THE IMPORTANCE OF MOISTURE DETERMINATION OF REFERENCE MATERIALS

APPLICATION NOTE: 25

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1. Introduction

Powdered certificated reference materials (CRM), e.g., coal and ores carry a certificate of traceability, or certificate of analysis, in which it is stated whether the certified analyte value is reported on a dry basis. The certificate of traceability for an ore tailing reference shown in Figure 1, states that the material needs to be dried for one hour prior to use. This implies that the certified value of carbon is on a 'dry-basis'. If such materials contain a few percent of moisture and no correctio is done, a significant bias in the results obtained on this material will be evident. The systematic error will increase with decreasing sample mass. In this application note, the effect of not taking moisture content into consideration is demonstrated.

2. Determination of Moisture Content

2.1 *Procedure*

The user laboratory is required to dry a portion (accurately weigh out 1.0 to 2.0 grams in triplicate) of the CRM material in air at 105 ^{o}C in a drying oven to constant mass to determine the moisture content. The procedure requires a crucible with a flat inner surface with a surface area not smaller than 10 cm^2 (this represents a 0.1 gram spread per cm^2). The CRM is weighed

into the crucible and spread evenly in the crucible using a spatula and dried to constant mass. A constant mass is the mass reached when, during the drying process, the difference between two successive weighing of the sample at an interval of minimum one hour, first heated, then cooled to room temperature, does not exceed 0.5% (m/m) of the last determined mass or 2 mg, whichever is the greater (ISO 11465: 1993). The difference in mass before and after drying is the moisture content. In correcting the certified analyte value for moisture content, a correction factor is calculated as:

$$\text{Moisture correction factor (MCF)} = \frac{100 - \%\text{Moisture at } 105^{\text{O}}\text{C}}{100} \qquad [1]$$

$$\text{Air dry basis concentration} = \text{MCF x certified value on a dry basis} \qquad [2]$$

2.2 *Moisture Results*

The mean moisture content determined at 105°C to constant mass on triplicate portions of LECO CRM 502-491, is 2.08% (Table 1).

Table 1. Triplicate moisture results obtained on LECO carbon certified reference material, 502-491.

Name	Moisture Average	Moisture (s)	Moisture %RSD
502-491	2.08%	± 0.0621 %	2.99%
Name	**Initial Mass**	**Moisture**	
502-491	1.5614 g	2.14%	
502-491	1.6491 g	2.01%	
502-491	1.5577 g	2.08%	

3. Calibration of LECO CS 744

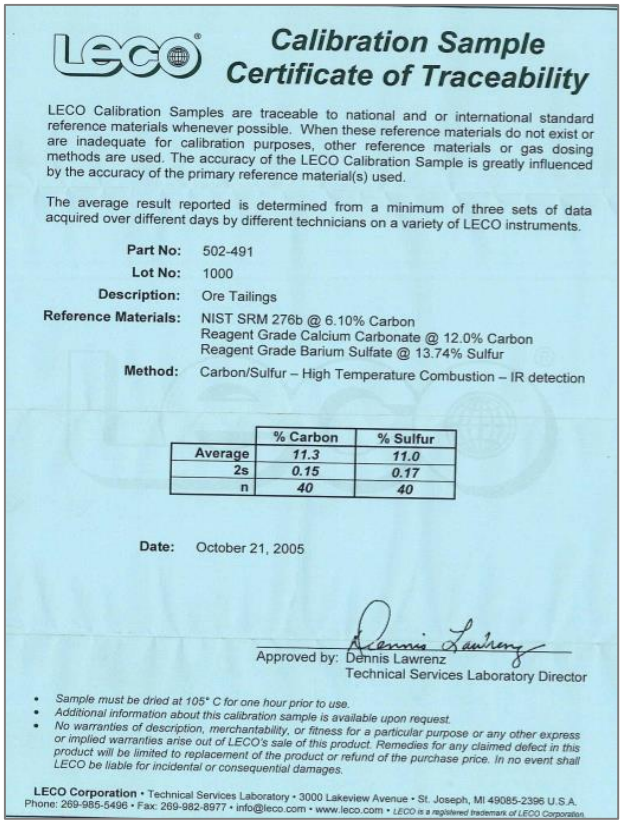
The LECO CS744 Analyser was calibrated using a range of masses of CRM 501-024. The resulting linear least squares regression was done using the certificate dry-basis value, as per the certificate (not given here), of 501-024 *i.e.*, 3.23 ± 0.02% C.

4. Certified Reference Material

LECO certified reference material 502-491 (Figure 1), was used as an independent calibration verification standard, *i.e.*, this standard was not used to make up the regression calibration as shown in Figure 2. The certified carbon value and stated measurement uncertainty for 502-491 are shown in Table 2. The certificate states that *"sample must be dried at 105ºC for one hour prior to use"*, which implies that the certified value is on a 'dry-basis'.

Table 2. Certified carbon value on a dry basis and two-sigma measurement of uncertainty for CRM 502-491.

Reference Material: 502-491		
% Carbon	11.3	±0.15



LECO

Calibration Sample Certificate of Traceability

LECO Calibration Samples are traceable to national and or international standard reference materials whenever possible. When these reference materials do not exist or are inadequate for calibration purposes, other reference materials or gas dosing methods are used. The accuracy of the LECO Calibration Sample is greatly influenced by the accuracy of the primary reference material(s) used.

The average result reported is determined from a minimum of three sets of data acquired over different days by different technicians on a variety of LECO instruments.

Part No: 502-491
Lot No: 1000
Description: Ore Tailings
Reference Materials: NIST SRM 276b @ 6.10% Carbon
Reagent Grade Calcium Carbonate @ 12.0% Carbon
Reagent Grade Barium Sulfate @ 13.74% Sulfur
Method: Carbon/Sulfur – High Temperature Combustion – IR detection

	% Carbon	% Sulfur
Average	11.3	11.0
2s	0.15	0.17
n	40	40

Date: October 21, 2005

Approved by: Dennis Lawrenz
Technical Services Laboratory Director

- Sample must be dried at 105° C for one hour prior to use.
- Additional information about this calibration sample is available upon request.
- No warranties of description, merchantability, or fitness for a particular purpose or any other express or implied warranties arise out of LECO's sale of this product. Remedies for any claimed defect in this product will be limited to replacement of the product or refund of the purchase price. In no event shall LECO be liable for incidental or consequential damages.

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Figure 1. Certificate of traceability for reference material ore tailings, 502-491.

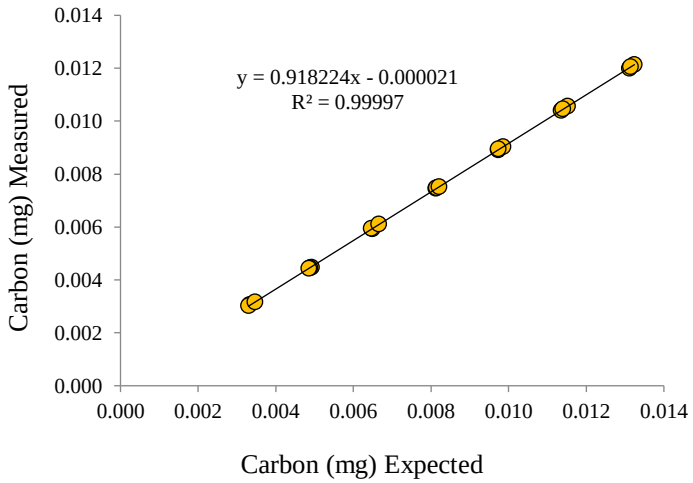

Figure 2. Linear least squares regression of carbon measured (mg) against the carbon mass expected (mg) from a range of increasing mass of CRM 501-024.

5. Converting "As Is" % Carbon to Dry basis

502-491 was weighed in quadruplicate without drying and analysed on the CS744 to give a mean value 11.04% C. Correcting for the moisture determined, will give the value on a dry basis. The calculations are shown below:

Mean % C = 11.04 %. Therefore, 11.04 % at a mean mass weighed of 0.1045 g is 0.0115368 g of carbon.

$$Grams\ C\ measured = \frac{11.04\%\ x\ 0.1045\ g}{100}$$

$$Grams\ C\ measured = 0.011537$$

$$Since, 0.1045\ g\ CRM\ contains\ 2.08\ \%\ mositure, then:$$

$$Grams\ moisture\ in\ 0.1045\ g = \frac{2.08\%\ x\ 0.1045\ g}{100}$$

$$Grams\ moisture\ in\ 0.1045\ g = 0.002174$$

$$Therefore, 0.1045 - 0.002174 = 0.10233\ g\ sample$$

$$Therefore, \% C = \frac{0.011537\ g\ C\ \ x\ 100\ g}{0.10233\ g} = 11.27\ \%$$

Summarising the above conversion of 'As-is' % carbon to dry basis % carbon:

$$\% C\ (dry) = \frac{100}{1 - Moisture}\ x\ \% C$$

$$\% C\ (dry) = \frac{100}{100 - 2.08}\ x\ \% C$$

$$\% C\ (dry) = 11.2_{(7)} = 11.3\ \% C$$

6. Correction for Moisture

The mean moisture content determined at 105°C to constant mass on triplicate portions of LECO CRM 502-491, is 2.08% (Table 1). The certified carbon concentration for 502-491 is 11.3±0.15% on a *dry basis*, as stated on the certificate of analysis (Figure 1). Calculating the moisture correction factor using equation [1]:

$$Moisture\ correction\ factor = \frac{100 - 2.08}{100} = 0.9792$$

Multiplying the factor of 0.9792 by the certified value as stated on the certificate of analysis on a dry basis gives the certified analyte concentration on an air-dry basis:

$$0.9792\ x\ 11.3\ \% \ = 11.06\%$$

The stated measurement uncertainty also needs to be corrected *i.e.*, 0.9792 x 0.15 = $0.14_{(7)}$, rounded to 0.15%. Therefore, the air-dry basis carbon concentration is, 11.1±0.15%. The dried CRM is weighed out in quadruplicate and analysed on a LECO CS744 Analyser. The mean value for the replicates is 11.04% C with a mean mass of the CRM used for analysis of 0.1045 g (Table 3).

Table 3. % Carbon as determined without drying of the CRM.

Name	**Carbon Average**	**Carbon Std. Dev.**	**Carbon %RSD**
502-491	11.04	0.04648	0.421
Name	**Sample Mass**	**% Carbon**	
502-491	0.1056	10.99	**% Carbon determined as is with no drying**
502-491	0.1024	11.11	
502-491	0.1026	11.07	
502-491	0.1074	11.04	

Conclusion

The user laboratory therefore has two choices:

1. Dry the CRM material, weigh out what is required for analysis and then place the dried mass into a desiccator. The moisture content does not require calculation as the laboratory report the assays on the dried sample *i.e.*, dry basis.
2. Weigh the CRM as is, with no drying, analyse, and then separately determine the moisture content. Correct the dry-basis CRM certified value for the moisture and recalculate the certified value as well as its stated measurement uncertainty.

Acknowledgements

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References

ISO 11465: 1993; Soil quality – Determination of dry matter and water content on a mass basis – Gravimetric method.