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**ELECTRODE TECHNOLOGY for  
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## **Characterization of Anode Materials**

*SESSION CHAIR*

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## IMPROVING THE PRECISION AND PRODUCTIVITY OF GREEN COKE VOLATILE MATTER ANALYSIS

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### Abstract

Volatile matter (VM) analysis of green petroleum coke is an important measurement for determining the calcination behavior and properties of calcined coke. Green cokes with high VM (>12%) are more difficult to calcine and result in a higher porosity and lower bulk density in calcined coke. This paper will review current methods for measuring the VM of green coke based on the ASTM quartz method, the platinum crucible method, and the macro thermo-gravimetric (TGA) method. Detailed experimental results comparing the quartz crucible and macro TGA methods are presented in the paper. When used in combination with a high speed rotor mill, automated TGA equipment offers significantly improved speed and precision, as well as the capability for simultaneous measurement of ash and moisture contents.

### Introduction

The aluminum industry uses carbon anodes made from calcined petroleum coke (CPC) and coal tar pitch. CPC is produced from green petroleum coke (GPC) by the thermal treatment process of calcination. A primary objective of calcination is to transform the carbon structure so that it becomes electrically conductive. During thermal treatment, volatile hydrocarbons left behind from the refinery coking process are driven from the GPC. These volatile hydrocarbons are known as volatile matter (VM) or sometimes volatile and combustible matter (VCM). The VM content of GPC is an important property that determines CPC properties such as bulk density [1] which impact anode quality and performance at smelters [2].

GPC is produced at refineries with delayed coker units. The coker converts residual oils from crude distillation to light products and GPC by thermal cracking. The refinery recovers the cracked products to produce motor fuels. The pyrolyzed solid product from the coking process contains between 8 and 15% VM. Laboratories can determine the amount of VM by the use of several analytical procedures. This paper compares VM results obtained from a thermo-gravimetric analysis (TGA) method [3] and a quartz crucible analysis [4] method. Sample preparation using automated sample milling equipment is also investigated.

### Background

VM in GPC comprises light hydrocarbons and hydrogen that are driven from the coke when it is heated above 300°C [5,6]. Condensable tars which are carbon, hydrogen and oxygen containing species, break down or thermally crack into lighter components such as methane as the sample is heated. Methane is released until ~800°C. In the VM analysis test, the coke sample is heated to 950°C. GPC also releases hydrogen and this can

continue at temperatures above 1000°C. Small amounts of sulfur, nitrogen, and oxygen compounds are also released during heating. The amount of VM in GPC is determined by coker operating conditions and the coker feedstock.

Measuring VM provides valuable information to refineries, calciners, and smelters. Refineries utilize VM measurements for process control feedback to determine the amount of unrecovered light products. Higher VM means that less light products are recovered. In some cases, this may be the preferred economic choice for the refinery. Coking units are usually the refinery bottleneck. Operating with less coking severity provides the coker and refinery with more capacity or throughput to process more residual oils. When throughput increases, the residual oils are heated to lower temperatures in the furnace. The endothermic coking reactions proceed at lower rates, which results in increases in the VM content in the GPC.

Over the past decade, refineries have increased capacity in this manner. When refineries process heavier crudes (i.e. higher specific gravity oils), they typically have more bottoms (residual oil) which make additional coke. More recently, refineries have looked to reduce costs including coker heating costs, which also increases GPC VM content. Figure 1 shows the weighted average VM content from all anode-grade GPC suppliers to Rain CII Carbon from 2002 to 2010. For this time frame, VM was determined by ASTM D6374 (Quartz Crucible Method).

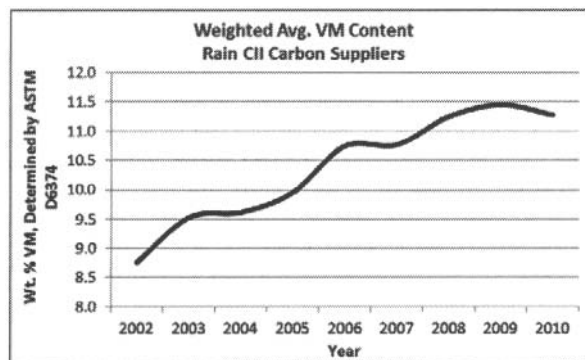


Figure 1: Weighted Average VM Content of Rain CII Carbon GPC, 2002 – 2010

Calciners and smelters use VM measurements to predict calcining behavior, calcined coke properties, and anode performance. GPC containing higher amounts of VM will produce CPC with a higher porosity [1] and lower bulk density [7]. Low bulk density CPC is undesirable since it can negatively impact anode densities and require additional coal tar pitch binder.

As the calciner in the supply chain from refineries to smelters, Rain CII Carbon has developed correlations between VM and vibrated bulk density (VBD). The relationship between VM content and CPC bulk density for a straight-run GPC is shown in Figure 2. This data was based on Rain CII Carbon's measurement of GPC VM and CPC VBD for a particular supplier over a two year period. KVBD is an internal VBD test measured on samples prepared to 8x14 Tyler mesh (1.18 – 2.36mm). It was initially developed by Kaiser Carbon, hence the name, Kaiser VBD or KVBD. Rain CII's calciners have used this test in its current form for over 40 years to track daily product VBDs.

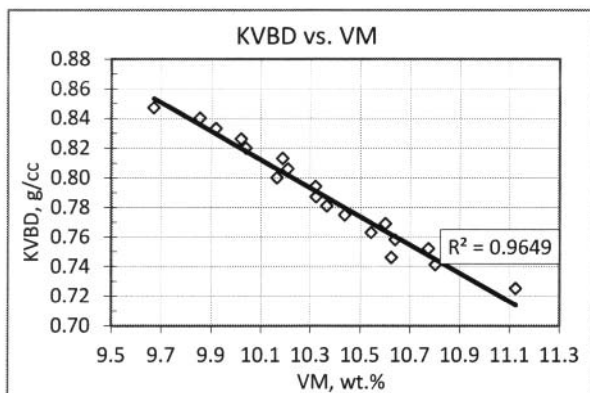


Figure 2: Correlation between KVBD and VM for one Rain CII Carbon Supplier.

Rain CII Carbon has, on occasion, rejected GPC shipments containing high VM. In addition to reducing CPC VBDs, high VM coke is more difficult to calcine. It is typically softer and finer in particle size than lower VM GPC. More heat is required to drive the VM from the coke and the finer particle size makes the coke bed more unstable. Fine coke does not tumble well in the kiln and becomes more insulating making it more difficult to achieve calcination real density targets.

#### Rain CII Carbon Measurement of VM Content

Prior to 2002, Rain CII Carbon utilized the platinum crucible method, ASTM D4421, to determine the VM content of GPC [8]. Rain CII Carbon determined that the quartz crucible method, ASTM D6374, resulted in 0.6% lower VM than the platinum crucible method and improved repeatability. Additionally, significant cost and time savings were possible with the quartz crucible method [9]. Based on this, Rain CII Carbon switched to using the quartz crucible method in early 2002.

In 2009, Rain CII Carbon participated in a VM round robin study with several other laboratories. One of Rain CII Carbon's GPC suppliers used a VM analysis procedure based on a TGA method and a different sample preparation method. The combination of using a TGA and a high speed rotor mill to prepare samples appeared to significantly reduce the sample analysis time and Rain CII Carbon became interested in the equipment. After preliminary testing, Rain CII purchased equipment in late 2010 and undertook an extensive comparison of the two methods. The results are presented in this paper.

## **Equipment Description and Information**

### Quartz Crucible Method and Equipment

The ASTM quartz crucible method utilizes one gram samples crushed to -60 mesh (-250µm). The samples are placed in quartz crucibles with covers and then placed in a sample rack that allows a laboratory to analyze up to 20 samples in a single run. The rack is loaded into a muffle furnace preheated to 950°C. The temperature drops initially and then recovers to 950°C and the samples are held for five to ten minutes as specified in the procedure. The rack is then removed from the furnace and allowed to cool before crucibles are placed in a desiccator. Final weights are determined once the samples have cooled to ambient temperature and the VM is calculated.

The equipment used for the quartz method is simple and readily available and this is a key benefit of the method. Quartz crucibles, covers, and crucible racks are available for commercial purchase. The furnace is a standard muffle furnace with the ability to maintain 950°C. A timer is also required to ensure samples remain in the furnace for the calibrated length of time. Figure 3 shows the quartz crucible method being used at Rain CII Carbon.

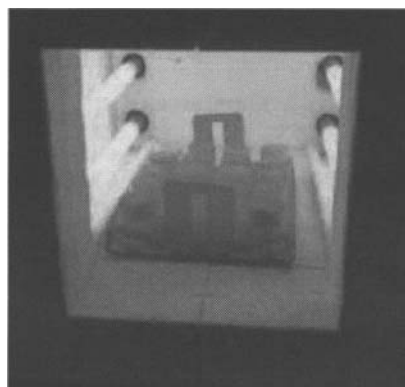


Figure 3: Quartz Crucible VM Method Equipment

### Sample Preparation for Quartz Crucible Method

The quartz crucible method requires samples to be crushed to -60 mesh (-250µm). Rain CII Carbon uses a jaw crusher for the first stage crushing and then a roll crusher for final crushing. Stage crushing is used where the roll crusher gap is gradually reduced until the required particle size is obtained. The ASTM procedure provides specific guidelines on how the sample should be crushed to avoid over-crushing.

### TGA VM Method and Equipment

The ASTM TGA method, D7582, also utilizes one gram samples crushed to -60 mesh (-250µm). The procedure does not specify sample preparation and crushing, only that all material should be crushed to -60 mesh. This is different from the quartz crucible method which gives specific guidelines to avoid over-crushing as discussed later in the paper.

Thermo-gravimetric analysis is a very common analytical method and there are numerous manufacturers of equipment available. In

this paper, a Leco TGA 701 analyzer was used for all the testwork, Figure 4. The TGA measures the weight loss in an enclosed furnace and the model used has a sample carousel that holds up to 19 samples (38 for dual configuration). It can measure total moisture, ash, volatile content or loss-on-ignition. The furnace can be controlled to 1000°C with uniform heating and heat ramping. Dual thermocouples provide feedback for temperature control.



Figure 4: Leco TGA701 Apparatus

Coke samples are placed in crucibles and weighed. For VM determination an inert atmosphere of nitrogen or argon is used. The apparatus first raises the temperature to 107°C for moisture determination, then to 950°C in 26-30 minutes. Samples are held at 950°C for seven minutes. The weight of the samples at the end of the heating cycle are measured to calculate the VM content. Ash analyses can then be performed on the samples using oxygen or air atmospheres. ASTM recommends heating the coke sample for three or more hours at 950°C ± 10°C.

#### Rotor Mill Sample Preparation

The Retsch ZM200 mill is one of several rotor mills available commercially. It is a high speed rotor mill that rapidly reduces sample particle size. The mill can be fitted with different size sieves depending on the intended use. For the results reported in this study, a 60 Tyler mesh (250µm) sieve was used. When the uncrushed sample is added to the mill, the high speed rotor pulverizes the sample until it passes through the 60 mesh sieve. This ensures that the entire sample is crushed to minus 60 mesh (250µm) and it also minimizes over-grinding of the sample. The Retsch mill is shown in Figure 5.



Figure 5: Retsch ZM200 Mill

## Experimental

The Rain CII Carbon Lake Charles Laboratory completed VM comparison tests between the TGA using the ASTM D7582 procedure and the quartz crucible method using ASTM D6374. Since the TGA also provides residual moisture and ash analysis results, a comparison was also made between the TGA ash results and those generated by the platinum crucible method using ASTM D4422.

VM analyses were completed in conjunction with testing of the high speed rotor mill. Sample preparation and analysis results using the rotor mill were compared to Rain CII Carbon's standard procedure for preparing samples to minus 60 mesh using a roll crusher.

A total of 209 samples were analyzed for the evaluation of the TGA and rotor mill. Correlations between TGA VM and ash analysis results and quartz crucible VM and platinum crucible ash analysis results were made. Potential contamination of samples by metals (primarily iron) from the mill and roll crusher was checked by analyzing samples using X-ray fluorescence (XRF) analysis.

Repeatability values were established for all methods based on the above testwork, including the different sample preparation methods.

## Volatile Matter Results and Discussion

### Volatile Matter with Roll Crusher Sample Preparation

The first studies were performed to determine what, if any, bias existed between TGA and quartz crucible analyses. Table 1 shows the averages and standard deviation difference between TGA and quartz VM analyses. In this case, all samples were prepared by roll crusher. Figure 6 shows the correlation between the two methods using 209 samples. The R<sup>2</sup> value of 0.94 indicates a strong overall correlation between the TGA analyzer and quartz method. The overall average for these samples was 11.02% by TGA and 11.50% by the quartz method VM for all samples ranged from 6.5% to 15.8%, as measured by the TGA.

Table 1: Average VM and Difference from TGA and Quartz VM

	209 Samples	
	TGA	Quartz
Average	11.02	11.50
Std. Dev. Of the Diff.	0.55	
VM Range	6.1% - 15.8%	

While a strong correlation exists between the methods, samples analyzed by the quartz method and the TGA method showed a greater difference with higher VM samples. Figure 7 shows the larger difference between samples with >12% VM compared to those with <12% VM.

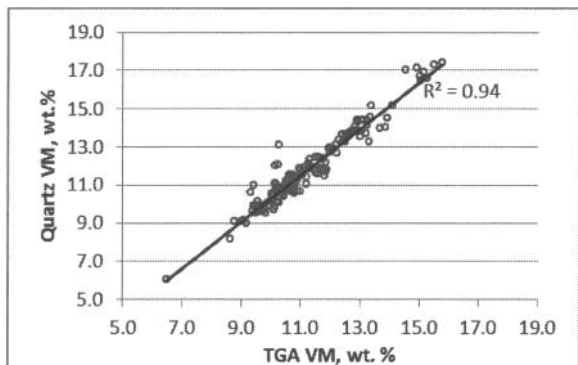


Figure 6: TGA and Quartz VM Correlation

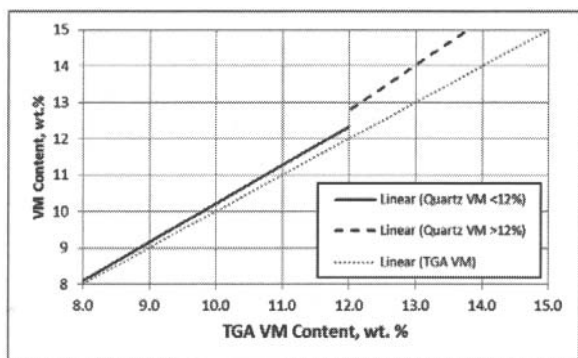


Figure 7: Quartz VM for samples Above and Below 12%

The average difference between the two methods on samples ranging from 6.1% to 12% VM is 0.24% lower for the TGA analysis. The average difference for samples ranging from 12.0% to 15.8% VM is 1.1% lower for the TGA analysis. Table 2 shows the values obtained by the quartz method compared to the TGA results. All samples for these analyses were prepared by roll crusher. The VM range was determined by TGA analysis.

Table 2: Averages for VM Below and Above 12%

	165 Samples <12%		44 Samples >12%	
	TGA	Quartz	TGA	Quartz
Average	10.41	10.65	13.29	14.39
Average Diff.	0.24		1.1	
VM Range	6.1% - 12.0%		12.0% - 15.8%	

**Effect of Residual Moisture on VM Analysis:** With the divergence of results at high VM levels, studies were conducted on two high VM samples prepared by roll crusher. Two high VM samples were prepared nine times by roll crusher and placed into a vacuum desiccator. Another set of samples were prepared by roll crusher and dried in an oven for 30 minutes at 105°C prior to analysis. Analysis of oven-dried samples resulted in virtually identical VM results. Samples stored in a vacuum desiccator showed less agreement between the TGA and quartz analysis. Table 3 shows these results.

Table 3: Vacuum Desiccation and Oven Drying VM Results

	Vacuum Desiccation		Dried for 30 Minutes	
	TGA	Quartz	TGA	Quartz
Sample 1				
Average	12.29	12.82	12.29	12.42
Average Diff.	0.53		0.12	
Sample 2				
Average	12.96	13.37	12.96	12.89
Average Diff.	0.41		(0.07)	

The results indicate that crushed samples readily absorb moisture and higher VM samples appear more susceptible to this. Rain CII Carbon has always placed samples in a vacuum desiccator after crushing as recommended in the ASTM D6374 procedure. This reduces moisture pickup but does not appear to eliminate it. A short drying step immediately prior to analysis removes residual moisture from the sample. It is worth noting that the TGA method removes residual moisture prior to VM determination.

Volatile Matter by TGA with Rotor Mill versus Quartz Crucible with Roll Crusher Sample Preparation

The VM methods were then compared by analyzing 39 bulk samples that were separately prepared and analyzed. Samples analyzed by the TGA were prepared using the rotor mill. Samples analyzed by quartz crucible were prepared by step-wise roll crushing. Table 4 summarizes the analytical averages and standard deviation of the differences (TGA minus quartz). The VM range was determined by TGA Analysis. Figure 8 shows a strong correlation between the two methods with differently prepared analysis samples.

Table 4: TGA with Rotor Mill vs. Quartz with Roll Crusher

	39 Samples	
	Rotor Mill and TGA	Standard Prep and Quartz
Average	10.2	11.1
Std. Dev. Of The Diff.	0.7	
VM Range	8.9% - 15.5%	

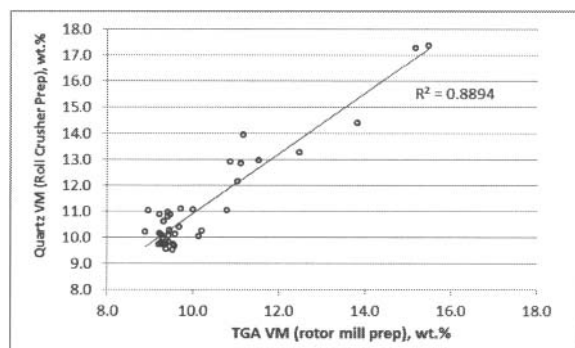


Figure 8: TGA (Rotor Mill Prep) and Quartz (Roll Crusher Prep)

**Repeatability:** Repeatability testing of the VM analysis was performed by analyzing an in-house coke standard, developed from an industry-wide round robin (RR 16) conducted by Rain

CII Carbon. The sample was analyzed 28 times for the TGA/ rotor mill combination and the same for the quartz crucible/ roll crusher combination. Statistics for each method are shown in Table 5. Figure 9 demonstrates improved repeatability of the TGA analyzer and rotor mill. The TGA analyzer exceeds both precision statements provided by ASTM.

Table 5: Repeatability Results for each VM Method

	RR16, 28 analysis	
	TGA	Quartz
Average	9.63	9.88
Std. Dev.	0.12	0.28
ASTM Repeatability	0.24	0.24

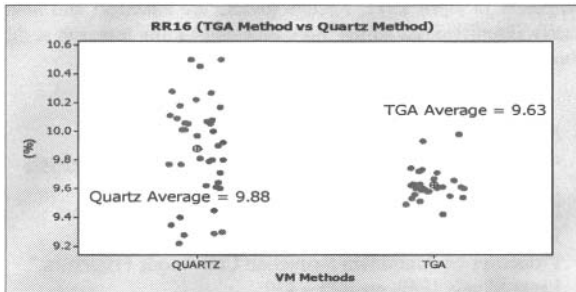


Figure 9: Data Plot for 28 Analyses of One Sample

**Ash Results and Discussion**

The ash method for the TGA was compared to the platinum crucible method. Ash analysis by the TGA is performed in an oxygen environment compared to the ambient air atmosphere used for the platinum crucible method. Samples for both the TGA and platinum crucible methods were prepared by roll crushing. The R<sup>2</sup> value of >0.99 indicates a strong correlation between the TGA analyzer and the platinum crucible ash method. Table 6 summarizes the analytical results. Figure 10 demonstrates the correlation between ash determined on the TGA and platinum crucibles. Ash range was determined by TGA analysis.

Table 6: Analytical Results for TGA and Pt Ash Comparison

	61 COMPARISONS	
	TGA	Pt
Average	0.45	0.43
Average Diff.	0.016	
Std. Dev. of the Diff.	0.048	
Ash Range	0.1% - 1.26%	

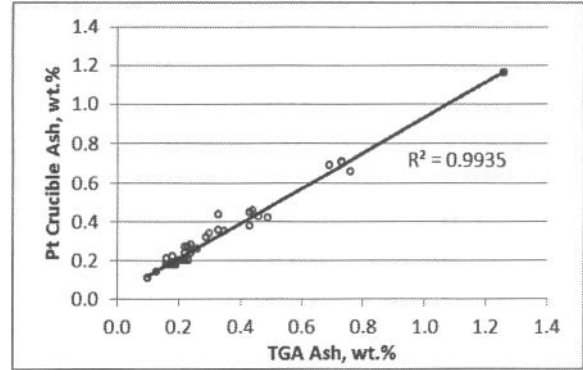


Figure 10: Ash Correlation - TGA (Rotor Mill) and Pt. Crucible (Roll Crusher)

**Repeatability**

Ash repeatability for the TGA was tested by analyzing our in-house coke standard (ash value 0.20 wt.%) and a National Institute of Standards and Technology (NIST) sample (Sample #2718, ash value 0.18 wt.%) on the TGA. Table 7 summarizes the statistics for each sample and demonstrates the repeatability of the TGA analyzer and rotor mill sample preparation. The TGA analyzer exceeds the ASTM repeatability for ash measured by ASTM D4422.

Table 7: TGA Repeatability Results for each VM Method

Standard Sample	Lab QC	NIST 2718
Standard Ash Value	0.20	0.18
No. of Analyses	13	9
Average	0.22	0.18
Std. Dev.	0.01	0.01
ASTM Repeatability	0.02	

**Rotor Mill Sample Preparation**

The laboratory tested for contamination introduced by the rotor mill during sample preparation. XRF tests showed little to no change in metals content for samples prepared by the rotor mill. Work in this area also showed that the rotor mill provided a more homogeneous sample than those prepared by roll crusher. Table 8 shows the average and standard deviation difference between samples prepared by rotor mill and roll crusher for XRF testing.

Table 8: XRF Differences, Rotor Mill and Roll Crusher Prep

	Element			
	Ni	Fe	V	Ca
Average	(0.0003)	0.0008	(0.0003)	0.0004
St. Dev.	0.0004	0.0013	0.0010	0.0015
Average	(0.03)	0.0018	(0.0006)	0.00003
St. Dev.	0.08	0.008	0.0007	0.0001

Additional tests were completed to compare the particle size of samples prepared to -60 mesh (-250µm) on the rotor mill and roll crusher. Unlike the quartz crucible method, the TGA method only states that the sample needs to be sized to minus 60 mesh. The quartz method calls for 40-55% of the crushed material to be

retained on the 120 Tyler mesh screen. Sizing data shows that the rotor mill will not meet the ASTM guidelines for the quartz crucible method. Table 9 shows sizing data obtained for samples prepared by rotor mill and roll crusher.

Table 9: Sizing Data for Rotor Mill and Roll Crusher Preparation

HGI	+65 mesh	+120 mesh	-120 mesh
	Rotor Mill		
56	3.1	29.2	67.7
65	4.7	22.1	73.2
100	5.2	14.2	80.6
Average	4.3	21.8	73.8
	Roll Crusher		
56	0.7	50.3	49.0
65	0.1	51.3	48.7
100	11.9	35.8	52.4
Average	4.2	45.8	50.0

### Improvement and Efficiency Gains

#### Rotor Mill

The rotor mill rapidly produces -60 mesh (-250µm) samples for VM, ash, or XRF analysis. The rotor mill decreased the sample preparation time by 12% per sample. Sample preparation time includes cleaning equipment after each sample is milled.

#### TGA Analyzer

The TGA analyzer was found to offer many potential benefits over the quartz crucible method. Of primary importance is improved safety. The laboratory technicians do not need to open furnace doors at high temperature or remove crucible racks at 950°C as required by the current quartz crucible method. Residual moisture is also completely removed from the VM samples prior to VM determination which improves the accuracy of the analysis.

The VM tests are completed in a nitrogen atmosphere which eliminates air oxidation or burning of the sample. The oxygen atmosphere used for ash analysis allows completion in six hours compared to eight to ten hours for the platinum crucible method. The TGA can complete VM and ash analysis in a single run for up to 19 samples; all data inputs are controlled by the CPU and internal balance, ensuring accuracy in all calculations.

### Conclusions

Utilizing the rotor mill and TGA analyzer, the following conclusions can be made:

- The combination of the rotor mill and TGA analyzer will produce lower VM results from 0.2% (VM<12.0%) to 0.8% (VM>12.0%) compared to the results obtained using the standard roll crusher preparation and quartz method.
- VM analysis precision will be improved to 0.12% using a rotor mill and TGA analyzer.
- Residual moisture did not influence TGA VM measurements because the method completely removes residual moisture prior to analysis.
- Vacuum desiccation of prepared samples did not eliminate moisture pickup prior to VM analysis by the quartz crucible method.

- Ash results using the rotor mill and TGA will decrease on average by 0.02%.
- No significant biases exist in any of the elements analyzed by XRF for samples prepared by the rotor mill.
- Compared to the quartz crucible method and roll crusher, the TGA/rotor mill combination offered a significant improvement in sample analysis times.
- The TGA also eliminates opening the muffle furnace door and handling objects near 950°C as done in the quartz crucible method. This makes it an inherently safer procedure.

Given the increasing variation in green coke quality for CPC production, VM measurements are becoming more important for our industry. Based on the benefits outlined above, the Rain CII Carbon Lake Charles lab switched to using the TGA/Retsch equipment in April 2011. Results to-date are excellent and have greatly simplified one of the more time consuming tests run at the laboratory.

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