

Utilizing Modified ASTM Coal Standard Methods to Characterize Woody Feedstocks

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Important Role of Standardized Methods

- Technology development, environmental compliance and commerce depend on accurate and consistent measurements
- Consistency of results measured for a parameter
 - Intralaboratory
 - Interlaboratory



For over 50 years, CONSOL Energy's analytical laboratory has been characterizing coal and coal-by products to support the activities of its mining operations and its research projects. CONSOL has long recognized the importance of measurement standardization in technology development, environmental compliance and commerce. Standard methods of analysis are essential to measurement consistency within our own laboratory as well as ensuring measurement consistency between coal buyer and seller laboratories.

ASTM International (formerly American Society for Testing and Materials (ASTM))

- ASTM D5 subcommittee for coal and coke
- Committee and Board leadership
- Leading method development



CONSOL has always encouraged its personnel to be actively involved in standards development and proliferation through the ASTM International (formerly American Society for Testing and Material (ASTM)) D5 subcommittee for coal and coke. Over the years, several generations of CONSOL scientists have served ASTM as committee chairpersons and as members of the board of directors. The CONSOL Energy laboratory has participated in the development and validation of many coal and coke standards and has contributed several of its own methods for adoption by ASTM. So it is safe to say that CONSOL has very deep roots in the standards communities.

Standard Organizations

- ASTM

- Recognized by US coal and power producers

- Committee D5, Coal and Coke

- Committee E , Refuse Derived Fuel D34.03.02 ,
Municipal Recovery and Reuse

- CEN

- Recognized by Biomass producers and consumers



While ASTM D5 methods are the benchmark for the US power industry and ASTM E methods address characterization of refuse derived fuels, these methods have not been validated for biomass. Specific biomass standards have been compiled by CEN but these standards are not widely used in the US and they have not been validated for the analysis of coal. As co-firing coal and biomass become more common, characterization of the two fuels is creating some issues for laboratories.

Utilizing Biomass to Produce Electricity

- As of 2005 – 23 states have renewable energy programs
- Total US electric production
 - Nonhydroelectric renewables 2.2%
- Energy Policy Act of 2005
 - >5% renewable electric energy in 2010-2012
 - >7.5% renewable electric energy in 2013 and beyond
- Firing or co-firing biomass qualifies in many states



As of 2005, 23 states have mandated renewable energy portfolio standards with the goal of increasing the production of “renewable” electricity from 2.2% annually to more than 7.5% annually by 2013. Co-firing biomass with coal is an attractive option for power generators to comply with the renewable energy mandates because most states recognize co-firing as a means of compliance and because co-firing can produce significant amounts of power from renewable sources with low capital investment. In many boilers, as much as 15% of the fuel can be replaced with biomass with little to no loss in boiler efficiency.

Analytical Issues Caused by Co-firing Biomass with Coal

- Collection and preparation
- Choice of methods
- Sensitivity of ASTM methods for biomass parameters that are present at concentrations much lower than are present in coal
- Precision and accuracy of methods not validated for biomass materials



However, co-firing biomass and coal creates some issues for laboratories that are accustomed to analyzing coal. How can the biomass be prepared and subsampled to ensure a homogeneous sample for analysis? When coal and biomass are co-fired, should ASTM methods be utilized for the coal analysis and CEN methods be utilized for the biomass analysis or can both materials be analyzed utilizing ASTM standards so that all results are on the same basis? Will ASTM D5 standards provide adequate sensitivity for low concentration analytes present in biomass? Will the accuracy and precision be equivalent to the accuracy that is obtained for coal samples?

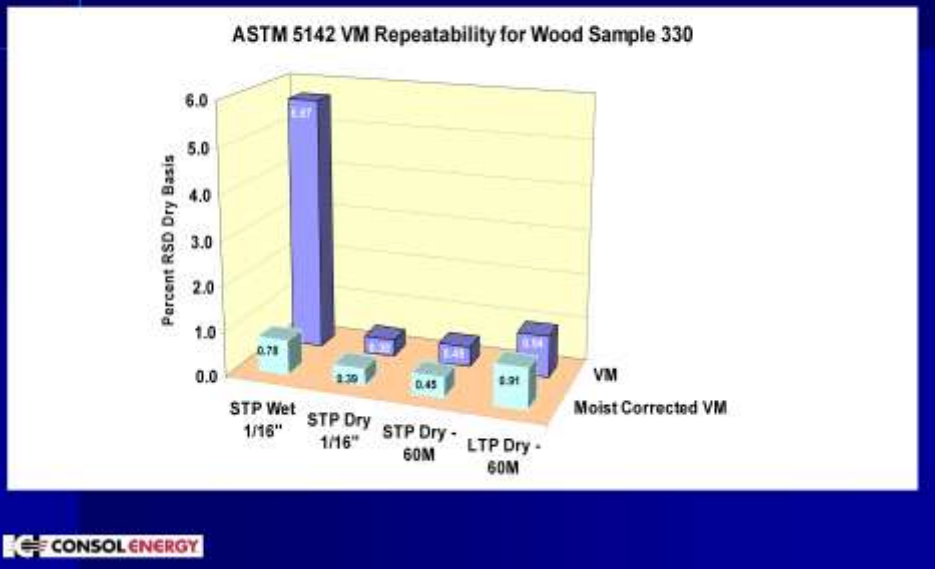
The purpose of this paper is to evaluate the applicability of ASTM D5 standard methods to the measurement of woody feedstock parameters. It will address preparation of the woody feedstock as well as the sensitivity, precision and accuracy of biomass characterization by CEN and ASTM D5 standard methods.

Sample Preparation

- Particle Size
 - 1/16" material (80-90% of samples was 60 mesh to 1/16")
 - -60 mesh material
- Repeatability of determinations for volatile matter and ash
- Moisture
 - Samples analyzed "As Received"
 - Samples analyzed "Dry"

Raw processing of wood often results in material with a top size as large as ½-1". The homogeneity (including the moisture content) is highly variable. Consequently, the particle size of the raw sample must be reduced prior to analysis to ensure that sample aliquots used for characterization are homogenous. Two samples of wood were analyzed to determine the effect of particle size on measurement results. Measurements were first made on two samples where the top size of 80-90% of the sample was in the 60 mesh to 1/16" size range. The samples will be referred to hereafter as the "1/16 inch" samples. A portion of the 1/16" sample was then dried, prepared to -60 mesh and was reanalyzed.

Volatile Matter - Repeatability




Homogeneity was assessed by analyzing 7 consecutive aliquots of the sample on the same day. Determination of volatile matter (VM) and ash content of the “wet” “as received” material resulted in volatile matter results with a relative standard deviation of 5.7% and 0.96% for wood samples 330 and 392 respectively. Correcting the results to a dry basis with the moisture concentration that was concurrently determined with the VM and ash improved the RSDs to 0.78 and 0.67, indicating the variability in the moisture concentration of aliquots as large as one gram is a significant source of VM imprecision for the “as received” material. This contribution was further verified by noting that the RSDs for the dried, “as received” material are identical for moisture corrected and uncorrected results. These results show the importance of determining the moisture concurrently or at least on the same day as the other parameters are determined when the moisture concentration of the sample is high.

Drying the sample and reducing the top size of the dry sample to -60 mesh resulted in little to no improvement in precision for one gram aliquots of the sample but as will be seen later in the presentation, reducing the size to -60 mesh did improve the precision when smaller sample aliquots were required for characterization. Consequently, samples were dried and prepared to -60 mesh to ensure homogeneity for the remainder of the testing presented in this presentation.

Comparison of Method Conditions for Moisture Methods


<u>Moisture Method</u>	<u>Sample Preparation</u>	<u>Temperature</u>	<u>Atmosphere</u>	<u>Termination of Analysis</u>
ASTM E871 (Refuse)	Reduce a sample of at least 22lbs by riffing. Maximum particle size 1in.3	103 ± 1°C	Not Specified	Δmass < 0.2% of original weight
CEN 14774 (Biomass)	Reduce a sample of at least 300g by riffing. Maximum particle size not specified.	105 ± 2°C	Air	Δmass < 0.2% of original weight
ASTM D5142 (Coal)	- 60 mesh sample	104 to 110°C	Air or Nitrogen	Until 2 successive weighings agree "within the plateau deviation specified for the instrument"



ASTM and CEN methods for moisture were reviewed to determine if there were differences in the method conditions that would cause significant differences in determination of the moisture, volatile matter and ash concentrations. The ASTM and CEN methods for moisture and VM specify very similar conditions.

Comparison of Method Conditions for Volatile Matter Methods

<u>VM Method</u>	<u>Sample Preparation</u>	<u>Temperature</u>	<u>Atmosphere</u>	<u>Termination of Analysis</u>
ASTM E872 (Refuse)	- 1 mm sample	950 ± 20°C	Not Specified	Maintain temperature for 7 minutes
CEN 15148 (Biomass)	- 1 mm sample	900 ± 10°C	"Out of contact with ambient air"	Maintain temperature for 7 minutes
ASTM D5142 (Coal)	- 60 mesh sample	950 ± 20°C	Nitrogen	Maintain temperature for 6 minutes



These methods would therefore be expected to provide equivalent results for moisture and VM.

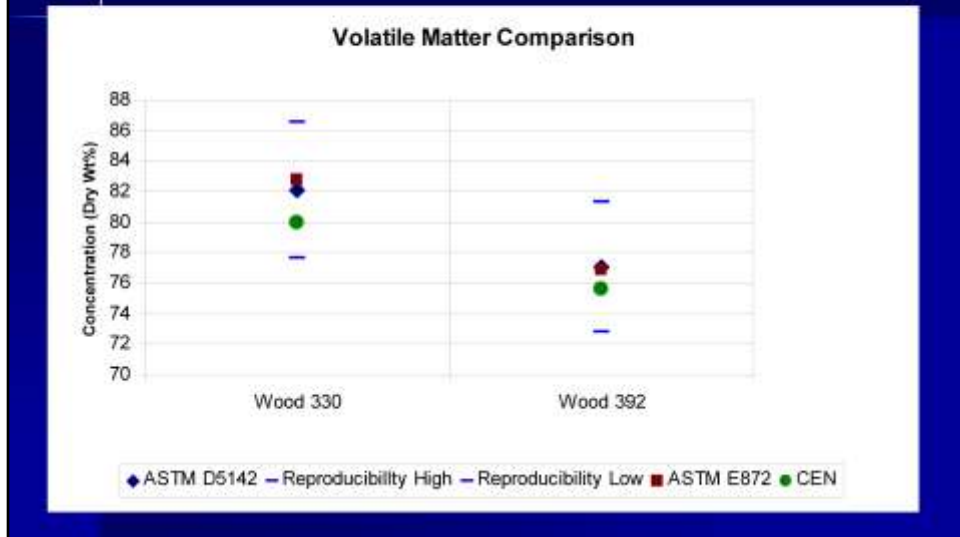
Comparison of Method Conditions for Ash Methods

<u>Ash Method</u>	<u>Sample Preparation</u>	<u>Temperature</u>	<u>Atmosphere</u>	<u>Termination of Analysis</u>
ASTM D1102 (Wood)	- 40 mesh sample	600°C	Not Specified	$\Delta\text{mass} < 0.2\text{mg}$
CEN 15148 (Biomass)	- 1 mm sample	550°C	Not Specified	$\Delta\text{mass} < 0.2\text{mg}$
ASTM D5142 (Coal)	- 60 mesh sample	700°C to 750°C	Oxygen	Until sample has reached a constant weight



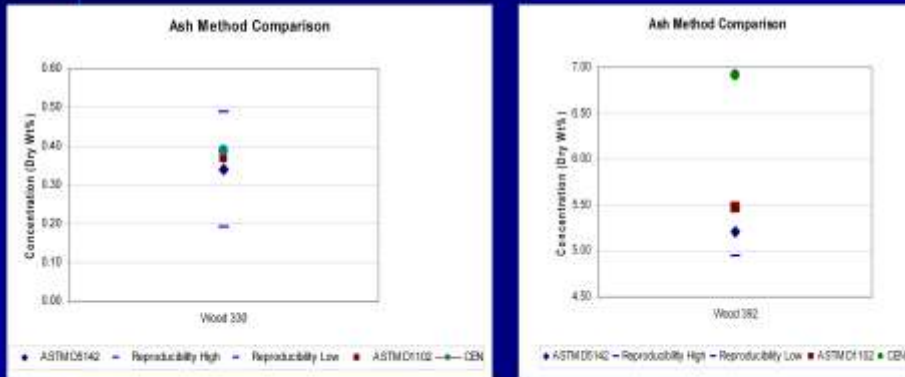
The ASTM and CEN methods for determining ash specify temperatures that differ by 200 °C. The effect of this temperature differential was evaluated

Volatile Matter – Method Comparison



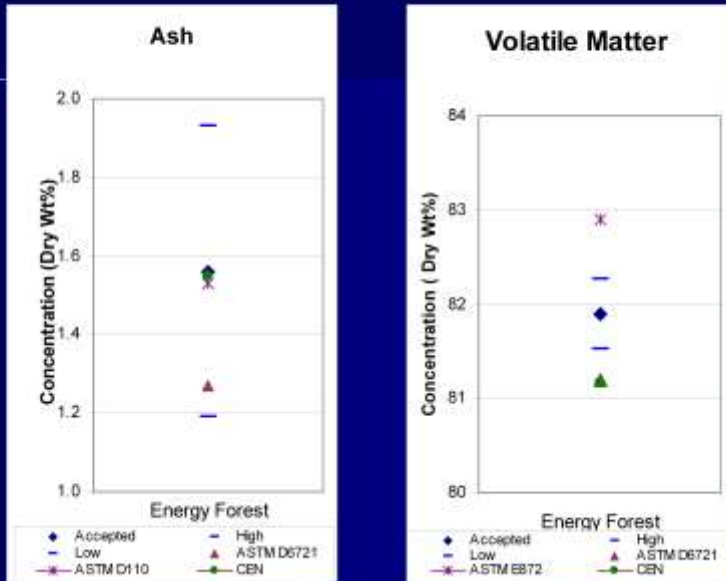
The equivalency of the three methods used to determine moisture, VM and ash was compared by analyzing reference materials and two wood samples. All three methods yielded VM results that were within the repeatability limits specified by ASTM 5142.

Ash – Method Comparison



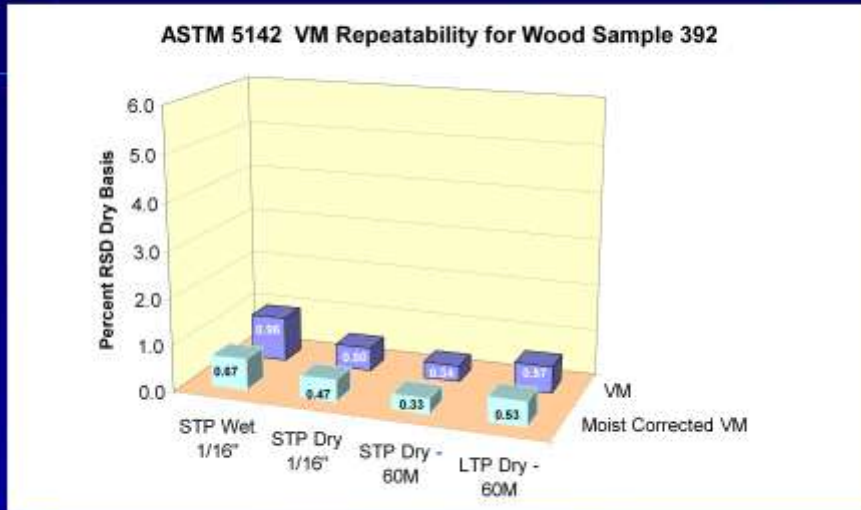
Ash results produced by ASTM D1102 are within repeatability limits for ASTM 5142. The ash result produced by the CEN method was within repeatability limits for sample 330.

Volatile Matter and Ash - Accuracy



The accuracy achieved utilizing ASTM 5142 was evaluated by analyzing the Energy Forest standard reference material NJV 94-3 obtained from the Swedish University of Agricultural Sciences. The ASTM 5142 ash results fell within the uncertainty limits provided with the standard. While the ASTM 5142 volatile matter result for the Energy Forest standard fell outside the uncertainty limits, the result was with 1% relative of the accepted value.

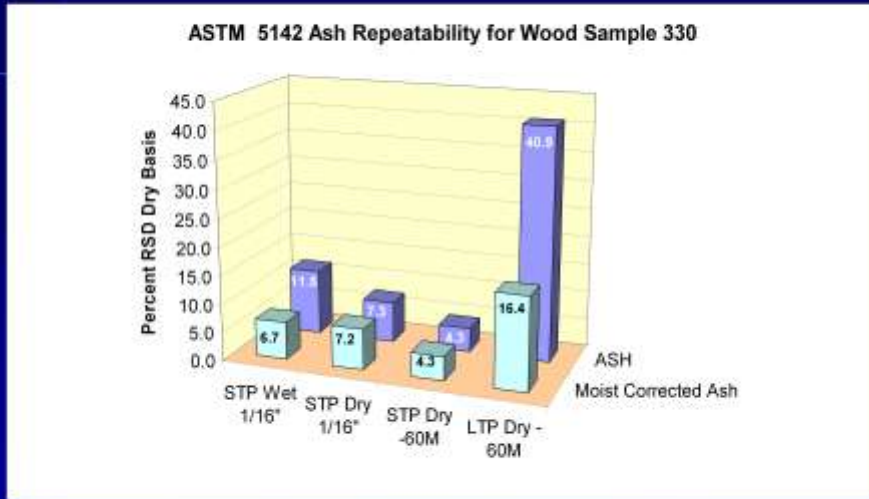
Volatile Matter - Repeatability



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The long term repeatability was evaluated by analyzing the dry, -60 mesh sample once per day on 7 different days. The RSD of the VM long term results were approximately two times higher than the RSDs measured during the short term tests but are still within the ASTM repeatability limits for VM

Ash - Repeatability



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and ash (Slide 15). Long term repeatability of the ash results were 3-4 times greater than the short term repeatability.

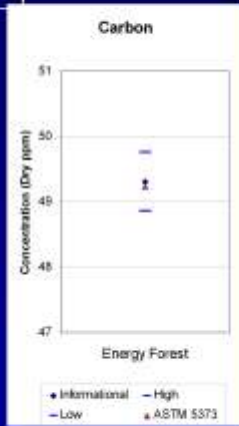
Comparison of Method Conditions for CHN Methods

<u>CHN Method</u>	<u>Sample Preparation</u>	<u>General Description</u>	<u>Combustion Temperature</u>	<u>Afterburner Temperature</u>
ASTM E777 (C and H Only) (Refuse)	-0.5 mm sample	Upon combustion of sample, C is converted to CO ₂ , H is converted to H ₂ O. Gases are captured in CO ₂ and H ₂ O specific "absorption trains". The weight gain of each respective train is calculated as weight percent C and H in the analysis sample.		850°C
CEN 15104 (Biomass)	- 1 mm sample	Upon combustion of sample, C is converted to CO ₂ , H is converted to H ₂ O, and N is converted to NO _x . CO ₂ and H ₂ O are detected by IR detectors, and NO _x is detected by a TC cell. The concentration of C, H, and N in the analysis sample are then calculated.		"According to Manufacturer's Specifications"
ASTM D5373 (Coal)	-60 mesh sample			850°C

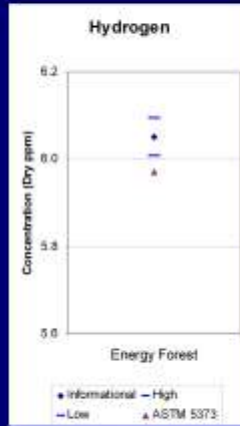


A comparison of the ASTM and CEN methods for determination of carbon, hydrogen and nitrogen indicates that the principle and conditions are very similar. All three methods would be expected to provide equivalent results.

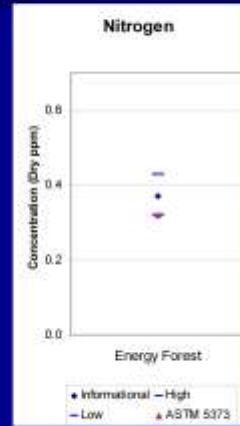
CHN – Accuracy of ASTM D5373



Average LQSI Difference
Absolute = 0.78 Wt%
Relative = 1.55%



Average LQSI Difference
Absolute = 0.26 Wt%
Relative = 4.39%



Average LQSI Difference
Absolute = 0.01 Wt%
Relative = 8.6%

The accuracy of the ASTM D5373, “Instrumental Determination of Carbon, Hydrogen and Nitrogen in Laboratory Samples of Coal and Coke” for wood samples was assessed by analyzing the Energy Forest reference material. The D5373 carbon and nitrogen results were within the accuracy limits provided with the reference material. The D5373 hydrogen result was slight outside of the acceptance limits for informational result provided with the reference material, but was within 5% of the accepted result. Analysis of three separate LQSI interlaboratory biomass samples yielded similar results, further confirming the applicability of ASTM 5273 to wood samples.

CHN - Repeatability



The precision was assessed by analyzing a wood sample repeatedly. The carbon and hydrogen repeatability improved significantly when the 1/6" size sample was dried prior to analysis showing significant moisture variability in the 50 mg sub samples used for the ultimate determinations. An additional 2-3 fold improvement in repeatability was noted when the sample size was reduced to -60M. This result is contrary to what was noted for proximate analysis and emphasizes the importance of particle size in minimizing sample variability when sample aliquots smaller than 1 g are analyzed. Increasing the sample size to 150 mg resulted in no further improvement to the repeatability indicating that the homogeneity of the -60M sample is adequate for sub sampling aliquots as small as 50 mg.

The long term precision was assessed by analyzing a wood sample on seven different days. As expected, the long term repeatability is 2-4 times larger than the short term repeatability but is still well within the ASTM 5373 repeatability limits for duplicate samples.

The instrumentation used in this study lacked the sensitivity to provide nitrogen results that had the same level of relative precision obtained for carbon and hydrogen. Relative precision is also an issue for coal samples where the ASTM repeatability at nitrogen concentrations in the range 0.69-1.57 weight % is permitted to be as high as 16%. While the ASTM 5373 relative precision for nitrogen determinations is high, the absolute precision is adequate for boiler applications

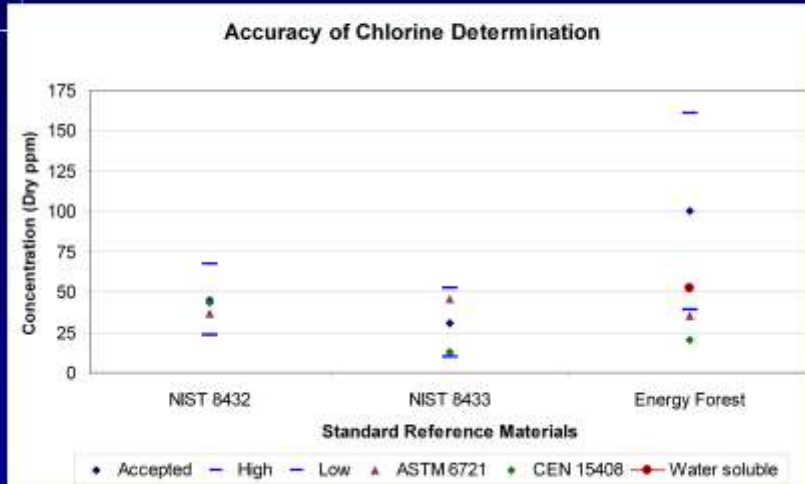
Comparison of Method Conditions for Chlorine Methods

<u>Chlorine Method</u>	<u>Sample Preparation</u>	<u>General Description</u>
ASTM E776 (Refuse)	Specified use of a "thoroughly mixed, air dried RDF sample."	Sample is combusted under O ₂ , Cl ⁻ is absorbed in alkaline solution and determined by potentiometric titration. (CONSOL uses ion chromatography rather than a potentiometric titration)
CEN 15408 (Biomass)	-1 mm sample	Same as above. Method is applicable only for concentrations > 25 ppm.
ASTM D6721 (Coal)	-60 mesh sample	The sample is combusted with a tungsten accelerator in a humidified stream of O ₂ . Chlorine is oxidized, converted to HCl, and the Cl ⁻ is captured in the electrolyte of the titration cell. The Cl ⁻ is determined quantitatively through microcoulometry.



ASTM E776 and CEN 15408 utilize high pressure oxygen bomb combustion of the sample followed by titration to determine chlorine. This method is labor intensive, slow, difficult to repeat, and is only moderately sensitive. Consequently, CONSOL uses ASTM D6721 for the determination of chlorine. In this method, the chlorine that is volatilized at high temperature is captured in a scrubber solution where it is titrated coulometrically.

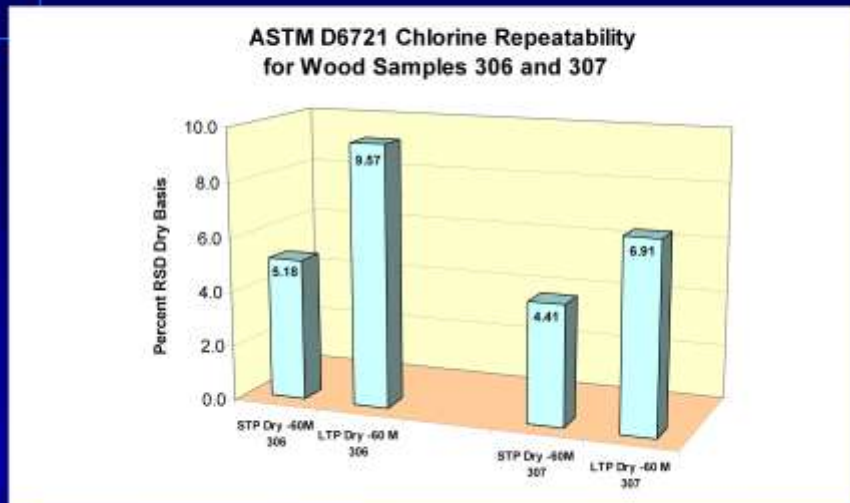
Chlorine - Accuracy



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The accuracy of chlorine methods was assessed by analyzing three standard reference materials. Chlorine results obtained by ASTM 6721 and CEN 15408 differed significantly. However, chlorine results obtained for the two NIST reference materials were within the very wide uncertainty limits provided with the accepted reference values. Both methods yielded a chlorine concentration that was much lower than the accepted value for the Energy Forest reference material. These results and determination of the water soluble chlorine in this reference material suggest that the informational value provided with the Energy Forest SRM may be suspect.

Chlorine - Repeatability



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The short term chlorine repeatability of ASTM D6721 was assessed by analyzing two wood samples seven consecutive times each on one day. The RSDs obtained were 5.1% and 4.4% respectively which are well within the ASTM repeatability limits for duplicate determinations.

The short term chlorine repeatability for CEN 15408 was 75.6%. Much of this imprecision was caused by high and variable concentrations of chlorine in the blank. Additional work would be required to use CEN 15408 as a viable method for determining chlorine in biomass.

The long term chlorine repeatability of ASTM D6721 was assessed by analyzing the two wood samples on seven different days. The RSDs obtained for the long term repeatability, 9.6% and 6.9% respectively, are a factor of two higher than the short term repeatability but are still within the ASTM D6721 repeatability criteria.

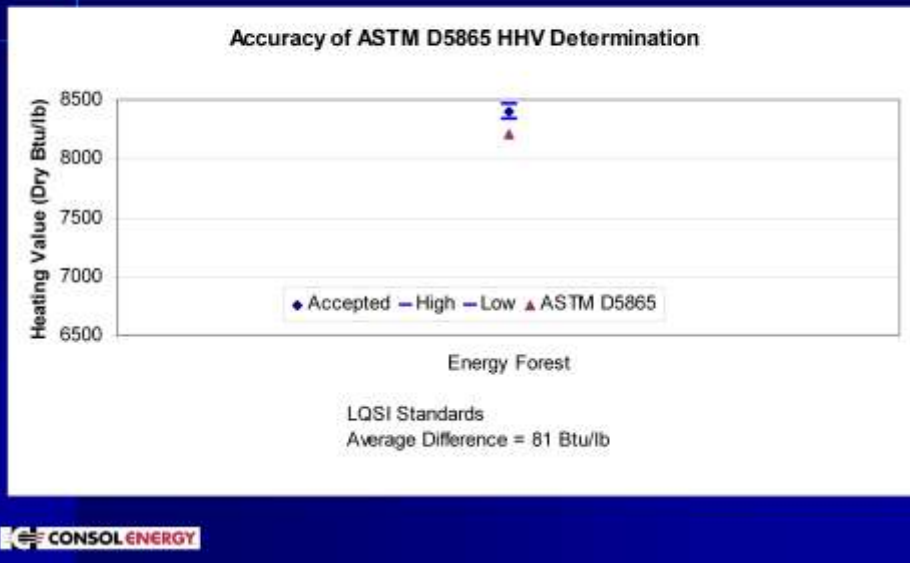
Comparison of Methods for Heating Value

<u>Heating Value Method</u>	<u>General Description</u>	<u>Repeatability</u>
ASTM E711 (Refuse)	Sample is burned in high pressure O ₂ in a bomb calorimeter under specified conditions. The heating value is calculated from the corrected temperature rise and the effective heat capacity of the calorimeter with allowances made for contributions from ignition energy, combustion of fuses, and thermal effects of side reactions such as the formation of Nitric Acid.	When HHV = 7900 BTU/lb, duplicates should agree within 32.3 BTU/lb
CEN 15400 (Biomass)		Duplicates should agree within 86 BTU/lb
ASTM D5865 (Coal)		Duplicates should agree within 50 BTU/lb



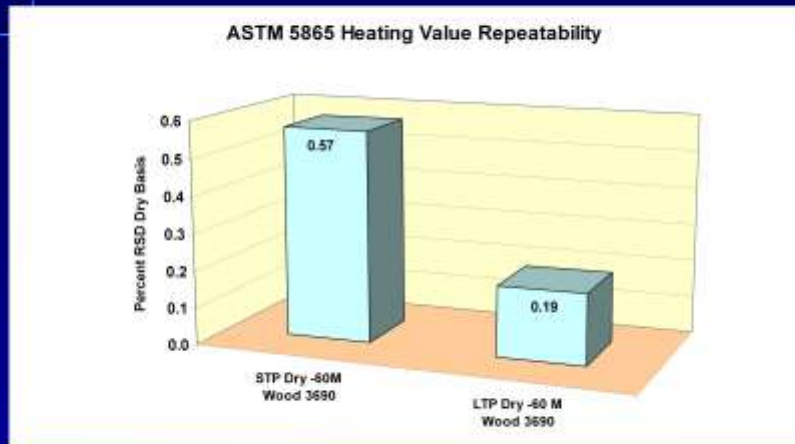
Both ASTM methods and the CEN method all employ an oxygen bomb calorimeter for the determination of heating value. Differences in the methods are minor so one would expect results produced by the methods to be equivalent

Heating Value - Accuracy



The accuracy of the ASTM D5865 was assessed by determining the heating value of the Energy Forest reference material. The ASTM D5865 result fell outside the uncertainty limits provided with the reference material but was within 2.3% relative of the accepted value. The average difference for the ASTM D5865 results for three LQSI biomass interlaboratory standards was 81 Btu/lb.

Heating Value - Repeatability



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The short term repeatability of ASTM D5865 was assessed by determining the heating value of a wood sample seven times on the same day. The RSD was 0.57% or 47 Btu, which is well within the ASTM D5373 repeatability limits.

The long term repeatability of ASTM D5865 was assessed by determining the heating value of a typical wood sample on four different days. The RSD of 0.19% was well within ASTM repeatability limits.

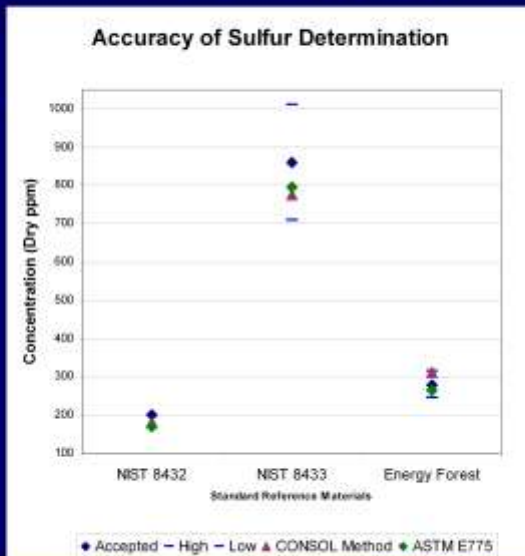
Comparison of Method Conditions for Sulfur

<u>Sulfur Method</u>	<u>Sample Preparation</u>	<u>General Description</u>
ASTM E775 (Refuse) and CEN 15408		Sample is combusted under O ₂ . SO ₄ is absorbed in a scrubbing solution and is determined by ion chromatography.
CONSOL ICPAES (Biomass)	-60 mesh sample	The sample is digested and is analyzed by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICPAES).
ASTM D4239 (Coal)		Sulfur is converted to SO ₂ in an oxygen rich environment. The SO ₂ is measured by infrared spectroscopy.



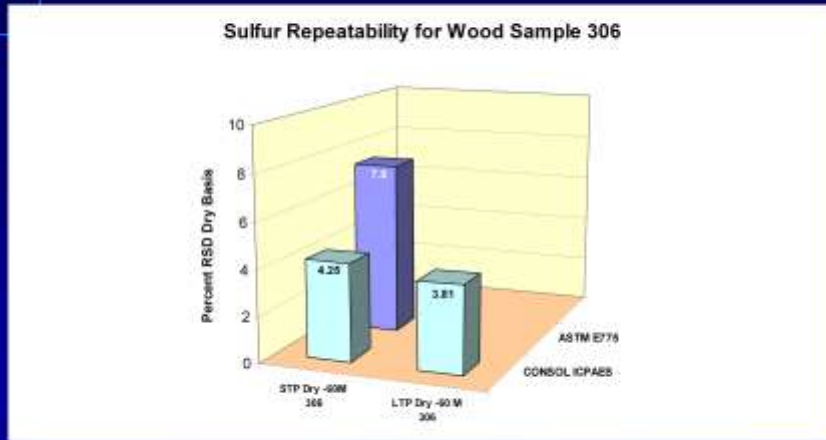
The most common method for the determination of sulfur in coal and coke is ASTM method D4239. This method determines sulfur by oxidation to SO₂ and subsequent detection by infrared spectroscopy. While the method is rapid and inexpensive, it provides a detection limit in the 300 ppm range which is not adequate for the determination of the low sulfur concentrations normally present in wood. ASTM E775 and CEN 15408 for the determination of sulfur in refuse derived fuels utilize the oxidation of the sulfur to sulfate via combustion in an oxygen bomb and subsequent determination of the sulfate in the bomb washings by precipitation or other means. This method is often subject to imprecision caused by incomplete combustion of the sample, irreproducible washing of the bomb and significant blank sulfur concentrations. Consequently, CONSOL developed a method that solubilizes the sulfur with caustic and acid, then determines the sulfur by inductively coupled plasma atomic emission spectroscopy.

Sulfur - Accuracy



Accuracy for the sulfur methods was accessed by analyzing three standard reference materials. The sulfur results obtained by the CONSOL method and ASTM E775 are within the uncertainty of the accepted values provided with the Energy Forest and NIST 8433 reference materials. NIST 8332 did not provide an uncertainty limit for sulfur, however the sulfur results produced by both the CONSOL and ASTM E775 methods were within 15% of the accepted values for all reference materials.

Sulfur - Repeatability



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The precision of the two sulfur methods was assessed by analyzing a wood sample seven times. The RSD for seven consecutive determinations of sulfur in the wood sample were 4.2% and 7.5% respectively for the CONSOL and the ASTM E775 methods. These methods yielded an absolute repeatability of less than 10 ppm sulfur compared to the very wide 300 ppm limit permitted by ASTM E775 for refuse derived fuels.

The long term repeatability was assessed by analyzing a wood sample on 3-4 different days. The RSD was 3.8% for the CONSOL ICPAES method. The unexpectedly lower RSD for long term repeatability may be an artifact of the small number of replicate determinations.

Conclusions

- ASTM coal and CEN methods for moisture, volatile matter, carbon, hydrogen, nitrogen and heating value are very similar and produce equivalent results.
- While ASTM coal and CEN methods differ for ash and chlorine, they produce equivalent results.
- Additional standards development is required by the standards organizations to provide accuracy and precision that is equivalent to the CONSOL method when sulfur concentrations are low.
- Comparison of ASTM and CEN methods for major and trace elements is in progress.



The applicability of ASTM coal and coke methods to woody feedstocks was evaluated. In many instances, the differences between the ASTM coal and coke, the ASTM refuse derived fuel and the CEN biomass standard methods are insignificant. In these instances, results produced by all methods are generally within the precision of the analytical measurements. In other cases, there are fundamental differences in the methods. Despite these differences, application of ASTM coal and coke methods to wood samples provides results for VM, ash, carbon, hydrogen, and sulfur results that are equivalent within the precision of the methods. Only the chlorine results produced by different methods are significantly different. For chlorine, the ASTM coal and coke method appears to provide results that are more accurate and precise than the CEN method.

The work in this paper provides evidence that ASTM coal and coke methods can be used to analyze both biomass and coal samples, particularly when co-firing necessitates that the samples be analyzed and reported on an equivalent basis

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