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Needs for NMS support for measurements of moisture in materials

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Department for **Innovation, Universities** & **Skills**

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ABSTRACT

Measurement of moisture content of materials is important in diverse areas of industry and research. This study reviews background information on the current state of moisture measurement, particularly measurement traceability and calibration. Evidence has been gathered from users and suppliers of moisture measuring equipment; university researchers; relevant groups across NPL, LGC, and overseas NMIs; and other UK and international experts as appropriate. User needs for NMS support for moisture measurement are reported. Recommendations are presented along with details of the plans for future work at NPL. These include contributions to NMS projects in the NPL Materials area, where moisture measurements can have some immediate impact.

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1. INTRODUCTION

1.1 Applications and needs for moisture measurement

Moisture adversely affects many materials and products in their dimensional stability, mechanical strength, microbial activity, corrosion and other chemical stability, handling characteristics, thermal properties and more. This affects thermal efficiency of buildings, and product quality in foods, pharmaceuticals, agriculture, solid and liquid fuel, concrete, timber, chemicals and materials processing. Moisture is critical to the performance of many materials, particularly coatings and adhesives, and hence reliable moisture measurement can be key to innovation in a wide variety of areas. Despite widespread interest in measuring material moisture content, there is a limited measurement traceability infrastructure currently in place.

The measurements needed vary significantly. In simple cases, the quantity of interest is average or bulk moisture content. In other cases it is surface or near-surface moisture. Some users would like to measure moisture profile in a material, and real-time changes in moisture profile, which are far more challenging to measure.

1.2 Previous study

In 1998 the NPL report “A study of the requirement for standards for the measurement of moisture in solid materials” [1] was published. The aim of the study was to find whether existing calibration practices, measurement traceability and documented standards meet the needs of industries that make these measurements.

Industrial sectors and major users of moisture measurement at that time were identified. Calibration arrangements were assessed by interviewing representative companies from these sectors and assessing how satisfactory they were and the commercial impact more accurate moisture content measurement would have.

Certified reference materials and user education were felt to be the areas that would improve the accuracy of moisture content measurements of those asked the most.

The previous study concluded that a way forward to a calibration service for instruments at NPL could not be identified at that time, due to the fact that calibrations are in most cases material specific. The recommendations made by the report included publicising the availability of certified reference materials among the UKAS accredited laboratories, the provision of further reference materials for the main industries that could benefit, encouraging instrument suppliers to provide realistic statements of uncertainty for use with their instruments and raising awareness of moisture content measurement issues amongst users and standards committees.

1.3 Background to project

The purpose of this report is to establish current background information and user needs in moisture content measurement as a case for National Measurement System (NMS) support. Projects have been identified in the NPL materials group which have relevant

moisture applications which would benefit from the support of a new measurement capability. A review of the current calibration and measurement techniques in use in UK industry is to be conducted to see what benefit a new capability at NPL providing traceability to moisture content measurements would have.

1.4 Study Methodology

A literature review was conducted of technical developments, published standards documents and trade association guidelines in the field of moisture content measurement since the last report was published.

Users and suppliers of moisture measuring equipment; university researchers; relevant groups across NPL, the Laboratory of the Government Chemist (LGC), overseas national measurement institutes (NMIs) and other UK and international experts were surveyed in a consultation process which sought to gain an understanding of current moisture content measurement requirements. The measurement techniques and calibration activities now in use in the various sectors were also examined.

The fields of plastics, composites and powdered materials are considered in some detail, as these are the areas within the NPL materials group that could immediately benefit from measurements of moisture content of materials.

Information was also gathered from training courses run by Mettler Toledo and TA Instruments, from the conference TAC 2008, and in passing from numerous contacts.

It should be emphasised that the study only addresses a selection of users and applications in this field, where the measurement needs are numerous and diverse. The general level of interest expressed was overwhelming, and it has not been possible to document all contacts and issues here.

1.5 Structure of report

Section 2 reviews the moisture content measurement techniques currently in use and looks at the technologies that have been developed over the past decade. Section 3 explains the methods of calibration employed for the instrument types described previously and how traceability for the measurements made is obtained. Section 4 details the consultation process that took place and analyses the results obtained from the survey questions asked. Section 5 summarises the requirement found by the consultation and Section 6 suggests immediate recommendations for improved accuracy in moisture content measurement. Finally, Section 7 describes the future activities planned at NPL in working towards the development of a traceability infrastructure to support reliable moisture measurements across research and industry.

2 MOISTURE CONTENT MEASUREMENT TECHNIQUES

Techniques for the measurement of moisture in solids can be classed as “absolute” (direct) or “inferential” (indirect) techniques. The absolute techniques of moisture measurement found to be in use in 1998 by the previous study [1] included distillation, Karl Fischer titration and thermogravimetric analysis. Indirect techniques in use at that time included electrical conductance, electrical capacitance, near infrared reflection (NIR), radio frequency and microwave absorption, neutron moderation and nuclear magnetic resonance (NMR). The measurement limitations and applicability of these techniques is described below along with techniques for moisture content measurement that have been developed in the last 10 years.

2.1 Terminology

In the conventional definition, “moisture content” does not consist exclusively of water, but may include other volatile substances which are not separately distinguished by a given measurement process. This convention has arisen because of the measurement and calibration methods that are considered to be “standard” for this area of measurement. When referring exclusively to the water present, the term “water content” may be clearer. However this term was not found to be adopted in any of the industries surveyed. This report adheres to the general usage of the term.

When expressing or interpreting values, care must be taken to distinguish between percentage moisture content and percentage of value. For instance, at a moisture content of 15 %, a change in moisture content of 3 % corresponds to 20 percent of value.

When considering water content, certain measurement techniques only detect the “free” water in a sample and consider this to be its moisture content. In other techniques the moisture content measurement is of both “free” and “bound” (physically or chemically) water because of the way the sample has to be prepared for measurement, or the physical principle behind the measurement. More advanced techniques are able to make separate measurements of the amount of free and bound water in the sample.

2.2 Absolute (direct) moisture content measurement techniques, calibration and associated problems

Although not infallible techniques, absolute measurements currently provide the highest level of accuracy available in moisture content measurement. Inferential (non-absolute) measurements can be referenced or checked against absolute methods, by applying both measurements to the same batch or sample of material, and comparing the results.

2.2.1 Traditional oven “loss on drying” method

A sample is weighed, dried using a separate oven or incorporated heating element above the balance pan at temperatures above 100ºC, and then weighed again to determine the mass of the moisture lost due to heating. Drying temperatures, durations and limits signifying the detection of an “end-point” of the measurement are specified for individual materials either by internal protocols or through following the directions of published standards.

Figure 1: Moisture Analyser, balance with incorporated infrared heating element.
Source: Sartorius

Moisture content through loss-on-drying methods can be defined as a percentage of its wet mass “wet basis” or dry mass “dry basis” :

$$\text{Moisture content “wet basis”} = \frac{m_w}{m_m} \times 100\% = \frac{m_w}{m_w + m_d} \times 100\% \quad (1)$$

$$\text{Moisture content “dry basis”} = \frac{m_w}{m_d} \times 100\% = \frac{m_m - m_d}{m_d} \times 100\% \quad (2)$$

where: m_w = mass of water, m_m = mass of moist material and m_d = mass of dry material.

Calibration of balances using reference weights gives traceability to oven loss-on-drying moisture content measurements.

It is thought that this technique measures the amount of “free” water being driven off but oven drying may drive off an unspecified amount of “bound” water as well leading to uncertainty in the result. Other volatiles in a sample may also be driven off upon heating or interfere with the driving off of water, creating uncertainty as any mass change observed may not be solely due to water loss.

Measurements can take minutes, hours and in some cases days to complete.

2.2.2 Gain on wetting - moisture diffusion coefficient determination

An alternative absolute use of calibrated balances is to determine the gain in mass on wetting of a dry sample as it is subjected to saturation by different environmental conditions, enabling a moisture diffusion coefficient of the sample to be determined. Combining the gain in mass information with the conditioning time of the sample allows moisture diffusion coefficients to be experimentally determined. These experimental values are often used to validate diffusion models that can then be used with confidence to theoretically predict material properties in future simulations.

A specimen is dried down to constant mass within specified limits prior to the conditioning of the sample. Repeated immersion of the sample in the conditioning environment takes place with mass measurements made at regular intervals. Once saturation of the sample has been deemed to have been reached (there is no further gain in mass within specified limits) the sample is dried again until constant mass is obtained. There are often discrepancies observed between the initial and final dry mass values that are due to the effects of water or baking causing the chemistry of the sample to change through phenomena such as leaching and carbonisation.

This information is important to manufacturers of materials who have to specify design values in the fields of construction, plastic and composite materials.

Measurements can take days or even weeks depending upon the material's properties and the limits defining when constant mass has been reached.

2.2.3 Thermogravimetric analysis (TGA)

Thermogravimetric analysers make measurements of mass loss as a function of temperature in order to evaluate the composition of samples. Thermogravimetric analysis can also be used to monitor the gain in mass of a sample if left subject to ambient conditions.

Top of the range thermogravimetric analysers have a balance capacity of less than 1g, a sensitivity of 0.1μg and a dynamic measurement range of around 100mg. More typical instruments in use have a higher capacity of around 100g and sensitivity of 1μg. Examples of analytical laboratories using this technique exist in the fields of pharmaceutical, polymer and organic / inorganic material production.

The principle behind thermogravimetric analysis (TGA) lies in the balancing of a sample and reference pan hung from either end of a beam with a central pivot. A current is applied to keep the balance steady, ensuring even heating of the sample in the surrounding furnace. The heating rate can be controlled such that it will slow down when the thermogravimetric analyser detects mass being lost to give a better resolution in these regions. An initial "zero" current reading (no load) is compared to that required to balance the pans when the material under test is placed in the sample pan. The change in current as mass is lost allows a calculation of the moisture content of the sample when comparing it to the "zero" current originally required to balance the empty pans.

As well as providing information about the moisture content in the sample, the content of free and bound water can also be distinguished. The user develops a knowledge of what is responsible for mass loss at different temperatures meaning that oven drying temperatures can be established for different materials. Thermogravimetric analysis can also be coupled with a mass spectrometer or Fourier transform infrared spectroscopy (FTIR) for improved sample qualification.

Reference materials are used to characterise thermogravimetric analysers providing a form of calibration, sodium tartrate dehydrate being commonly used. Manufacturers have also developed their own weight loss standards. [2]

Temperature as well as mass calibration is required for traceable thermogravimetric analysis measurements. A thermocouple is used to measure the sample temperature which has to be located close to the sample, how close is open to interpretation from the user.

Problems can occur when a dry purge gas (N_2) is used with samples bearing a large free water content as this can serve to saturate the gas causing additional initial weight loss not due to the furnace.

Measurements can take minutes or sometimes up to an hour or two to complete.

2.2.4 Karl Fischer Titration

Karl Fischer titration is most ideally suited to measuring moisture content of liquids, but can be applied to finely ground solids (and, in fact, to gases). Ground-up samples are stirred into a liquid reagent chemical mix, so that the water is taken up by the reagents. Titration is carried out, with a reaction which converts the water present into sulphuric acid and hydrogen iodide. The end point, when all water has reacted, is detected from a change in either voltage or current between electrodes immersed in the liquid. The process is almost entirely automated in many commercially-available instruments. These are divided into two variants; volumetric and coulometric. In the coulometric method the titrant chemical is produced by electrolysis, for convenience and accuracy.

This method generally requires grinding and pre-weighing of samples and, as for gravimetric analysis, these potentially carry uncertainties which must be borne in mind. It is also important to consider how completely moisture can be transferred from the ground sample to the reagent mixture.

Karl Fischer titration can perform sensitively even down to very low moisture contents. For samples containing more than 1 mg of moisture, manufacturers claim uncertainties of 0.5 % to 1 % of result, although this figure would not include any allowance for uncertainties particular to handling solid samples (see section 3.2). Some suppliers offer reference (liquid) samples for calibration purposes. The moisture content of the reference material is verified by the manufacturer through thermogravimetric analysis and Karl Fischer titration of the sample batch. In some cases these are traceable to a NIST CRMs alcohol of certified water content (NIST SRM 2890).

Problems with Karl Fischer titration involve actually getting the water content out of the compound matrix. If this is possible then it is a very accurate technique. This can

prove to be problematic for products that are poorly soluble in the reagents used. Solvents of different kinds can be used to better release the water from samples. It is necessary to monitor titration curves to ensure all the water in the sample is detected completely.

Some materials are incompatible with this type of analysis, being strong oxidising or reducing agents or chemicals that react with the Karl Fischer reagent.

Karl Fischer titration has sometimes been found to give different moisture content results to loss-on-drying methods as it detects bound as well as free water in a sample.

More efficient and reproducible results are obtainable if automated sample changers are used in conjunction with Karl Fischer titrators, enabling up to 13 samples to be titrated in unattended operation. The samples are automatically transferred into a temperature-controlled oven from where the evolved water is transferred to the titration cell via an applied gas flow.

2.3 Inferential (indirect) moisture content measurement techniques, calibration and associated problems

2.3.1 Resistance

Meters or probes which use the resistance of the measured material derive values of the moisture content present through a conversion factor inbuilt into the device at manufacture. The conversion factors give a form of traceability as they are calculated from comparison measurements made by the instruments against oven based loss-on-drying type measurements at the point of manufacture.

The resistance scale is set by the instrument manufacturer against traceable standard resistors. A check standard is provided with the instrument that should result in a listed moisture content reading within acceptable limits.

Other conductive substances in the material, for example salts and wood preservatives, can cause errors in the measurements made with resistance probes. Accuracy is also affected by inhomogeneities in the material and the depth to which probes are inserted as surface effects can dominate.

Not considered the most accurate of techniques, resistance probes are used more as a basic indication than an absolute measurement device in the fields of wood, agricultural produce, and building materials.

2.3.2 Capacitance

The dielectric constant of a material increases with increasing moisture content. The use of capacitance techniques to calculate moisture content values from measured dielectric constants of materials is used both online and in laboratories in the agricultural produce, wood and food stuff sectors. These measurements are usually in the microwave or radiofrequency (RF) ranges. They are effective non-contact and non-destructive.

Calibration taking into account material type and particle size allows dielectric constant measurements to be used to give values of moisture content. Two other variables have a significant impact on the dielectric constant of a material other than moisture content: density and temperature. Temperature can be measured and compensated in measurements but variations in density can be a significant problem to accuracy if precautions are not taken to control homogeneity in the sample used. However, researchers have recently made progress in compensating for sample density [3, 4].

The rapid, non-contact and non-destructive nature of these measurements makes them suitable for on-line moisture content measurements in the fields of paper, wood, agricultural produce, foodstuffs and building materials. Microwave based instruments could in theory be used to make moisture content measurements of any non metallic product, providing appropriate calibration is carried out beforehand. Penetration depth depends on the moisture range being measured (the wetter the material, the less penetration).

The measurements are most accurate when moisture is uniformly distributed throughout the sample, without surface moisture or moisture gradients from drying.

2.3.3 Dielectric Spectroscopy

Dielectric spectroscopy is a special case of the capacitance method above. The dielectric properties of a medium are measured as a function of frequency and can be used with the appropriate calibration to convert measurements of permittivity into values of moisture content.

This technique requires calibration for the material under test to be performed in advance. Reference materials of known moisture content used to build up calibration data through comparison of permittivity results against values of moisture content of samples from the same batch determined by oven loss on drying or Karl Fischer titration.

With this technique low levels of moisture content can be detected, down to 0.1 % moisture content of a bulk material. It is also possible to get a through-sample moisture content profile in simple structures, although calibration of this is problematic.

Problems in industrial use can include the proximity of the coaxial sensor to the online materials and the fact that on complex industrial lines, microwave dryers can interfere with the measurement signal. The dimensions of materials and their physical form can prove problematic too as they may change during the course of the measurement. Temperature changes modify the energetic states of the water molecule dipoles, affecting the results seen.

2.3.4 Near Infrared (NIR) spectroscopy

Near infrared spectroscopy shows a strong spectral signature for water and may in some cases be able to distinguish between free and bound water**.** The main technique employed involves measuring the diffuse reflectance of the transmitted signal and is not a measurement of bulk water content as only the first millimetre or two of a surface are

probed. Near infrared techniques are most effective at measuring the moisture content of granular or particulate materials like tobacco, flour, food products, clay, proteins, sugar and pharmaceuticals (tablets and powders).

Figure 2: NIR measurement of food
Source : NDC Infrared

Measurements have been made spanning the entire range from 0 to 100 % moisture content, but usually a smaller range is selected depending upon the application for which it is intended. Instruments are calibrated against Karl Fischer and gravimetric techniques at the point of manufacture. Accuracy is quoted at ± 0.1 % moisture content but this is subject to the application and product type.

Problems involving particle size, fibre concentration and colour of product affecting results have largely been overcome with the higher end of the range instruments now available by making measurements at multiple wavelengths and development of the algorithms used.

A second moisture measurement configuration measures diffuse transmission of the near infrared signal through a product as it passes along a production line. This is used in the quality control of high-density paper (400gsm) and board.

Both approaches are widely used in process control, where the rapid measurement response time is used to alter variables such as production line speed, as well as in laboratories.

In some cases, additional measurements of fat, protein and nicotine in product can be derived from near infrared spectroscopy measurements.

2.3.5 Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance is a non-destructive technique that can be used to determine the moisture content of most materials including foodstuffs, agricultural produce and powders.

The technique determines a through-sample profile of the content and mobility of hydrogen present in the material. Moisture content is proportional to the hydrogen content and the molecular mobility of the hydrogen allows determination of the binding energy of the water meaning bound and free water can be determined separately. The measurement usually involves applying a high magnetic field, and is unsuitable for ferromagnetic materials.

Moisture content traceability comes from comparisons against measurements made from the same sample set to oven loss-on-drying methods.

The content of oils and other volatiles can also be measured provided appropriate calibrations have been completed.

2.3.6 Time domain reflectometry (TDR)

Time domain reflectometry is a non-destructive technique used to measure the dielectric permittivity of soil, grain and other media into which the measurement probe must be inserted.

An electromagnetic wave is generated in a step pulse with a fast rise time, which propagates along the length of the measurement probe. Where an impedance mismatch occurs this causes an electromagnetic discontinuity, which reflects the signal back along the length of the probe. The travel time and magnitude of reflected signals are recorded and used to evaluate the materials dielectric permittivity. Moisture content is inferred from these measurements through empirical and dielectric mixing models relating moisture content to measured dielectric permittivity. Accurate TDR measurement requires material specific calibration. [5]

The principle of TDR can also be applied to measurements using a flanged open-ended co-axial line probe, which generates microwaves and measures the return signal reflected from a sample.

2.4 Progress in moisture measurement techniques in the past decade

Many moisture measurement methods have been incrementally developed in recent years. Other methods are emerging, at the research stage.

2.4.1 Data logging and networking

Across most of the instrument types described in sections 2.2 and 2.3 the provision of software with instrumentation has been a major development since the publication of the previous NPL report. [1]. Instrumentation is now supplied with integral data logging

in many cases and the networking of devices allows data from many measurement sources to be collected together at a central point, more recently wirelessly. This can provide a better overall description of the moisture content of a sample through simultaneous measurements at different points. Measurements of the same sample type made across sites worldwide can now also be networked to enable the results to be centralised in order to provide more accurate calibration data updates to be sent to the instruments.

2.4.2 Dielectric spectroscopy

In the last decade there has been development of calibration equations which are independent of temperature variation, bulk density and granular material type (oats, wheat, corn, barley) [3], [4] so that moisture content predictions can be made without having to generate calibration data for each material or meter type.

2.4.3 Terahertz spectroscopy

Terahertz spectroscopy has been used to measure the water content in pharmaceutical products, agricultural produce [6], foodstuffs and leaves [7].

Terahertz measurement is similar in principle to those in the microwave and RF ranges. Most dielectric materials, such as air, plastic and wood, are weak absorbers of terahertz radiation where as strong absorption is seen in water and moist materials. The benefit of working at terahertz is the potential for high resolution at the millimetre scale, or below. There may be also potential for through sample moisture content.

At present terahertz instrumentation is laboratory-based, relatively expensive and cumbersome, but it is believed that in 5 to 10 years it would become a viable technique for moisture content measurement. This would require development into industrially usable form.

2.4.4 Other techniques

Numerous other approaches are emerging, as evidenced in research journal publications.

Fibre optic sensors for humidity (rather than moisture) have been researched by a number of workers. They incorporate surface features such as a hygroscopic coating, or diffraction gratings, which alter the reflected light signal in response to humidity changes. While optical fibres offer interesting benefits of multi-point or distributive measurement, and non-electrical sensing principle, they are not yet commercially available as hygrometers. Trial work with optical fibres embedded in concrete has shown that they may be usable to measure material moisture content [8].

A non-destructive, non-contact ultrasound measurement technique is being developed for the determination of moisture levels in wood [9]. It is concluded that the technology has great potential to be developed into an automated device, which could be used to control wood drying and sterilisation processes.

NPL is trialling a surface acoustic wave (SAW) technique for measuring near-surface moisture content. If the approach proves viable, this would fill a useful niche in enabling measurement of moisture content in surface coatings.

Other techniques gaining acceptance include spectral soil moisture content measurement from space, and concrete moisture measurements using x-ray absorption.

2.5 Equilibrium relative humidity measurements

Measurements of equilibrium relative humidity (ERH) or water activity (A_w) are widely used in some sectors where they can give some information about the moisture condition of materials. ERH is linked to moisture content of materials (most closely related to the "free" water content), but does not give this information directly.

Air humidity measurements in a sealed environment above the surface of drying screed and floor slabs are used to infer the moisture content of flooring through the principle of equilibrium relative humidity. Humidity measurement traceability is required, as strict standards have to be met for flooring to be compliant. By measuring the relative humidity in the measurement box; after equilibrium conditions have been reached, this value of equilibrium relative humidity is used to provide information about the moisture content of the screed or concrete slab below. Calibration is carried out against saturated salt solutions that will produce known reference relative humidities above them or by comparison against another traceably calibrated RH measuring instrument.

This principle is also applicable to situations where a humidity probe can be immersed in an environment where the temperature and humidity are dominated by the material under test. Examples of this include hoppers full of grain or stacks of paper.

3 CALIBRATION AND TRACEABILITY

The UK has some traceability infrastructure for moisture measurement, but it is limited.

The Laboratory of the Government Chemist (LGC), the UK NMI for chemical measurements, provides moisture analysis using Karl Fischer titration. Although the UKAS-accredited measurement service is available to general customers, the majority of measurements made are for users within the organisation, in support of other work carried out by LGC.

A large number of organisations have UKAS testing accreditation for activities that include an element of moisture measurement. While these must employ measurement traceability as far as it is available, many of these moisture tests are primarily assessed for their compliance with published methodologies, rather than being referenced or checked against physical moisture standards.

Users of traditional "loss on drying" type measurements, obtain traceability through calibration of balances using calibrated reference weights. Additionally, in thermogravimetric analysis, temperature calibration is required to give traceability to the measurements made.

The majority of inferential devices are calibrated by comparison against an absolute method at the point of manufacture and returned to the manufacturers for future calibration checks. Comparison measurements are made on samples of materials similar to those which are to be measured by the instrument that have been conditioned by the laboratory to a range of moisture content values.

3.1 Certified reference materials

Certified reference materials offer a method of checking or calibrating moisture measuring instruments by providing users with ready made samples of specified moisture content levels, with associated uncertainties. They prove particularly valuable for users who are unwilling to take their instruments out of service for calibration. The values of moisture content and uncertainty are calculated from the results obtained from absolute measurements made at various laboratories of samples from the same batch of homogenous reference material. Provided that users follow the storage and handling instructions provided with the materials, it is assumed that the reference value of the material remains true and the users instrument's readings can be compared to this as a form of calibration.

UK supplier LGC Promochem does not advertise certified reference materials specifically for water, but does sell a few certified materials in which the moisture component is stated – sterilised cream, beef/pork meat, processed meat, rapeseed, canned pet food, poultry feed and bituminous coal.

Outside the UK there is some provision of certified reference materials for moisture, but this is limited:

- Producers of certified reference materials are listed at http://www-naweb.iaea.org/nahu/nmrm/nmrm2003/prod.htm#BCR

- NIST certified reference materials for moisture in liquids (various oils and alcohols) http://www.cstl.nist.gov/acd/839.02/environmental.html#table7

- The Institute for Reference Materials and Measurements (IRMM) is the international body focusing on certified reference materials. It hosts the web resource ERM-CRM http://www.erm-crm.org/html/homepage.htm with partners LGC and BAM.

The following certified reference materials with specified moisture contents were found by searching the COMAR database: http://www.comar.bam.de

BCR 302 Crystalline cellulose whose water sorption isotherms (sorbed mass fractions) have been measured at a variety of humidities (referred to as water activities) ranging from mass fraction 2.13 % (over saturated solution of lithium chloride - nominally 11 %rh) to 13.27 % (over barium chloride - nominally 90 %rh). For purpose of checking performance of COST 90 procedure (evaluation of food water activities). Expressly not recommended for use as a calibrant, according to the certificate.

SMRD 2000 Certified fresh meat reference material : lean pork, water, potato flour and nitrite salt. Material has to be homogenised before analysis. Moisture content is

between 68.5 % and 69 % as per ISO 712 (M 01/1). A certified value of moisture content 68.8 % is quoted with an uncertainty of 0.129 g/100g at the *k*=1 confidence level. No inhomogeneity was detected for moisture during duplicate analysis of 30 randomly selected samples at one laboratory. The analytical method used to determine the moisture content was drying at 100-110 °C.

The material is intended for use in the control of instruments and methods in major nutrient and elemental analysis of meat and meat products.

BCR 563 Common Wheat Flour, for use on verifying satisfactory performance of stated methods and instruments. Moisture content 13.95 % with an uncertainty of 0.04 g/100 g at a *k*=1 confidence level. Drying at a temperature between 130 °C and 133 °C and weighing was the method used to determine the moisture content according to ISO 712 (M 01/1). A NIR instrument was used to determine the homogeneity of the moisture content in the flour, assessing "within" sample variability. Inhomogeneity was not detected. It is recommended that the user perform the test of interest on at least 2 independent samples.

RM 84 Acid Casein, suitable for regular performance control in chemical analysis and validation of a laboratory's own methods. Water content is listed as being 9.32 g/100g with an uncertainty of 0.22 g/100g at a $k = 2$ confidence level. Especially for use in protein analysis at high contents.

RM85 Sodium caseinate, suitable for regular performance control in chemical analysis and validation of a laboratory's own methods. Water content is listed as being 6.86 g/100g with an uncertainty of 0.05 g/100g at a $k = 2$ confidence level. Especially for use in protein analysis at high contents.

RM 700 Boiled sausage, suitable for use in regular performance control in chemical analysis as well as validation of a laboratory's own methods. Water content is listed as being 60.66 g/100g with an uncertainty of 0.28 g/100g at a $k = 2$ confidence level.

BCR-446, BCR-447 and BCR-448 Rapeseed of (respectively) low, medium and high oil content, with moisture certified as supporting information for the main quantity certified (oil content). Measurements were made using pulsed NMR. The certified contents of "moisture and volatiles" range between 7.0 g/100g and 7.7 g/100g, with a *k*=2 relative uncertainty of about 1 percent.

Overall, although there are a few certified reference materials available, their applicability is narrow, and some are not intended for use as calibrants for moisture. Certainly, CRMs are not available for the majority of applications. In general they are only available in small amounts.

3.2 Sample preparation and handling

Sample preparation and handling may be the greatest source of uncertainty in using reference materials for moisture content calibration (or indeed in moisture measurement generally). Care must be taken that any batch from which samples are taken is prepared to be as homogenous as possible and that storage temperatures and conditions are consistent with those specified by the procedure followed.

Moisture is easily lost or gained during grinding of samples prior to measurement. Also, for “loss on drying” methods it must be borne in mind that samples with large surface area soak up water again as soon as they come out of the oven. Some estimates suggest that an almost instantaneous regain of several percent of the normal moisture content can be expected.

In connection with both Karl Fischer titration and loss-on-drying methods, weighings may need to be corrected for air buoyancy if the material differs from that for which the balance is "compensated" (usually steel or brass, if anything). In normal room conditions it should be sufficient to assume that the displaced air has a density of 1.20 kg m^{-3} with a standard deviation of 1.3 percent of value or less. However a material such as wood may have a density of only 500 kg m^{-3}, whereas steel is approximately 8000 kg m^{-3}. Ignoring air buoyancy could thus lead to an error of up to 0.2 % in overall mass, which would give an error of 2 % of result in evaluating a moisture content of 10 %. Weighings at temperatures other than room temperature would require different degrees of air buoyancy to be considered.

Some users assess the uncertainties due to the effects of sample handling on moisture content, but this is not widespread practice.

3.3 Other Calibration methods and checks

Reference artefacts are available for some moisture measuring instruments which allow checks of correct and stable operation of the instrument, without relating to values of moisture content.

Reference artefacts are available for near infrared spectroscopy instruments. These are in the form of glasses doped with rare earth metals at varying thicknesses to simulate (nominal) moisture content of matrix materials. They are clearly marketed as stability checks rather than calibrated references.

Wood moisture meters which measure conductivity between electrodes are usually calibrated electrically, using boxes which contain fixed resistances. This is mainly a stability check, although they are marketed as “calibrators”.

3.4 Other aspects of standardisation

There are numerous published standards (ISO, EN and national documents) that define standard methods for moisture measurement or calibration. These go a long way towards harmonisation and quality assurance of moisture measurements, although the protocols differ significantly from one industry to another.

Legal metrology is standardised though the international Organisation for Legal Metrology (OIML). NPL provides the UK technical input into OIML TC17/SC1, which handles standards on grain moisture and wood moisture testing. These have a strong emphasis on pattern approval of instruments.

The International Committee on Weights and Measures (CIPM) deals with moisture

content within its chemical metrology committee (CCQM). There is also some interest in moisture content standardisation within thermometry, in the Humidity Working Group (CCT/WG6). However there have been no inter-NMI key comparisons of moisture content measurements (of materials), so far.

3.5 Keynote presentation on standardisation from TAC 2008

An international authority on standardisation in thermal analysis Roger Blaine (Board member of ASTM International, and Applications manager of TA Instruments) gave a keynote presentation titled: *Regulatory requirements, standard methods and reference materials* at TAC 2008 - Thermal Analysis and Calorimetry 2008 **"**Ensuring Accuracy and Relevance", 1 - 2 April 2008, Teddington, UK.

Moisture is a small part of the field covered by this speaker, but from a US and global perspective, key points for CRMs generally were:

Trends [in reference materials generally]:
- Increasing regulatory requirements
- Many standard methods available (e.g. ASTM International)
- Declining availability of reference materials from national metrology institutes (e.g. NIST, LGC, PTB)
- Growing availability of reference materials from secondary sources (e.g. TA Instruments, Mettler-Toledo)

Industries most affected:
- Pharmaceutical
- Suppliers to the automobile industry
- Large chemical producers
- Analytical and calibration laboratories

Pharmaceutical requirements
- IQ/OQ/PQ (installation qualification, operational qualification, performance qualification)
- Software validation (developed using a structured methodology, tested, supported and escrowed [data secure])
- Regular calibration (annually by supplier or third party, using certified and traceable reference materials).

Automobile industry and analytical laboratories
- ISO 9001 – A General Quality Initiative for Development, Manufacturing and Service
- ISO 16949 – Requirements for ISO 9001:2000 for Automotive Production
    - Section 7.6 Control of Measuring Devices
    - Calibration at Specific Intervals By Services Accredited to ISO 17025
- ISO 17025 – Requirements for Calibration Laboratories - Sections 5.6.21 and 5.6.31 "Wherever possible, calibration materials shall be traceable to a National Metrology Institute"
- A2LA (American Association for Laboratory Accreditation) and EA counterparts
    - Requires accredited organizations to only use accredited suppliers

  - Requires calibration using materials traceable to a national metrology institute

ASTM International goals:
- To have a standard end-use calibration method for each signal generated by thermal analyzers, calorimeters and rheometers.
- To have certified and traceable reference materials available for each standard

Comments on the market for CRMs generally:
- Supply is limited and declining
- CRMs are typically under priced (i.e. fail to cover development costs) also commenting: “Better to have some materials at a higher price than no materials at a lower price”.

Development practices of TA Instruments (TAI) as a leading company in this field:
- No duplication of already available materials
- Priority given to measurements for which there are no reference materials
- Primarily to benefit TAI users (but generally applicable where practical)
- Provide traceability (in addition to certified value) wherever practical
- Work with other organizations (such as ASTM International) wherever practical
- Selection criteria: rank order the development of candidate materials with regard to:
  - Number of retail sales
  - Availability of any (or some) reference materials in this class
  - Ease of preparation

Reference material classes:
- Pure material – property is assumed to be that quoted in the literature (e.g., modulus of spring steel) Quality = “fair”
- Consensus reference materials – property is the mean of a series of measurements made in different laboratories (e.g., oxidation induction time material) Quality = “good”
- Traceable reference materials – property certified by the supplier with processes traceable to a SRM from a national metrology institute (e.g., curie temperature materials) Quality = “better”
- Standard reference materials – property certified by a national metrology institute (e.g., indium melting temperature and enthalpy) Quality = “best”

Overall, this gives a picture of a continuing and widespread need for CRMS (for all types of analysis, not just moisture) and a vision of how this need could be addressed.

4. CONSULTATION OF USERS / SUPPLIERS OF MOISTURE MEASUREMENT INSTRUMENTATION

4.1 Consultation selection process

Those consulted included users and suppliers of moisture measuring equipment; university researchers; relevant groups across NPL, LGC, overseas NMIs and other UK and international experts. A list of interested parties since the last report [1] had been maintained and further leads generated through consultation were followed up. In total around 25 people were interviewed from NPL in fields ranging from polymeric and composite materials to biomaterials science. Approximately 30 external contacts were consulted across industries including construction, food science, pharmaceutical production and instrument manufacture.

4.2 Interview format

Participants in the consultation were contacted by e-mail, telephone and in person and asked to answer questions from a detailed questionnaire. Questions asked included the materials with which the interviewee had experience of moisture content measurement, the techniques they had used, whether there was any method of traceable calibration employed and what the commercial benefits of improved accuracy in moisture content measurement would be to their field of work.

4.3 Summarising the participants of the survey

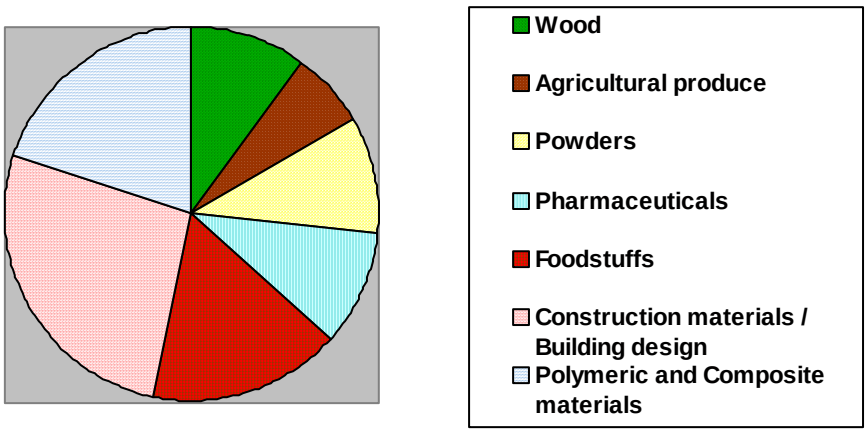

Figure 3: Pie chart showing survey respondents by industrial sector

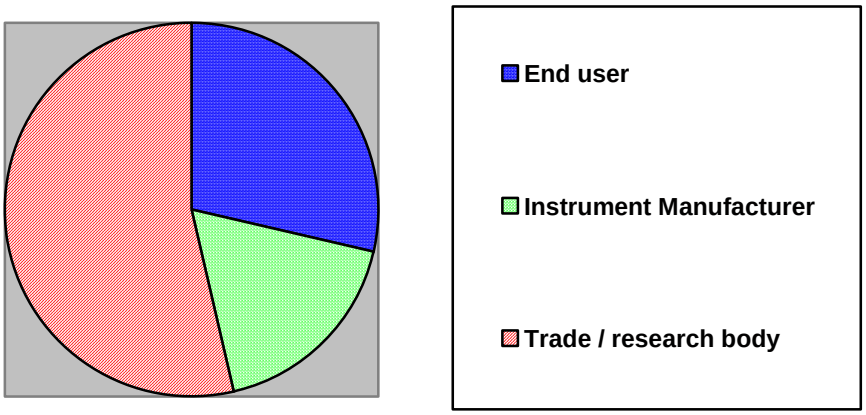

Figure 4: Pie chart showing respondent experience of moisture content measurement

4.4 Moisture in material – how it affects the sector, and measurement types employed

4.4.1 Wood

Moisture content measurements are made on timber in storage to check environmental conditions are not causing rot or similar deterioration in the wood and to detect the point at which it has dried to a workable level. The moisture content of wood is also responsible for dimensional changes, which are an important consideration for many applications. Moisture content measurements of wood in existing buildings are also made again to check that the material is not damp. The moisture content measurements made in building investigation are not very accurate or well regulated. The resistance gauges used are seen as more of a tool for a surveyor than a measurement device.

The moisture content range measurable is between 6 % and 100 % but in practice readings above 30 % moisture content are generally meaningless, as wood has reached its saturation threshold at this point. The uncertainty of resistance moisture measurements in wood is said to be around 2 % of the value measured.

At moisture content levels above 20 % moisture content bio-organisms can start to grow and start damaging timber. At around 30 % moisture content timber reaches the fibre saturation point and all possible bound water is absorbed. Further increases in moisture content are then due to the presence of free water in the timber.

Conductivity type instruments are used to measure the DC resistance of wood between two pins inserted into the material. A scale is developed for a particular wood type with calibration tables for other wood species supplied to correct for other readings obtained. The depth of probe insertion determines whether surface or bulk moisture content measurements are being made. It is recommended that measurements should be made along the grain of the timber.

On line capacitance measurements are used in saw mills where, when employing good practice, workable results can be achieved using the 2 % of value uncertainty in moisture content that instrument manufacturers quote for measurements made with this technique.

Figure 5: Measuring the moisture content of wood with resistance probes
Source: GE sensing Protimeter

4.4.2 Agricultural Produce

Most end users in agriculture require a cheap (less than £1000), rapid and easy to use device for online and at line measurements of moisture content. Near infrared reflectance, capacitance and resistance moisture meters techniques are used in the agriculture industry for this purpose. Microwave moisture meter technology is being tailored for continuous control of the moisture of grain [10].

Grain contracts specify moisture content levels during storage which if not met lead to financial penalties for the farmer. The moisture content of cereals at harvest ranges between 13 % and 19 % depending on the weather in the season. A safe enough moisture content level for drying grain for storage without spoilage is between 9 % and 14 % dependant on grain type. If stored above these levels grain can be subject to quality reduction through microbial degradation, mould growth and mite infestation leading to crop loss. Excessive drying is wasteful and can lead to splitting and cracking of grain and reduced returns for grain merchants. Importantly, it also reduces the profit on sales by weight.

Calibration is performed through comparison of moisture measurements made by the loss-on-drying oven technique with those made by the near infrared reflectance

measurements of material from the same sample set. Measurements of moisture content in flour are said to have been made with reproducibility of ~0.25 % of value and repeatability of ~ 0.05 % of value using the oven drying method.

4.4.3 Powders

The moisture content of a powder affects the flow properties of the bulk material and cracking can occur when the powders are then compacted if moisture levels are not properly controlled. Powdered materials are pressed to form a range of products including metal components, ceramics, bricks and pharmaceutical tablets.

Karl Fischer titration, thermogravimetric and oven loss-on-drying techniques are all used in laboratories to measure the moisture content of different types of powder. Near-infrared spectroscopy and microwave techniques are used for on-line measurement of moisture content in powders.

Near-infrared reflectance does not measure bulk water, just a millimetre or two into a surface and so may not provide an accurate measurement of the moisture content of the powder. Microwave techniques have been suggested for measurement of bulk properties of non-metallic powders in a rapid and non-destructive way [11].

“Green cracking” is defined as cracking in a pressed component before the sintering or firing stage of manufacture. It is believed that any increase in the moisture content of a powder above a specified level increases the risk of cracking.

More accurate moisture content measurement in powders would lead to more consistency of product and less requirement for reprocessing.

It was estimated by one respondent that 80 % of materials in use today start off their lives as powders.

4.4.4 Pharmaceuticals

Moisture control and airtight packaging of pharmaceuticals is of extreme importance as the effectiveness and lifetime of drugs can be affected by their exposure to moisture. When tablets are manufactured from powders, the caking (tablet formation) is related to moisture content in the bulk powder as described above in section 4.4.3.

It is thought that in the area of powder flow in the pharmaceutical industry that there is adequate measurement in place using near infrared reflectance and microwave techniques on-line in place to give information about the product’s moisture content whilst in the dryer.

Powder is sampled after batch drying, prior to tablet pressing. The inlet moisture content of the pharmaceutical ingredients is more than 10 % to 20 %. After processing and drying the product has moisture content between 1 % to 3 %. The moisture content needs to be known as the drying process is stopped once a specified moisture content has been reached. The product is allowed a tolerance of the order of ±0.1 % moisture content of the required value for quality assurance purposes. Those surveyed in the pharmaceutical industry thought their on-line moisture content measurement

requirements were adequately covered by existing measurements of powders using near infrared reflectance and microwave techniques.

If an exact moisture content specification of a product is required then loss-on-drying and Karl Fischer titration type measurements are made. Different moisture content results have been observed between Karl Fischer titration and loss-on-drying methods and this is believed to be due to the wet chemistry method detecting bound water as well as free water.

Freeze dried pharmaceuticals have to be dried to a certain level of moisture content, which is checked by Karl Fischer titration analysis of a sample from a batch during production. Ensuring the product reaches the required level of moisture content during freeze drying is important as it ensures the same state is returned to upon rehydration. Samples may not go back into solution if they are over-dried as hydrophobic surfaces can be formed upon drying. Under drying reduces the period of acceptable storage of Freeze-dried products.

4.4.5 Foodstuffs

Moisture content measurement in foodstuffs can be used to improve the taste, feel and appearance of a product, and is critical for determining legal limits and specifications. As well as being a measure of product quality, moisture content is an important indicator in food safety.

Loss-on-drying type measurements and Karl Fischer titration are used by laboratories to determine moisture content specifications of foodstuffs. The “Dean and Stark” method is an alternative chemical method used for the determination of moisture content in, for example, spices, by distillation and collection of the water. Many laboratories in the UK that employ the loss-on-drying technique for moisture content determination of foodstuffs have UKAS testing accreditation for their measurements which are traceable through calibrated balances. Uncertainties of these loss-on-drying moisture content measurements are said to be less than 0.5 % of value.

The range of moisture content measured in foodstuffs ranges from ~ 1 % (coffee powder and oils) to near 100 % (aqueous solutions - drinks).

Secondary measurements are also made using resistance, capacitance and near infrared spectroscopy techniques. These instruments are calibrated by comparison with absolute techniques. An additional benefit of using near infrared spectroscopy is that wastage of product can be reduced through improved monitoring of constituents (moisture, fat, protein) during production.

Measurement of moisture content is also used in production process control; for example, where extruders are used to make snacks from ground maize. Microwave sensors are built into the walls of the extruder to monitor moisture content.

“Ready meals”, which consist of multiple components, will heat up at different rates in a microwave oven due to differing moisture and salt contents in the constituents.

Figure 6: NIR reflectance used to measure moisture content in crisps
Source : Thermofisher Scientific

4.4.6 Construction materials and building design

In the area of building design, a better understanding of the effect of moisture content in building materials and the relationship between this and the physical properties of the materials over time would lead to improved predictions of building characteristics. Moisture content is a vital parameter when determining thermal conductivity through walls. It would be useful to be able to quantify the moisture content effects on the properties of building materials and incorporate this into testing procedures. This is of enormous importance in the drive for “carbon reduction” to reduce global warming.

The presence of moisture accelerates corrosion of any steel reinforcement in structures. Any damp revealed in inspection of such buildings, is used to prompt the repair or treatment of these areas before serious damage occurs.

Moisture content measurement issues for construction materials begin with proving compliance with a specification at the point of manufacture, giving confidence in the durability and strength of a product. Building materials manufacturers have to quote design values which include thermal and moisture diffusion coefficients. Increased confidence in these values through traceable measurements may provide an edge in the marketplace. A loss-on-drying method for measuring the moisture content of core samples taken from concrete is described by the standard EN 772 [12] Moisture content is not a required parameter to be quoted in the materials data sheet supplied by manufacturers. The moisture content of building materials is not so important at the point of sale; more so once it is in place and subject to environmental effects. A parameter which is quoted on the materials data sheet is dimension change (shrinkage) caused by drying. There are testing procedures that cover this measurement, again in EN 772. [12]

Typically moisture contents in the range 8 % – 12 % are measured in cured concrete and an uncertainty of 10 % of value is acceptable for those making conductivity-type measurements. Moisture content of other building materials ranges from 5 % to saturation in brickwork, and from 3 % to 7 % in insulating material.

In the laboratory, gravimetric analysis of concrete is used to experimentally determine moisture content. When a new concrete structure is being built then conductivity measurement probes can be cast into the material. Wet concrete is a good ionic conductor, which becomes a good insulator when dry. Conductivity measurements in concrete are affected by temperature and the ionic concentration of the material.

The moisture content of existing structures can be measured by drilling holes and inserting probes which are then backfilled with mortar. A problem is that this may measure the moisture content of the mortar rather than the structure of interest. A cavity can be drilled into a structure and an automated sensor inserted and left to take humidity measurements, which can be used to infer the moisture content of the materials through the equilibrium relative humidity principle (see section 2.5).

The moisture content of wet concrete is measured at the plant during manufacture but there is currently a lack of measurement taking place to ensure this level remains the same at the site upon delivery.

Concrete must dry to a certain level before screeding and certain roofing materials can be laid on top of it. Screed must also have dried to an appropriate level before flooring is laid on top of it. This measurement is traditionally made through ERH measurements, which can take a long time to provide stable readings (mainly because of the slowness of the curing process itself).

Uncertainties of around 10 % of value are considered acceptable in moisture content measurements concerning structural health, as the measurements (in difficult situations) are more about moisture distribution than accuracy. Ultimately a customer requires a lifetime prediction of the structure under test, which is made from a combination of measurement data and theoretical modelling.

There is currently a lot of research into flood-resistant materials and the need for more airtight, low energy buildings to which moisture content measurements will contribute important information.

4.4.7 Polymeric and composite materials

Increased moisture content in a polymer can lead to loss of molecular weight, loss of electrical insulation properties and the potential for mechanical failure due to environmental stress cracking. When samples are under tensile stress, moisture uptake increases as cracks and defects are opened up allowing more moisture to be absorbed. Increased moisture content reduces viscosity of polymers by a factor of 100 as it cuts polymer chains making the materials flow more easily.

Excessive moisture during the processing of polymers can lead to hydrolysis, chain scission and foaming in extreme cases. Over-drying can lead to condensation reactions

occurring. More accurate online moisture content measurement during the drying of polymers would give more confidence in the final product and less chance of degradation during processing.

When considering composite materials, moisture within an adhesive is not a problem in itself, rather the ingress of moisture within the interface of a polymer and substrate. This can chemically un-bond an interface and result in de-lamination.

A great deal of the measurements made in this area at NPL are to determine moisture diffusion coefficients of samples through gravimetric methods described in section 2.2.2 using the procedural standard ISO 62 [13]. Diffusion coefficients of materials are dependant upon the conditions they are exposed to.

The range of moisture content measured in materials when making diffusion measurements was between 0 % and 5 % with an uncertainty of 1 % of value. The traceability of these measurements comes through the calibrated balance used and the validated diffusion equations used to predict the moisture content within the layers of composite materials.

It is desirable to be able to measure moisture content as a function of depth in composite sample. Nuclear magnetic resonance was believed to be the only available technique that could profile samples in this manner at present.

The NPL Materials Team, together with a company called Anaglyph, has developed software called Component and Composite Design Analysis (CoDA) which is a design analysis package used to predict properties of composite materials of various geometries (http://www.npl.co.uk/server.php?show=ConWebDoc.1680). It contains a moisture related module allowing the analytical calculation of the rate at which moisture diffuses into a sample of a single material type and designated thickness. Parameters regarding the material's condition must be entered before any calculations are made which enable a moisture diffusion coefficient to be evaluated for the material. The material's properties can be assumed to be the same as those provided with the software (synthetic) or manually entered from the results of experimental data or from manufacturer's data sheets. The software can also predict the physical expansion of a material at different moisture contents.

Limitations of the CoDA software's use when predicting moisture diffusion into materials are that it can only use a single diffusion coefficient and so only works for solid materials of a single phase at present and not composites. Diffusion of moisture can only be predicted in one dimension, "through-the-thickness", and edge effects are ignored. Predictions of moisture diffusion can be made for a material with one side only exposed to the moisture source (considered to be either 100 %rh or immersion in water) or with both sides exposed to the moisture source.

Another software tool, TherMOL 3D has been developed at NPL to model the transient heat or mass transfer through multi-layered and multi-material systems in three dimensions. TherMOL 3D has also been developed for application to inverse modelling problems and adopts optimisation methods and the NPL Grid to reliably determine material and model parameters, aiding the design of new products and improving efficiency in the manufacturing process.

Below is a link to TherMOL 3D online information:

http://www.npl.co.uk/server.php?show=ConWebDoc.1918

The models developed are used to calculate properties of materials, which can then be used in finite element modelling. This aids the accuracy of design when using these materials and is especially useful in the evaluation of properties in situations where these are un-measurable. TherMOL 3D has also been linked with damage mechanics models to predict cracking in composite laminates subject to transient diffusion.

TherMOL 3D is also being adapted to model transient mass diffusion in biomaterials.

4.4.8 Other Measurement needs found during consultation

The following sectors were not surveyed in great detail but were either mentioned as areas where moisture content measurement had a potential to benefit the industry in the future or where it was already sufficiently served by current practices.

Chemicals:

In the chemical testing field there are reported to be no specific outstanding calibration, instrumental or methodology issues regarding moisture measurement. Laboratories appear to be well aware of the "critical points" and conduct best practice routinely including the necessary measures to control these like weighing to constant temperature, temperature profiling of instruments (ovens) and using desiccators to store cooling samples.

Laboratories do not tend to use reference materials for moisture, but participate extensively in UKAS organised proficiency schemes to demonstrate their competence in this area of testing.

Nuclear:

All waste above a certain class of radioactivity has to be stored in a retrievable manner, and monitored. Measuring moisture content accurately would enable the nuclear industry to better understand the behaviour of stored radioactive waste and the properties of the concrete encapsulating the waste stored in steel drums over time. This would increase confidence that the nuclear waste in storage is safe.

The difficulties of practical measurement of moisture content either inside a drum or of the surrounding concrete depend on the intensity of the radiation. The constraints include: strict exposure limits for workers; radiation damage of various types that can affect sensors and all electronics; the need for radiation screening where possible (while still sampling); the need for in-service checks or calibrations. The conditions pose challenges even to methods such as microwave absorption and neutron moderation, which are among the more robust non-contact methods.

Biomaterials:

Biomedical applications of moisture measurement in advanced materials include the following:

The moisture content of soluble stitches could be measured so that their lifetime could be more accurately determined. The solubility is tuned through the composition of the polymers used.

Plastic bone screws degrade inside the body, which is problematic as currently this occurs from the core outwards rather than the outside in, leaving a hollow structure rather than encouraging bone growth. Degradation products are also released by the bone screw into the body. Improved measurement of the composition of the bone screws prior to insertion and in vivo would help this problem. A better understanding of bone screw materials would lead to a more durable, fit for purpose product - meaning fewer repeat operations for patients.

Biocompatible polymers are used to coat cochlear ear implants providing an impermeable barrier around the implant. Moisture content and permeability are important.

Theoretical modelling of moisture transfer - the biomaterials group at NPL looked at the diffusion of cultures through the gels in which tissue scaffolds are encapsulated using the TherMOL 3D software tool.

Energy:

The moisture content of coal can effect how much energy is required for firing and can be controlled if monitored. Moisture can cause problems with pulverised coal when it is used as a fuel as clumping can occur causing blockages.

Improved online measurement of drying effects in production lines can reduce energy wastage, through avoiding over drying of products.

Use of bio fuels at low temperatures is highly dependent on moisture content and an upper limit of 0.05 % (500mg / kg) is specified by an international standard EN 14214. [14]

Surface coatings sector:

For hard, wear-resistant coatings, moisture in the coating is not an issue as they are effectively impenetrable, but moisture on the surface can cause problems. Moisture ingress occurs with more porous coatings. Coatings that are semi-permeable (resistant to ingress, but not trapping moisture when it does permeate) are generally preferable in most applications.

The Paint Research Association (PRA) conducts research into coatings for wood, masonry and metals. They are currently conduct permeability determination of coatings rather than (quantitative) moisture content measurement. The tests follow the ASTM Standard D 1653 “Determination of water vapour permeability”. [15]

Below is a link to the PRA permeability testing procedure :

http://www.pra-world.com/technical/testingphysicalpermeability.htm

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The Paint Research Association do not make measurements of the moisture content of the coating itself, although this was of some interest to them.

Tobacco:

Product quality and bulk handling properties of tobacco are affected by moisture content, which may be raised to as much as 50 % for certain stages in its processing, before reaching a final moisture content of around 12 % to 13% once dry. If tobacco were drier than this it would fall out of cigarettes and if it was any wetter then staining of the cigarette paper would occur.

There are strict requirements by HM Customs and Excise who rate the taxable value of the tobacco and tobacco products, which are assessed by weight, taking into account moisture.

Measurements are made using loss-on-drying laboratory methods and near infrared spectroscopy online. Near infrared spectroscopy is accurate enough for current moisture content measurement requirements where the main interest is in checking consistency of product and can also give information about the nicotine content in the product.

There have been instances in the past where a proficiency test has been carried out with a set of samples sent across those in industry making moisture content measurements to check the consistency of results. However a certified reference material in the field is said to not be available and would prove beneficial.

Electronic Components:

Barrier materials are applied to electronic circuitry to prevent moisture coming into contact with sensitive electronic components. This is achieved by one of two methods: by building a “brick” of polymer material around the sensitive components or through the use of a conformal coating. Conformal coatings have advantages that they can be removed to allow repairs to the components inside and are good at dealing with cyclical environmental conditions but they do allow a larger degree of moisture permeation than the “brick” method.

Organic Electronics:

Encapsulation of devices is used to prevent damage to components through oxidation with cathode materials being particularly sensitive to water and oxygen. Normally encapsulation is effective enough when using glass substrates but there is an increasing demand for flexible substrates and encapsulation materials.

Improved moisture content measurement accuracy in this field would allow more quantitative characterisation of different substrate and encapsulation materials used when making organic electronic devices (for example lighting, displays, photo-voltaics

and transistors). There is particular interest in the determination of water diffusion rates through flexible displays made through layering different materials.

4.5 Common technical issues in survey findings

Sampling was widely quoted to be the main difficulty in achieving reliable measurements. In some cases, the problem was said to be that the bulk material is inhomogeneous. In other cases, it was sample handling that introduced errors.

Sample conditioning, where it is necessary, may be complex. It is not easy to ensure that the moisture content is uniform in a material, or that the moisture profile of a sample in the laboratory is as it would be in a natural environment.

There was no clear definitive absolute technique found for moisture content measurement, since the preferred method depended on the material under test and whether a measurement sought to be able to differentiate between free and bound water content. Where both techniques were employed some users trusted the results of Karl Fischer titration over gravimetric techniques and vice versa.

When making loss-on-drying measurements problems arise when trying to weigh hot samples directly from the oven as this generates convection currents on the balance. Cooling the sample in an open laboratory leads to adsorption of water taking place into the dry sample causing erroneous results. A common technique used is to put the dried sample in a desiccator with silica gel at the bottom and allowing it to cool before weighing at room temperature.

Although most participants surveyed considered moisture content to mean just the water content of a sample, rather than the content of water and other volatiles, it was conceded that with the oven loss-on-drying technique it was impossible to differentiate between the two when mass loss was observed.

Those using indirect measurement techniques tended to be happy with the accuracy with which their measurements could be made, as absolute accuracy was not as important to them as relative values and consistency of results.

Reference materials were found to be of great use for end users in sectors for which they were available, allowing calibration and equipment checks to be carried out without having to take instruments out of service. As long as the handling and storage instructions that the materials are supplied with were followed, users felt that the results achieved could be compared to the certified values of moisture content with confidence.

Where a standardised procedure was available for measurement of a particular material type these were still open to a certain amount of interpretation by those following them and a user dependency in results was observed in many instances.

4.6 Technical issues and problems found from the survey specific to particular sectors

4.6.1 Wood

There are still no authoritative wood species tables in existence for use with resistance-type instruments. As an example, one manufacturer provides a “Timber Species Group Table” which lists corrections for readings from wood types that fall outside those from the standard scale. Tables in existence are specific to each country and instrument manufacturer.

Within species of wood there are differences seen in moisture content measurements using conductivity-type instruments, as the properties of timber vary depending on the environment in which trees are grown. If grown near to the sea, salt in the air can be absorbed and increase the conductivity.

Temperature changes the resistance of wood, and there is no authoritative reference data for this relationship. Recommendations from manufacturers include making a correction of + 0.5 % moisture content for every 5 °C below 20 °C and -0.5 % moisture content for every 5 °C above 20 °C. These corrections are only stated as approximate values. Water-borne preservatives are also said to cause over-readings of 1 %-2 % in moisture content.

4.6.2 Agricultural Produce

Discrepancies in the measured moisture content in grain have been observed when the procedural standards of two different countries were followed at the same laboratory. This could cause disputes in international trade. Worldwide standardization of the procedure followed when measuring moisture content in grain using the loss-on-drying oven technique was considered highly desirable.

The Home-Grown Cereals Authority (HGCA) published a report and practical user guidelines on the subject of maximising the accuracy of moisture meters in 2008 [16], [17]. This report includes comparisons between capacitance and resistance moisture meters with the reference values found by following the oven drying routine reference method ISO 712 [18] of a ground grain sample.

All probes and capacitance meters measure whole grain samples, whereas resistance meters require a ground sample of grain. The extent to which a sample is ground prior to measurement can cause errors in readings. Readings were found to be lower by 1 % moisture content when grinders with a worn mechanism were used to prepare the grain. [16]

Figure 7: Grain moisture meter with grinder
Source : HGCA

When using meters, farmers are told to allow a safety margin for any moisture content measurement of ±0.5 % as errors of this magnitude were frequently observed between meter and oven readings. Errors were seen to be even larger than this in very wet, very dry and freshly harvested grain. There is greater variability in the moisture content of freshly harvested grain than with grain that has been stored for some time.

Sufficient time must be allowed, for both meters and probes, for equilibration with the temperature of the grain to be reached before a stable reading can be expected.

4.6.3 Powders

Experiences of Karl Fischer titration to measure moisture content in powders found that it was expensive and too time consuming to prove useful for the powder processing industry. Problems with at-line measurements of powders centre around making sure the small sample being measured is representative of the large amount of material on-line.

4.6.4 Pharmaceuticals

When making exact moisture content measurement of a product using loss-on-drying techniques, problems encountered include operator dependency due to how an individual followed a procedure. Individual company procedures are developed specifying drying time and temperature recommendations. These factors, along with the balance type used, can cause differences to be observed in the same measurements made at different production sites across the world.

Charring observed on the balance pan during moisture content determination using loss-on-drying instrumentation with an incorporated heating element can be a sign of potential loss of organic matter. This contributes a source of error to the mass measurement made.

4.6.5 Foodstuffs

An operator dependency in loss-on-drying results is again observed. In the more automated microwave heating loss-on-drying methods this is less apparent.

Traceability and uncertainty are not major concerns for many foodstuff moisture content measurements, rather reproducibility of results and compliance with regulations. Any calibration method can be used, as long as it has been agreed by the parties interested in the measurement, for example trade partners.

The Campden and Chorleywood Food Research Association (CCFRA) run a workshop "Principles of Near Infrared (NIR) Analysis" which covers the measurement principles and calibration techniques of near infrared spectroscopy when applied to cereals and milled produce. (http://www.campden.co.uk/training/cmb7.htm)

One user spoke of reference materials such as meat or baby food which are made up on their site. A 50-100g can of product is opened and put into sealed pots. These pots remain useable for about 3 weeks if stored in a fridge. From their experience of regular drift and quality control checks, the product in the unopened can remains stable for around 3-4 years. Certified reference materials of various food types can also be purchased from establishments such as NIST and LGC Promochem and can be found on the COMAR database (though only a few are moisture CRMs). (See section 3.1).

4.6.6 Construction materials and building design

Accepted values of thermal and moisture diffusion coefficients for materials used in building design are, in general, taken from test reports written as long as 40 years ago and have not been verified since. Measurements at NPL of a typical wall (brick-cavity-airbrick-plaster) saw a 20 % difference in experimental values of thermal and moisture diffusion coefficients compared to those calculated theoretically using the accepted values.

Hygroscopic absorption causes the chemistry of some building materials to change. Moisture can cause a chemical reaction in a material and sometimes carbon dioxide is taken up by the sample as a by-product of this causing a change in mass which cannot be separated from that due to a change in moisture content.

For a meaningful calibration of a conductivity type instrument it would have to be calibrated using a reference material identical to that of the product that was to be measured. Within products of the "same" material there will be variations throughout in density of material composition. The reference materials used are conditioned for several weeks at controlled temperatures and humidities for several weeks until they are assumed to have equilibrated. A loss-on-drying method is used to check the moisture content of these materials.

4.6.7 Polymeric and composite materials

This is an area where there are interests in better knowing bulk moisture content, and also moisture profile and diffusion. Where published tests of moisture are employed, some shortcomings are observed. The ISO-62 standard [13] is not very precise about

the drying procedure (“wipe with a clean cloth”) and time period before weighing after drying (“within 1 minute of removal from conditioning environment”) leading to an operator dependency being observed in results.

Leaching can occur when samples are submerged in water: when moisture enters the material, other substances are displaced resulting in uncertainty as to what is responsible for the changes in mass observed.

4.7 Commercial issues from survey responses

Where moisture measurement is used as a parameter for manufacturing process control, improved accuracy would provide faster response times to the point at which the desired level of moisture content in a product has been met. Reducing production process times by as little as half a second can lead to substantial increases in profit margins.

The signal from a gauge can be used to alter variables such as line speed which can save time and money in drying processes. Dryers can be turned off the moment the product has reached the required moisture content level, increasing productivity, reducing product overheating and saving costs in the form of reduced energy use in drying and less requirement for treatment of flue gases. Changes in product moisture content from an expected value can help manufacturers foresee problems with their dryers at an earlier stage and take action in advance before a fault develops.

Moisture content measurements are also used to ensure fair trade in the tobacco, agricultural produce and foodstuffs industries where the CCFRA has, in the past, been called in to check the performance of end users instruments to settle disputes between companies.

5 SUMMARY OF REQUIREMENT FOUND

The main requirements are given in the following paragraphs, and a concise summary of requirements and possible actions is given further below in Table 1.

5.1 Measurement

Many measurement users contacted in this work were highly knowledgeable; but not all are. Workshops and meetings within and across sectors on the subject of moisture content measurement would enhance knowledge transfer of best practice and problems encountered amongst end users and trade bodies. Instrument manufacturers in attendance would be able to make the end users more aware of the options that other available technology may offer them when making moisture content measurement. It would be valuable to provide answers to technical enquiries, such as being able to recommend instrument types suitable for applications e.g. within NPL’s scope of giving technical advice.

Good practice guidelines such as that produced by the Home-Grown Cereals Authority [16] for measurement of moisture content in grain would be beneficial for end users if produced for other sectors.

Proficiency tests within industries could be conducted, with artefacts or reference materials being circulated amongst companies to test the consistency of the measurements being made. This would prove of more immediate benefit to some sectors than the provision of a calibration service for the measuring instruments themselves. Where procedural standards used to measure moisture content appear to differ between countries, or simply between methods, it would be valuable to have clarification.

Industries could benefit from instrument manufacturers providing more realistic estimates of the uncertainty associated with using their equipment. NPL may eventually be able to help with uncertainty analysis in the form of consultancy or with repeatability and reproducibility measurements.

Within NPL, a moisture measurement capability could support other NMS projects in the Materials Team.

5.2 Calibration

Unless universal methodologies for calibration can be devised, any calibration service for an instrument has to be material specific, making it difficult to provide an all-encompassing solution. However a “universal” reference material or materials would be highly desirable, if that could be achieved

Many of the sectors surveyed said that they would benefit from reference materials made specifically for the products they worked with.

It would aid some process measurement industries if the reference materials supplied were in large enough quantities such that they could flow down the production line, giving a calibration in situ, relevant to the actual measurement situation.

For some types of measurement, a facility for calibrating moisture-measuring instruments would be a valuable way of providing measurement traceability

Table 1 Summary of identified moisture measurement needs and possible actions

Measurement need	Possible action
Technical advice/ knowledge transfer on moisture measurement.	Continue to build NMS expertise and outreach. Website FAQs KT club or KTN meetings.
Good practice guidelines.	Could be written and disseminated in collaboration with sector specialists or trade bodies.
Estimates of reproducibility for certain measurements (instruments).	Instrument comparative studies.
Estimates of reproducibility for certain methods (published standards).	e.g. Provide reproducibility data for ISO 62. Similar others.
Support for uncertainty estimation.	NMS Programme knowledge transfer, or consultancy as NPL builds moisture knowledge base.
Measure moisture in coatings / surface layers.	SAW trial measurements, NIR measurements. Cooperation with PRA.
Measure powders to relate moisture to flow-related cracking in green compacts.	Portable at-line measurement.
Measurements of moisture profile, with calibration / traceability.	Develop calibration approaches in cooperation with researchers in relevant techniques (e.g. time domain reflectometry, dielectric spectroscopy, others).
Diverse need for measurements in polymers including several NPL-based NMS projects.	Support through NPL moisture measurement facility encompassing several approaches.
Traceable calibration of instruments for moisture measurement.	Develop reference moisture facility on recognised principle (e.g. loss on drying) or combination of principles. Disseminate traceability.
New moisture reference materials for particular sectors/applications.	Research/development/dissemination of new CRMs collaborating with sectors. LGC Promochem would be logical outlet.
“Universal” or widely applicable CRMs for moisture.	Research of novel CRMs and approaches to harmonising their application.
Equivalence of certain moisture measurement methods.	Laboratory comparative study or round-robin comparative study of standard samples.
Equivalence of results from different labs (e.g. those UKAS accredited).	Round-robin proficiency tests.
Reconcile differences reported between KF and “loss on drying” reference methods.	Comparative studies of two reference methods for different samples.
Reconcile differences reported between published nominally equivalent international standard methods.	Comparative studies of methods on standard substance(s).
Ensure representation of UK interests on international standards bodies.	Working groups of OIML, CIPM, EURAMET.
Harmonise/collaborate with other NMIs.	EURAMET project on strategy for moisture standards.

6 FURTHER WORK

6.1 Actions proposed

Among the items listed, a number are already proposed actions within Project UP10 of the current NMS Materials and Thermal Programme; namely to:

- Build capability at NPL for some basic moisture measurements to consolidate NPL's knowledge base and support existing NMS projects, particularly:
    - To acquire, gain practical use, and study of a selection of moisture measurement instruments and techniques, resulting in an NMS initial capability to make some types of moisture measurement. This will enable recommendations for longer-term work with the aim being to establish routes for traceability through instrument calibrations or the use of reference materials.
    - To execute moisture determinations according to *ISO 62: Determination of water absorptio*n aiming to provide reproducibility data for inclusion in the revised standard
    - Experimental at-line powder measurements (for powder flow for green compacts). These would be desirable for enhanced process control in advanced powder-route materials.
    - There will also be a trial of surface acoustic wave (SAW) technique, (already used to determine mechanical properties of materials and coatings), as a method of measuring moisture content in coatings.
- Represent UK interests in moisture measurement in committees of EURAMET, OIML TC17/SC1, and CIPM CCT/WG6. In particular, a number of other European national measurement institutes are involved in, or embarking on, activity in this area of measurement, and NPL has agreed to lead a EURAMET "Collaboration in research" project to look at strategy for this.

These actions are expected to lead to recommendations for longer-term work.

6.2 Future direction

Ultimately, it may be desirable to establish a greater level of NMS support for measurements of moisture content, supporting measurement good practice and innovation in this field. This would involve some or all of: good practice guidance through publications, events and consultancies, and measurement services such as calibration of instruments or certified reference materials. It would be desirable to promote an emphasis towards "outcome-based" verification (through calibration, checks against reference materials, and proficiency testing) instead of heavy reliance solely on standardisation of procedures.

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