METROLOGICAL TRACEABILITY OF MOISTURE CONTENT MEASUREMENTS IN PLANT-ORIGIN BULK MATERIALS

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Abstract:
This document explains advantages and disadvantages of the measurement methods for the moisture content determination of plant-based materials in order to identify the best one which can provide metrological traceability to SI units.

The term "moisture" is generic and, to have proper Calibration and Measurement Capabilities (CMCs) and Certified Reference Materials (CRMs), a better specification of the measurand should be given. Currently, no CMCs for moisture content measurement in the plant-origin bulk materials, as well as respective CRMs, are available in the KCDB. Undoubtedly, those CMCs and CRMs are crucially needed to provide metrological traceability in this area.

Keywords: Karl Fischer titration, plant matrix

1 INTRODUCTION

The moisture content is one of the most important characteristics of plant-origin bulk materials, which is necessary to support fair trade in the grain market. To determine moisture content, industrial laboratories mostly use the air-oven reference methods [1 – 5]. In the reference method, a test portion of most cereals is dried at a temperature of about 130 °C for a few hours.

Also, the absolute methods described in ISO standards [4, 5] can be used by specialized laboratories. In the absolute method a test portion is dried under reduced pressure and kept at about 50 °C for up to one month, until the constant mass is reached.

The main disadvantage of reference methods is that the completeness and specificity of moisture removal are not guaranteed [6, 7]. Absolute methods are difficult to perform and require considerable time.

Other techniques, such as the Karl Fischer titration, provide high selectivity to water determination. In this case, water molecules are usually extracted by the dried methanol [8] and it is assumed that extraction is full.

2 PURPOSE

In this paper we review methods for the moisture content measurement in plant-origin materials determination. The main aim of this work is to select a way for creating the plant matrix CRMs that would provide traceability to SI to support CMC claims.

3 MATERIALS AND METHODS

Methods described below are applied for wheat, rice (paddy, husked and milled), barley, millet, rye, oats, triticale, sorghum in the form of grains, milled grains, semolina or flour, maize, pulses, and other plant matrix objects.

a. Karl Fisher method

The Karl Fischer (KF) method is a widely used technique for the accurate determination of water content in various plant-origin materials.

The KF method is based on the chemical reaction between iodine and water in the presence of sulphur dioxide and a base. The reaction runs in a specialized titration measuring instrument. The KF reaction can be formulated as follows [9]:

$I_2 + SO_2 + 2H_2O \rightarrow 2HI + H_2SO_4$

For determining the water content, two different kinds of KF method are used: volumetric KF titration, where the injection of an iodine solution is carried out using an automatic burette (suitable for samples with high water content: 100 mg/kg - 100%); coulometric analysis according to KF, where iodine is formed in the cell as a result of electrochemical oxidation (suitable for samples in which water is present in trace or low amounts: 1 mg/kg - 5%). In modern realization of both kinds of KF methods is possible to use special supplementary equipment, such us ovens,

autosamplers, mills, temperature-controlled cells, automated filling/emptying of cells, magnetic stirrers, etc. All such supplementary equipment make the KF method more precise and reproducible, faster, ready-to-use, economically effective and environmentally friendly.

Figure 1: Karl Fischer volumetric titrator

b. Oven absolute method

A test portion of the laboratory sample is dried under reduced pressure, at a temperature in the range (45 – 50) °C, in the presence of a desiccant, until constant mass is reached.

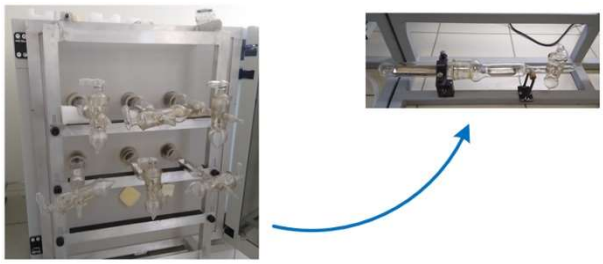

Figure 2: Oven absolute method equipment

c. Oven reference method

A test portion of the laboratory sample (previously ground and/or conditioned, if needed) is dried (100 - 135 °C) under conditions which provide a result maximally corresponding to one obtained by the absolute oven method.

4 DISCUSSION

The main disadvantage of the reference methods, described in ISO standards [4,5], is the absence of knowledge on the chemical nature of evaporated substances, that may be both water and some other volatile compounds.

In contrast to reference methods, described in ISO standards, KF method provides measurement of water content only. Using the KF titration method for moisture content measurements in plant matrix CRM would provide traceability to SI to support CMC claims.

The oven absolute method has high precision and acceptable specificity (only traces of volatile organic substances could evaporate from test portion).

Advantages and disadvantages of these methods are presented below.

Table 1: Advantages and disadvantages of reference oven method [4,5]

Advantages	**Disadvantages**
Easy to apply	Low water selectivity
Small period of time per measurement	High electricity consumption
Commercially available equipment	Low accuracy

Table 2: Advantages and disadvantages of Karl Fisher method

Advantages	**Disadvantages**
Absolute method; provide traceability to SI	Poison reagents
High water selectivity	More expensive
Small period of time per measurement	Needs skilled staff
Commercially available equipment	Medium precision
Small electricity consumption	

Table 3: Advantages and disadvantages of absolute oven method [4,5]

Advantages	**Disadvantages**
Acceptable water selectivity (expected)	Highest period of time per measurement
High precision (U (0.95; k=2; n=10) ≈ 0.03 %)	Needs skilled staff
Commercially available equipment	High electricity consumption

The comparison of the oven reference methods with KF method and the corresponding "adjustment" of working methods is a common practice [3, 11, 12]. For example, the ASAE S352.2 standard [3] includes only those oven methods for which the documented comparison with the KF titration was carried out; such studies were made for a several dozens of plant matrix measurands. Also, the absolute oven method "is intended to serve as a standard for checking and perfecting other methods for the determination of moisture content" [4].

Applying KF and absolute oven methods to the same sample and comparing the obtained results seems ~~a~~ very promising. There are many reasons to consider both methods as selective; their results are expected to be comparable. On the other hand, the questions concerning the correctness of these methods and the ways of their implementation will arise. Particularly, the comparison of both methods will allow to answer the question regarding the water selectivity of the absolute oven method. Additionally, such study will provide an estimation

of the sufficiency of water extraction in the KF method.

If the correspondence of both methods results is found to be sufficient, it will allow to produce corresponding CRMs by assigning the relevant property value by means of KF method and absolute oven one as well. In this case the traceability to SI could be provided.

In previous works the precision of KF method was not very high [10]. Nevertheless, the usage of only KF titration for such CRMs characterization seems promising by means of new KF equipment, developed in recent years; such equipment provides higher precision of the method.

5 SUMMARY

Plant matrix CRMs for measurement laboratories using KF titration method for moisture content measurements in plant-origin bulk materials are needed. With those CRMs it will be possible to establish metrological traceability and to support a fair trade in the grain market. Comparing the results of KF and absolute oven methods seems a very important and useful starting point.

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