

# Reconciling Differences in Coal and Coke Volatile Matter Yields Determined by Two ASTM Methods

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## VOLATILE MATTER IN COAL AND COKE

- Volatile matter is considered to be "Those products, exclusive of moisture, given off by a material such as gas or vapor, determined by definite prescribed methods which vary according to the nature of the restrict."
- Some of the constituents of coal volatile matter are hydrogen, carbon monoxide, methane and other hydrocarbons, tar vapors, ammonia, and some organic sulfur- and oxygen-containing compounds. Some noncombustible gases derived from the decomposition of organic materials in coal (such as carbon dioxide and water vapor) are also considered constituents of coal volatile matter.
- Volatile matter is used to:
- Assess the burning rates of coal
- Indicate coke yield upon carbonization
- Help establish the ranks of coals

## **VOLATILE MATTER YIELDS**

#### Factors that affect volatile matter yields are:

- Moisture in coal
- Heating rates of samples
- Final temperature
- Plastic properties in coals

#### Parameters examined in these studies include:

- Moisture, ranks of coal, and pre-drying samples
- Sample heating ratesFinal temperatures
- Isolating and analyzing volatile matter fractions

## ASTM VOLATILE MATTER PROCEDURES

#### D 3175 (Fieldner Furnace)

• One gram of the analysis sample in a platinum crucible with a tight fitting lid is lowered into a minimum free space vertical tube furnace preheated to 950°C ±20°C and heated for 7 minutes. After cooling and weighing the mass loss is recorded.

## D 7582 (Macro TGA)

• One gram sample of the analysis sample in ceramic crucibles with lids on a 20-position carousel are heated at a rate that reaches  $950^{\circ}\text{C} \pm 10^{\circ}\text{C}$  in a 26-30 min time period. An internal balance weighs the covered crucibles at regular intervals while the temperature of the furnace is raised. The  $950^{\circ}\text{C}$  temperature is held for 7 minutes and the mass loss is recorded.

#### **For Both Procedures**

Volatile matter = mass loss - residual moisture

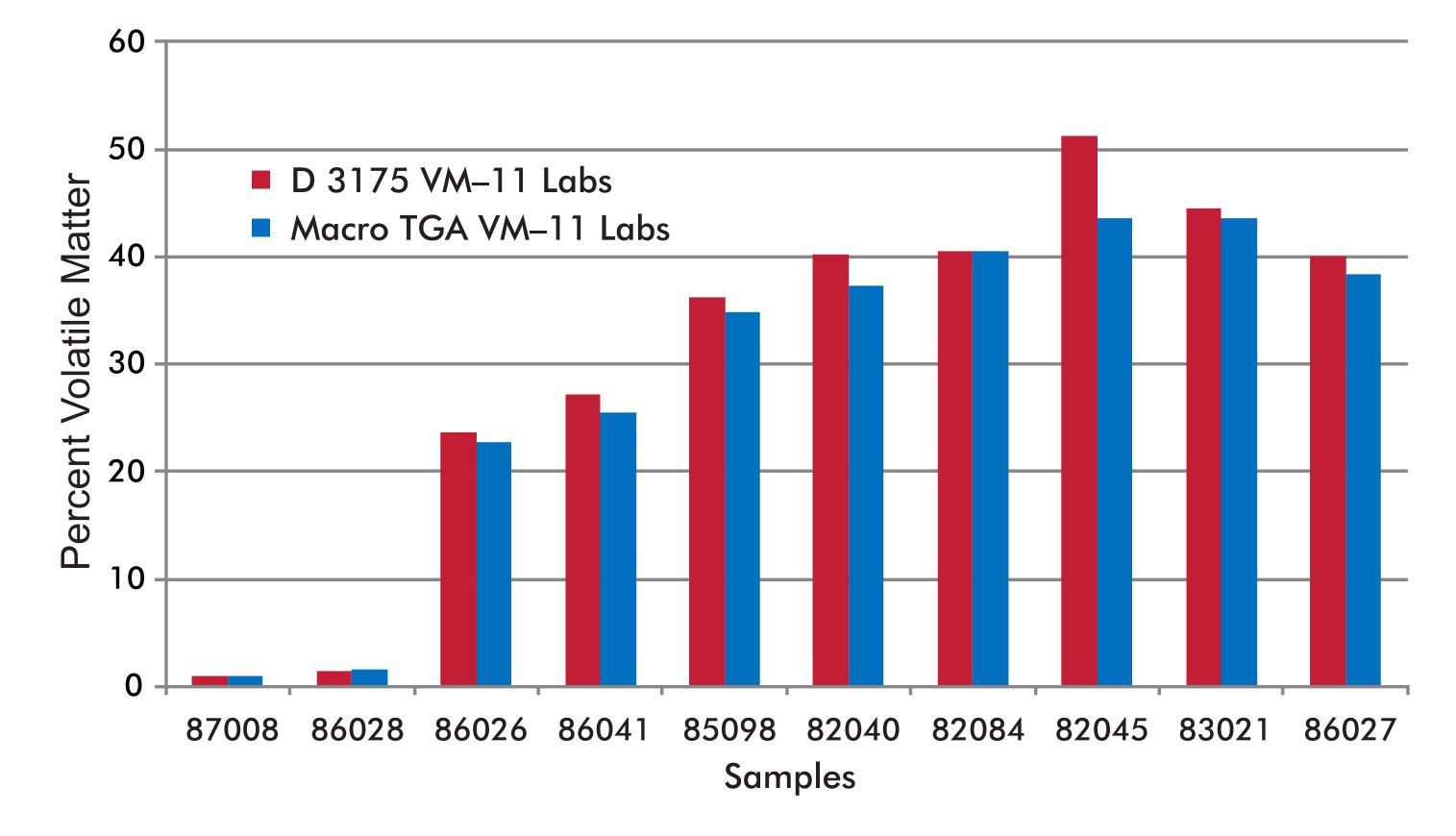


Figure 1. Dry Volatile Matter Values from 1986-87 ASTM Interlabaratory Study

# COMPARISON OF ASTM D 3175 AND MACRO TGA VM VALUES

#### For Different Ranks of Coal

- D 3175 VM values are higher than macro TGA VM values for bituminous coals.
- D 3175 VM values are similar to macro TGA VM values for subbituminous and lignitic coals.
- D 3175 VM values are slightly lower than macro TGA VM values for anthracite coals and cokes.

#### **Precision of Volatile Matter Measurements**

• The precision of macro TGA volatile matter measurements are generally better than D 3175 volatile matter measurements. D 3175 measurements in interlaboratory studies have wider ranges and higher standard deviations, as shown in Figure 2.

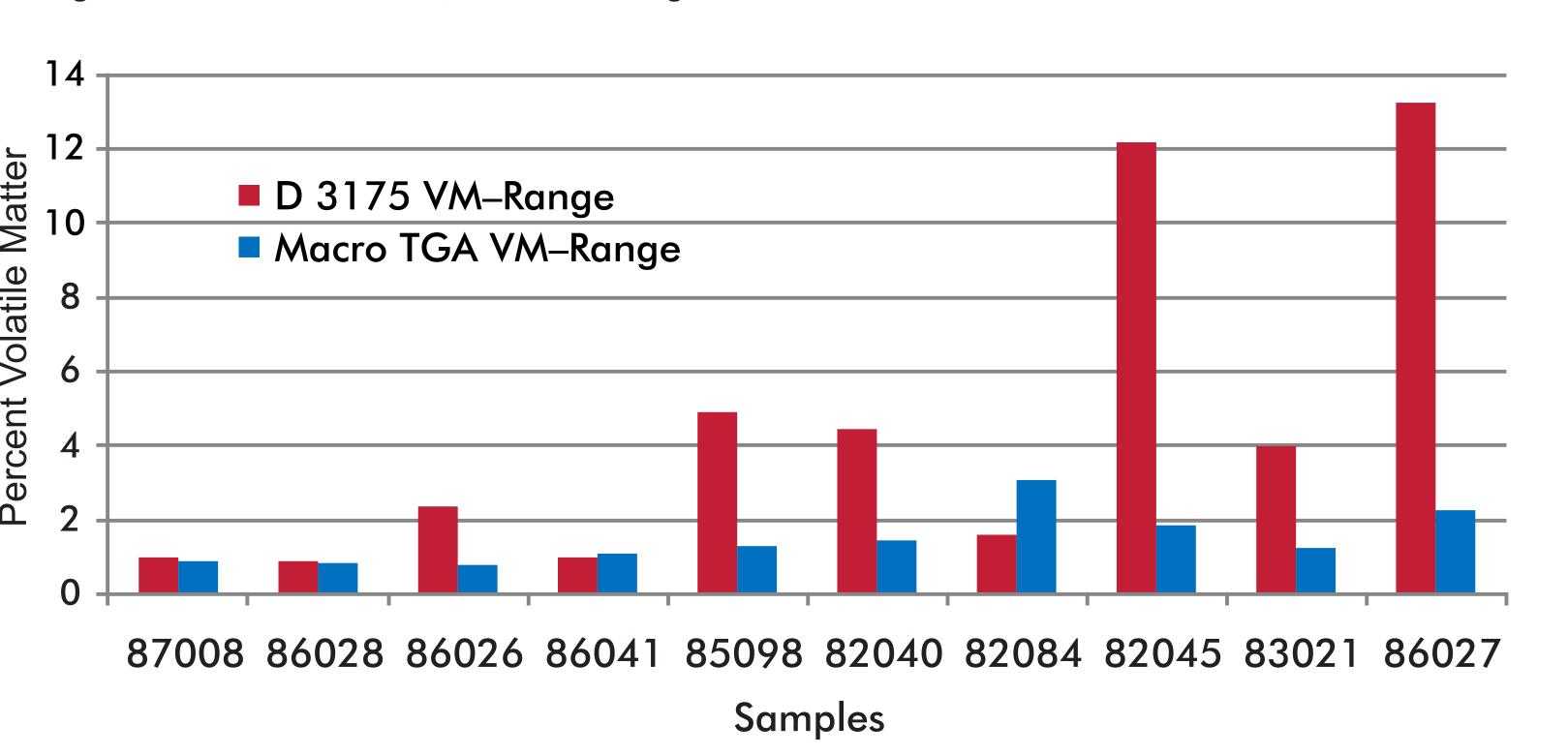


Figure 2. Ranges of Dry Volatile Matter Values from 1986-87 ASTM Interlaboratory Study

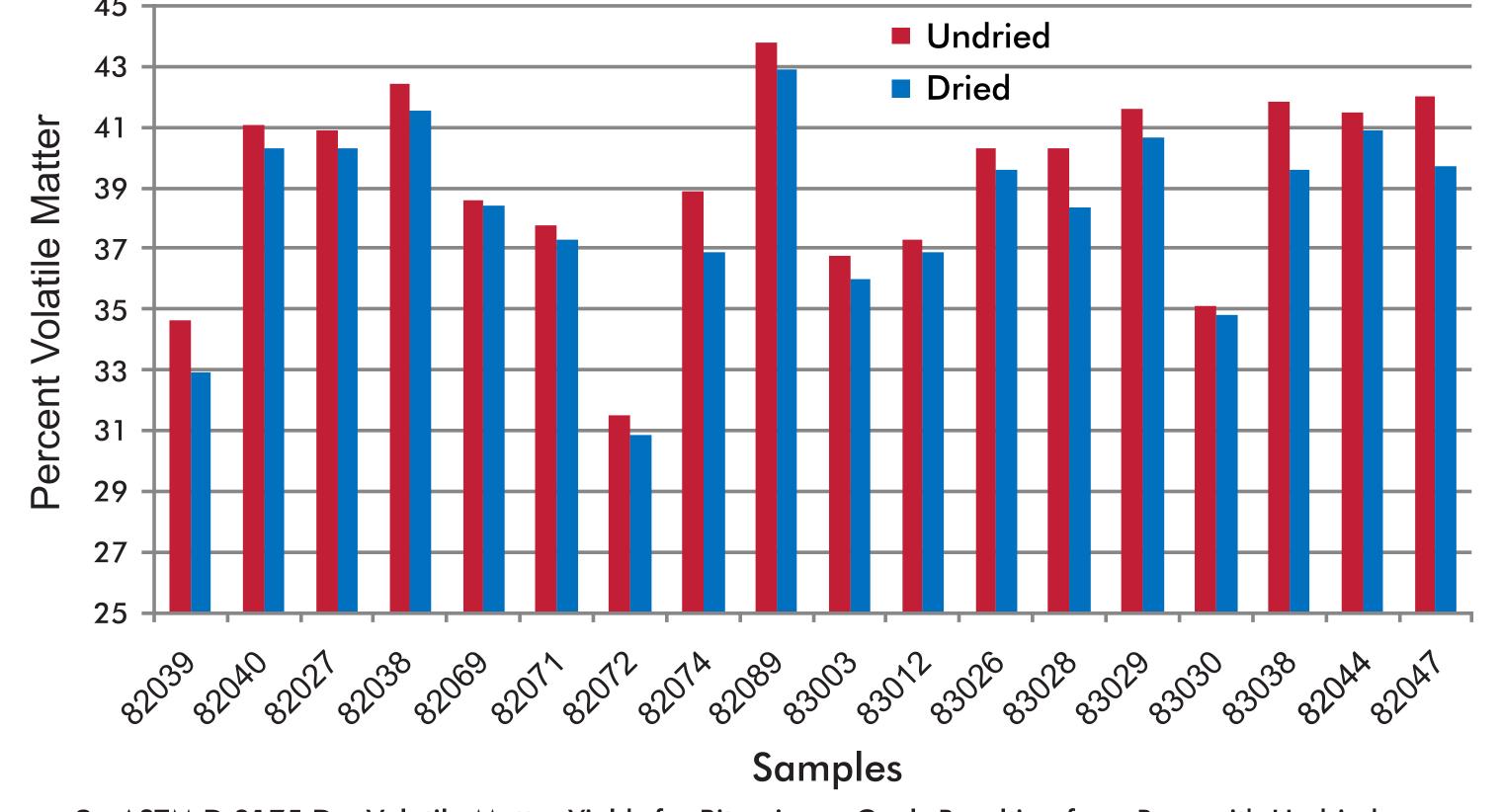
## OUTLINE OF STUDIES

#### **Pre-drying Samples**

• D 3175 VM values were measured for 18 bituminous coals. Samples of the same coals were dried and the VM measured. All VM values of the dried coals were lower than the D 3175 VM values, as shown in Figure 3, by an average of 0.94%.

#### Heating Rates Study with LECO TGA 601

- The VM yields as a function of the macro TGA furnace ramp rate were measured for 9 bituminous and 7 subbituminous and lignitic coals. Heating rates used were 10, 20, 30, and 40°C/min. These VM values along with D 3175 VM values with an effective heating rate of 420°C/min were used to prepare Figures 4 and 5.
- Isolation and analysis of volatile matter fractions.



**Figure 3.** ASTM D 3175 Dry Volatile Matter Yields for Bituminous Coals Resulting from Runs with Undried and Dried Samples

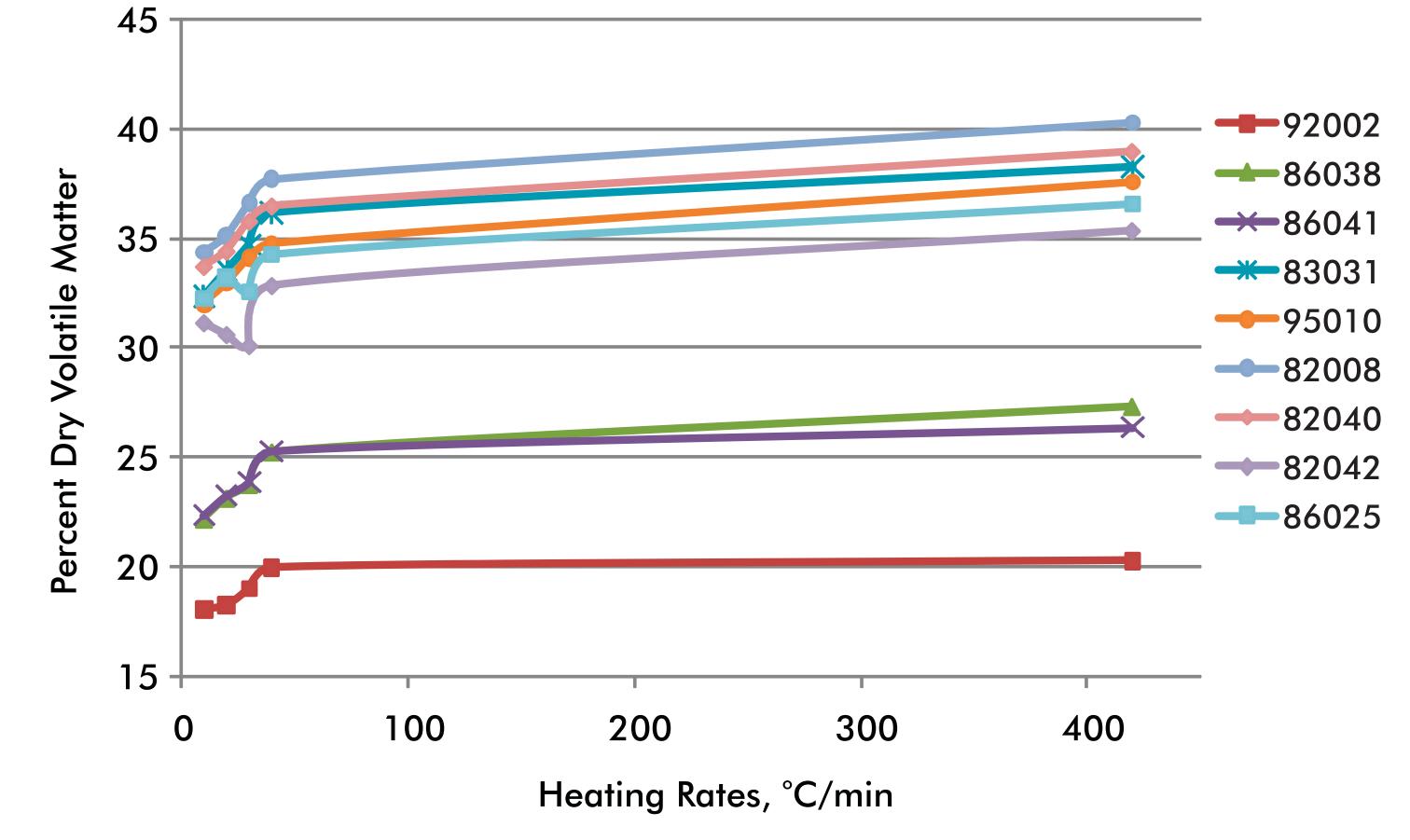
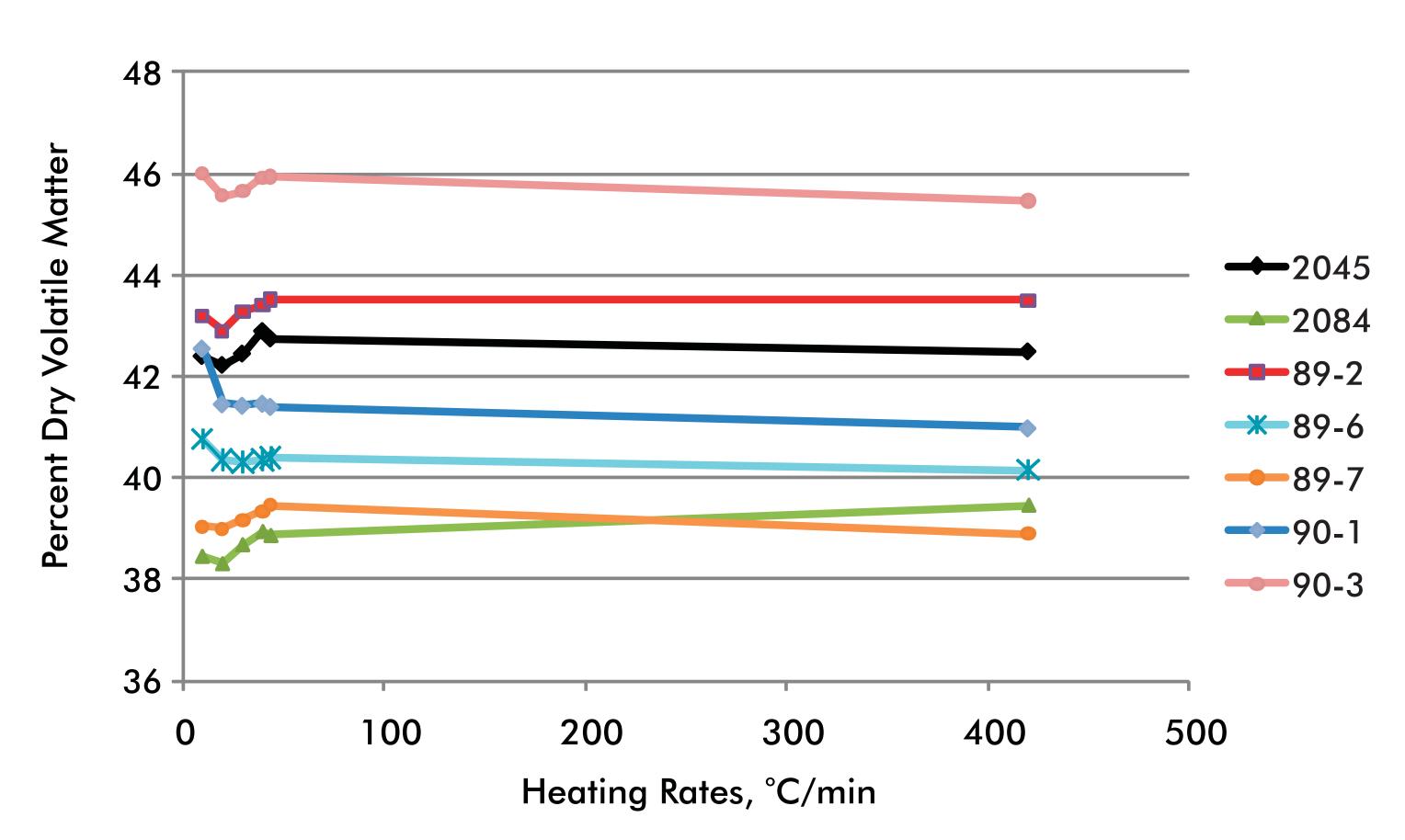
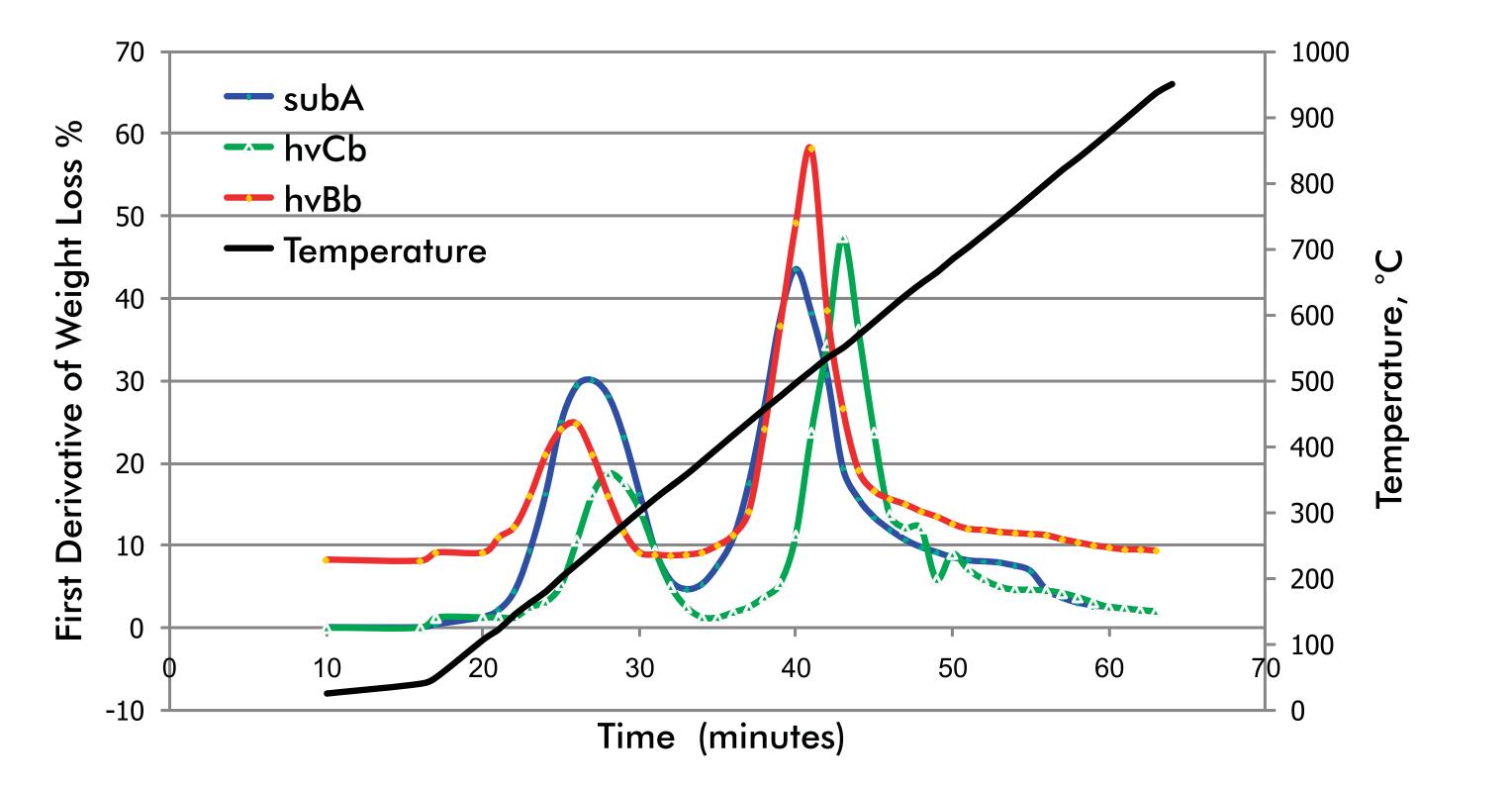


Figure 4. Plot of Dry Volatile Matter Yields as a Function of the Heating Rate for Bituminous Coals



**Figure 5.** Plot of Dry Volatile Matter Yields as a Function of the Heating Rate for Subbituminous and Lignitic Coals



**Figure 6.** Differential Thermogravimetric Plots of 2 Bituminous Coal and a Subbituminous Coal Showing Areas of Maximum Mass Losses During Heating

## CONTROLLED PYROLYSIS EXPERIMENTS

A LECO Model 601 Macro TGA was used in control pyrolysis experiments to heat coal samples in nitrogen to selected final temperatures (400°C, 650°C, and 950°C) to isolate volatile matter fractions. The 400°C and 650°C temperatures were selected to coincide with materials evolved in the 100-400°C, and 400-650°C ranges, as indicated by the differential thermogravimetric (DTG) plots of the three coals, as shown in Figure 6. The solid residues from the experiments were analyzed for carbon, hydrogen, nitrogen, sulfur, and oxygen (by difference). Using the measured values and the mass losses during the controlled pyrolysis experiments, the elemental analysis of the residues and volatile matter on a "raw coal basis" were calculated. As an example, Table 1 shows the results for the hvCb coal.

Samples from hvCb Coal							
	Raw Coal	400°C Residue	400°C Volatiles	650°C Residue	650°C Volatiles	950°C Residue	950°C Volatiles
% Yield		97.04	2.96	68.22	31.78	63.18	36.82
% Carbon	77.47	76.48	0.99	55.84	21.63	54.08	23.39
% Hydrogen	5.54	4.98	0.55	1.74	3.80	0.343	5.20
% Nitrogen	1.75	1.73	0.01	1.44	0.30	0.903	0.84
% Sulfur	5.29	4.94	0.34	2.75	2.54	2.56	2.73
% Oxygen	9.96	8.89	1.07	6.45	3.51	5.29	4.66

**TABLE 1.** Dry, ash-free (DAF) analytical values of residues from controlled pyrolysis experiments with hvCb coal calculated to a raw-coal basis.

Figure 7 illustrates graphically how sulfur is lost from the different coals as a function of the pyrolysis temperature. The amount of sulfur lost from the coal during pyrolysis is very significant, since any sulfur remaining in the residue would be converted to  $SO_2$  during ashing and trapped by the alkali and alkaline earth oxides formed from minerals during the pyrolysis. The amount of ash determined for coal samples ashed after the volatile matter determination is generally less than the ash determined directly on coal samples.

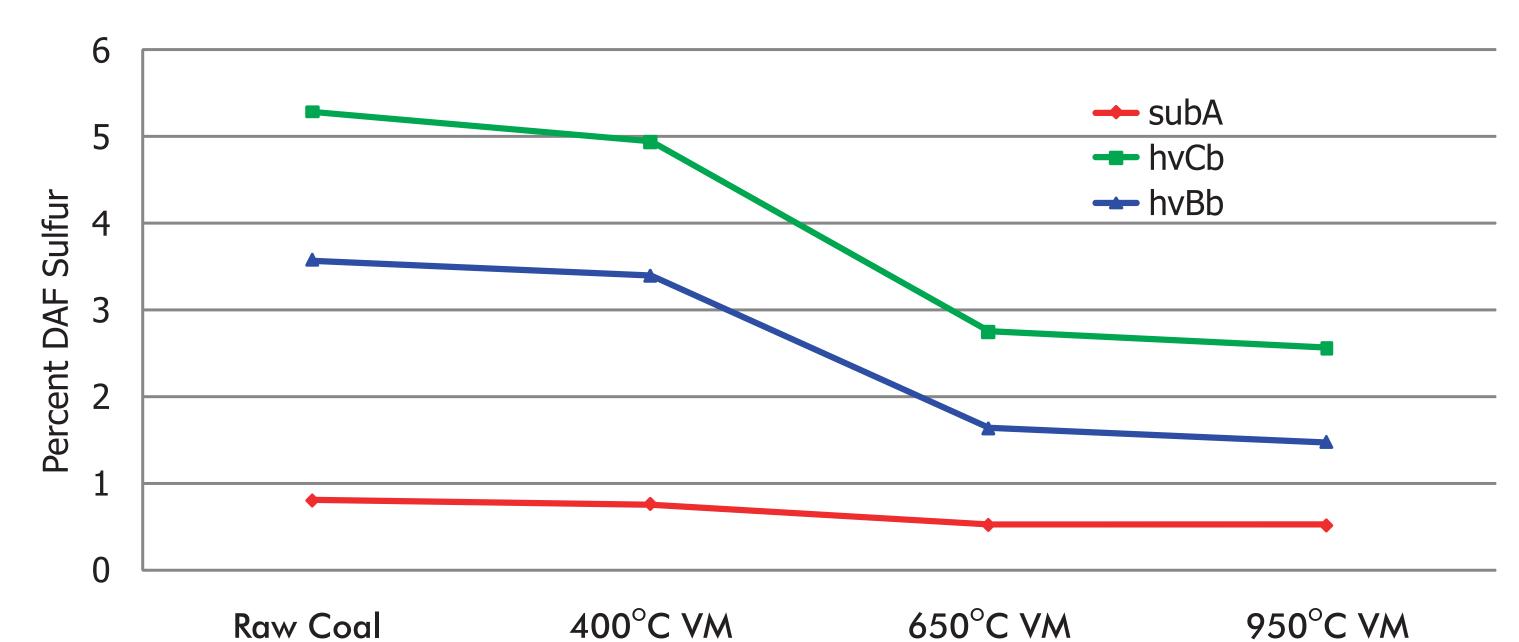
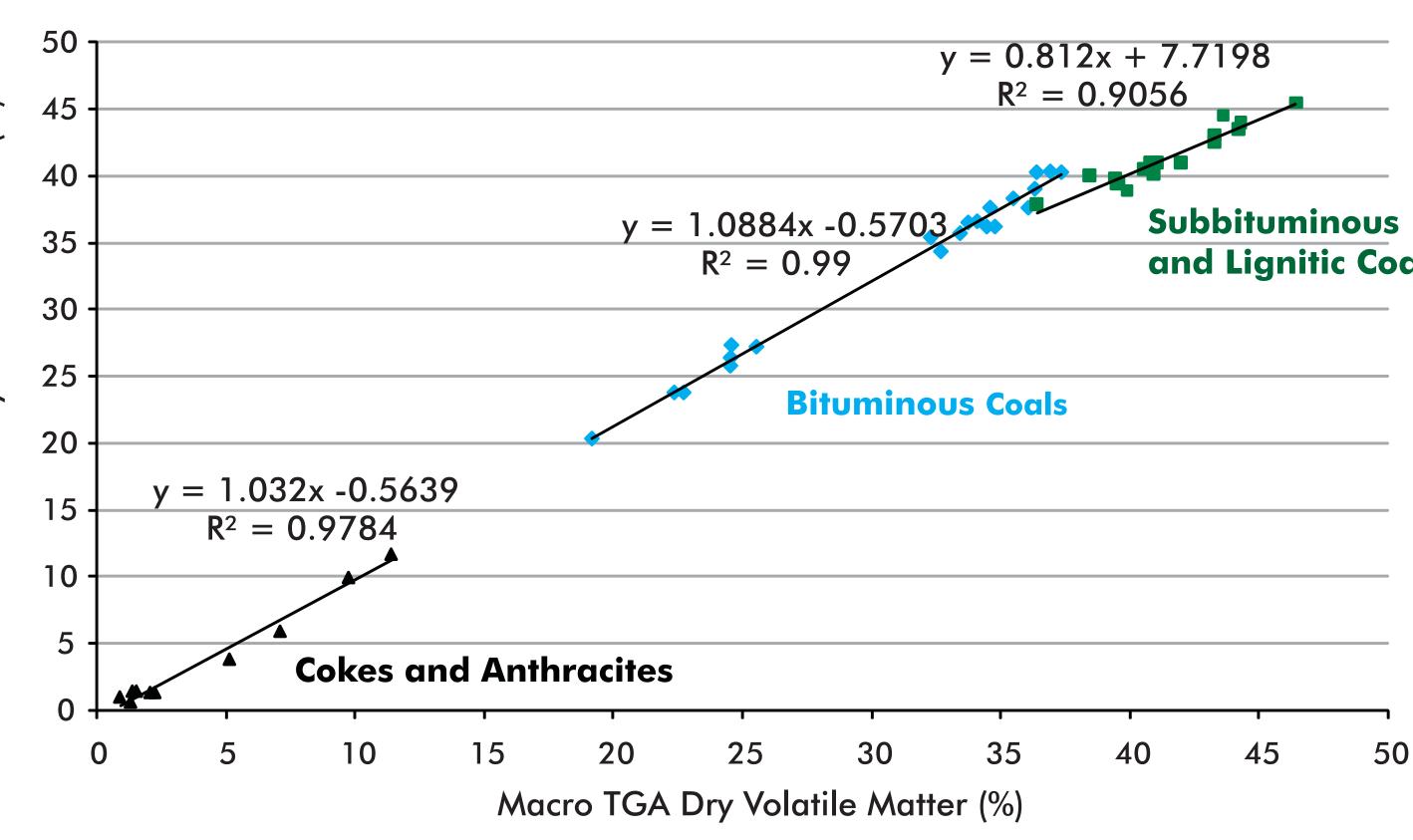


Figure 7. DAF Sulfur Values in Pyrolyzed Residues after VM Release

A considerable amount of data collected in three separate studies over a period of 23 years is being offered as a general procedure to reconcile the differences between the D 3175 and macro TGA volatile matter values. In addition to the data collected in this study, data collected in an ASTM interlaboratory study conducted in the mid 1980's<sup>1</sup>, and an ASTM interlaboratory study conducted in 2008<sup>2</sup> were used to construct a plot of D 3175 and macro TGA dry volatile matter values. Linear regression of the data show equations with R<sup>2</sup> values of 0.99 for the bituminous coals. The cokes give the next best R2 of 0.978, while the R<sup>2</sup> value of 0.906 for subbituminous coals shows a less favorable but good fit for the wide range of data used. The regression equations are very useful for predicting the relationship between the two methods for the different groups of coals and cokes.

## RECONCILING D 3175 AND MACRO TGA VOLATILE MATTER DIFFERENCES

Using the equation for bituminous coals in Figure 8, a bituminous coal with a macro TGA 35% dry volatile matter, the corresponding D 3175 dry volatile matter is 37.52%. As for the 2.52% difference, 0.94% can be attributed to the moisture in coal. The remaining 1.58% is attributed to the plastic properties of bituminous coals. The rapid heating (420°C/min) of the coals in the D 3175 procedure and lower heating rate (44°C/min) take bituminous coals through the plastic stage where a variety of reactions alter the nature of the solid carbon matrix material. This alteration leads to a greater release of material as volatile matter.



**Figure 8.** Plot of Dry Volatile Matter Values Determined by Two ASTM Methods with Regression Lines and Equations

## OBSERVATIONS AND CONCLUSIONS

- The volatile matter yield in most coals and cokes is a function of the heating rate, with bituminous coals most affected by heating rate differences.
- Coal moisture is a very important factor in the determination of volatile matter. All pre-dried coals examined in this study exhibited lower volatile matter yields than undried analysis samples of coal. This effect is more pronounced for high moisture coals (subbituminous and lignitic coals).
- ASTM Method D 3175 is more affected by the moisture in coals, as compared to the macro TGA method (Method D 7582). An alternate D 3175 procedure with rapid pre-drying is used for subbituminous and lignitic coals because of this effect. This study showed pre-dried bituminous coals had 0.94% lower volatile matter yields.
- Controlled pyrolysis experiments in nitrogen using the macro TGA, along with elemental analysis, offers procedures for determining the reduction of various elements and components from coal during heating.
- Predictive equations were developed from the three separate studies of various coals and coke samples, as shown in Figure 8. The best agreement is for bituminous coals, followed by anthracites and cokes, and then subbituminous and lignitic coals. In 2006 a Task Group in the ASTM D0.21 Subcommittee conducted a study involving a comparison of macro TGA volatile matter values with those from D 3175. A plot of the bituminous coal data with a linear regression forced through zero yielded a slope of 1.0692. The data was collected on NIST SRMs and 3 international coals. If the bituminous coal data used for Figure 8 is forced through zero the slope is 1.0707. The agreement between this study and the D05.21 Subcommittee study is excellent.
- The major source of volatile matter differences in bituminous coals, as determined by the ASTM D 3175 and macro TGA methods, is attributed to the plastic properties of the coals.
- Data from the different studies shows good agreement, especially considering that it was collected over a 23-year period in different studies with several different versions of the same type of instrumentation. This agreement shows the historical consistency in the two methods.

### REFERENCES

- 1. RR:D05-1012, Research Report for ASTM Standard Test Method D 5142, ASTM International, West Conshohocken, PA.
- 2. RR:D05-1038, Research Report for ASTM Standard Test Method D 7582, ASTM International, West Conshohocken, PA.

