New Primary Standards for Establishing SI Traceability for Moisture Measurements in Solid Materials

NEW METHODS FOR ESTABLISHING SI TRACEABILITY FOR MOISTURE MEASUREMENTS IN SOLID MATERIALS

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Abstract

A European research project METefnet addresses a fundamental obstacle to improving energy intensive drying process control: due to ambiguous reference analysis methods and insufficient methods for estimating uncertainty in moisture measurements, the achievable accuracy in the past was limited and measurement uncertainties were largely unknown. This paper reports the developments in METefnet that provide a sound approach for removing the obstacle: SI unit realisations for water mass fraction with demonstrated equivalence, new certified reference materials, two new transfer standard instruments, a novel calibration method for surface moisture and software tools for uncertainty analysis. The results show that an equivalence of 0.2 %w has been achieved between water mass fraction realisations and the developed methods are applicable to wide range of materials.

Keywords: Air temperature; Calibration; EURAMET; Heat transfer; Intercomparison

1 Introduction

Moisture content of solid materials is important in a vast range of applications. The presence of water influences in pharmaceuticals, carbon-fibre composites, polymers, food powders, biomass, paper, and many others – during processing, storage and use. In drying and combustion processes water has major effect on energy consumption/generation due to its large latent heat of evaporation. Thus, significant advancements in energy efficiency can be achieved by improving moisture control. In various production processes, water influences active ingredients, mechanical quality, product stability and shelf life. Errors and inconsistencies in moisture measurement and control lead to increased wastage and decreased process speed and throughput.

Reliable measurement and quantifying the reliability in moisture measurements pose various challenges. The most fundamental one is the measurand itself: applying a measurement method you may measure water content alone while with another one you actually measure water and other liquid or volatile contents. For example, results obtained with the widely recognised loss-on-drying methods take into account water and other volatiles while only water is determined with the coulometric Karl Fischer titration method. Also, disseminating traceability and estimating uncertainty are challenging in moisture measurements. Overall there is a need in the moisture field to reduce dependence solely on method-based standardisation of procedures, moving instead towards outcome-based verification of measurement results.

A 3-year European research project METefnet was started in 2013 to develop unambiguous principles, methods and equipment for establishing and disseminating SI traceability to measurements of moisture in solids. The project addresses a wide range of materials relevant to industrial production of pharmaceuticals, polymers, foodstuff, animal feed, biomass, wood products, and others [1].

This paper summarises the major outcomes of the METefnet project including new primary standards for water mass fraction in solids, new reference materials and transfer standard systems for moisture, a calibration method for surface moisture meters, methods and tools for estimating uncertainty and first steps towards a more coherent moisture metrology infrastructure in Europe. By analysing the outcomes, conclusions are drawn about the potentiality of the SI traceability based on calibrations and reference materials in quality assurance of moisture measurements.

2 Background

When determining gravimetrically the moisture content (w_{mc}) applying loss-on-drying methods (LoD) the result is obtained as a percentage of its wet mass (wet basis) or dry mass (dry basis):

$$w_{mc,wet} = \frac{m_{w^*}}{m_m} \times 100\ \%\text{mc} = \frac{m_{w^*}}{m_{w^*}+m_d} \times 100\ \%\text{mc} = \frac{m_m - m_d}{m_{w^*}+m_d} \times 100\ \%\text{mc} \quad (1)$$

$$w_{mc,dry} = \frac{m_{w^*}}{m_d} \times 100\ \%\text{mc} = \frac{m_m - m_d}{m_d} \times 100\ \%\text{mc} \quad (2)$$

where: m_w* = mass of water and other volatiles determined as the mass loss during drying of a material sample, m_m = mass of the material sample before drying and m_d = mass of the material sample after drying. This method is most widely recognized for moisture determination for its simplicity and fundamentality. However, the duration and the conditions in each part of the process (weighings, handling the sample, heating in an oven, cooling down) affect significantly on the results. Because of differences in water evaporation when heating, water adsorption when cooling, chemical decomposition etc. with different materials, a large number of standardised methods with different heating temperatures and durations for different materials have been set up in industry to obtain acceptable level of reproducibility. A review of LoD methods and relevant standards is presented in [2].

Coulometric Karl Fischer titration (cKF) provides another fundamental approach to moisture determination. When measuring moisture in solids, the titration setup needs often to be equipped with a sample oven. In this case, the method is analogous to LoD but instead of measuring mass loss we measure the actual amount of water evaporated from the sample (n_w) and determine finally the water mass fraction (w_w):

$$w_w = \frac{n_w M_w}{m_m} \times 100\ \%\text{w} = \frac{m_w}{m_m} \times 100\ \%\text{w} \quad (3)$$

Here m_w and M_w are the mass of evaporated water and the molar mass of water, respectively. The uncertainty sources of the cKF method are rather well known but quantitative information on the actual uncertainty contributions is very limited in the literature [3].

There are many other faster and more practical indirect techniques available for measuring moisture in solids in laboratories and on site such as electrical conductance and capacitance, microwave, infrared (IR), nuclear magnetic resonance (NMR) etc [2,4,5]. Most of the methods are highly material specific, and

frequent calibration with representative material samples is needed to obtain the accuracy level needed in the measurements. Certified reference materials (CRM) would provide simplest way to ensure the reliability of a calibration but in terms of moisture range and material there are only a very limited number of CRMs available [6]. Therefore, the calibrations are usually performed by comparing an instrument reading with the corresponding result of LoD analysis from measurements of parallel samples taken from a process. Surface moisture meters are calibrated using samples with homogenous moisture distribution although large moisture gradients are characteristic to the surfaces of interest.

3 Methods

3.1 Moisture measurands and unit realisations

To investigate and demonstrate the feasibility of water mass fraction as an unambiguous measurand in moisture measurements several primary realisations were developed and validated and compared to each other. At the Centre for Metrology MIKES of VTT Technical Research Centre of Finland Ltd (VTT MIKES) and the Danish Technological Institute (DTI) new primary standards were set up by combining LoD in well controlled environment with hygrometer-based and water-trap-based water vapour detection, respectively. Figures 1a and 1b show the schematic diagrams of these primary standards.

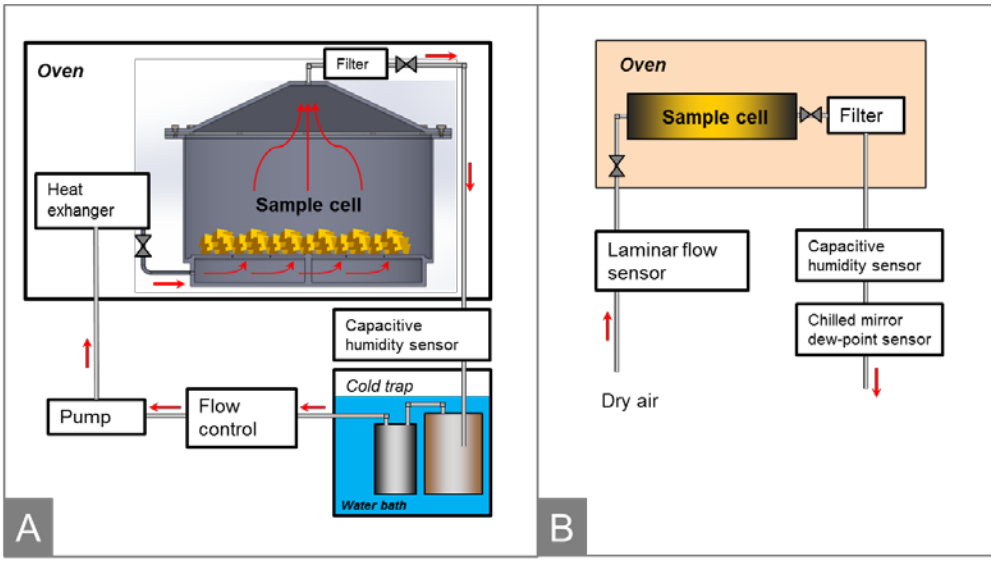

Figure 1: Schematic drawings of the primary standards for water mass fraction developed at a) VTT MIKES and b) DTI. The balances used for weighing the sample cells are not shown in the drawings.

The primary realisation at the National Physical Laboratory (NPL) is based on a commercial evolved water vapour analyser in which a sample of max. 2 g is flushed with dry nitrogen during heating and the

evaporated water is determined with a phosphorus pentoxide humidity sensor. By careful characterisation of the water vapour detection and each component in the analysis process, requirements for a primary standard were fulfilled. University of Tartu (UT) carried out a comprehensive uncertainty analysis for a commercial cKF titrator equipped with an oven sample processor. More detailed information about these realisations is published elsewhere [7-11].

Three inter-laboratory comparisons with different types of materials were carried out with these new primary realisations and with LoD and cKF methods at several other national metrology institutes, i.e. Istituto Nazionale di Ricerca Metrologica (INRIM) in Italy, Instituto Nacional de Tecnologia Industrial (INTI) in Argentina, National Institute of Metrology (BRML-INM) in Romania, National Institute of Metrology (NIMT) in Thailand, TÜBİTAK Ulusal Metroloji Enstitüsü (UME) in Turkey, National Institute for Standards (NIS) in Egypt and Ural Research Institute for Metrology (UNIIM) in Russia. The materials used in the comparisons were: polycaprolactone polymer (about 0.2 %w), wood pellets (about 8 %w), α-D-lactose monohydrate (about 5 %w), calcium oxalate monohydrate (about 12 %w) and sodium succinate dibasic hexahydrate (about 40 %w). The comparisons are reported in full elsewhere [12-14].

3.2 Means to disseminate SI traceability

Three approaches were chosen in this work to develop better tools for disseminating traceability in bulk moisture measurements: 1) searching new reference materials for certification, 2) combining a microwave moisture sensor with a material sample stabiliser and 3) developing a new moisture analyser operating in a wide frequency range from radio frequencies to micro waves. Detailed information about these developments are given elsewhere as indicated below.

The NPL primary standard was used to study candidate reference materials. Based on these studies three of the materials were selected for certification [15]. In addition, the candidate materials were also studied in one of the inter-laboratory comparisons.

To enable usage of a wide range of materials in validations and comparisons demanding moisture measurement applications, a portable system was developed at INRIM in which constant ambient conditions for a reference material are maintained during transport. A microwave sensor was developed for carrying out the comparative measurements on site [16].

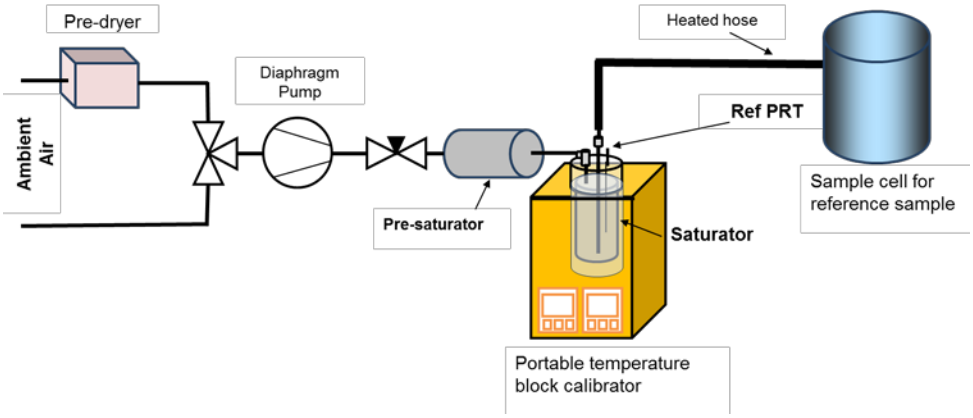

Figure 2: Schematic drawing of the system developed by INRIM for maintaining a reference sample in stable ambient conditions.

To reduce the material sensitivity in moisture measurements, Centre Technique des Industries Aérauliques et Thermiques (CETIAT) designed a new instrument that measures complex permittivity of a moist material by using radio-frequency wave and microwave at a low energy level [17, 18]. The system comprises a Virtual Network Analyser (VNA) and two non-resonant and broadband measurement cells: the capacitive one (Figure 3a) covers the frequency range 1MHz to 400 MHz while the coaxial cell (Figure 3b) operates in the range 200 MHz to 5 GHz. The instrument was validated at CETIAT and tested in one of the inter-laboratory comparisons.

A: B:

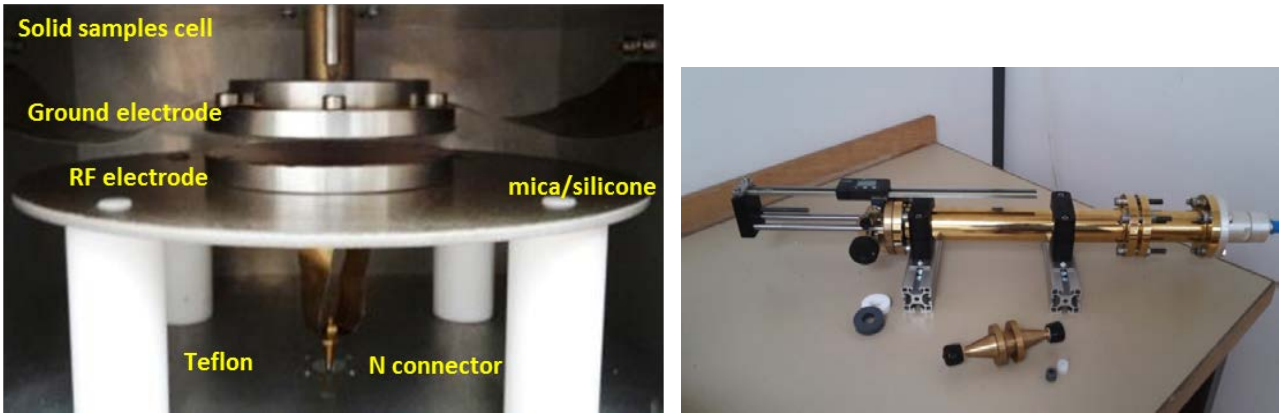

Figure 3: Photographs of the capacitive (A) and coaxial (B)measurement cell developed by CETIAT.

To achieve improved representativeness of surface moisture meter calibrations, a new calibration system was developed at University of Ljubljana (UL) [19]. By controlling ambient conditions in opposite sides of a material layer, moisture gradient close to the surface can be controlled (see Fig. 4). The performance of the system was analysed by simulation in cooperation with Università degli Studi di Cassino e del Lazio Meridionale (UNICLAM) and by experiments in cooperation with UME.

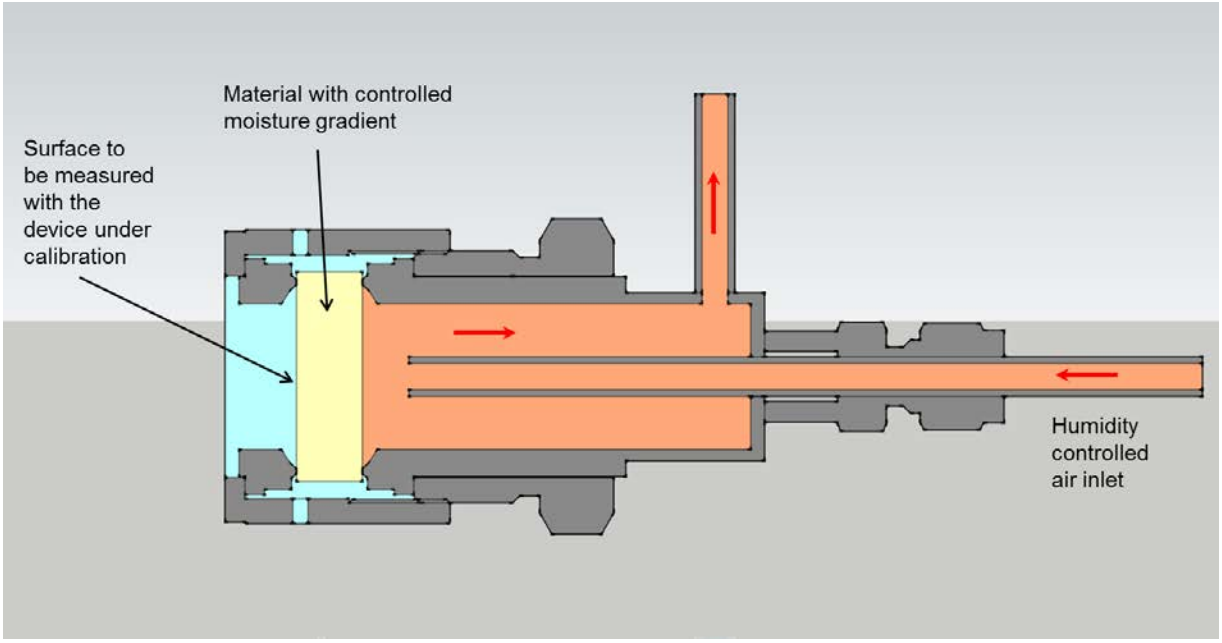

Figure 4: Schematic drawing of the calibration system developed at UL for surface moisture meters.

3.3 Uncertainty estimation methods

Uncertainty analysis methods applied in moisture measurements are mostly insufficient for establishing SI traceability. Estimating moisture gradients and their contribution to the measurement uncertainty is very challenging. For the purpose, numerical simulation methods and software were developed and validated by UNCLAM, INRIM and DTI [20]. Another challenging error source is the effect of handling and transporting samples. This was studied experimentally with wood and paper materials in several cases by BRML INM, Czech Metrology Institute (CMI), INRIM, NIS, UME and VTT MIKES [21, 22].

Comprehensive uncertainty analyses were carried out for the primary realisations and the other LoD and cKF methods used in this work. These were compared within the inter-laboratory comparisons.

4 Results

4.1 Equivalence of water mass fraction measurement techniques

Figures 5 to 9 summarise the results of the inter-laboratory comparisons. Although multiple results are shown for most of the measurement methods, each result within single comparison was obtained with different measurement equipment.

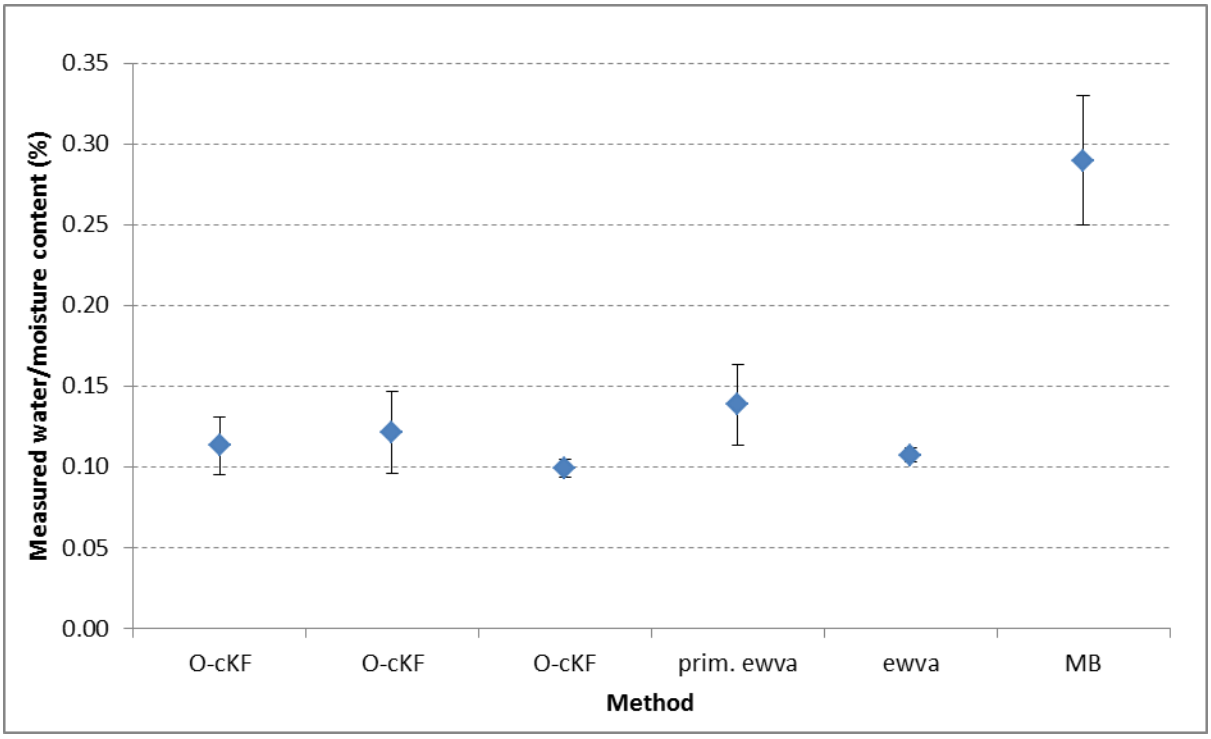

Figure 5: Results obtained with different methods in the inter-laboratory comparison with polycaprolactone polymer. Each result was derived with different measurement equipment. O-cKF = coulometric Karl Fischer titrator with oven, prim. ewva = the NPL primary standard, ewva = evolved water vapour analyser, MB = moisture balance. Error bars show estimated uncertainties at about 95 % confidence level.

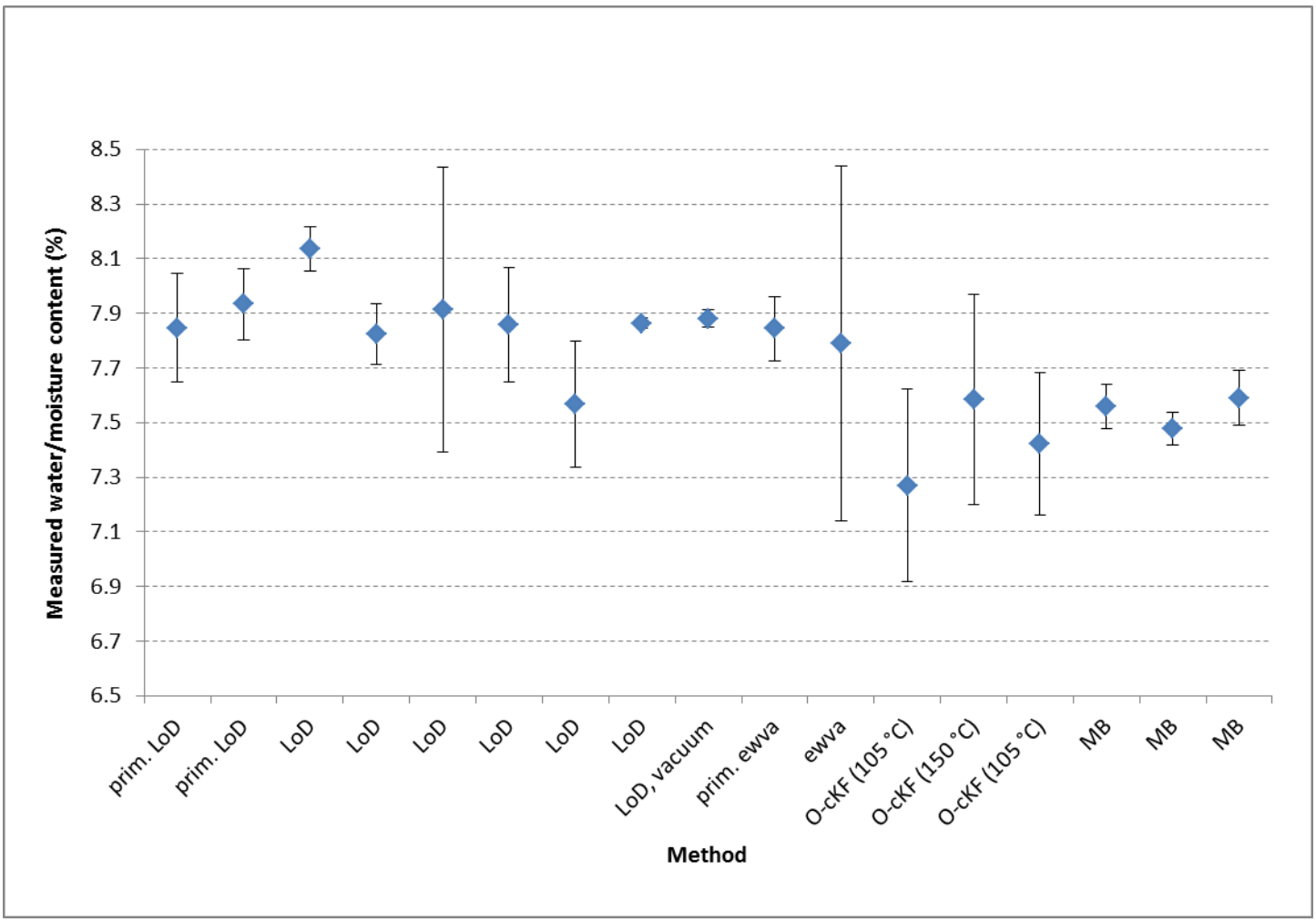

Figure 6: Results obtained with different methods and instruments in the inter-laboratory comparison with wood pellets. O-cKF = coulometric Karl Fischer titrator with oven, ewva = evolved water vapour analyser, LoD = oven drying system, MB = moisture balance. The primary standards are indentified with ‘prim’. Error bars show estimated uncertainties at about 95 % confidence level.

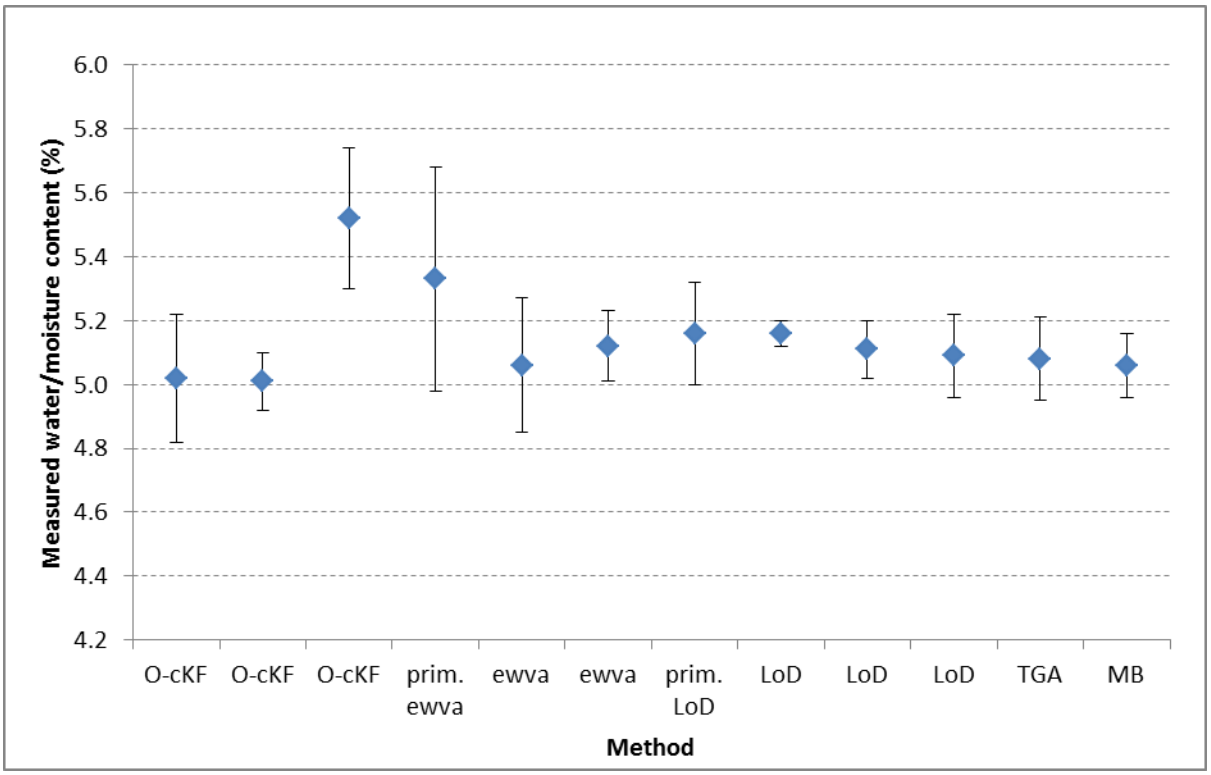

Figure 7: Results obtained with different methods in the inter-laboratory comparison with α-D-lactose monohydrate. Each result was derived with different measurement equipment. O-cKF = coulometric Karl Fischer titrator with oven, ewva = evolved water vapour analyser, LoD = oven drying system, TGA = thermogravimetric analyser, MB = moisture balance. The primary standards developed in this project are identified with ‘prim’. Error bars show estimated uncertainties at about 95 % confidence level.

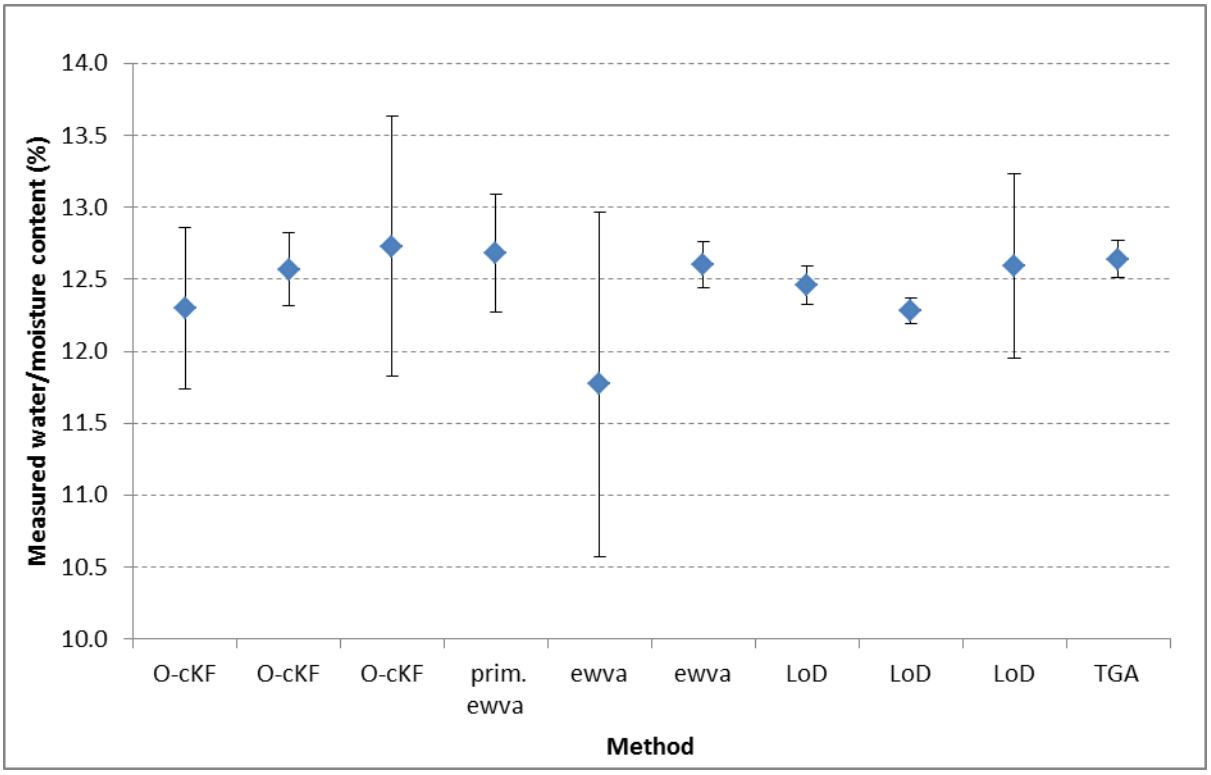

Figure 8: Results obtained with different methods in the inter-laboratory comparison with calcium oxalate monohydrate. Each result was derived with different measurement equipment. O-cKF = coulometric Karl Fischer titrator with oven, ewva = evolved water vapour analyser, LoD = oven drying system, TGA = thermogravimetric analyser, MB = moisture balance. The primary standards developed in this project are identified with 'prim'. Error bars show estimated uncertainties at about 95 % confidence level.

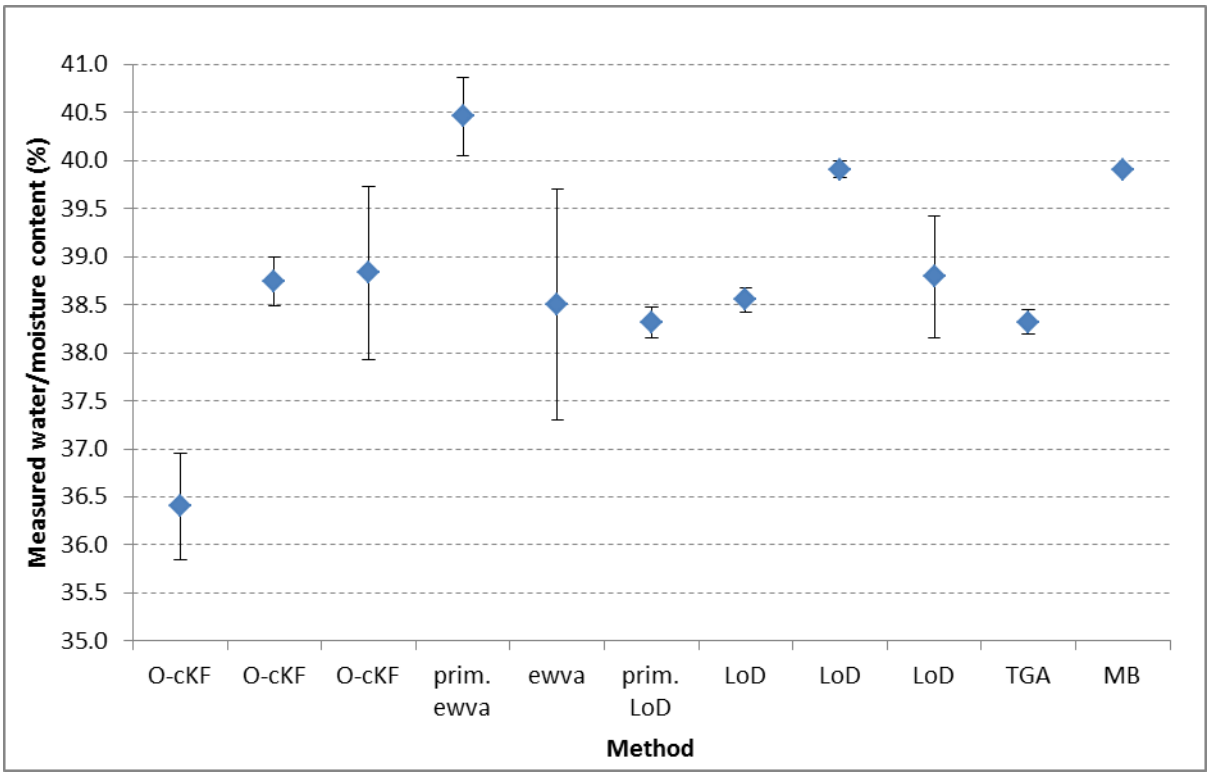

Figure 9: Results obtained with different methods in the inter-laboratory comparison with sodium succinate hexahydrate. Each result was derived with different measurement equipment. O-cKF = coulometric Karl Fischer titrator with oven, ewva = evolved water vapour analyser, LoD = oven drying system, TGA = thermogravimetric analyser, MB = moisture balance. The primary standards developed in this project are identified with 'prim'. Error bars show estimated uncertainties at about 95 % confidence level.

The inter-laboratory comparisons showed that in general, the measurement results of different materials with different water contents are in a good agreement, indicating a good equivalence of the techniques. LoD measurements were not successful with the polymer samples due to very low moisture level and possibly non-aqueous volatiles but cKF and ewva showed a good agreement. The agreement between water specific and non-water specific methods indicate low concentrations of non-aqueous volatiles in the pellets and powders used as the sample materials. With wood pellets, cKF tends to show lower water mass fraction due to short heating time. However, cKF results with better agreement can be achieved by measuring at several oven temperatures and modelling water release and decomposition in the sample [23]. The result 'O-cKF (150 °C)' in Figure 6 was obtained applying this method while the result 'O-cKF (105 °C)' on the left was measured using the same titrator. The results of the sodium succinate dibasic hexahydrate water content measurements from the different laboratories were found be more scattered than the other two powders. This is thought to be due to two reasons: one is that all of the water in the material was not completely detected, indicated by measured water content values below its theoretical hydration level. Secondly, it appears that in addition to water, this material contains other volatiles or decomposes during the sample heating which makes the results different for water specific and non-water specific measurement techniques.

4.2 Effectiveness of developed means to disseminate SI traceability and estimate uncertainty

All the materials used in the inter-laboratory comparisons showed good stability. Extensive tests for the three powders show that they are suitable for certification [15]. The inter-laboratory comparison results demonstrate the feasibility of disseminating SI traceability using the new reference materials after certification.

Validation tests carried out for the transfer standard instruments developed at INRIM and CETIAT show that these instruments provide better reliability in wide ranges of water content and materials than achievable before in validations and comparisons of reference moisture equipment [16, 18].

Experimental validations of the numerical simulation method developed by UNICLAM demonstrated its usefulness in estimating moisture gradients drying applications and surface moisture measurements (an example is given in Fig. 10).

The studies on the effects of handling and transporting samples demonstrated well the importance of these effects on the reliability of moisture measurements. Because of the dependence on exposure times and ambient conditions, the net effect is often observed as deviation in analysis results but also drift type effect can be observed. Exposure to ambient air should always be minimised. In transport and storage, it is most important to use well sealed containers or bags with high resistivity to water permeation. Despite efforts to minimise the effects, they cannot be omitted from an uncertainty analysis. Main tool for quantifying changes in the water content of a sample is weighing a sample container with and without the sample. However, it should be noted that also non-aqueous volatiles may contribute to the mass change during handling the samples. On the basis of the studies on sample handling and transport, a good practice guide was written [24].

5 Discussion

The cooperation within this work demonstrated the importance of well-defined quantities and units. As people from very wide range of industrial and scientific fields are involved with moisture measurements, terms and notations have large variation. As far as reporting measurement results is concerned, the ambiguity of moisture content due to volatiles is one problem. For example, the term ‘water content’ is more specific than ‘moisture content’ but it may refer to mass or volume based quantities and to dry or wet basis. Therefore, in this work we used water mass fraction as the primary measurand because it is unambiguous and well defined in terms of a SI base quantity (mass). Mass fraction is also included in the SI brochure published by BIPM [25]. As moisture results are most often reported in terms of percent, there is a great danger of confusion between estimates and relative uncertainty values. Therefore, symbol ‘%w’ is used for the unit of water mass fraction. The METefnet consortium has prepared a recommendation document on the definitions of quantities, units, symbols and terminology for moisture measurements. This will serve as a basis for further work in the international metrology community and wider to obtain generally accepted principles of SI traceability in moisture measurements.

The METefnet project has shown that with a European initiative significant advancement can be achieved in a metrology field with highly fragmented expertise and resources. For providing efficient metrology services to European industry, a coherent moisture metrology infrastructure is needed where national metrology institutes and designated institutes specialise in different subfields of moisture measurements but collaborate closely with each other.

6 Conclusion

The major outcomes of the METefnet project are summarised in this paper. For establishing SI traceability for moisture in solids, two new primary standard systems were constructed, an evolved water vapour analyser was upgraded to a primary standard instrument and a coulometric Karl Fischer titrator with sample oven was thoroughly analysed. To provide appropriate tools for disseminating SI traceability, new reference materials and transfer standard systems for moisture, a calibration method for surface moisture meters, methods and tools for estimating uncertainty were successfully developed. The inter-laboratory comparisons show that the uncertainty estimation methods applied by the participants are appropriate and an uncertainty level of 0.2 %w at 95 % confidence level was achieved with the primary realisations of water mass fraction.

This work provided solid basis establishing SI traceability in moisture measurements with the water mass fraction as the primary measurand. Further work is needed to provide more efficient methods for industrial measurements. Wide international cooperation is needed to obtain generally accepted principles of SI traceability in moisture measurements and internationally recognised measurement capabilities at national metrology institutes for moisture in various materials.

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