

SUMMARY REPORT

DEVELOPMENT OF AN IMPROVED IMPINGER-BASED METHOD FOR USE IN MEASURING HCl EMISSIONS FROM CEMENT KILNS

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INTRODUCTION

The measurement of gaseous hydrochloric acid (HCl) in Portland cement kiln effluent has been the topic of many technical and regulatory discussions over the past years. Measuring HCl from cement kiln stacks and by-pass ducts poses great challenges because of the relative reactivity of the HCl with the cement kiln dust and other components of the measurement system.

It may be necessary for facilities producing cement and lime to measure HCl for the purposes of: 1) determining MACT Standard applicability, 2) establishing emissions inventories for air permits, 3) demonstrating compliance with future state/local regulations, and/or 4) determining the performance of HCl continuous monitors. To make these determinations, HCl emissions must be measured with a known degree of accuracy at the level of concern (usually 3-10 PPM). Therefore, the Portland Cement Association (PCA), its member companies, and the National Lime Association (NLA) funded this laboratory study.

The objectives of the laboratory study were:

- 1) To improve the understanding of the complex HCl measurement issues and techniques,
- 2) To resolve the problem associated with measuring HCl by EPA impinger Method 26/26A (40 CFR part 60) relative to the infrared-based instrumental analyzers, and
- 3) To derive an improved impinger-based measurement method that is acceptable to industry and that can be proposed as an ASTM and/or EPA test method.

BACKGROUND

In the past, numerous studies regarding HCl measurement from various effluent matrices have been conducted by EPA and by industry. Much of this work has fueled speculations regarding how and why these measurement methods failed in the various applications, and has evolved sometimes-mythological explanations about the reported results. Many issues remain misunderstood about the measurement of reactive condensable gases such as HCl, and much of the applicable knowledge from successful emissions tests has not been disseminated through the regulatory and measurement community.

Work sponsored by the Portland Cement Association in 1996 resulted in developing Fourier transform infrared (FTIR) and gas filter correlation (GFCIR) based measurement methods that were validated by the cement industry using EPA Method 301. Some of this work involved the concurrent measurement of HCl using EPA Method 26/26A (a less costly impinger-based method that may provide comparable results.) Because of sampling system discrepancies between the methods, results for Method 26/26A were low relative to GFCIR measurements. The EPA subsequently indicated in its proposal of the Portland cement MACT Standard (March 1998) that validation of Method 26/26A was required on a kiln by kiln basis using an infrared-based analyzer.

In the summer of 1998, substandard GFCIR work was performed by EPA contractors in gathering data for a future proposed MACT standard in the Lime industry. The results from these tests were used by the EPA to disallow use of the GFCIR test method in their promulgation of the Portland cement MACT Standard (June 1999). This EPA decision forces cement companies to use FTIR as their only option for measuring HCl in major source applicability determinations.

Because of these circumstances, the Portland Cement Association and the National Lime Association wanted to demonstrate that simple modifications to Method 26/26A can produce data of known accuracy and precision, and can provide results comparable to instrumental infrared analyzers. Demonstration of method equivalency should allow member companies to choose which measurement technique best fits the technical and economical requirements of the particular test situation.

PROJECT DESCRIPTION AND APPROACH

This study was intended to solve the immediate measurement problem of Method 26/26A and the IR-based methods in the most cost-effective manner. As such, a comprehensive study that determined the specific chemical reactions and mechanisms that cause the previously observed discrepancies between Method 26/26A and the IR-based methods was not conducted.

The laboratory study was conducted at the Clean Air Engineering headquarters located in Palatine, Illinois on July 21 through 28, 1999. Clean Air provided the laboratory facilities, the FTIR instrumentation and conducted the ion chromatographic analyses of the impinger solutions. This was an optimum facility to conduct these studies because of the proximity to the PCA Campus.

The laboratory study was divided into simple and more complex experiments that investigated the adsorptive nature of glassware and two common types of filter media as a function of sampling system temperature and degree of conditioning (exposure to HCl in simulated cement and lime kiln effluent). Experiments were conducted using HCl calibration gases and simulated effluent in the presence of both cement kiln and lime kiln dusts (CKD and LKD) using FTIR to quantify HCl. Comparative experiments were then performed between the FTIR and the modified impinger method to determine; 1) the degree to which these methods agreed with each other, and 2) the degree to which they could quantify accurately HCl at concentration levels of concern to industry.

The experimental design dated June 2, 1999 was followed. Some deviations from the initial experimental plan were necessary as the iterative nature of the study revealed where time saving measures and more effective experiments could be performed. The following presents the results for the study. Referenced tables and figures start on page 7 of this document.

EXPERIMENTAL SUMMARY, RESULTS AND CONCLUSIONS

PART I – Effects of Measurement System Temperature and Filtration Media

Fresh and conditioned Method 26 glassware and filter holders were assembled and the time required to achieve a stable 99% upscale response for dry HCl calibration gas (10 PPM) was measured at 250°F and 350°F. Teflon and ultra high purity quartz filters manufactured by Pallflex were evaluated also to determine the degree of HCl adsorption versus time.

Figure 1. Presents a schematic of the experimental apparatus, and Table 1 details the experimental conditions used for the entire study.

Part I - Results

The time required to achieve a stable 99% upscale and downscale (zero) measurement system response was greater than 50 minutes for 15 PPM of HCl at 250°F and a 2 liters per minute flowrate using fresh (off the shelf) glassware. The time for conditioned glassware at these same conditions was greater than 40 minutes. The time to achieve a stable upscale and downscale response at 350°F for the same 15 PPM HCl standard was reduced to about 25 minutes for unconditioned glassware.

Because of the large time discrepancy between the two temperatures, all ensuing experiments were conducted at the 350°F temperature condition.

Using the same experimental conditions and conditioned glassware, the time required to achieve a stable upscale and downscale result was reduced to about 20 minutes.

A stable HCl response time for both the quartz and Teflon coated filters were virtually identical (about 20 minutes) to the FTIR by-pass response time. Both types of filtration media gave acceptable

responses in simulated effluent versus the FTIR only (by-pass) measurement. A graphical representation of the filter versus FTIR by-pass response is presented in Figure 2.

Part I Conclusions

- Using a 350°F measurement system temperature reduced the measurement system response time by a factor of 2. This suggests that some of the past noted discrepancies between Method 26 and the infrared method results were based on the large temperature difference between the methods. (350°F for the IR methods and 250°F for Method 26/26A)
- The measurement system response time for conditioned glassware was less than that for fresh glassware. It is expected that the time to condition the glassware is a function of the relative surface area of the glass. These experiments used a 3' glass lined probe and 3" diameter filter holders and filters. This suggests that some of the past noted discrepancies between Method 26 and the infrared method results were due to lack of glassware equilibration with the effluent.
- The ultra high purity quartz and Teflon coated filtration media gave similar responses to the HCl in simulated effluent.
- Measurement system flowrate versus response time could not be varied due to the physical constraints of the FTIR system. It is expected that increasing the sample flow can reduce measurement system response time.

PART II – Adsorption Studies

A. HCl Evolution Studies

Samples of two cement kiln dusts and one lime kiln dust (50:50 mixture of the two samples provided from Montevallo kilns 3 and 4) representing various degrees of calcination, free lime and chloride content were loaded onto quartz filters. Simulated effluent was directed through each of 1.0-g samples at 350°F. An FTIR was used to determine whether HCl could be evolved from the dust at measurement system temperatures.

Table 2 details the results of the CKD and LKD analysis, the Colton CKD was not used in the first studies.

Part II A Results

Gaseous HCl was not evolved from the CKD or LKD samples under the experimental conditions used during this study. This was true even with Ravena CKD which has a chloride content of approximately 0.8%. (At 2 lpm and 1.0-g. of CKD sample, 44 PPM of HCl can be released theoretically.)

B. HCl Adsorption Studies on CKD and LKD with Simulated Effluent

Samples of the same two cement kiln dusts and one lime kiln dust (50:50 mixture of the two samples provided) were loaded onto quartz filters and simulated effluent was directed through each of 0.05-g samples to determine the effect of CKD and LKD on quantifying HCl. The concentration of water vapor, oxygen and HCl was held constant while the concentration of SO₂ was varied as each experiment progressed. During the LKD experiment ammonia was added also to determine the effect of quantifying HCl.

Part II B - Results

Figure 3 presents a schematic of the Part II experimental apparatus, and Figures 4 through 6 present a graphical representation of the HCl adsorption results on the dust samples.

The presence and amount of SO₂ in the simulated effluent greatly affects the observed HCl concentration as depicted in Figures 5 and 6. These dust samples demonstrated a preferential

adsorption of SO₂ over HCl. As expected, addition of ammonia decreased the observed concentration of HCl as measured by the FTIR. This phenomenon is depicted in Figure 6.

Part II – Conclusions

- HCl is not evolved at 350°F from CKD or LKD using typical measurement system temperatures. This eliminates one source of suspected potential bias.
- All of the dust samples adsorbed HCl. This suggests that an effective HCl measurement system should minimize the collection of particulate matter during sampling.
- The adsorption of HCl by the CKD and LKD samples is greatly affected by the relative concentration of SO₂ in the effluent. The dust samples preferentially adsorb SO₂ over HCl. This suggests that effluent having a higher relative SO₂ concentration at the inlet to a baghouse will allow more HCl to pass through the filter cake collected on the bags. (An ESP likely will not exhibit as great of an effect due to the lack of filter cake through which the effluent passes.)
- As expected, the addition of ammonia to the simulated effluent reduces the amount of gaseous HCl that reaches the detector. This is presumable due to the formation of NH₄Cl.

PART III - FTIR/Modified M26 Comparison Studies

Samples of all three cement kiln dusts and one lime kiln dust (50:50 mixture of the two samples provided) were loaded onto quartz filters. Two sets of filters containing 0.05g samples were assembled for each experiment; one for the FTIR and one for the modified impinger method. The impinger method was modified to use pre-conditioned glassware (glassware previously passivated by HCl and simulated effluent), and was operated at 350°F temperatures rather than the 250°F specified by the Method 26.

Simulated effluent was directed simultaneously through the FTIR and the impinger train to compare the HCl concentration results. These experiments were conducted at two water vapor concentrations and at three HCl concentrations. The impinger method and the FTIR run were exactly 60 minutes in duration. The impinger train collected approximately 120 liters of gas sample.

A blank run using no dust was conducted to compare directly the FTIR and impinger results in the absence of dust. The HCl certified gas standard also was analyzed directly by both methods.

Figure 7 presents a schematic of the experimental apparatus

Figures 8 through 16 present a graphical representation of the FTIR response with time during these experiments. These graphs are annotated to contain information regarding the percent water vapor concentration, and the expected results.

Figures 17 through 21 are bargraphs that directly compare the FTIR and impinger results to each other and to the expected value. Dilutions of a manufacturer's certified 165-PPM standard ($\pm 5\%$ accuracy) were performed to generate the HCl concentrations used during this study. The dilution system consisted of a series of mass flow meters that were calibrated against a digital flow meter having a NIST traceable calibration.

The expected values depicted in the bargraphs was calculated three separate ways; 1) the expected value based on the manufacturer's certified analysis and application of dilutions factors, 2) the expected value based on direct cylinder analysis by the FTIR and application of dilution factors, and 3) the expected value based on direct analysis of the cylinder by the impinger train and application of dilution factors. In each case the error of the observed FTIR and M26 measurement is a combination of the calibration gas uncertainty, the error of the calibrated dilution system, and the error of the analytical methodology used (in this case the FTIR quantification algorithm and the ion chromatographic analysis of the impinger solutions).

Part III - Results

The FTIR measurement results were generally higher than expected and the modified impinger method was generally lower than expected at concentration levels approximating 5-20 PPM.

At the 10-PPM HCl concentration level, the FTIR results were approximately 3-6 PPM (30-60%) higher than the value expected based on the certified tag value. The modified impinger results were approximately 0.8 to 3 PPM (8-30%) lower than the value expected based on the certified cylinder tag value.

At the 4.5 PPM HCl concentration level, the FTIR results were approximately 2 PPM (40%) higher, and the impinger results were approximately 1 PPM (20%) lower than the expected value based on the certified tag value.

At the 17 PPM HCl concentration level, the FTIR results were approximately 11 PPM (45%) higher, and the impinger results were approximately 1 PPM (3%) lower than the expected value based on the certified tag value.

From time to time the water injection system had to be refilled during the course of these experiments. This led to the discovery of an unexpected phenomenon. The observed HCl concentration varied proportionately with effluent water vapor content. The Figures 8-16 clearly demonstrate that when water vapor is decreased (refilling the syringe), the observed HCl concentration also decreases.

Part III – Conclusions

- Operating the FTIR and the impinger measurement system at the same temperature with the same filtration media produces results that are similar. This is perhaps the most important aspect in obtaining comparable results for highly reactive gases in difficult to measure effluent.
- The experiments conducted during this study were operated at the 350°F. It is recommended that this temperature is used after baghouse and ESP controlled kilns where effluent temperatures typically exceed 350°F. For cooler stacks, the measurement system temperature should be at least 20°F higher than the effluent temperature to prevent condensation of the gas stream, but not so high as to vaporize material condensed on the particulate matter.
- In most cases, the FTIR results were higher and the impinger based results were lower than the value expected from the certified tag value. The FTIR results are likely high due to a non-linearity effect, which can be corrected using software, and adding additional calibration values below 10 ppm to the analytical program. The impinger results are within 20% of the value (1ppm) at the 5 PPM concentration level. This is likely the expected accuracy of the method.
- The direct correlation of HCl with percent water vapor may be explained by an adsorption effect. When water vapor is present, it occupies sites in the measurement system at the molecular level. Perhaps by hydrogen bonding with the fluorinated groups in the Teflon sampling components. Removing water vapor frees the active sites so that HCl can be adsorbed. The rapid displacement of HCl by water vapor as the moisture level is again increased suggests that the water is preferentially adsorbed in the system over HCl.

DISCUSSION AND RECOMMENDATIONS.

Numerous comparative studies between impinger-based and IR-based HCl measurement methods were conducted in the past using greatly disparate temperatures, and filtration media. The impinger testing was performed using freshly cleaned glassware, while the instrumental IR-based methods employed sample line conditioning with effluent before starting the run. Impinger-based methods are also designed to collect particulate matter effectively even when single point non-isokinetic sampling was

performed, while the instrumental IR-based methods sometimes take measures to reduce the amount of particulate collected (by turning the nozzle backwards, etc.). An additional source of error between the methods is the primary calibration standards used, and the degree of infrared analyzer linearity in the measurement range.

Together, the combination of sampling system temperature differences, degree of sample component conditioning, and the amount of particulate matter collected can more than account for differences encountered in the past comparative measurement results.

Simple modifications to Method 26 such as raising the temperature, conditioning the front half of the sampling train components, and reducing the amount of particulate matter collected can be made so that the results are comparable to those provided by infrared methods.

Perhaps the most important issue that became evident during the course of these experiments is that measuring HCl accurately at the 3-10 PPM level of concern is very challenging. Given a 20-30% level of accuracy for both methods (under the best circumstances) means that a relative error of from 0.5 to 3 PPM can be realized at any time. This makes it difficult if not impossible for a large facility having 3 or more kilns to determine major source status under the Clean Air Act Amendments.

Further work in this area should focus on how to measure HCl more accurately at low concentrations. Design of a sampling probe configuration that rejects particulate matter is recommended, along with field testing of the modified method. Testing of the impinger method should be conducted using a paired train configuration so that the precision of the method can be determined. Additionally, a means of co-adding HCl calibration gas (similar to analyte spiking) while sampling will determine the relative accuracy of the method at levels of concern to industry.

With respect to the infrared -based measurement techniques, use of a sampling probe that minimizes or rejects particulate matter is also recommended. Additionally, measures to more accurately quantify HCl at low concentrations should be taken. This includes adding HCl calibration points below 10 ppm to the software program, and ensuring that measurement system zero procedures are conducted and that the measurement system can actually achieve a zero reading for HCl.

Table 1 – Experiment Description and Simulated Effluent Matrix for Parts I-III

Experimental Condition	% H₂O Vapor	HCl – PPM	SO₂ – PPM	% - O₂	NH₃ - PPM
PART I Quartz Vs Teflon Filters	7%	10	245	15%	None
PART II HCl Evolution Studies 1.0 g of CKD and LKD on UHP quartz filters at 350°F	10%	None	109	5%	None
PART II Dust Adsorption Studies 0.05 g Ravena CKD 0.05 g San Antonio by-pass CKD 0.05 g Montevallo LKD	7% 7% 7%	15 15 15	245/475/0 0/245/475 0/245/475	15% 18% 18%	None None O/10/40
PART III Method 26/FTIR Comparisons 0.05 g Ravena CKD 0.05 g San Antonio by-pass CKD 0.05 g Colton CKD 0.05 g Montevallo LKD 0.05 g Ravena CKD 0.05 g San Antonio by-pass CKD 0.05 g Colton CKD 0.05 g Montevallo LKD	6% 6% 6% 6% 12% 12% 12% 12%	9 9 9 9 9 9 25 5	212 212 212 212 200 200 200 200	15.5% 15.5% 15.5% 15.5% 14.5% 14.5% 13.5% 15%	None None None None None None None None