

VALIDATION TESTING OF THE DRAFT ASTM IMPINGER METHOD FOR MEASURING GASEOUS CHLORIDE EMISSIONS FROM MINERAL CALCINERS

Test Report

Prepared for: National Lime Association 200 North Glebe Road Arlington, VA

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Chemical Lime Company Draft Test Report

November 2000

Prepared for:

National Lime Association 200 North Glebe Road Arlington, VA

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Executive Summary

Emission Monitoring Incorporated was hired by the National Lime Association (NLA) to conduct validation testing of a draft method for measuring gaseous chlorides in lime kiln emissions. Dr. L. Kinner of Emission Monitoring in conjunction with Mr. G. Cobb and Mr. F. Shaw of AirSource Technologies Inc. performed the field-testing.

The draft method (attached in Volume II Appendix A) is entitled "Measurement of Gaseous Chlorides and Fluorides from Mineral Calcining Exhaust Sources – Impinger Method -Z8662Z " and its development is under the auspices of the American Society for Testing and Materials (ASTM). The gaseous chlorides collected by this method are all attributed to hydrogen chloride gas.

A test plan and quality assurance project plan were prepared and reviewed by members of the NLA. A copy of the plan is included in Volume II Appendix B.

Method validation testing was conducted at two facilities. One facility had a scrubber controlled kiln system and the other had a baghouse controlled kiln system. This report describes the test program performed at Chemical Lime Company - Ste. Genevieve, Missouri, (baghouse) from September 10-12, 2000. Testing at this facility provided a low concentration sample matrix (<10 ppm) from which to conduct the validation.

Data acquired by the Draft ASTM Method were evaluated using the statistical analysis procedures for bias and precision contained in EPA Method 301 (40 CFR Part 63, Appendix A – Section 6.3). In this capacity, paired samples of lime kiln effluent were acquired simultaneously using the ASTM method. One of the samples from the pair was spiked with a small amount of gaseous hydrogen chloride at the end of each run. Twelve sets of the paired samples were acquired to provide 12 spiked and 12 unspiked pairs of data sets. The combination of 12 spiked samples and 12 unspiked samples provided a means to determine the accuracy and precision of the draft method.

The bias of the method using Method 301 calculations is -0.03 mg with a t-value of 0.05 for this type of sample matrix. These results indicate a statistically insignificant bias when compared to the critical t value of 2.201. The in-stack concentration levels evaluated during this validation test ranged from about 0.5 ppm to 7 ppm.

The Method 301 statistical analyses results using paired trains indicates that the method has a relative standard deviation (RSD) of about 38% for the unspiked samples and 18% for the spiked samples.

The effluent concentration level of HCl was observed to change during Runs 1 and 2, 4 and 5, and 9. The reason for the HCl concentration changes are not known; however, variable HCl concentration levels in lime kiln effluent have been observed during past testing using Fourier transform infrared spectrometry¹.

The fact that the HCl concentration levels were variable during testing had the effect of increasing the apparent imprecision of the method when using the paired train sampling approach. A detailed discussion regarding the precision of the method is presented in Section 4 of this report.

In addition to conducting the Method 301 statistical analyses, the percent recovery for each spiked sample was also calculated. The results ranged from a low of 74% recovery to a high of 150% recovery with an average of 111% for the 12 runs. The 150% result is suspected to be an outlier data point because the remaining 11 spiked samples were within 30% of the expected value. The average percent recovery removing the outlier data point is 108%.

¹ Test Report Prepared for US EPA "Lime Kiln Source Characterization – Draft Final Report Austin White Lime Company" Prepared by Eastern Research Group, EPA Contract 68-D70007, December 1998.

1.0 BACKGROUND AND INTRODUCTION

Existing HCl measurement methods such as USEPA Method 26/26A (40 CFR Part 60 Appendix A) have been reported to have both high and low biases in many measurement applications. In 1994, the US EPA recognized the inaccuracies of Method 26/26A, and a directive was issued to solve the problems associated with the method, or to find a better measurement method for measuring HCl at low concentration levels².

Since that time, Fourier transform infrared (FTIR) methods such as Methods 320 and 321 (Part 63) have been developed for measuring HCl. Although, FTIR instrumentation is highly qualified to measure HCl in the gaseous form, the technique is constrained at low HCl concentration levels. Low concentration level measurements of HCl by FTIR are difficult because; 1) reference spectra and calibration gases can be inaccurate, 2) measurement systems can have highly variable detection limits, 3) many FTIR instruments can have HCl non-linearity problems that may go uncorrected by the operator, and 4) sampling systems often require in excess of 100 feet of heated transfer line to direct the effluent to the instrumentation, and this transfer line can scrub HCl.

The fact that the FTIR is problematic for measuring HCl at low concentration levels was demonstrated numerous times during FTIR testing at lime producing facilities. During these tests, the analyte spike quality assurance procedures did not meet the criterion defined by Methods 320 or 321 at concentration levels below 10 ppm as demonstrated by low analyte spike recoveries ³.

This issue is significant because accurate low concentration level measurements are needed by many industrial facilities. A laboratory study was conducted during the summer of 1999 that investigated many of these phenomena. A report was prepared that details these issues and presents the basis for developing a new method for measuring HCl (g) and conducting this field validation 4 .

The purpose of the test program was to evaluate the method entitled "Measurement of Gaseous Chlorides and Fluorides from Mineral Calcining Exhaust Sources – Impinger Method." This method is currently in draft form and its development is under the auspices of the American Society for Testing and Materials (ASTM). The evaluation approach used EPA Method 301 to perform a method "validation". The gaseous chlorides collected by this method are attributed to HCl (g).

Two lime kiln systems provided the sample matrix for this test program. This report describes the testing conducted at Chemical Lime Company - Ste. Genevieve Missouri facility. Results from the second test program are described in the report entitled "Validation Testing of the Draft ASTM Impinger Method for Measuring Gaseous Chloride Emissions from Mineral Calciners – Mississippi Lime Company Test Report".

The calciner system at Chemical Lime consisted of a rotary kiln with a pre-heater tower in combination with a baghouse for the purpose of dust collection. The effluent matrix contained concentration levels of HCl that ranged from about 0.5 ppm to 7 ppm.

² Memorandum dated March 14, 1994 from James Crowder Industrial Studies Branch Chief, United States EPA to Gilbert Wood Emission Measurement Branch Chief requesting a new or revised test method to measure HCl from Portland Cement and Secondary Aluminum Facilities. Docket to the Portland Cement NESHAP – Item number II-B-45.

³ Reference #1 – Testing at Austin White Lime Company and Test Report Prepared for US EPA, "Lime Kiln Source Characterization – Draft Final Report – Huron Lime" Prepared by Eastern Research Group, EPA Contract 68-D70007

⁴ Kinner, Peeler, and Willis "Development of an Improved Impinger-Based Method for Measuring Gaseous Chloride Emissions from Mineral Calciners", Air and Waste Management Association Annual Meeting – Salt Lake City, Utah, June 19, 2000.

2.0 DESCRPTION OF METHOD VALIDATION AND APPARATUS

This test program was performed at Chemical Lime Company's pre-heater equipped kiln designated as Kiln #2. The kiln was operated under conditions considered to be representative of normal production and in accordance with the facility operating permit.

Testing was conducted at the stack location. Twelve sets of paired sampling trains were operated in succession to total 24 samples for the method validation testing. Figure 2-1 presents a schematic of the paired sample train and spike apparatus.

Before starting Run 1, a conditioning run was performed to passivate any active sites within the probe and filter box. The impinger contents from this run were discarded.

The draft ASTM method prescribes collecting about 120 liters of gas into four midget impingers containing a solution of dilute sulfuric acid (0.1 N). The gas sample is collected for one-hour at a rate of 2 liters per minute. Sample gas is withdrawn from a single point in the stack or duct. Analysis of the impinger train sample is performed using ion chromatography, a method that analyzes total chloride ions in the solution. Concentration data only were collected during this validation test program.

After the end of each one- hour sample run, one sample train of the pair was spiked with a concentration of HCl calibration gas, equivalent to about 10 ppm. For this validation test, the amount of HCl spiked into the impinger trains was about three times the concentration of the unspiked samples. This level was chosen to provide validation of the method at the 10 ppm level, and because no previous HCl data were available from this facility.

The spiking procedure is detailed in section 11.2.6 of the draft method and consists of adding HCl calibration gas (about 30 liters for this application) into the sampling train upstream of the particulate matter filter. The spike gas flow rate was adjusted to be greater than the total sample flow so that the excess spike gas was vented out the probe. This enabled the meter box and pump to function identically to conditions encountered during sample collection.

Conducting a gaseous spike into an impinger train is very ambitious. Spiking with a gaseous standard adds much in the evaluation of this method because the spike had to pass through the filter, and thus it evaluated the scrubbing potential of the lime dust on the particulate filter cake.

Figures 2-2 and 2-3 present digital images of the method under actual application at the Mississippi Lime facility.





Figure 2-2 Sampling Apparatus in Testing Application



Figure 2-3 Sampling Apparatus with Spike Assembly Attached

3.0 DATA QUALITY OBJECTIVES

The test program data quality objectives and achieved data quality are summarized in the following tables.

Table 3-1 Data Quality Objectives Method 301

Target Analyte	Bias	Precision	Data Completeness Target
HCl (g)	t value <2.201 for 12 pairs	? 50% Relative Standard Deviation	100%

These data quality objectives were chosen to reflect the acceptable bias and precision detailed in Section 6.3 of EPA Method 301^{-5} .

The following table shows the actual data quality achieved during this field test.

Table 3-2 Achieved Data Quality Method 301

Target Analyte	Bias	Precision	Data Completeness
HCl (g)	Bias = -0.03 mg	38% RSD for unspiked samples	100%
		18% RSD for spiked samples	
	t value = 0.05 for 12 pairs		
	t<2.201		

These results are presented in Tables 4-1 (bias) and 4-2 (precision).

An additional data quality objective for calculating the spike recovery from each impinger train pair was set at 70% to 130% of the expected value. Table 3-3 summarizes the findings from this analysis.

Table 3-3 Spike Recovery Data Quality Objectives and Data Quality Achieved

Target Analyte	Accuracy Expected	Accuracy Achieved*
HCl (g)	Spike Recovery 70% to 130% of	74% - 119%
	Expected Value	

*An outlier data point of 150% was observed during one spike

These results are presented in Table 4-3.

⁵ EPA Method 301 CFR Part 63, Appendix A, Section 6.3. December 1992.

4.0. RESULTS

The target data completeness of 100% was achieved during this test program.

During testing the underlying effluent HCl concentration changed from run to run. This had the affect of increasing the %RSD of the unspiked samples when applying the 301 statistics to paired instead of quad samples. Table 4-1 demonstrates how the variable effluent HCl concentrations dramatically affect the precision results.

It was originally planed that quadruplet sampling trains would be used to evaluate this method, however, the heater in the filter box of one of the paired trains was found to have a short relative to ground at the start of the first tests. Because testing started on Sunday (9-10-00), there were no provisions to have a replacement heater delivered. The decision was made to proceed with testing on Sunday and Monday by acquiring 12 sets of paired runs (instead of 6 sets of quad runs) in order to obtain the requisite 24 samples.

4.1 Method 301 - Precision

Using paired trains instead of the planned quad train approach had the effect of further magnifying the apparent imprecision of the method due to the underlying HCl effluent concentration changes. In order to perform the Method 301 statistical analyses, one uses 2 unspiked samples and two spiked samples (quad samples) to determine the difference in the results from each pair. Six sets of these quad trains are conducted, and the differences in each of the pairs are used to perform the statistical analyses. If quad trains are used, then effluent concentration changes are not as great an issue because both pairs should collect the same milligram catch. If paired trains are used, then calculating the difference of the spiked and unspiked pairs is performed using samples acquired sequentially in time rather than simultaneously.

A graphical depiction of the underlying effluent concentration level changes is presented in Figure 4-1. This graph presents a comparison of the spiked and unspiked sample values, and the results when the spike amount is subtracted from the spiked train results. It is apparent from the graph that the spiked, unspiked, and "spike removed" samples follow the same trend with time. This trend is due to changes in the underlying effluent HCl concentration.

Applying the Method 301 statistical analyses for precision is not appropriate for sources with variable effluent concentration levels using the paired train approach. Therefore, a procedure to remove the effluent variability was used that consisted of generating an "unspiked" sample result from the spiked sample train.

The procedure consisted of first subtracting the amount of HCl spike gas added into the spiked sample train. This effectively produced an "unspiked" sample to compare to the true unspiked sample of the pair. Although this approach is not perfect because it has errors associated with the spike procedure, it does effectively remove the underlying effluent concentration changes. Method 301 statistical analyses for precision were then applied to this data set (See Table 4-2).

Based on EPA Method 301 statistical analyses of these data, the method has a relative standard deviation of 38% for the unspiked samples using the approach described above, and 18% for the spiked samples. According to Method 301 (Section 6.3), a candidate method is acceptable if the precision is <50% RSD.

4.2 Method 301 - Bias

The bias of the method using the Method 301 calculations is -0.03 mg, with a t-value of 0.05. These very low values indicate that the method has insignificant bias when comparing to the critical t value of 2.210.

According to EPA Method 301 (Section 6.3), a method provides valid data if the t-test shows that the bias is statistically insignificant. The Method 301 statistical results for bias are presented in Table 4-1.

4.3 Spike Recovery Results

Although not a requirement of Method 301, the percent recovery for each spiked sample was calculated to present the results in terms of expected versus observed values. This was done by determining the value of the amount of spike collected relative to the amount expected.

The results ranged from a low of 74% spike recovery to a high of 150% spike recovery with an average of 111% for the 12 runs. The 150% result is suspected to be an outlier data point because the recovery for the remaining 11 spiked samples was within 30% of the expected value. Removing the 150% outlier data point results in an average percent recovery of 108% for the 11 runs. The 30% criterion is generally accepted as the basis for "valid" data produced by instrumental test methods using Fourier transform infrared spectrometry⁶.

The spike recovery results do not indicate that the method has significant bias because the average spike recovery for the population of samples was greater than 100%.

Table 4-3 presents all of the pertinent sample collection data and the corresponding percent recoveries for each of the spiked sample trains.

The data file prefixes were named as follows;

CGA50A and 50B – Calibration gas audits of the gas cylinder used for spiking – duplicate analyses CVAL – Chemical Lime validation runs

The analytical laboratory report prepared by Resolution Analytics Inc. is attached in Volume II Appendix C, and raw data sheets, calculations, and gas meter calibrations are contained in Volume II Appendix D of this report.

⁶ EPA Method 321 40 CFR Part 63, Appendix A – Section 9.3.2

Chemical Lime





Paired Sample Run Number

Table 4-1 Chemic	al Lime - Meth	od 301 Statistical	Analysis of Paired Tr	ain Samples							
	_			Differences		D://					
Comple Nome	ma aatab	mg amerence		Difference	Coursed	Difference Spiked Daire	Coursed				
	ing catch	between pairs	mg spike added	Unspiked Pairs	Squared	Spiked Pairs	Squared				
	0.00	2.04	1 71	0.15	0.02	0.69	0.46				
CVALIIB	2.12	2.04	1.71	0.15	0.02	-0.06	0.40				
CV/AL 12A	0.23										
CVAL12A	1.44	1 21	1 73								
OVALIZD	1.44	1.21	1.75								
CVAL21A	1 12										
CVAL21R	3.26	2 14	1 71	-0 14	0.02	-0.84	0.71				
017.122.13	0.20			0.11	0.02	0.01	0.11				
CVAL22A	0.98										
CVAL22B	2.42	1.44	1.76								
-											
CVAL31A	0.41										
CVAL31B	2.42	2.01	1.71	0.88	0.77	0.91	0.83				
CVAL32A	1.29										
CVAL32B	3.33	2.04	1.76								
CVAL41A	1.18										
CVAL41B	3.25	2.07	1.74	-0.16	0.03	-0.19	0.04				
CVAL42A	1.02										
CVAL42B	3.06	2.04	1.70								
CVAL51A	0.10										
CVAL51B	2.80	2.70	1.76	1.07	1.15	0.36	0.13				
CVAL52A	1.17										
CVAL52B	3.16	1.99	1.72								
0.41.044											
CVAL61A	1.21		4.70	0.40	0.40	0.54	0.00				
CVAL61B	3.32	2.11	1.73	-0.40	0.16	-0.54	0.29				
C)/A1 62A	0.91										
CVAL62R	0.01	1.07	4 74								
CVAL02D	2.70	1.97	1.74								
Moon Unspiked	0.80		Sum	1.40	2.14	-0.08	2.45				
Mean Sniked	2.50		Sum	1.40	2.14	-0.30	2.43				
Mean mg Added	1 73		Sdu	0.42		Standard Deviatio	n of the uns	niked "A" s	amples		
mean mg Aaaea			Sds	0.42		Standard Deviatio	n of the snik	ed "B" sam	nles		
			%RSDu	52.83		% Relative Stands	ard Deviatio	n of unspike	noo d samples		
			%RSDs	18.07		% Relative Stands	ard Deviation	n of sniked	samnles		
			Bias	-0.03		Mean of Spiked - Mean unspiked - Mean mg added					
			SDM	0.62		Square root of the sum of the squares of spiked and unspike			unspiked		
			t	0.05		Absolute value of	Bias/SDM				
			t < 2.201	bias not statistically	significant						
					3						
			The precision resu	Its for unspiked	samples a	re biased by the	effluent o	oncentra	tion chance	ies	
Note: A trains unsp	iked, B trains s	piked									

Table 4-2 Chemical Lime - Spike minus Unspiked Paired Train Samples										
Sampla Nama	ma catch	ma sniko oddod	anikad sample - snike added	Difference	Squared					
		my spike audeu	Spiked Sample - Spike added	Unspikeu raiis	Squareu					
CVAL11B	2.12	1.71	0.41	0.34	0.11					
		•••••								
CVAL12A	0.23	4.70	0.00	0.54	0.00					
CVAL12B	1.44	1./3	-0.29	-0.01	0.26					
CVAL21A	1.12									
CVAL21B	3.26	1.71	1.55	0.43	0.19					
CVAL22A	0.98									
CVAL22B	2.42	1.76	0.66	-0.32	0.10					
0) (AL 04 A	0.44	ļ]								
	0.41	1.71	0.71	0.20	0.00					
CVAL31B	2.42	1.71	0.71	0.30	0.09					
CVAL32A	1.29	I								
CVAL32B	3.33	1.76	1.57	0.28	0.08					
CVAL41A	1.18									
CVAL41B	3.25	1.74	1.51	0.33	0.11					
CVAL42A	1.02		 [
CVAL42B	3.06	1.70	1.36	0.34	0.12					
CVAL51A	0.10									
CVAL51B	2.80	1.76	1.04	0.94	0.88					
CVAL52A	1.17									
CVAL52B	3.16	1.72	1.44	0.27	0.07					
CVAL61A	1.21									
CVAL61B	3.32	1.73	1.59	0.38	0.15					
CVAL62A	0.81									
CVAL62B	2.78	1.74	1.04	0.22	0.05					
Mean Unsniked	0.80	Sum		3.00	2 21					
Mean Sniked	2 50	Sum		5.00	2.21					
Mean mg Added	1.73	Sdu		0.31						
Medit mg Addes		%RSD	[38.74						
		/orce_			1					
		Effluent variations re	moved from data set							
N-te. A traing upon	list D trains		<u> </u>							
INOTE: A TRAINS UNSP	iked. B trains s	SDIKED	i de la companya de l		1					

Image: Property into the state of	Table 4-3 Cl	hemical Lim	e Calculati	ons for CLC S	pike Recoveries														
Calculation																			
Califiering back with supple Deployee Analyse State of the supple Deployee Analysee Analyse State o																			
Obs Obs <td>Calibration C</td> <td>Gas Audit Sa</td> <td>ample Dupl</td> <td>licate Analysis</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td> <td>25.40</td> <td></td> <td></td> <td></td> <td></td> <td></td> <td></td>	Calibration C	Gas Audit Sa	ample Dupl	licate Analysis									25.40						
Colored 216 200 200 201 200		Mg HCI	Vdry (L)	Meter Temp C	Meter Temp K	Std Temp	Pressure " H	3	Pressure torr	Std Pressure	DSCM Collected	mg/dscm	ppm	Avg					
Construint Vision Construint Construint <thconstruint< th=""> Construint Construi</thconstruint<>	CGA50A	2.18	32.01	30	272	2 293	1	30	762	760	0.03	5 63.03	3 41.53						
Consiste Visite Visite Subset Subse	CGA50B	2.13	31.41	28	271	293	6	30	762	760	0.034	4 62.51	1 41.18	41.36	5				
Chemical Lines: Velocitica Description Description <thdescription< th=""> Description <thdescripti< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td></thdescripti<></thdescription<>																			
Bit Rift 4 My ECI Vary Li	Chemical Li	me Validatio	on Runs - S	Spike Cylinder	41.4 ppm									In-Stack Concentrat	ion Values				
CMULTA LOU LOU <thlou< th=""> <thlou< t<="" td=""><td>Run # 1</td><td>Mg HCI</td><td>Vdry (L)</td><td>V spike dry (L)</td><td>Meter Temp C</td><td>Meter Temp K</td><td>Std Temp</td><td></td><td>Pressure " Hg</td><td>Pressure torr</td><td>Std Pressure</td><td>DSCM Collected</td><td>DSCM Spike added</td><td>mg/dscm</td><td>ppm</td><td>mg spike added</td><td>% Recovery</td><td></td><td></td></thlou<></thlou<>	Run # 1	Mg HCI	Vdry (L)	V spike dry (L)	Meter Temp C	Meter Temp K	Std Temp		Pressure " Hg	Pressure torr	Std Pressure	DSCM Collected	DSCM Spike added	mg/dscm	ppm	mg spike added	% Recovery		
CMAILTS 21.00 30.00 40 330 288 2023 777 766 0.011 0.008 Dead Location of the Value and	CVAL11A	0.08	125.07	no spike	35	308	6	293	29.03	737	76	0.12	2	0.66	0.43	NA			
Bay EC Bay EC Value 1 and 1, 1 Main 1	CVAL11B	2.12	120.18	30.05	40	313	5	293	29.03	737	76	0.11	1 0.03	19.42	12.80	1.71	119%	1	
Rin P2 My Fiel Voly 2, V spile dry 12, More Tang C Mor														In-Stack Concentrat	ion Values				
CMA126 0.4 11.2 Log 20.0 1.20 MA	Run #2	Mg HCI	Vdry (L)	V spike dry (L)	Meter Temp C	Meter Temp K	Std Temp		Pressure " Hg	Pressure torr	Std Pressure	DSCM Collected	DSCM Spike added	mg/dscm	ppm	mg spike added	% Recovery		
CMALTAP 14.4 17.10 30.1 30.2 30.2 20.0 73.7 70 0.11 0.03 13.00 80.0 17.7 744 CMALTAP 13.00 0.050 0.0500	CVAL12A	0.23	121.97	no spike	32	305	5	293	29.03	737	76	0.1	1	2.00	1.32	NA			
Band di Viglici Viglici <t< td=""><td>CVAL12B</td><td>1.44</td><td>121.02</td><td>30.1</td><td>39</td><td>312</td><td>2</td><td>293</td><td>29.03</td><td>737</td><td>76</td><td>0.1</td><td>1 0.03</td><td>13.06</td><td>8.60</td><td>1.72</td><td>74%</td><td></td><td></td></t<>	CVAL12B	1.44	121.02	30.1	39	312	2	293	29.03	737	76	0.1	1 0.03	13.06	8.60	1.72	74%		
Bit Rue 3 Bit Rue 3 <t< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>In-Stack Concentrat</td><td>ion Values</td><td></td><td></td><td></td><td></td></t<>														In-Stack Concentrat	ion Values				
CVAL2A 1.02 SEE 0 SEE 0 <th< td=""><td>Run #3</td><td>Mg HCI</td><td>Vdry (L)</td><td>V spike dry (L)</td><td>Meter Temp C</td><td>Meter Temp K</td><td>Std Temp</td><td></td><td>Pressure " Hg</td><td>Pressure torr</td><td>Std Pressure</td><td>DSCM Collected</td><td>DSCM Spike added</td><td>mg/dscm</td><td>ppm</td><td>mg spike added</td><td>% Recovery</td><td></td><td></td></th<>	Run #3	Mg HCI	Vdry (L)	V spike dry (L)	Meter Temp C	Meter Temp K	Std Temp		Pressure " Hg	Pressure torr	Std Pressure	DSCM Collected	DSCM Spike added	mg/dscm	ppm	mg spike added	% Recovery		
CML2F 3.5 3.5 3.5 3.5.	CVAL21A	1.12	121.65	no spike	35	308	5	293	29.03	737	76	0.1	1	9.98	6.57	NA			
Name Name <th< td=""><td>CVAL21B</td><td>3.26</td><td>120.45</td><td>30.1</td><td>42</td><td>2 315</td><td>5</td><td>293</td><td>29.03</td><td>737</td><td>76</td><td>0.1</td><td>1 0.03</td><td>29.99</td><td>19.76</td><td>5 1.71</td><td>117%</td><td></td><td></td></th<>	CVAL21B	3.26	120.45	30.1	42	2 315	5	293	29.03	737	76	0.1	1 0.03	29.99	19.76	5 1.71	117%		
Bun H Mart Horizon Variable value due due due due due due due due due d														In-Stack Concentrat	ion Values				
CVAL228 0.04 Total SN organization 0.01 0.01 0.01 0.00 0	Run #4	Mg HCI	Vdry (L)	V spike dry (L)	Meter Temp C	Meter Temp K	Std Temp		Pressure " Hg	Pressure torr	Std Pressure	DSCM Collected	DSCM Spike added	mg/dscm	ppm	mg spike added	% Recovery		
CMAL28 Lob GOAL Coal Coal <t< td=""><td>CVAL22A</td><td>0.98</td><td>120.53</td><td>no spike</td><td>38</td><td>311</td><td></td><td>293</td><td>29.03</td><td>737</td><td>76</td><td>0.1</td><td>1</td><td>8.86</td><td>5.84</td><td>NĂ</td><td></td><td></td><td></td></t<>	CVAL22A	0.98	120.53	no spike	38	311		293	29.03	737	76	0.1	1	8.86	5.84	NĂ			
Number Number<	CVAL22B	2.42	120.49	30.75	45	5 318	6	293	29.03	737	76	0.11	1 0.03	22.47	14.80	1.73	90%		
Num FG Mg HCI Vortunal Aug HCI Vortunal Vortunal Aug HCI Vortunal Aug HCI Vortunal Aug HCI Vortunal <														In-Stack Concentrat	ion Values				
CVAL31 0.41 20.08 /m 20 /m	Run #5	Mg HCI	Vdry (L)	V spike dry (L)	Meter Temp C	Meter Temp K	Std Temp		Pressure " Hg	Pressure torr	Std Pressure	DSCM Collected	DSCM Spike added	mg/dscm	ppm	mg spike added	% Recovery		
CVAL36 Q42 Q307 Q307 Q43 Q34 Q303 Q303 Q304	CVAL31A	0.41	120.85	no spike	41	314	1	293	29.03	737	76	0.11	1	3.78	2.49	NA			
Mare Mode Mare Team Mare Team <t< td=""><td>CVAL31B</td><td>2.42</td><td>120.67</td><td>30.75</td><td>48</td><td>321</td><td></td><td>293</td><td>29.03</td><td>737</td><td>76</td><td>0.1</td><td>1 0.03</td><td>22.65</td><td>14.92</td><td>1.71</td><td>114%</td><td>,</td><td></td></t<>	CVAL31B	2.42	120.67	30.75	48	321		293	29.03	737	76	0.1	1 0.03	22.65	14.92	1.71	114%	,	
Hun B My LP Vight Gy LV Vight														In-Stack Concentrat	ion Values				
CVAL328 1.29 1.20 1.20 1.20 1.20 1.20 1.20 1.20 1.47 7.56 PA VCAL328 3.33 12.33 30.83 23.00 7.78 760 0.11 0.00 10.82 10.86 6.89 N4 CVAL414 1.18 11.49 poste 30.83 30.83 23.80 23.80 738 760 0.11 0.00 10.82 10.74 11.47 7.74 11.27 VCAL414 1.38 12.40 20.00 738 760 0.11 0.00 10.82 10.74 11.27 11.47 11.47 11.48 10.43 10.43 10.43 10.43 10.43 10.43 10.43 10.43 10.43 10.43 10.43	Run #6	Mg HCI	Vdry (L)	V spike dry (L)	Meter Temp C	Meter Temp K	Std Temp		Pressure " Hq	Pressure torr	Std Pressure	DSCM Collected	DSCM Spike added	mg/dscm	ppm	mg spike added	% Recovery		
CVAL28 3.33 121.39 3.08 4.49 3.79 2.95 7.76 0.11 0.03 3.00.6 19.82 1.76 110% Run #7 Mg HCl Vdy (L) Vspike drv (L) Meet Temp C Meet Temp C Sid Temp Pressure torn Sid Pressure DSCM Collected DSCM Spike adds mg spike addsd Mg RCl Vdy (L) Vspike drv (L) Meet Temp C Meet Temp C Mg RCl Vdy (L) Vspike drv (L) Meet Temp C	CVAL32A	1.29	120.64	no spike	39	312	2	293	29.71	755	76	0.1	1	11.47	7.56	NA			
Mer Mer <td>CVAL32B</td> <td>3.33</td> <td>121.39</td> <td>30.83</td> <td>46</td> <td>319</td> <td>)</td> <td>293</td> <td>29.71</td> <td>755</td> <td>76</td> <td>0.1</td> <td>1 0.03</td> <td>30.08</td> <td>19.82</td> <td>1.76</td> <td>110%</td> <td>,</td> <td></td>	CVAL32B	3.33	121.39	30.83	46	319)	293	29.71	755	76	0.1	1 0.03	30.08	19.82	1.76	110%	,	
NB_RU FU Var(L) V sple dv(L) Verter Temp K Stort Temp Pressure Tem														In-Stack Concentrat	ion Values				
CVALL1A 1.16 119.49 no spike 33 306 2.293 2.09 7.39 760 0.11 0.03 2.9.45 1.7.4 1.7.4 CVALL1B 3.25 30.3 3.3 3.33 3.33 3.36 29.09 7.39 760 0.11 0.03 29.55 1.7.4 1.7.4 112% CVAL42A 1.02 121.50 no spike 40 313 233 20.09 7.39 760 0.11 0.03 29.55 1.6.81 1.7.4 112% CVAL42A 1.02 121.57 30.19 4.65 318 233 20.09 7.39 760 0.11 0.03 28.10 1.6.81 1.7.7 113% CVAL42B 3.06 121.57 30.19 4.65 SCM Collected DSCM Collected<	Run #7	Ma HCI	Vdrv (L)	V spike drv (L)	Meter Temp C	Meter Temp K	Std Temp		Pressure " Ha	Pressure torr	Std Pressure	DSCM Collected	DSCM Spike added	ma/dscm	ppm	mg spike added	% Recovery		
CVAL41B 3.25 120.56 30.3 39 312 29.3 29.09 7.39 760 0.11 0.03 29.53 19.45 1.74 112% Run 88 Mg HCI Vdry (L) V spike dry (L) Meer Temp C Meer Temp K Std Temp Pressure timp Std Temp Pressure timp Std Temp Mg HCI Vdry (L) V spike dry (L) Meer Temp C Meer Temp K Std Temp Pressure timp	CVAL41A	1.18	119.49	no spike	33	3 306	5	293	29.09	739	76	0.1	1	10.61	6.99	NĂ			
No. 10 No. 10<	CVAL41B	3.25	120.56	30.3	39	312	2	293	29.09	739	76	0.1	1 0.03	29.53	19.45	1.74	112%	,	
Nu n B Mu h Cl Vory (L) V spike dry (L) Meter Temp C Meter Temp C Stal Temp Pressure 190 Pressure 190 <t< td=""><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td></td><td>In-Stack Concentrat</td><td>ion Values</td><td></td><td></td><td></td><td></td></t<>														In-Stack Concentrat	ion Values				
CVAL42A 1.02 121.50 no spike 40 133 293 29.09 739 760 0.11 9.22 6.08 MÅ 0 CVAL42B 3.06 121.57 30.19 45 318 293 29.09 739 760 0.11 0.03 28.10 16.51 1.70 113% Run #9 Mg HCI Vdry (L) V spike dry (L) Meter Temp C Meter Temp K Std Temp Pressure torr Std Pressure DSCM Collected DSCM Sche added mg/scm mg/scm mg/scm mg/scm mg/scm mg/scm mg/scm mg/scm 1.76 100 12.25 no.51 NA 1.76 150% outlier CVAL51B 2.80 121.52 no.site Accouncerration Values mg/scm 1.76 150% outlier 1.76 150% outlier Run #10 Mg HCI Vdry (L) V spike dry (L) Meter Temp C Meter Temp K Std Temp Pressure 'Hg Pressure	Run #8	Mg HCI	Vdry (L)	V spike dry (L)	Meter Temp C	Meter Temp K	Std Temp		Pressure " Hg	Pressure torr	Std Pressure	DSCM Collected	DSCM Spike added	mg/dscm	ppm	mg spike added	% Recovery		
CVAL42B 3.06 1.75 3.0.9 4.5 3.16 2.3.9 7.39 7.60 0.11 0.03 2.8.10 1.7.5 1.7.7	CVAL42A	1.02	121.50	no spike	40	313		293	29.09	739	76	0.1	1	9.22	2 6.08	B NA			
Imp MpL MpL <td>CVAL42B</td> <td>3.06</td> <td>121.57</td> <td>30.19</td> <td>45</td> <td>318</td> <td>5</td> <td>293</td> <td>29.09</td> <td>739</td> <td>76</td> <td>0.1</td> <td>1 0.03</td> <td>28.10</td> <td>18.51</td> <td>1.70</td> <td>113%</td> <td></td> <td></td>	CVAL42B	3.06	121.57	30.19	45	318	5	293	29.09	739	76	0.1	1 0.03	28.10	18.51	1.70	113%		
Run #0 Mg HC1 Vdry (L) V spike dry (L) Meter Temp C Meter Temp K Std Temp Pressure 'Hg														In-Stack Concentrat	ion Values				
CVALS1A 0.10 121 58 no spike 32 306 233 2300 739 760 0.11 0.037 0.57 NA CVALS1B 2.80 121.26 30.6 37 310 293 29.09 739 760 0.11 0.03 251.3 165 1.76 150% outlier Run #10 Mg HCI Vay led fry (L) Vay led fry (L) Meter Temp C Neter Temp K SId Temp Pressure frr TSI Pressure DSCM Collected DSCM Collected DSCM Collected DSCM Collected DSCM Spike added fmg/dscm ppm mg spike added % Recovery 10.22 6.73 NA 10.22 6.73 NA 10.23 6.73 NA NA	Run #9	Mg HCI	Vdry (L)	V spike dry (L)	Meter Temp C	Meter Temp K	Std Temp		Pressure " Hq	Pressure torr	Std Pressure	DSCM Collected	DSCM Spike added	mg/dscm	ppm	mg spike added	% Recovery		
CVAL51B 2.80 121.26 30.6 37 310 29.3 29.09 739 760 0.11 0.03 25.13 16.66 1.76 150% outlier Run #10 Mg HCI Vdry (L) V spike dry (L) Meter Temp C Meter Temp K Std Temp Pressure 'Hg Pressure 'Hg Pressure 'Temp' 739 760 0.11 0.03 29.30 19.31 1.72 112.26 NA 10.22 6.73 NA 10.22 10.73 NA 10.22 0.73 NA 10.22 6.73 NA 10.22 10.63 NA 112% 112% 112% 112% 112% 112% 112% 112% 112% 112% 112% 112% 112% 112% 112% 112% <td>CVAL51A</td> <td>0.10</td> <td>121.58</td> <td>no spike</td> <td>32</td> <td>305</td> <td>;</td> <td>293</td> <td>29.09</td> <td>739</td> <td>76</td> <td>0.1</td> <td>1</td> <td>0.87</td> <td>0.57</td> <td>NA</td> <td></td> <td></td> <td></td>	CVAL51A	0.10	121.58	no spike	32	305	;	293	29.09	739	76	0.1	1	0.87	0.57	NA			
Image: bit in the start of the sta	CVAL51B	2.80	121.26	30.6	37	310)	293	29.09	739	76	0.1	1 0.03	25.13	16.56	1.76	150%	outlier	
Run #10 Mg HCI Vdry (L) V spike dry (L) Meter Temp C Meter Temp C Meter Temp C Std Temp Pressure tring Std Pressure DSCM Collected DSCM Spike added mg/dscm ppm mg spike added % Recovery (IIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIIII														In-Stack Concentrat	ion Values				
CVAL52A 1.17 122.21 no spike 31 304 233 29.09 739 760 0.11 0.03 10.22 6.73 NA 0.4 0.01 0.01 0.01 0.03 29.30 19.31 1.72 112% 0.00 0.01 0.03 29.30 19.31 1.72 112% 0.01 0.03 29.30 19.31 1.72 112% 0.01 0.01 0.03 29.30 19.31 1.72 112% 0.01 0.01 0.01 0.03 29.30 19.31 1.72 112% 0.01 0.01 0.01 0.03 29.30 19.31 1.72 112% 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.01 0.03 30.04 19.79 1.73 114% 0 0.01 0.03 30.04 19.79 1.73 114% 0 0.01 0.03 30.04 19.79 1.73 114% 0 0 0.01 0.03 30.04 19.79 1.73	Run #10	Ma HCI	Vdrv (L)	V spike dry (L)	Meter Temp C	Meter Temp K	Std Temp		Pressure " Ha	Pressure torr	Std Pressure	DSCM Collected	DSCM Spike added	ma/dscm	ppm	mg spike added	% Recovery		
CVAL52B 3.16 118.49 30.06 40 313 293 29.09 739 760 0.11 0.03 29.30 19.31 1.72 112% Run #11 Mg HCI Vdry (L) V spike dry (L) Meter Temp C Meter Temp	CVAL52A	1.17	122.21	no spike	31	304		293	29.09	739	76	0.1	1	10.22	6.73	NA	,,		
Image: Construction of the second o	CVAL52B	3.16	118.49	30.06	40	313		293	29.09	739	76	0.1	1 0.03	29.30	19.31	1.72	112%		
Run #11 Mg HCl Vdry (L) V spike dry (L) Meter Temp C Meter Temp K Std Temp Pressure * Mg Pressure torr Std Pressure DSCM Collected DSCM Spike added mg spike added % Recovery CVAL61A 1.21 121.40 no spike 32 305 233 29.09 739 760 0.11 10.67 7.03 NA <														In-Stack Concentrat	ion Values				
CVAL61A 1.21 121.40 Instact Concentration NA Instact Concentration <td>Run #11</td> <td>Ma HCI</td> <td>Vdrv (L)</td> <td>V spike dry (L)</td> <td>Meter Temp C</td> <td>Meter Temp K</td> <td>Std Temp</td> <td></td> <td>Pressure " Ha</td> <td>Pressure torr</td> <td>Std Pressure</td> <td>DSCM Collected</td> <td>DSCM Spike added</td> <td>ma/dscm</td> <td>ppm</td> <td>mg spike added</td> <td>% Recovery</td> <td></td> <td></td>	Run #11	Ma HCI	Vdrv (L)	V spike dry (L)	Meter Temp C	Meter Temp K	Std Temp		Pressure " Ha	Pressure torr	Std Pressure	DSCM Collected	DSCM Spike added	ma/dscm	ppm	mg spike added	% Recovery		
CVAL61B 3.32 121.06 30.12 39 312 293 29.09 739 760 0.11 0.03 30.04 19.79 1.73 114% N #12 Mg HCl Vdry (L) V spike dry (L) Meter Temp C Meter Temp K Std Temp Pressure "Hg Pressure "T DSCM Collected DSCM Spike added mg/spike added % Recovery 1.73 114% CVAL62B 0.81 121.56 no spike 30.11 304 29.09 739 760 0.11 0.03 30.04 19.79 1.73 114% 110% CVAL62B 2.78 120.86 30.11 36 309 293 29.09 739 760 0.11 0.03 24.95 16.44 1.74 110% Avg. % Recovery Re	CVAL61A	1.21	121.40	no spike	32	305	5	293	29.09	739	76	0.1	1	10.67	7.03	NA	,,		
Orice Description Description <th< td=""><td>CVAL61B</td><td>3.32</td><td>121.06</td><td>30.12</td><td>39</td><td>312</td><td>,</td><td>293</td><td>29.09</td><td>739</td><td>76</td><td>0.1</td><td>1 0.03</td><td>30.04</td><td>19.79</td><td>1 73</td><td>114%</td><td></td><td></td></th<>	CVAL61B	3.32	121.06	30.12	39	312	,	293	29.09	739	76	0.1	1 0.03	30.04	19.79	1 73	114%		
Run #12 Mg HCl Vdry (L) V spike dry (L) Meter Temp C Meter Temp K Std Temp Pressure * Hg Pressure torr Std Pressure DSCM Collected DSCM Spike added mg spike added % Recovery CVAL62A 0.81 121.56 no spike 31 304 293 29.09 739 760 0.11 0.03 24.95 16.44 1.74 17.0 4.70 NA 100 0 0 0 0 0 0 0 0 0 0 0 0 0 0.01 0.03 24.95 16.44 1.74 17.0 NA 100 0	OTTLEOTE	0.02	121100	00.12				200	20.00			0.1	0.00	In-Stack Concentrat	ion Values				
CVALE2A 0.81 121.56 In optice 31 304 293 29.09 739 760 0.11 0.03 24.95 16.44 1.74 110% CVAL62B 2.78 120.86 30.11 36 309 293 29.09 739 760 0.11 0.03 24.95 16.44 1.74 110% 4.09, % Recovery CVAL62B 2.78 120.86 30.11 36 309 293 29.09 739 760 0.11 0.03 24.95 16.44 1.74 110% 4.09, % Recovery Avg. % Recovery Avg. % Recovery Avg. % Recovery Avg. % Recovery	Run #12	Ma HCI	Vdry (L)	V spike dry (L)	Meter Temp C	Meter Temp K	Std Temp		Pressure " Ha	Pressure forr	Std Pressure	DSCM Collected	DSCM Spike added	mg/dscm	nnm	ma spike added	% Recovery		
CVAL62B 2.78 120.86 30.11 36 309 293 29.09 739 760 0.11 0.03 24.95 1.74 110% CVAL62B 2.78 120.86 30.11 36 309 293 29.09 739 760 0.11 0.03 24.95 16.44 1.74 110% 10% <td>CVAL624</td> <td>0.81</td> <td>121 56</td> <td>no snike</td> <td>31</td> <td>304</td> <td></td> <td>203</td> <td>29.09</td> <td>739</td> <td>76</td> <td>0.1</td> <td>1</td> <td>7 14</td> <td>4 70</td> <td>NA</td> <td><i>/////////////////////////////////////</i></td> <td></td> <td></td>	CVAL624	0.81	121 56	no snike	31	304		203	29.09	739	76	0.1	1	7 14	4 70	NA	<i>/////////////////////////////////////</i>		
CVAL = Chemical Line validation runs Company Compa	CVAL62B	2 78	121.00	30 11	36	309	1	203	29.09	739	76	0.1	1 0.03	24.95	16.44	1 74	110%		
Image: CVAL = Chemical Line validation runs Image: CC	OTALOZE	2.70	120.00	00.11		, 000	·	200	20.00	100	70	0.1	0.00	24.00	10.44		110/0		
CVAL = Chemical Lime validation runs						1	1								4 60	Ava Unspiked	1110/		COVERV
CVAL = Chemical Line validation runs Image: CVAL = Chemical Line validation ru	-	1	1	1		+	1								4.05	, rivg. onspiked	11170	Δνα %	o over y
CVAL = Chemical Line validation runs Image: Comparison of the comparison	1														1			Recovery	
CVAL = Chemical Line validation runs 16.45 Avg. Spiked 108% Outlier "A" trains unspiked Image: CVAL = Chemical Line validation runs 10.45 Avg. Spiked 108% Outlier	1														1			Removing	
"A" trains unspiked IO-70 (Ng. Spiked) IO-70 (Ng. Spiked) IO-70 (Ng. Spiked) "A" trains unspiked IO	CVAL - Cher	mical Lime v	alidation run	IS											16.45	Ava Spiked	109%	Outlier	
	"Δ" traine une	niked				+	1								10.40		100/0	June	
	"B" trains onl	ked				1	1								1			1	

5.0 DATA CONTROL OBJECTIVES

HCl Calibration Gas

The spike gas used for this testing program was a certified compressed HCl calibration gas prepared in a dry nitrogen balance. Because the accuracy certification for HCl standards is limited to ? 5%, the certified value of this cylinder was verified by two independent means. Independent verification of the gas value was first conducted using FTIR spectroscopy, and then an impinger train analysis of the gas was conducted in the field. (See Table 4-3 for CGA50A/B analysis.)

This cross checking mechanism provided for analysis using two separate analytic techniques (infrared and ion chromatography), and enabled more accurate representation of the true value of the cylinder gas.

A copy of the cylinder gas manufacturer certification is included in Appendix E.

Table 5-1 summarizes the certified cylinder gas value, the results from the independent FTIR analysis of the gas and the results of the impinger analysis of the gas.

HCl Calibration Gas	Analysis Values
Certified Value	52.3 ppm
FTIR Analysis	43.7 ppm
Impinger Analysis	41.4 ppm
CGA50A and 50B average	

Table 5-1 Analysis of the HCl Calibration Standard

A conversation on October 5, 2000 with Mr. Ted Neeme of Spectra Gas (the individual who signed the gas manufacturer certificate of analysis) revealed that FTIR spectrometry is used to analyze the HCl gas after it is placed into the cylinder. An independent FTIR analysis of this gas by Prism Analytical Technologies Inc. (Mt Pleasant, MI) revealed that the cylinder value was about 20% less (8.6) ppm than that indicated by the certified value. Furthermore, the independent FTIR analysis was within 5% (2.3 ppm) of the impinger based analysis, which used a completely different analytical technique to quantify the HCl concentration. The disagreement between the certified value and the two separate independent analyses is problematic, and continues to cause concern for industries that must rely on accurate calibration gases for measuring HCl⁷.

For the purpose of calculating spike recoveries, the average value from the direct analysis of the cylinder gas by the duplicate impinger trains was used (41.4 ppm). This approach is consistent with the procedures and calculations prescribed by EPA FTIR Methods 320 and 321 (equations 3 &4) where direct analysis of the cylinder gas is used as the basis for calculating spike recovery.

Special Apparatus

The draft ASTM Method places strict requirements on the operating temperature of the front half (probe and filter) of the sampling train. This is necessary in order to prevent condensation and minimize reactions of the HCl with the materials of fabrication. In order to meet the temperature requirements of the method, the front half of the sample train was designed and fabricated to be specific for this method and validation approach.

The front half of the sampling train has: a single sample probe with two separate heated sections, two sets of filters, proportionally controlled heaters to maintain the probe and hot box temperatures within the

⁷ Personal conversations with Dr. Marty Spartz On-Line Technologies (November 2000), Mr. Les Keepper Prism Analytical Technologies (October 2000), Dr. Robert Spellicy IMACC (June 2000), and Dr. Jeff LaCoss Eastern Research Group (August 1995 and August 1998)

prescribed range, and provisions for delivering a gaseous spike into the sampling system at a point immediately upstream of the particulate filter.

Because it has been demonstrated that lime kiln dust adsorbs HCl (g) ⁴, the front half of the sampling train has a unique feature that is designed to reject as much particulate matter as possible. This design feature consists of a large pore 25-micron stainless steel frit with a particulate shield welded on one side. The assembly is fitted on the end of the probe and remains in-stack (with the shield positioned in the flow stream to deflect particles). This arrangement allows small particles and gases to pass into the sampling system and primary particulate filters (0.3 micron), and is similar to designs used by instrumental test methods such as gas filter correlation.

6.0 CONCLUSIONS

The Method 301 validation of the draft ASTM HCl Method met the data quality objectives of the test program. Method 301 statistical analyses of the data indicate the method has an insignificant bias at concentration levels less than 10 ppm as indicated by the very low bias and critical t values.

The percent recovery range of the spiked samples (within 30% of the expected values) further supports the method accuracy at this low concentration level.

The precision of the method in this concentration range is between 18% and 38% RSD.