the 1970s employ an acid distillation sample pretreatment step to dissociate cyanide from metal-cyanide complexes and separate cyanide from the matrix. Acid distillation is known to cause either negative or positive analytical biases depending upon the composition of the sample matrix being tested. In fact, the U. S. EPA Solutions to Analytical Chemistry Problems with Clean Water and Methods[(1)] ("Pumpkin Guide") notes; "Next to oil and grease, cyanide is the pollutant for which the most matrix interferences have been reported."

On April 17th, 2012, the U.S. EPA Administrator signed a Methods Update Rule (MUR) approving new analytical methods for testing of pollutants in wastewater under the Clean Water Act.[(2)] Six ASTM methods (including ASTM D 7511-09e2) covering sampling, preservation, and analysis of free, available and total cyanide species were included in the final MUR. Facilities with National Pollutant Discharge Elimination System (NPDES) permits can now use ASTM D 7511-09e2[(3)] to test wastewater samples for regulatory compliance reporting.

ASTM D 7511-09e2 uses narrow-band, low- watt UV irradiation to decompose metal-cyanide complexes in samples at ambient temperature in a continuously flowing acidic stream. Reducing and complexing reagents, combined with ambient temperature UV digestion minimize the formation of matrix interferences. Elimination of the sample distillation step enables measurement of cyanide at lower concentrations with improved precision.

Instrumentation for Cyanide Analysis by ASTM D 7511-09e2

ASTM D 7511-09e2 defines design and performance characteristics a flow injection analysis (FIA) instrument should possess to perform the method. Among the design features needed for this in-line UV digestion, gas-diffusion amperometry method are a UV digestion module with a 312-nm lamp, a gas diffusion manifold with a hydrophobic membrane, an amperometric detector equipped with a silver working electrode, an AgCl reference electrode, and a Pt or stainless steel counter electrode.

The CNSolution™ 3100 Cyanide Analyzer (Figure 1) is a compact, modular, laboratory instrument that meets the requirements stated in ASTM D 7511-09e2.

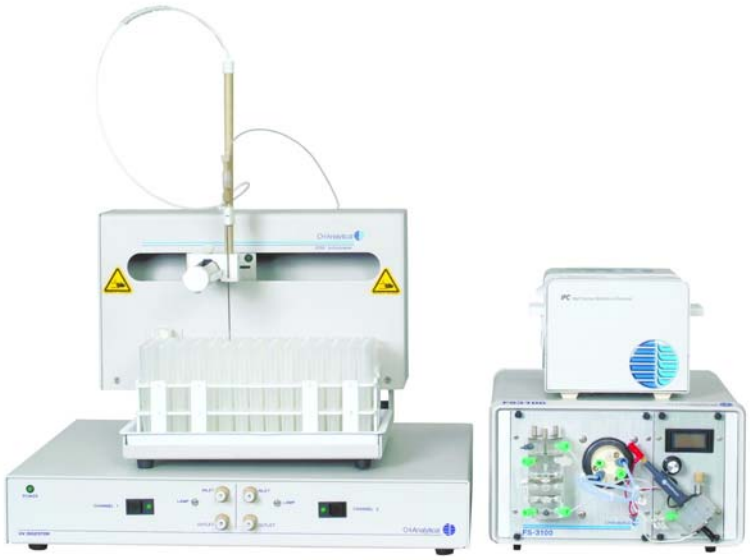

Figure 1. OI Analytical CNSolution™ 3100 Cyanide Analyzer for ASTM D 7511-09e2

Advantages of ASTM D 7511-09e2 for Lab Operation

Laboratories gain a number of operational benefits by employing ASTM D 7511-09e2 for cyanide analysis beyond a reduction in matrix interferences and improved analytical performance[(4)].

ASTM D 7511-09e2 does not require the preliminary acid distillation step specified in method 335.4.[(5)] Eliminating the distillation step provides laboratories the following operational advantages.

- Higher sample throughput
- Lower labor costs
- Lower cost per analysis for reagents and consumables
- Eliminates analyst exposure to hazardous reagents (boiling, concentrated sulfuric acid and pyridine)

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Sample Throughput

Figure 2 illustrates the maximum capacity possible when performing manual distillation and analysis by 335.4 compared to in-line UV digestion and gas-diffusion amperometry per ASTM D 7511-09e2. The maximum capacity is based on the samples possible to distill in an 8 hour work day using a 10-position Midi distillation block, a 21-position MICRO DIST apparatus, or a CNSolution™ 3100 cyanide analyzer configured to run ASTM D 7511-

09e2. Data for the Midi and MICRO DIST distillations are from a supplier website and probably overstate potential capacity by not taking into account factors such as operator fatigue, coffee breaks, etc. Data for the CNSolution™ 3100 analyzer is based on the number of samples it can run in an 8 hour period at 1 minute per injection with simultaneous UV-digestion and analysis of samples by ASTM D 7511-09e2.

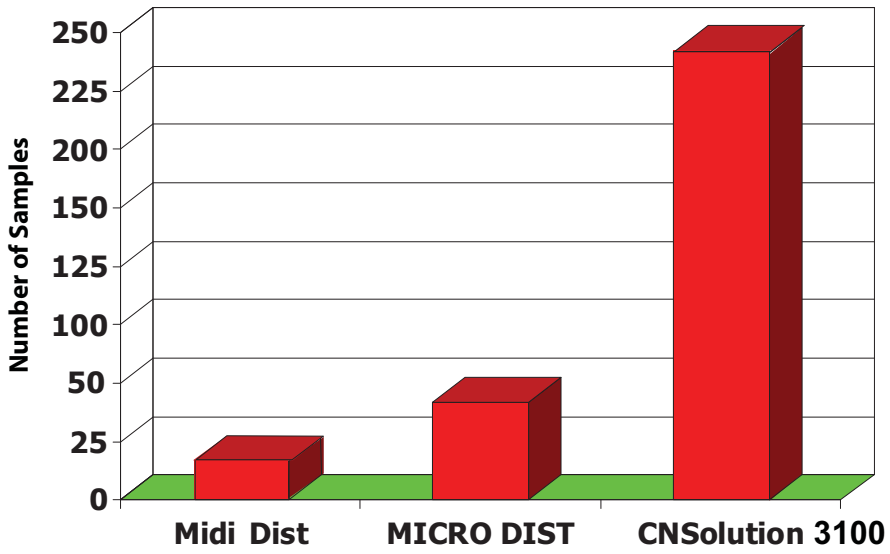

Figure 2. Sample throughput in an 8-hour shift for manual distillation and analysis by Method 335.4 versus in-line UV digestion and analysis by ASTM D7511-09e2

Labor Costs

Figure 3 illustrates the estimated annual labor costs required for manual distillation and analysis of 40 samples per month by method 335.4 versus in-line UV digestion and analysis by ASTM D 7511-09e2. A cost of $15.00 per hour for technician time was used in these estimates.

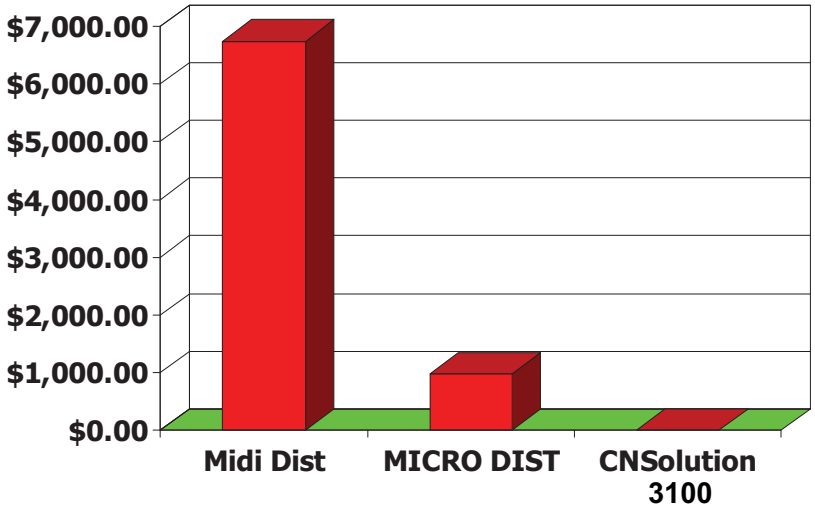

Figure 3. Estimated annual labor cost for distilling and analyzing 40 samples per month by Method 335.4 versus ASTM D 7511-09e2

The labor involved in performing midi distillations includes estimated time spent on glassware setup, disassembly and washing. Labor also includes hands-on labor associated with pipetting samples and reagents ($MgCl_2$, NaOH, etc.). The MICRO DIST apparatus uses disposable polypropylene distillation tube, which eliminates some of the labor costs associated with re-usable Midi distillation glass tubes/flasks.

ASTM D 7511-09e2 uses automated in-line UV digestion instead of a manual distillation step so there are no labor costs for sample distillation.

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 3100 there are no disposable costs associated with it.

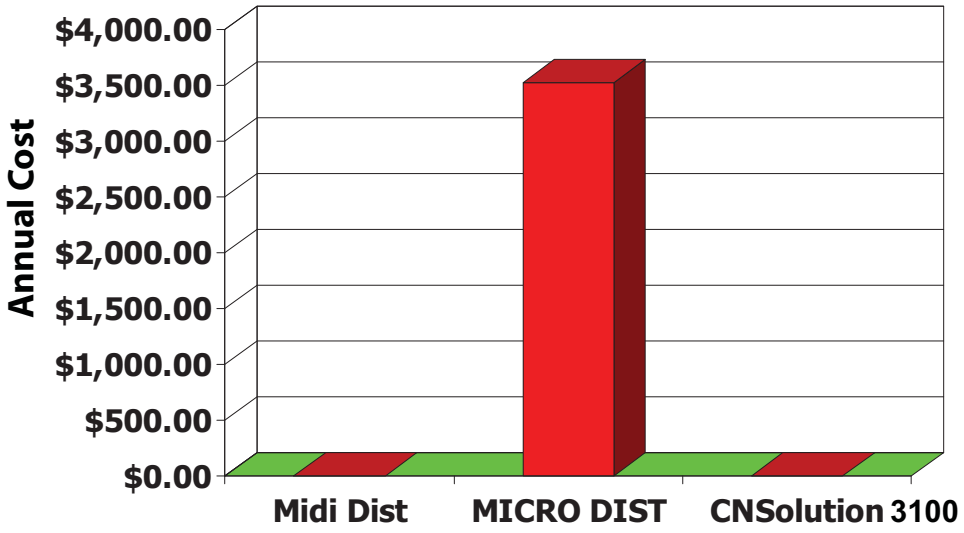

Figure 4. Estimated Annual Cost of Using Disposable Polypropylene Tubes to Distill and Analyze 40 Samples per Month

Reagent and Consumables Cost Per Analysis

Figure 5 presents the estimated cost per analysis of reagents and consumable items to perform cyanide analysis by method 335.4 versus ASTM D 7511-09e2. While the MICRO DIST apparatus uses reduced amounts of reagents, the potential savings is offset by the high cost of disposable polypropylene distillation tubes. The larger volume of reagents required to perform Midi distillations increases its cost per analysis. The cost per analysis for performing

ASTM D 7511-09e2 on a CNSolution™ cyanide analyzer is less than $1.00 because no distillation reagents or consumables are required.

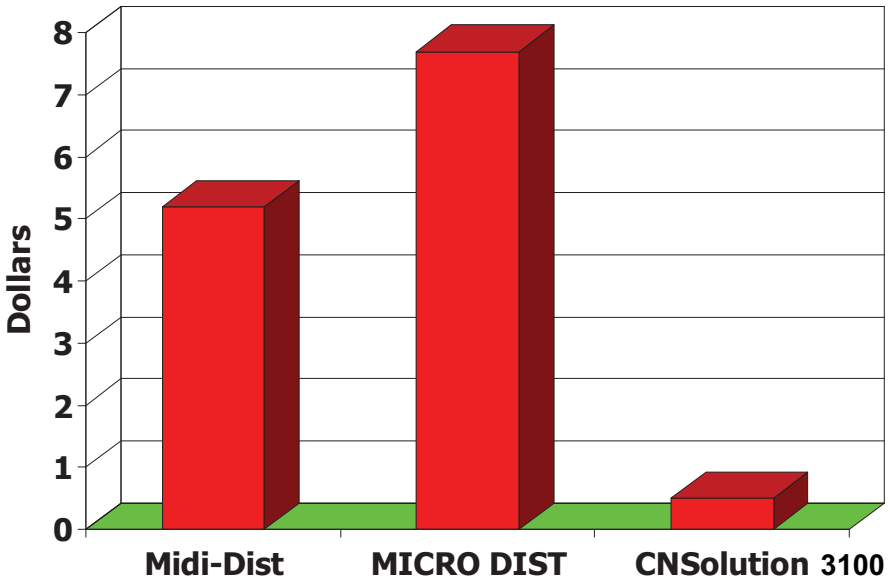

Figure 5. Estimated reagent and consumable cost per analysis for cyanide analysis by Method 335.4 versus ASTM D 7511-09e2

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.

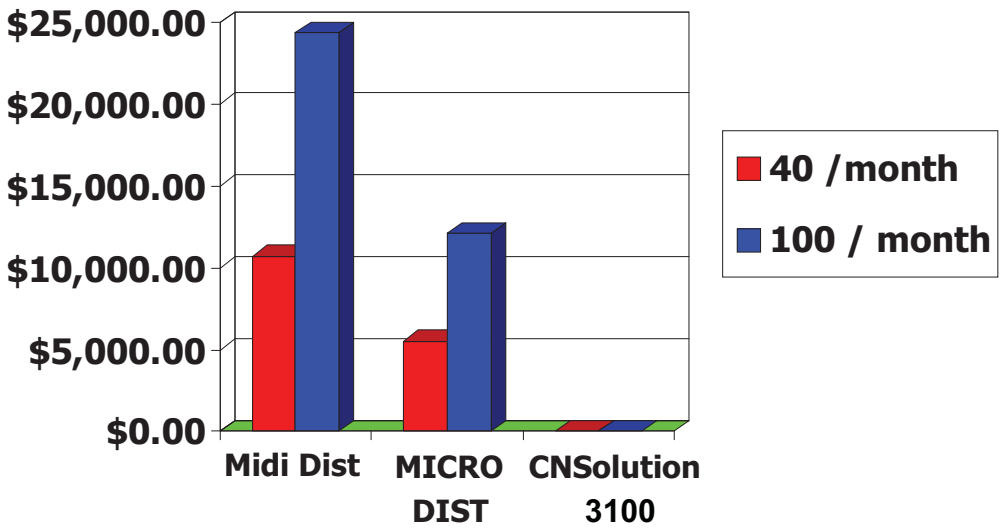

Figure 6. Estimated Total Annual Operating Costs for Acid Distillation versus Gas-diffusion Amperometry Cyanide Methods

ROI Analysis Worksheets

The preceding sections of this whitepaper identified and compared factors affecting the cost of performing total cyanide analysis by a method requiring acid distillation (335.4) versus ASTM D 7511-09e2, which employs automated in-line UV digestion. Sample throughput, labor, disposable plastic distillation tubes, cleaning reusable distillation glassware, distillation reagents, waste generation and disposal all affect the cost per analysis and annual operating cost.

The operating practices and cost structure in each lab are different requiring compilation of lab-specific costs for use in return on investment (ROI) calculations. Cost comparisons for total cyanide analysis of 40 and 100 samples per month are provided as representative examples.

Cost Comparison for Total Cyanide Analysis of 40 Samples Per Month

Table 1: Labor (Time) Required for Distillation

Task/Labor in Minutes	Micro Dist (21 Samples)	Midi Dist (10 Samples)	CNSolution 3100
Setup Time	15	30	0
Warm Up Time	15	30	0
Distillation Time (per sample)	30	120	0
Cool Down Time	0	15	0
Clean Up and Tear Down Time	5	30	0
Total Time in Minutes per Batch	65	225	0

NOTE: Total Cyanide analysis by ASTM D 7511-09e2 does not require an acid distillation step. The UV digestion module of the CNSolution 3100 automates dissociation of metal-cyanide complexes and does not require any direct labor.

Table 2: Monthly Labor Costs for Distillation of 40 Samples

	Micro Dist	Midi Dist	CNSolution 3100
# of Samples per Month	40	40	0
# Samples per Batch	21	10	0
# Batches per Month	2	4	0
Time Spent per Month (hours)	2.17	15	0
Technician Salary ($ per hour)	15	15	15
Labor Cost per Batch (includes overhead)	$81.25	$562.50	$0.00
Total Labor Cost per Month	$162.50	$2,250.00	$0.00

Table 3: Annual Labor Costs for Distillation of 40 Samples per Month

	Micro Dist	Midi Dist	CNSolution 3100
# Batches per Year	24	48	0
Time Spent per Year (hours)	26	180	0
Technician Salary ($ per hour)	15	15	15
Labor Costs per Year (includes overhead)	$975.00	$6,750.00	$0.00

Table 4: Total Annual Cost of Consumables for Distillation of 40 Samples per Month

Required Consumable	Micro Dist	Midi Dist	CNSolution 3100
Micro Dist Tubes (each)	7	NA	0
# Batches per Year	24	48	0
# Tubes per Batch	21	0	0
# Tubes per Year	504	0	0
Total Consumable Cost per Year	$3,528.00	NA	$0.00

Table 5: Total Annual Cost of Reagents for Distillation of 40 Samples per Month

Required Reagent	Micro Dist	Midi Dist	CNSolution 3100
Sulfuric Acid	$10.00	$100.00	$0.00
Sulfamic Acid	$23.20	$232.00	$0.00
Magnesium Chloride	$37.20	$372.00	$0.00
Sodium Hydroxide	$35.80	$358.00	$0.00
Reagent Labor	$129.48	$1295.00	$0.00
Total Reagent Cost per Year	$235.68	$2,357.00	$0.00

Table 6: Initial Cost for Distillation / UV Digestion Equipment

	Micro Dist	Midi Dist	CNSolution 3100
Micro Dist	$4,000.00	NA	NA
Midi Apparatus + all glassware	NA	$8,000.00	NA
UV Digestion Module + supplies	NA	NA	$5,500.00
Total Initial Investment	$4,000.00	$8,000.00	$5,500.00
Total Amortized Investment (5 Years)	$800.00	$1,600.00	$1,100.00

Table 7: Annual Cost of Total Cyanide Analysis by Distillation Method 335.4 versus ASTM Method D 7511-09e2

	Micro Dist	Midi Dist	CNSolution 3100
Labor (sample preparation)	$975.00	$6,750.00	$0.00
Consumables (sample preparation)	$3,528.00	$6,750.00	$0.00
Reagents (sample preparation)	$235.68	$2,357.00	$0.00
Total Cost (labor, consumables, reagents)	$4,738.68	$9,107.00	$0.00
Amortized Capital Equipment (sample preparation)	$800.00	$1,600.00	$1,100.00
Total Cost	$5,538.68	$10,707.00	$1,100.00

NOTE: Calculation assumes the cost of the measurement step is equivalent.

Table 8: Labor (Time) Required for Distillation

Task/Labor in Minutes	Micro Dist (21 Samples)	Midi Dist (10 Samples)	CNSolution 3100
Setup Time	15	30	0
Warm Up Time	15	30	0
Distillation Time (per sample)	30	120	0
Cool Down Time	0	15	0
Clean Up and Tear Down TIme	5	30	0
Total Time in Minutes per Batch	65	225	0

Table 9: Monthly Labor Costs for Distillation of 100 Samples

	Micro Dist	Midi Dist	CNSolution 3100
# of Samples per Month	100	100	0
# Samples per Batch	21	10	0
# Batches per Month	5	10	0
Time Spent per Month (hours)	5.16	37.5	0
Technician Salary ($ per hour)	15	15	15
Labor Cost per Batch (includes overhead)	$193.45	$1,406.25	$0.00
Total Labor Cost per Month	$921.20	$14,062.50	$0.00

Table 10: Yearly Labor Costs for Distillation of 100 Samples per Month

	Micro Dist	Midi Dist	CNSolution 3100
# Batches per Year	57.1	120	0
Time Spent per Year (hours)	61.9	450	0
Technician Salary ($ per hour)	15	15	15
Labor Costs per Year (includes overhead)	$2,321.43	$16,875.00	$0.00

Table 11: Total Annual Cost of Consumables for Distillation of 100 Samples per Month

Required Consumable	Micro Dist	Midi Dist	CNSolution 3100
Micro Dist Tubes (each)	$7.00	NA	0
# Batches per Year	57	120	0
# Tubes per Batch	21	0	0
# Tubes per Year	1200	0	0
Total Consumable Cost per Year	$8,400.00	NA	$0.00

Table 12: Total Annual Cost of Reagents for Distillation of 100 Samples per Month

Required Reagent	Micro Dist	Midi Dist	CNSolution 3100
Sulfuric Acid	$25.00	$250.00	$0.00
Sulfamic Acid	$58.00	$580.00	$0.00
Magnesium Chloride	$93.00	$930.00	$0.00
Sodium Hydroxide	$89.50	$895.00	$0.00
Reagent Labor	$323.70	$3,237.00	$0.00
Total Reagent Cost per Year	$589.20	$5,892.00	$0.00

Table 13: Initial Cost for Distillation / UV Digestion Equipment

	Micro Dist	Midi Dist	CNSolution 3100
Micro Dist	$4,000.00	NA	NA
Midi Apparatus + all glassware	NA	$8,000.00	NA
UV Digestion Module + supplies	NA	NA	$5,500.00
Total Initial Investment	$4,000.00	$8,000.00	$5,500.00
Total Amortized Investment (5 Years)	$800.00	$1,600.00	$1,100.00

Table 14: Annual Cost for Total Cyanide Analysis by Distillation Method 335.4 versus ASTM D 7511-09e2

	Micro Dist	Midi Dist	CNSolution 3100
Labor (sample preparation)	$2,231.43	$16,875.00	$0.00
Consumables (sample preparation)	$8,400.00	$0.00	$0.00
Reagents (sample preparation)	$589.20	$5,892.00	$0.00
Total Cost (labor, consumables, reagents)	$11,310.63	$22,767.00	$0.00
Amortized Capital Equipment (sample preparation)	$800.00	$1,600.00	$1,100.00
Total Cost	$12,110.63	$24,367.00	$1,100.00

NOTE: Calculation assumes the cost of the measurement step is equivalent.

Summary and Conclusions

ASTM D 7511-09e2 is USEPA-approved for total cyanide analysis of NPDES wastewater samples and does not require a preliminary acid distillation step. This method was specifically developed to mitigate interferences and analytical biases associated with acid distillation and provide more accurate test results.

Laboratories moving away from cyanide analysis methods with acid distillation pretreatment steps can significantly reduce their operating costs, improve data quality, and meet regulatory compliance requirements.

Worksheets enabling laboratories to compile their specific costs and perform ROI calculations have been provided to determine the cost savings associated with total cyanide analysis by ASTM D 7511-09e2.

References

1. Solutions to Analytical Chemistry Problems with Clean Water Act Methods, U. S. EPA Office of Science and Technology, March 2007.

2. U. S. EPA Clean Water Act Analytical Methods - Recent Regulatory Changes; http://water.epa.gov/scitech/methods/update/cwa/update_index.cfm.

3. ASTM D 7511-09e2 Standard Test Method for Total Cyanide by Segmented Flow Injection Analysis, In-line Ultraviolet Digestion and Amperometric Detection, ASTM International, West Conshohocken, PA, www.astm.org.

4. OI Analytical Application Note #3515, Cyanide Analysis - Reducing Laboratory Operating Costs without Compromising Data Quality or Regulatory Compliance, 2010.

5. USEPA Method 335.4: Determination of Total Cyanide by Semi-Automated Colorimetry, in Methods for the Chemical Analysis of Water and Wastes, EPA-60014-79-020, U.S. Environmental Protection Agency, National Exposure Research Laboratory, Cincinnati, Ohio, 1979.

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