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Comparison of methodologies for determining the carbon content in wood

Comparação de metodologias para determinar o teor de carbono em madeira

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ABSTRACT: New procedures seek to subsidize studies on biomass and carbon in forests and wood, mainly of tropical species. Thus, the work aimed to compare four methods of carbon determination in wood. A pre-dried sample of tropical wood was prepared and previously ground. In this sample, the carbon content was determined, applying four different methodologies, namely: conversion of organic matter, volumetric method, colorimetric method and dry combustion (LECO). The Tukey test was performed to determine the difference between the carbon levels obtained by each method. As a result, all methods differed statistically from each other: the colorimetric method underestimated the levels of organic carbon in a tropical wood; although widely used, the volumetric method has become obsolete; and the organic matter conversion method requires specific conversion factors for each material. So, from the environmental point of view and accuracy in obtaining data, the dry combustion method, in addition to being the closest to the standard, is also the one that generates less waste, being the most suitable to determinate carbon in wood.

Keywords: Colorimetric method. Conversion of organic matter. Dry combustion (LECO). Organic carbono. Volumetric method.

RESUMO: Novos procedimentos buscam subsidiar estudos sobre biomassa e carbono em florestas e madeira, principalmente de espécies tropicais. Assim, o trabalho teve como objetivo comparar quatro métodos de determinação de carbono em madeira tropical. Uma amostra pré-seca de madeira tropical foi previamente preparada e moída. Nesta amostra, foi determinado o teor de carbono, aplicando quatro metodologias diferentes, sendo estas: conversão da matéria orgânica, método volumétrico, método colorimétrico e combustão a seco (LECO). O teste de Tukey foi realizado para determinar a diferença entre os teores de carbono obtidos por cada método. Como resultado, todos os métodos diferiram estatisticamente entre si: o método colorimétrico subestimou os níveis de carbono orgânico na madeira de espécie tropical; embora amplamente utilizado, o método volumétrico tornou-se obsoleto; e o método de conversão de matéria orgânica requer fatores de conversão específicos para cada material. Portanto, do ponto de vista ambiental e da precisão na obtenção de dados, o método de combustão a seco, além de ser o mais próximo do padrão, também é o que gera menos desperdício, sendo o mais adequado para determinar o carbono na madeira.

Palavras-chave: Carbono orgânico. Combustão a seco (LECO). Conversão da matéria orgânica. Método colorimétrico. Método volumétrico.

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INTRODUTION

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Carbon dynamics are constantly modified by human activities, especially with regard to changes in land use and occupation and use of fossil fuels. The concern with climate change and global warming increased the need to assess the amount of carbon stored in the most diverse compartments of the Earth, contributing to the growing obligation to evaluate its determination processes in organic waste and in the soil.

The process of carbon determination of a material occurs through the transformation of organic matter into carbon dioxide (CO_2), could this occur through dry or wet combustion (SATO *et al*., 2014). The method selection will depends on aims, costs, maintenance of the equipment and structure of the laboratory where the analyzes will be carried out, beyond the fact that variations in the results may occur depending on the methods applied and the composition of the materials (CARMO; SILVA, 2012).

The increase in the number of researches, carried out in university laboratories and research institutes, has led to an increase in the amount of discarded waste, which causes problems in management, especially in the disposal and monitoring of liquid waste. Therefore, it is necessary to develop and/or adapt existing methodologies to reduce material generated in scientific environments(HO; CHEN, 2018).

It is worth noting that some methods, such as volumetric, although adapted from the original methodology (ARAUJO *et al*., 2020), generate large contaminant residues, not to mention the difficulty in obtaining some reagents, such as sulfuric acid. Therefore, the use of clean technologies for laboratory analysis to determine the carbon content in plant samples contributes to the updating of the old methods and accurace in obtaining the results.

Dry combustion is based on an automated technique of the analytical process for fast, precise and accurate determination of results (SOON; ABBOUD, 1991). In addition to being less laborious than techniques such as volumetric and colorimetric methods, it does not use toxic reagents (WANG; ANDERSON, 1998), not to mention that the measurement by elementary analyzers presents an important precision to verify changes in the carbon content and stock, whether caused by the climate or by site management practices (WRIGHT; BAILEY, 2001).

The constant improvement of techniques due to the emergence of new technologies, in addition to reducing costs, stimulates the development of fast, accurate and low environmental impact analysis methodologies(BERNARDI; OKA; DE SOUZA, 2010). Some methodologies have already been improved and updated in the literature, emerging some using procedures based on guidelines for environmental preservation and validation of analytical data. Such procedures seek to subsidize studies on biomass and carbon in forests and wood, mainly of tropical species.

Thus, the work aimed to compare four methods of carbon determination in topical wood, namely: conversion of organic matter, volumetric method, colorimetric method and dry combustion (LECO).

2 MATERIAL AND METHODS

2.1 SAMPLE PREPARATION AND MOISTURE CONTENT DETERMINATION

In the experiment, a sample of tropical wood previously prepared was used, being preserved in an airtight glass container until the time of analysis. This sample was previously dried in an oven for 72 hours at a temperature of 65ºC and ground in a Wiley knife mill(BEZERRA NETO; BARRETO, 2011).

The moisture content of the sample was determined using the gravimetric method. Glucose P.A. also had the moisture content determined to calibrate the volumetric and colorimetric methods for determining the total carbon content. Five repetitions were taken for each material.

2.2 METHODS

2.2.1 Conversion by organic matter content

The method was developed from the determination of the levels of mineral residue in the sample, whose difference in mass is equivalent to the content of organic matter in the plant tissue. For this purpose, previously dried and tared porcelain crucibles were used, in which 2.0 g of the sample were added.

This material was taken to the heating plate in order to carbonize the samples until the smoke release ceases (BEZERRA NETO; BARRETO, 2011). The crucibles were taken to a muffle regulated at a temperature of 575±25ºCfor four hours. After that time, they were placed in the desiccator to cool and then weighed. The organic matter content was determined due to the loss of mass by calcination of the sample, being:

$$OM = [\,C + CM] - CT$$

On what: OM is organic matter (g), C + CM is crucible mass + calcined material (g) and CT is crucible tare (g).

After determining the amount of organic matter, a conversion factor equal to 2.22 (MALAVOLTA, 2006) was used to estimate the carbon content in the tropical wood, using five replications.

2.2.2 Volumetric method

To perform the volumetric method, 0.1 g of the sample was weighed in digestion tubes, adding then 20 mL of 1.0 N potassium dichromate (with the aid of a volumetric pipette) and 10 mL of concentrated sulfuric acid (ARAUJO *et al*., 2020). The tubes were closed and taken to warm boiling for five minutes (±105ºC) in a digesting block.

After heating, the tubes were gently shaken for one minute and left to stand for 30 minutes. Then, the material was transferred to 500 mL erlenmeyers flask with the aid of 200 mL of distilled water. 10 mL of concentrated phosphoric acid and 1 mL of diphenylamine were added to each erlenmeyer flask. The excess of the oxidant was titrated with 0.5 N ammoniacal ferrous sulfate solution, until the purple color turned green. The results were evaluated according to the methodology developed by Bezerra Neto and Barreto (2011). Five repetitions were also performed.

2.2.3 Colorimetric method

To perform the colorimetric method, 0.1 g of wood sample was weighed in a 250 mL conical flask, in which 10 mL of potassium dichromate in sulfuric acid were added; the conical flasks were stirred for 10 minutes, and then left to stand for an hour. Then, 50 mL of distilled water were added and the mixture was left to decant for 12 hours. After decanting, the supernatant liquid was analyzed in a spectrophotometer with a wavelength of 650 nm(SILVA, 2009).

A standard carbon curve was prepared using 0 mg, 20 mg, 40 mg, 60 mg, 80 mg and 100 mg of glucose P.A., following the same methodology, and from the reading of the absorbance of the standards, in the Microsoft Office Excel software, a regression equation was obtained to calculate the carbon content in tropical wood. Five repetitions were also performed.

2.2.4 Dry combustion

After preparation, the samples were weighed in porcelain crucibles and taken to LECO equipment, model C-144, to determine the carbon content by dry combustion.Calibration was performed using the Rice Flour Organic Analytical Standard reagent. The determination was made by sending information from the equipment directly to a coupled computer software, which generates a digital file. Five repetitions were also performed.

2.3 COMPARISON BETWEEN METHODS

The comparison between the methods was carried out through analysis of variance (ANOVA) and the averages were compared by the Tukey test at 5% probability using the RStudio 1.1.463 program. The homogeneity of variances was observed by the Cochran test.

3 RESULTS

The levels of mineral residue found for the wood of brazilian tropical species corresponded to an average of 2.2242%, with standard deviation of 0.2158 and coefficient of variation of 9.7029%. Therefore, the organic matter content in the sample is 97.7758%. The organic fraction of dry tropical wood corresponds to a range of 97-99% of the material's mass, thus corroborating the results found in this work (KLOCK; ANDRADE, 2013).

Applying the conversion factor for total carbon, equal to 2.22 (MALAVOLTA, 2006), it was determined that by this method the total organic carbon content in the tropical woodcorresponds to 44.0432%.Finally, it was possible to evaluate and compare the methods for determining the total organic carbon content for the tropical wood sample, with the results shown in Table 1, with the variances being homogeneous by the Cochran test.

Table 1. Mean carbon content (%) in a tropicalwood sample by different methodologies

Method	Mean (%)	Stantard deviation	Coefficient of Variation (%)
Dry combustion	45.5064 a	0.2174	0.4778
Conversion of organic matter	44.0432 b	0.0972	0.2208
Volumetric	40.3025 c	0.4950	1.2281
Colorimetric	24.4548 d	0.6120	2.5027

Means followed by the same letter do not differ statistically from each other, according to the Tukey test at the 5% probability level. %CV = 1.07; smd = 0.74475

4 DISCUSSION

The most used methods in Brazil for the determination of carbon are the volumetric, using potassium dichromate, and by converting the organic matter, through the muffle, employing a factor for the conversion of carbon into organic matter, being the conversion of low cost and canbe performed in most laboratories (CARMO; SILVA, 2012).

Regarding the colorimetric method, despite the ease of execution, it generates chromium residues that must be properly treated, which causes cost burdens(ZHU, 2003). In addition, in relation to the other methods, it underestimated the values of total organic carbon in a tropical wood, with the lowest levels.

In the literature it is widespread that the carbon content in wood, of the most diverse species, is between 45% and 50%. However, there are reports of values close to 40% or above 50% (TRUGILHO *et al*., 2010; SANQUETTA *et al*., 2016), which reinforces the need for more accurate analysis methods.

Thus, since it has an average content of 24.4548%, the colorimetric method would be discarded to determine the carbon in wood, requiring further improvement of the technique, since its values were very different when compared to the averages presented in the literature and those observed by the other methods in this work.

Despite being widely used, the volumetric method has become obsolete, since its use generates a large amount of chemical waste, in addition to the possibility of systematic errors caused by the analyst. Another point that contributes to the lack of technique would be the need for authorization from higher agencies to purchase some inputs, such as sulfuric and phosphoric acids.

As an advantage, the volumetric method is simple to perform, not requiring more expensive equipment, such as colorimetric and dry combustion; however its main disadvantages are the high amount of reagents, the execution time and the low precision, as it requires more careful techniques(CHATTERJEE *et al*., 2009; SAMPAIO *et al*., 2012).

The difficulty of the organic matter conversion method is the use of the conversion factor that corresponds to each specific material, another drawback is the time to perform the analysis, since in general the muffles are small and the time for calcination of the material is high.

The dry combustion method, in turn, can also generate a systematic error, in relation to the true value of the quantity, being one of the reasons, the lack of calibration of the machine. However, when properly calibrated, it presents high precision and accuracy in the results.

Methods performed in an automated way, as they present low variation between results, in the same sample, require a smaller number of repetitions, not to mention that they use certified reagents with greater purity with reduced environmental impacts, being the most suitable then(SOON; ABBOUD, 1991). The disadvantage of this method is the high cost of execution and maintenance of the equipment(CARMO; SILVA, 2012).

Therefore, for all these considerations, the dry combustion method is the most suitable for determining the carbon content in a plant sample.

5 CONCLUSION

Analysis methods carried out in an authorized manner show less error and require a smaller number of repetitions. Besides that, from the environmental point of view and accuracy in obtaining data, the dry combustion method, in addition to being the closest to the

standard, is also the one that generates less waste, being the most suitable to determinate carbon in tropical wood.

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