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Determination of Ash in Biomass

Laboratory Analytical Procedure (LAP)

Issue Date: 7/17/2005

A. Sluiter, B. Hames, R. Ruiz, C. Scarlata,
J. Sluiter, and D. Templeton

Technical Report
NREL/TP-510-42622
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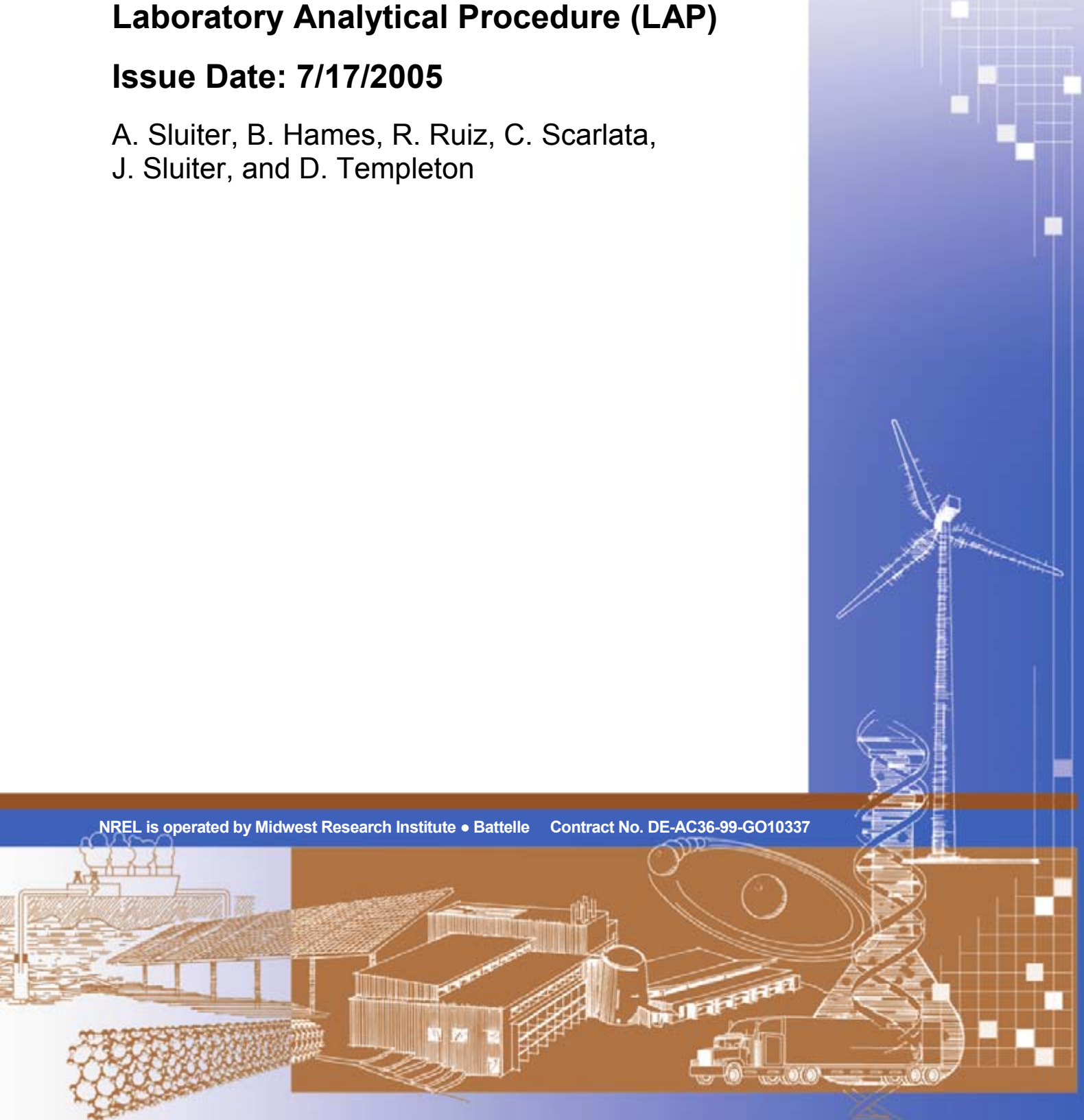

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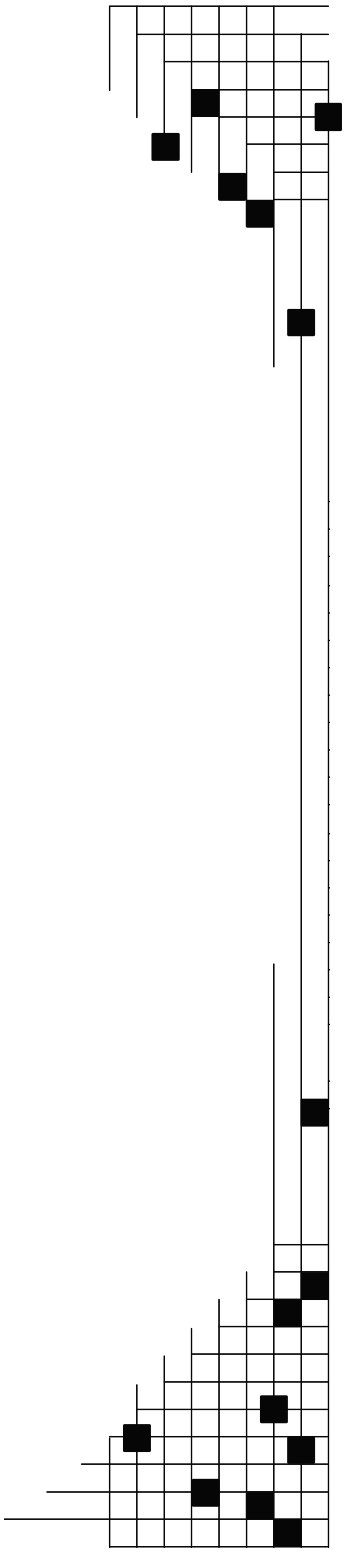

National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, Colorado 80401-3393
303-275-3000 • www.nrel.gov

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Procedure Title: Determination of Ash in Biomass

Laboratory Analytical Procedure

1. Introduction

1.1 The amount of inorganic material in biomass, either structural or extractable, should be measured as part of the total composition. Structural ash is inorganic material that is bound in the physical structure of the biomass, while extractable ash is inorganic material that can be removed by washing or extracting the material. Extractable ash can be the result of soil remaining in the biomass. Refer to LAP "Total Mass Closure" for information on where to utilize this procedure.

1.2 This procedure is substantially similar to ASTM Standard Method Number E1755-01 "Standard Method for the Determination of Ash in Biomass"

1.3 This test method covers the determination of ash, expressed as the percentage of residue remaining after dry oxidation at 550 to 600^{o}C. All results are reported relative to the 105^{o}C oven dry weight of the sample.

2. Scope

2.1 This procedure is applicable to hard and soft woods, herbaceous materials, agricultural residues, wastepaper, and solid fraction process samples.

2.2 All analyses should be performed in accordance with an appropriate laboratory specific Quality Assurance Plan (QAP).

3. Terminology

3.1 *Oven dry weight (ODW)*- the weight of biomass mathematically corrected for the amount of moisture present in the sample at the time of weighing

3.2 *Prepared biomass*- biomass prepared according to LAP "Preparation of Samples for Biomass Compositional Analysis".

3.3 *Ash*- The inorganic residue left after dry oxidation at 575°C.

4. Significance and Use

4.1 The ash content is a measure of the mineral content and other inorganic matter in biomass and is used in conjunction with other procedures to determine to total composition of biomass samples.

4.2 This procedure is used, in conjunction with other procedures to determine the chemical composition of biomass samples, see LAP "Summative Mass Closure for Biomass Samples".

5. Interferences

5.1 None

6. Apparatus

6.1 Muffle furnace, equipped with a thermostat, set to 575 $\pm$ 25 °C or equipped with optional ramping program

6.2 Analytical balance, accurate to 0.1 mg.
6.3 Desiccator containing desiccant
6.4 Ashing crucibles, 50 mL, porcelain, silica, or platinum
6.5 Porcelain markers, high temperature, or equivalent crucible marking method
6.6 Ashing burner, ignition source, tongs, and clay triangle with stand
6.7 Convection drying oven, with temperature control of 105 ± 3°C, optional

7. Reagents and materials

7.1 Reagents
7.1.1 None
7.2 Materials
7.2.1 None

8. ES&H Considerations and Hazards

8.1 Use appropriate safety measures when handling open flame.
8.2 When placing crucibles in a furnace or removing them, use appropriate personal protective equipment, including heat resistant gloves.
8.3 Follow all applicable NREL chemical handling procedures

9. Sampling, Test Specimens and Test Units

9.1 Care must be taken to ensure a representative sample is taken for analysis.
9.2 LAP "Preparation of Samples for Biomass Compositional Analysis" should be performed prior to this analysis
9.3 LAP "Determination of Solids in Biomass" should be performed at the same time that samples for ash analysis are weighed out. Alternately, 105°C oven dry biomass may be used, eliminating the need for total solids corrections.

10. Procedure

10.1 Using a porcelain marker, mark an appropriate number of crucibles with identifiers, and place them in the muffle furnace at 575 ±25 °C for a minimum of four hours. (Marking crucibles with a porcelain marker will permanently mark them, so a generic identifier is recommended.) Remove the crucibles from the furnace directly into a desiccator. If using a furnace set to 575 ± 25 °C, cool for a specific period of time, one hour is recommended. Record the cool time. Weigh the crucibles to the nearest 0.1 mg and record this weight.
10.2 Place the sample back into the muffle furnace at 575 ± 25°C and dry to constant weight. Constant weight is defined as less than ± 0.3 mg change in the weight upon one hour of re-heating the crucible.
10.3 Weigh 0.5 to 2.0 g, to the nearest 0.1 mg, of a test specimen into the tared crucible. Record the sample weight. If the sample being analyzed is a 105°C dried test specimen, the sample should be stored in a desiccator until use. If air dry samples are used, LAP "Determination of Total Solids in Biomass" should be performed at the same time, to accurately measure the percent solids for correction. Each sample should be analyzed in duplicate, at minimum.

10.4 Ash the samples. *Use step 10.4.1 if using a muffle furnace set to 575 ± 25 °C. Use step 10.4.2 if using a muffle furnace with a ramping program.*

10.4.1 Ash the samples using a muffle furnace set to 575 ± 25 °C.

10.4.1.1 Using an ashing burner and clay triangle with stand, place the crucible over the flame until smoke appears. Immediately ignite the smoke and allow the sample to burn until no more smoke or flame appears. Allow the crucible to cool before placing it in the muffle furnace. Alternately, a furnace with a temperature ramping function may be used to avoid pre-ignition.

10.4.1.2 Place the crucibles in the muffle furnace at 575 ± 25 °C for 24 ± 6 hours. When handling the crucible, protect the sample from drafts to avoid mechanical loss of sample.

10.4.1.3 Carefully remove the crucible from the furnace directly into a desiccator and cool for a specific amount of time, equal to the initial cool time of the crucibles. Weigh the crucibles and ash to the nearest 0.1 mg and record the weight.

10.4.1.4 Place the sample back into the muffle furnace at 575 ± 25 °C and ash to constant weight. Constant weight is defined as less than ± 0.3 mg change in the weight upon one hour of re-heating the crucible. When allowing samples to cool in a desiccator, it is necessary to maintain the initial cool time.

10.4.2 Ash the samples using a muffle furnace equipped with a ramping program.

Furnace Temperature Ramp Program: Ramp from room temperature to 105 °C
Hold at 105°C for 12 minutes
Ramp to 250 °C at 10°C / minute
Hold at 250 °C for 30 minutes
Ramp to 575 °C at 20 °C / minute
Hold at 575 °C for 180 minutes
Allow temperature to drop to 105 °C
Hold at 105 °C until samples are removed

10.4.2.1 Place the crucibles in the muffle furnace and begin the ramping program. When handling the crucible, protect the sample from drafts to avoid mechanical loss of sample.

10.4.2.2 Carefully remove the crucible from the furnace directly into a desiccator and cool. Weigh the crucibles and ash to the nearest 0.1 mg and record the weight.

10.4.2.3 Place the sample back into the muffle furnace at 575 ± 25°C and ash to constant weight. Constant weight is defined as less than ± 0.3 mg change in the weight upon one hour of re-heating the crucible

11. Calculations

11.1 If an air dry sample was used, calculate the oven dry weight (ODW) of the sample, using the average total solids content as determined by the LAP "Standard Method for the Determination of Total Solids in Biomass".

$$ODW = \frac{Weight_{\ air\ dry\ sample}\ x\,\%\,Total\ solids}{100}$$

11.2 Calculate and record the percentage ash on an ODW basis.

$$\%\ Ash = \frac{Weight_{\ crucible\ plus\ ash} - Weight_{\ crucible}}{ODW_{sample}} x\ 100$$

11.3 To report or calculate the relative percent difference (RPD) between two samples, use the following calculation

$$RPD = \left(\frac{(X_1 - X_2)}{X_{mean}} \right) \times 100$$

Where:

X_1 and X_2 = measured values
X_{mean} = the mean of X_1 and X_2

11.4 To report or calculate the root mean square deviation (RMS deviation) or the standard deviation (st dev) of the samples, use the following calculations.
First find the root mean square (RMS), of the sample using

$$RMS = x_m = mean = \sqrt{\left(\frac{\sum_1^n x}{n} \right)^2}$$

Then find the root mean square deviation, or standard deviation, using

$$RMS deviation = \sigma = stdev = \sqrt{\frac{\sum_1^n (x_i - x_m)^2}{n}}$$

Where:

x_m=the root mean square of all x values in the set
n=number of samples in set
x_i=a measured value from the set

12. Report Format

12.1 Report ash as a percentage of the ODW of the sample. Report the percent solids, if applicable. Standard deviation and relative percent difference may also be reported.

13. Precision and Bias

13.1 *Round robin testing* – For a report documenting an international round robin test of biomass analysis methods, including this procedure, see Milne et al., 1992.

14. Quality Control

Reported Significant Figures or decimal places: Determined by data quality objectives and laboratory specific Quality Assurance Plan.

14.1 Replicates: Run all samples and method verification standards, if applicable, in duplicate, at minimum.
14.2 Blank: An empty aluminum dish or crucible should be run through the analysis. The dish should be weighed empty, ashed, and reweighed. The difference in weight must be less than the equivalent of a 0.5% error.
14.3 Relative percent difference criteria: Each sample must reproduce ash content $\pm$ 0.5 wt %.
14.4 Method verification standard (MVS): A MVS, such as a QA/QC sample, should be run in duplicate with every batch.
14.5 Sample size: 1-4 grams. If there is insufficient sample, the result should be flagged and the lack of precision noted.
14.6 Sample storage: If applicable, oven dried samples should be stored in a desiccator until ready to use.
14.7 Standard storage: Not applicable
14.8 Standard preparation: Not applicable
14.9 Definition of a batch: Any number of samples that are analyzed and recorded together. The maximum size of a batch will be limited by equipment constraints
14.10 Control charts: MVS or a QA/QC material should be control charted to verify reproducibility
14.11 Others: Biomass can rapidly gain or lose moisture when in contact with air. During the weighing steps, minimize the amount of time the sample and crucibles are exposed to the air.

15. Appendices

15.1 None

16. References

16.1 Moore, W., and D. Johnson. 1967. *Procedures for the Chemical Analysis of Wood and Wood Products*. Madison, WI: U.S. Forest Products Laboratory, U.S. Department of Agriculture.
16.2 NREL CAT Task Laboratory Analytical Procedure #005 "Standard Method for Ash in Biomass".
16.3 TAPPI Test Method T211, "Ash in Wood and Pulp." *In Tappi Test Methods.* Atlanta, GA: Technical Association of the Pulp and Paper Industry.
16.4 Milne, T. A.; Chum, H. L.; Agblevor, F. A.; Johnson, D. K. (1992). "Standardized Analytical Methods" Biomass & Bioenergy. Proceedings of International Energy Agency Bioenergy Agreement Seminar", 2-3 April 1992, Edinburgh, U.K. Vol. 2(1-6), 1992; pp. 341-366
16.5 ASTM E1755-01 "Standard Method for the Determination of Ash in Biomass" In *2003 Annual Book of ASTM Standards, Volume 11.05.* Philadelphia, PA: American Society for Testing and Materials, International.