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“ – Reference method for water content in wood chips.

Title:
SOFT - Reference Method

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1. Introduction

Water mass fraction in biofuels is, according to the relevant ISO-standard [1], found by loss-on-drying. This method has some fundamental issues, since the drying takes place at 105 °C, at which other volatile organic compounds can also evaporate, and the loss is thus, as previously described by Samuelsson et al [2], [3] not only from the weight loss caused by the evaporation of water.

As the standard asks for a minimum of 300 g of biofuels and a scale with a resolution of at least 0.1 g, this could convince users that the water content of biofuels can be found to an uncertainty as low as 300.0/0.1 g/g ≈ 0.03 %.

Realistically, this is not the case though. In order to give the water content of a sample, the instruments used to perform the measurement have to be traceable to the SI-system. Practically this means, that although it is possible to measure a weight change with an accuracy of 0.1 g, this weight change is not necessarily only due to loss of water, and as such, the accuracy of the instrument does not equal the uncertainty of the measurement.

To counter the issue of other compounds evaporating from the sample, we need to quantify the water content using another method than the loss-on-drying. Specifically, we need to quantify the water using a method which detects all the water, and nothing but the water, and using instruments, where the calibration chain towards the SI base units is intact.

As one of the only institutes in Europe, Danish Technological Institute has a set-up for exactly this sort of measurements.

2. Method

The method used for the reference system is kept as similar to the corresponding ISO-standard as possible. As such we use a sample of at least 300 g and heat it to 105 °C ± 2 °C for at least 24 hours or until no more water is evaporated.

The reference method distinguishes itself by the following:

1. The sample is placed in a closed metal container, having an input gas port, an output gas port, and a port for a thermometer.
2. A known flow of dry gas is passed through the input gas port, over the heated sample, absorbing the water as it is released by the wood chips and out the output gas port.
3. The water content of the gas is found post-sample by means of equipment capable of measuring the dew point temperature of the gas.

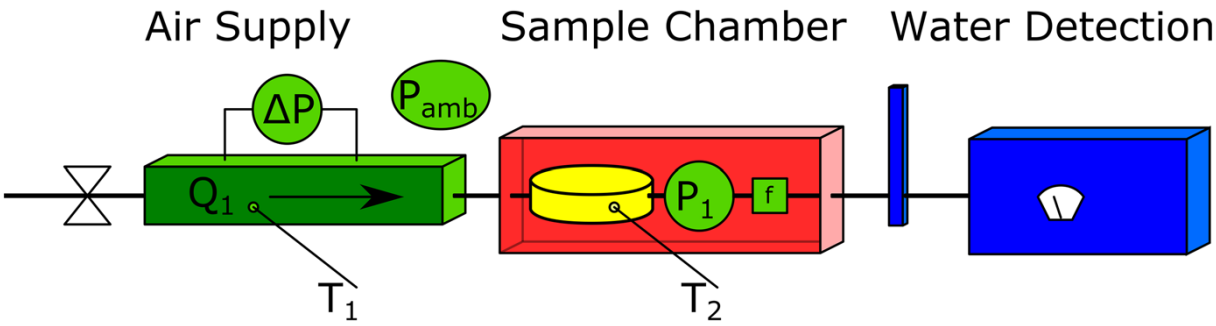
By integrating the gas flow multiplied by the water content over time, the total water content from the sample is found as described in Østergaard & Nielsen [4].

For comparison with the ISO-standard [1], the mass of the wet and dry sample are found by weighing.

As the system measures the water content of the air, the result shows the water released from the sample, disregarding any other compounds released in the process.

A sketch of the set-up is seen in Figure 2.1.

Figure 2.1: sketch of the set-up. The reference system consists of equipment for measuring air-flow, temperatures, pressure and dew-points.



2.1. Description (mass fraction)

The water content measured by the reference method is directly dependent on the amount of sample used for the measurement. Consequently, the water mass fraction is reported. This result is found like the water content in the ISO standard [1]. The current standard defines the moisture content as $M_{ar} = \frac{m_{wet} - m_{dry}}{m_{wet}} \cdot 100$, while the moisture content using the reference set-up is found as $w_{mc,wet} = \frac{m_{H_2O}}{m_{wet}} \cdot 100$, where m_{wet} is the mass of the wet sample, m_{dry} is the mass of the dried sample, and m_{H_2O} is the mass of the water content released from the sample during drying.

2.2. Traceability

The reference set-up at Danish Technological Institute has an unbroken chain of calibration for all measured parameters. As such, all devices used are directly traceable to the SI system with known uncertainties.

The parameters required to perform the measurements are:

- Dew point/water vapour pressure
- Gas flow
- Atmospheric pressure
- Pressure at sample chamber
- Ambient temperature
- Temperature at sample chamber

All instruments recording these parameters are calibrated, either in Danish Technological Institute's own accredited laboratories, or at external, accredited, laboratories.

For the mass measurements performed, traceability to the SI system is ensured by using a calibrated comparator with a calibrated 5 kg mass – the closest to the mass of the chamber, weighing in at around 5.4 kg.

2.3. Uncertainty

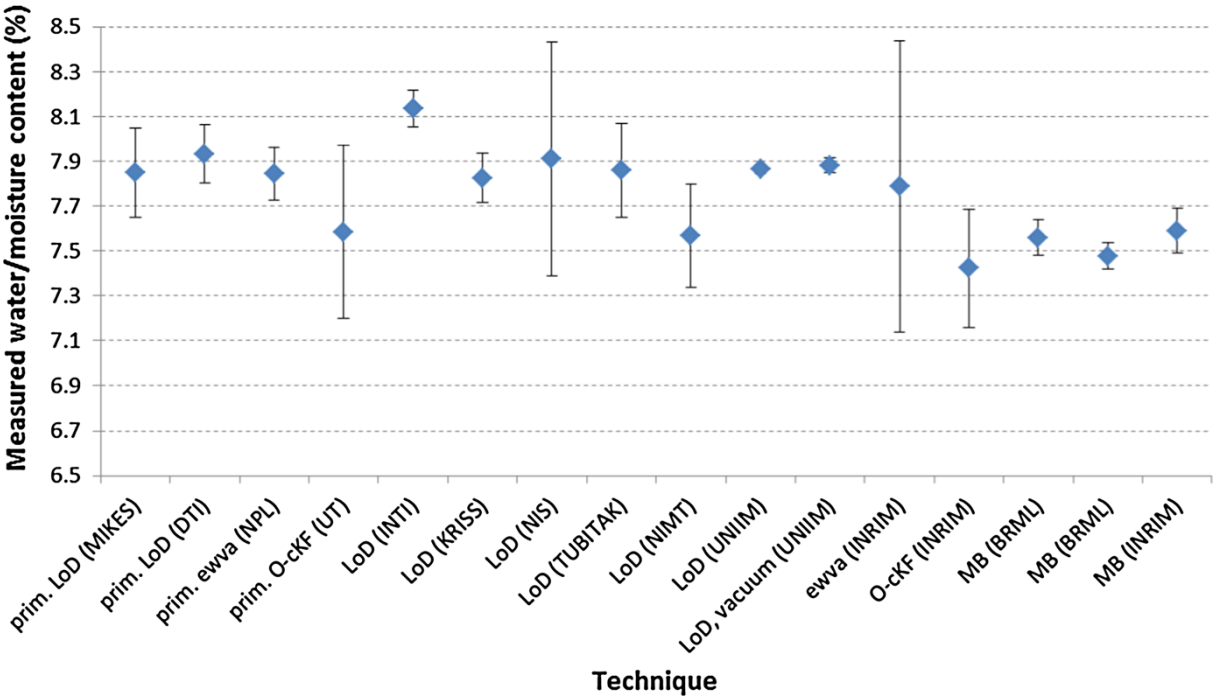
The uncertainties from the individual sensors are combined in the final measurement to give an uncertainty for the total moisture content of the sample.

As the interaction between the different measures and the result is highly non-linear, the final uncertainty is found by means of a Monte Carlo simulation, combining the individual uncertainties, as described by Østergaard & Nielsen[4].

2.4. Validation by comparison

The reference system was validated in a large international comparison, where multiple institutions measured water content from samples, all originating from the same population. The measurements were conducted using a multitude of different techniques, including Coulometric Karl Fischer, electrolytic cells, water vapour analyser, and dew point detection. The sample used for the intercomparison was wood pellets with a moisture content just below 8 % (wet basis). The results of the intercomparison is found in Heinonen et al [5] and seen in Figure 2.2. In general, it is seen, that the reference set-up at Danish Technological Institute (no. 2 from the left) performs well against the other set-ups at the metrology institutes around Europe and the world.

Figure 2.2: Comparison of reference systems for measuring material moisture in wood pellets



3. Results

In the current work, 3 samples of wood chips, originating from the same population, are studied. The three samples are dried using the reference set-up at Danish Technological Institute, giving the moisture content of the sample. Simultaneously, the mass of the sample is measure before and after drying (corresponding to the loss-on-drying method normally applied to water content determination in wood chips). This allows us to find the moisture content as prescribed by the ISO-standard [1]

The results from both reference set-up and as found from the standard are seen in Table 1.

Table 1: Results from reference set-up compared with results from loss-on-drying

Sample	Moisture content reference method	Uncertainty (k=2)	Lowest possible uncertainty (k=2)	Moisture content from loss-on-drying
1	22.29 %	0.58 %	0.45 %	22.44 %
2	31.73 %	0.85 %	0.64 %	31.49 %
3	30.87 %	0.79 %	0.62 %	31.18 %

The results from the loss-on-drying agree well with the reference system, indicating that the amount of evaporated material, not being water, is below the uncertainty of the reference system's uncertainty. Consequently, the uncertainty from the loss-on-drying results has to be at least as high as the uncertainty on the reference method. The minimum uncertainty obtainable from the reference method is 2 % of the mass of the water, in this case corresponding to an uncertainty of the moisture content of 0.45 % - 0.64 % (k=2).

All three samples originate from the same population, showing that the uncertainty of the moisture content of the sample is significantly larger than the uncertainty of the method used for measuring the moisture content.

This means, that in order to get a good estimate on the moisture content of a population of wood chips, focus should be on obtaining proper random samples from the population, since the uncertainty of the measurement is much lower than the variation within the population.

4. Conclusion

A reference system is used to verify the loss-on-drying moisture measurements performed on wood chips. The results from loss-on-drying are comparable with the reference measurements, within the expanded uncertainty of the reference system.

The reference system brings traceability to the measurements, ensuring that the moisture content describes the actual moisture content, and not mass loss due to evaporation of other compounds. The uncertainty of the loss-on-drying method must be increased to at least the uncertainty from the reference method, as described in GUM [6].

The sample variation between samples originating from the same population is significantly larger than the uncertainty of a single measurement. This means, that in order to

give a representative value for the moisture content of the population, attention must be placed on proper sample preparation and sufficient samples, as much as on the analysis method.

5. Bibliography

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