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Laboratory Analytical Procedure (LAP)

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National Renewable Energy Laboratory

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1. Introduction

1.1 The determination of total carbon, hydrogen, and nitrogen in bio-oils is important as these values can be used to track the carbon balance of production processes as well as calculate total oxygen content by difference. Oxygen content of bio-oils is a key metric for production and upgrading strategies as these are typically aimed at reducing oxygen and producing hydrocarbons which can be used to generate renewable fuels and chemicals. Oxygenates in bio-oils contribute to poor hydrocarbon miscibility, high acidity, high viscosity, and poor stability [1].

1.2 Combustion-based ultimate analysis is used to determine the weight percent (wt%) of C, H, and N in bio-oils and upgraded products. Ultimate analysis uses high temperatures and a pure oxygen environment to completely combust organic compounds to carbon dioxide (CO_2), water (H_2O), and nitrogen oxides (NO_x). In this procedure the amount of C and H in the sample are quantified by measuring resultant CO_2 and H_2O with an infrared radiation cell (IR). For N, NO_x is reduced to nitrogen (N_2) which is measured with a thermal conductivity cell (TC), providing total N content.

2. Scope

2.1 This procedure uses combustion analysis to determine the weight percent of C, H, and N in fast pyrolysis oil (FP), catalytic fast pyrolysis oil (CFP), distillate range hydrotreated oil products (HT), and aqueous phases isolated from FP and CFP oils.

2.2 This procedure is similar to ASTM D5291 Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants [2]. The sample preparation procedure, instrument parameters, and quality control have been optimized for the analysis of pyrolysis bio-oils. As with D5291, this procedure is not recommended for highly volatile materials with vapor pressures in the range of gasoline such as non-distilled HT pyrolysis products and naphthas derived from HT FP or CFP. Consult with your instrument manufacturer for guidance on analysis of high volatility samples.

3. Terminology

3.1 *Bio-oil* – The crude liquid product of converting solid biomass into a liquid via fast pyrolysis or other thermochemical conversion process.

3.2 *Pyrolysis* – Chemical decomposition of organic materials by heating in the absence of oxygen.

3.3 *Fast Pyrolysis (FP)* – Pyrolysis conducted with rapid heating and short residence time; typically, less than 10 seconds.

3.4 *Catalytic Fast Pyrolysis (CFP)* – Fast pyrolysis conducted in the presence of a catalyst (can be either in-situ or ex-situ).

3.5 *Hydrotreated Bio-oil (HT)* – The product of a process that uses high heat, high pressure, hydrogen, and catalyst to remove oxygen from bio-oil.

4. Interferences

4.1 Bio-oils may contain volatile components that are susceptible to evaporation, with higher vapor pressure samples (> 3 psi) being more difficult to handle. Note, this procedure is similar to ASTM D5291 in that it is not generally suitable for the analysis of samples with vapor pressures near that of gasoline range fuels [2]. The weight percent values for C, H, and N will be inaccurate if the sample loses mass to evaporation after the initial weight has been recorded and prior to combustion. Thus, calculation of oxygen by difference will be inaccurate and biased high as mass lost to evaporation will be reported as oxygen in the oil. Three techniques may be used to help minimize evaporation.

1. The sample is prepared physically as close as possible to sample introduction and analyzed immediately. This reduces time for evaporation to occur.
2. Aluminum oxide powder (Al_2O_3) or similar combustion aid may be used to minimize evaporation.
3. If applicable, a sealed capsule can be used to prevent evaporation. This is only applicable to instruments that can allow for the use of sealed capsules. Consult with the instrument manufacturer to determine if this strategy is appropriate.

5. Apparatus

5.1 Analytical balance with precision to 0.1 mg

5.2 Elemental Analyzer Instrument and Software (LECO CHN628 Series or equivalent)

6. Reagents and Materials

6.1 Reagents

6.1.1 Aluminum oxide (Al_2O_3)- LECO- (Com-Aid for Liquids, Part No. 501-427 or equivalent)

6.1.2 Ethylenediaminetetraacetic acid (EDTA) Calibration Standard – LECO- (Part No. 502-092 or equivalent)

6.1.3 m-Cresol – 99% purity (Sigma Aldrich Part No. C85727 or equivalent)

6.2 Materials

6.2.1 Tin Foil Cups – (Supplier LECO, Part No. 502-186-200 or equivalent)

6.2.2 Microdispenser Pipette (100 µL) (VWR Cat # 53506-201, or comparable)

6.2.3 Capillary Bores (100 µL, for microdispenser) (VWR Cat # 53508-499, or comparable)

6.2.4 Small Metal Spatula with long narrow head – (Supplier LECO, Part No. 501-614 or equivalent)

6.2.5 Sample Cup Holder, can use anything that will hold Tin Foil Cups – (Supplier LECO, Part No. 604-373 or equivalent)

6.2.6 Tweezers – Standard Lab Supply

7. Environmental Safety and Health Considerations and Hazards

7.1 The instrument furnace is operated at high temperatures (950°C) in pure oxygen. Follow all safety procedures recommended by the instrument manufacturer.

7.2 Follow all applicable chemical handling procedures.

7.3 Follow all applicable waste disposable and handling procedures.

7.4 Consult SDS of all reagents and samples for proper handling and disposal.

8. Sampling, Test Specimens, and Test Units

8.1 Bio-oil should be allowed to reach room temperature and thoroughly homogenized to obtain a representative sample.

8.2 Exposure to oxygen and heat should be minimized to prevent sample degradation prior to analysis.

9. Procedure

9.1 Refer to your instrument operation and instruction manual for definitions and more in-depth explanations.

9.2 If needed, prior to start of analysis replace furnace crucible. Note: use of Al_2O_3 or similar combustion aid will accelerate filling of the crucible with ash. Determine how many runs can be performed before the crucible requires replacement to prevent overfilling. For the LECO 628 instrument used to develop this LAP, approximately 30 runs with Al_2O_3 will fill crucible (10 samples run in triplicate).

9.3 Prepare instrument for operation (bring furnace to temperature, leak check, system check, etc.). Consult operation manual for recommended daily operation checks.

9.4 Create method for bio-oil analysis.

9.4.1 EDTA is used for calibration in this procedure. Other compounds may be used to calibrate instrument response as appropriate. Calibrate instrument prior to this procedure following the instrument manufacturer's recommendations.

9.4.2 The following are the system parameters used for bio-oil analysis [3]. These settings have been found to work well with bio-oils using the LECO system. Consult equipment manuals for appropriate settings with other systems.

Analysis Parameters			
Furnace Temperature		950°C	
Afterburner Temperature		850°C	
Element Parameters			
	Carbon	Hydrogen	Nitrogen
Baseline Delay Time	0 seconds	0 seconds	10 seconds
Min Analysis Time	20 seconds	40 seconds	40 seconds
Comparator Level	100.00	100.00	100.00
Endline Time	1 second	1 second	2 seconds
Conversion Factor	1.00	1.00	1.00
Significant Digits	5	5	5
IR Baseline Time	1 second		
TC Baseline Time	10 seconds		
Burn Profile			
Burn Steps	**Time (seconds)**		**Furnace Flow**
1	40 seconds		High
2	30 seconds		Medium
3	30 seconds		High
Ballast Parameters			
Equilibrate Time		30 seconds	
Not Filled Timeout		300 seconds	
Aliquot Loop			
Fill Pressure Drop		200 mm Hg	
Equilibrate Pressure Time		8 seconds	

9.5 Conditioning: Prepare 3 conditioning samples to prepare the instrument for analysis. Conditioning the instrument prior to determinations has been found to improve performance of the LECO system used to develop this LAP. Consult with instrument manual for suggested conditioning and instrument preparation if applicable.

9.5.1. Prepare three samples of EDTA at approximately 100 mg by weighing into tin foil cup. Twist tin foil cup to seal sample according to manufacturer's recommendations. Alternative sources of carbon and hydrogen such as paper (e.g. Kimwipe) or unused samples from previous days can also be used in place of an EDTA standard as these runs will not be used in any instrument calculations, only to condition the instrument.

9.5.2. If using carousel autosampler, confirm the autosampler is set so the number 1 slot will drop in the first conditioning sample. Next, put a conditioning sample in autosampler slots 1, 2, and 3.

9.5.3. Enter the three conditioning samples in the instrument software. Enter a mass of 1.0 g for each sample. Check to make sure the correct slot and method is assigned for each sample.

9.6 Blank Correction: Log in ten blank runs. The average blank value will be use as the zero value for the instrument.

9.6.1 Enter 1.0 g for sample mass for each blank. Check to make sure the correct autosampler slot and method is assigned for each sample. For the LECO software it is necessary to login blank samples as blanks for the system to correctly apply this to the daily calibration. Consult instrument manual for proper sample login.

9.6.2 After blank analysis is complete, highlight the last 5 runs in the software. The LECO software will automatically calculate average value and standard deviation (SD) for the highlighted cells. For LECO CHN628 the SD for each element should be less than or equal to 0.002% (20ppm) [3]. A value higher than this may indicate the instrument has not yet equilibrated. More blank samples may be needed to achieve adequate precision.

9.6.3 Set the blank value following instructions in instrument software manual.

9.7 Drift Correction: Prepare and login five drift standards using EDTA. Note, drift correction should be performed each day or when the check standard (9.8) is out of tolerance. If calibration has been performed on the day of analysis drift is not necessary. Drift is used as a daily calibration correction after initial instrument calibration per the operations manual.

9.7.1 Place sample cup holder on the balance and place tin foil in cup holder. Tare balance. Weigh ~0.10 to 0.15 g EDTA into the tin foil cup. Remove the tin foil from the balance and twist to seal. Return to balance.

9.7.2 If using LECO software login sample as the appropriate drift standard. Enter sample mass into sample line in instrument software.

9.7.3 Place sample in correct position on autosampler and start analysis.

9.7.4 Repeat steps above for the other four drift standards.

9.7.5 Highlight the last three standards after analysis is complete to calculate the average, standard deviation, and relative standard deviation (or perform the calculation manually). For LECO CHN628, the relative standard deviation (RSD) for carbon and nitrogen should be less than 0.5% and less than 1% for hydrogen. If precision is not met this may indicate a problem with the instrument or weighing technique. The method shall be evaluated for sources of imprecision before moving to the next steps.

Note: A minimum of three standards is needed to perform drift correction. This procedure recommends analysis of 5 replicates as the LECO system often requires additional conditioning after blank analysis. Consult with instrument manufacturer for recommended calibration procedures.

9.7.6 Highlight the last three standards (after confirming adequate precision) and select drift in the instrument software to adjust the calibration for instrument drift.

9.8 Daily Check Sample: m-cresol

9.8.1 Place sample cup holder on balance and place tin foil cup in holder. Tare balance. Weigh 0.15 - 0.20 g of Al_2O_3 into the tin foil cup. Make a small cavity in the center of the Al_2O_3 and tare the balance.

9.8.2 Using microdispenser carefully add 100 µL of sample (~0.1 g) to the cavity in the Al_2O_3.

9.8.3 Enter sample mass into instrument software. If using LECO software the check sample should be logged in as the appropriate standard to allow the analysis to compare measured values to limits automatically.

9.8.4 Add ~0.25 g of Al_2O_3 ± 0.025 g, just enough to fully cover the cresol. It is important to ensure the whole sample is covered but minimize Al_2O_3 use as much as possible.

9.8.5 Remove the tin foil from the balance and twist to seal. Note: Too much Al_2O_3 has been added if the sample cannot be sealed or it is too big to fall

into furnace. Take care to minimize Al_2O_3. Additionally, take care to ensure no sample leaks out while sealing the foil cup. If any liquid escapes, discard and reprepare.

9.8.6 Place sample in correct position on autosampler and start analysis.

9.8.7 It is recommended to perform sample analysis as quickly as possible after preparation to minimize or prevent sample evaporation.

9.8.8 Repeat steps above for an additional two samples (three total check samples).

9.8.9 Evaluate values of the triplicate analyses. Calculate percent oxygen as in 10.2. Calculate the average and RSD (typically done in the instrument software for C and H) and compare to the table provided in Section 12. If values are outside the limits provided preform a 4^{th} analysis to determine if one sample prep may have been done incorrectly. If the final three analyses do not meet these criteria it can indicate poor sample prep technique or an issue with the instrument. Sources of poor precision and accuracy shall be corrected before performing analysis of samples.

9.9 Sample preparation for lower viscosity oils.

9.9.1 Apply small amount of sample on Al_2O_3 to determine sample preparation method. Typically, lower viscosity sample preparation method is used for FP oils, HT oil products, and aqueous samples. These tend to be relatively free flowing, similar to the m-cresol check sample or water. Higher viscosity oils tend to be CFPs or aged FPs, which are typically difficult to sample with a pipet.

9.9.2 If sample has lower viscosity follow the procedure described above in 9.8.1 through 9.8.7 (identical procedure to m-cresol check standards). Run samples in triplicate.

9.10 Sample preparation for higher viscosity oils.

9.10.1 Place sample cup holder on balance and place tin foil in cup holder. Tare balance and use microdispenser to add ~0.1 g of sample directly to the tin foil cup. Another sample introduction method may be needed if sample is very viscous. If the sample cannot be drawn with a pipet, a small spatula can be used to transfer the sample.

9.10.2 Enter sample mass into software.

9.10.3 Add ~0.4 g of Al_2O_3 on top of sample. It is important to make sure the whole sample is covered.

9.10.4 Remove the tin foil from the scale and twist to seal. Note: Too much Al_2O_3 has been added if the sample cannot be sealed or it is too big to fall into furnace. If any liquid escapes, discard and reprepare.

9.10.5 Place sample in correct position on autosampler and start analysis. Run samples in triplicate.

10. Calculations

10.1 **O wt% wet basis** (includes contribution of O and H wt% from water)

O wt% wet basis = 100 - (C wt % + H wt% + N wt%)

10.2 **O wt% dry basis** (corrected for wt% O from water; water content determined by Karl Fischer LAP: NREL/TP-5100-80968)

$$O\ wt\%\ dry\ basis = \frac{O\ wt\%\ wet\ basis - (0.889\ x\ H2O\ wt\%)}{100 - H2O\ wt\%} * 100$$

10.3 **C wt% dry basis**

$$C\ wt\%\ dry\ basis = \frac{C\ wt\%\ wet\ basis}{100 - H2O\ wt\%} * 100$$

10.4 **H wt% dry basis** (corrected for wt% H from water; water content determined by Karl Fischer LAP: NREL/TP-5100-80968)

$$H\ wt\%\ dry\ basis = \frac{H\ wt\%\ wet\ basis - (0.111\ x\ H2O\ wt\%)}{100 - H2O\ wt\%} * 100$$

10.5 **N wt% dry basis**

$$N\ wt\%\ dry\ basis = \frac{N\ wt\%\ wet\ basis}{100 - H2O\ wt\%} * 100$$

11. Report Format

11.1 Report the mean, SD, and RSD values for each sample.

12. Precision and Bias

12.1 Intra-laboratory precision of m-cresol was determined using a LECO CHN628 instrument over the course of a four-month period with replicate analyses from three analysts totaling 150 data points. The results of this analysis are provided in the table below. In normal execution of this procedure the m-cresol control sample should fall within these limits for triplicate analyses. If values fall outside these limits it may indicate issues with sample preparation or with the instrument. Users are encouraged to

perform replicate analyses to establish intra-laboratory precision for their instrument. Contact instrument manufacturer for guidance on expected precision and accuracy.

Element	Actual Value	RSD Limit	95% Confidence Interval	Low Limit	High Limit
C	77.7	0.4	0.6	77.0	78.3
H	7.5	1.6	0.2	7.4	7.9
O	14.8	2.5	0.7	14.0	15.4

12.2 The interlaboratory precision of this method has not yet been determined.

13. Quality Control

13.1 Monitor the average value and precision of the m-cresol control sample over time to ensure adequate method performance.

14. References

[1] Bridgewater A.V., *Upgrading Biomass Fast Pyrolysis Liquids.* Environmental Progress and Sustainable Energy 2012, 31 (2), pp. 261-268.

[2] ASTM D5291-16, Standard Test Methods for Instrumental Determination of Carbon, Hydrogen, and Nitrogen in Petroleum Products and Lubricants. ASTM International: West Conshohocken, PA.

[3] Application Note 203-821-462, Carbon, Hydrogen, and Nitrogen in Hydrocarbons, 2013, LECO Corporation; Saint Joseph, MI, USA

[4] CHN628 Series: Instruction Manual. LECO Corporation; Saint Joseph, MI, USA

[5] Joel Miscall, Earl D. Christensen, Steve Deutch, Jack R. Ferrell III, Determination of Water content in Bio-oils by Volumetric Karl Fischer Titration. Golden, CO: National Renewable Energy Laboratory. NREL/TP-5100-80968.