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REPORT

A study of the requirement for standards for the measurement of moisture in solid materials

Stephanie A Bell

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ABSTRACT

This report discusses the needs of UK industry for standards for measurements of moisture in solid materials, and the benefits of providing such standards.

Industrial sectors which are major users of measurements of moisture in solids have been identified. Representative companies in these industries have been interviewed to assess how satisfactory they find existing arrangements for calibration, and what commercial impact this issue has. The needs for calibration traceability, where they exist, are recorded, together with cases where needs might be expected but do not in fact arise. Methods of satisfying these needs are proposed.

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Centre for Mechanical and Acoustical Metrology
National Physical Laboratory
Teddington, Middlesex
United Kingdom
TW11 0LW

Approved on behalf of Managing Director, NPL
by Dr Graham Torr, Head, Centre for Mechanical and Acoustical Metrology

CONTENTS

Page

LIST OF TABLES

LIST OF FIGURES

1 INTRODUCTION

1.1 OBJECTIVE

This report gives an overview of the extent of the requirement in the UK for standards for calibration for measurements of moisture in solid materials. The aim of this study was to find whether existing calibration practices, measurement traceability and documented standards meet the needs of industries which make these measurements.

1.2 BACKGROUND

Moisture content of materials affects their properties in various ways. Properties such as mechanical strength, corrosion, biological action (eg mould), electrical conductance, bulk handling characteristics, and price when sold by weight are just some of the matters which are influenced by the extent and form of water present.

1.3 STUDY METHODOLOGY

Background information was gathered using surveys of market information, published articles and scientific papers, instrument manufacturers' literature, published standard documents (BSI, ISO, OIML, etc.), directories and databases of business and research, and other literature.

The requirements of users were investigated in interviews by telephone or face to face. Those consulted were a variety of users of these measurements, as well as representative trade associations, research organisations, instrument manufacturers and suppliers, and technical officers of UKAS (United Kingdom Accreditation Service).

The study focused on measurements of moisture content in materials, without dwelling on related usage of humidity measurements in air. Although air humidity is of relevance, measurement infrastructure for this is already in place. It is only discussed here in cases when users make this measurement as a poor alternative to directly measuring material moisture content. Moisture content of liquid substances is also not discussed here, although some of the issues for moisture in solids are common to liquids.

1.4 STRUCTURE OF THE REPORT

In what follows, Section 2 gives a detailed background to measurement of moisture in solid materials, including definitions, phenomena related to moisture in solids, and methods of measurement. Section 3 discusses calibration issues and the main reference methods. Section 4 considers the requirements for measurement and calibration of devices, as detailed in various literature sources. Section 5 reports the findings of consultations with parties interested in measuring moisture content of materials. Section 6 summarises the findings and draws some overall conclusions, and Section 7 suggests further actions which should be considered.

2 MOISTURE MEASUREMENT

2.1 DEFINITIONS

The moisture content of a material is normally expressed as a percentage of its dry mass ("dry basis") unless "wet basis" is specified.

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 which 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.

2.2 HOW MOISTURE AFFECTS MATERIALS

The typical moisture content of organic substances in equilibrium with air at 50 percent relative humidity (50 %rh) spans approximately 2% to 30%. However, moisture contents outside these ranges are often found. The issues relating to some particular materials are briefly given below.

2.2.1 Wood

The moisture content of wood governs whether the wood or adjacent materials will suffer rot or similar deterioration. Moisture stability (rather than moisture content itself) is significant for wood in other ways. Most importantly, wood suffers dimensional changes if its moisture content changes. This leads to splitting and shrinkage of the wood, and peeling of coatings.

2.2.2 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, though it is finally much lower. 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.

2.2.3 Chemicals

In the mass-production of chemicals, the chemical reactions and subsequent properties of the materials can be affected by moisture content. Drying processes in this industry often have environmental implications, since solvents other than water may be driven off in large amounts. For pharmaceuticals, the potency and lifetime of drugs can be affected by their exposure to moisture, and physical properties such as caking (tablet formation) are also affected.

2.2.4 Paper

Paper changes dimensionally and in strength according to its moisture content at manufacture and in storage and use. Wrongly conditioned paper becomes visibly puckered. The moisture content of paper surfaces during printing is also critical, affecting the print adhesion and quality of finish.

2.2.5 Construction materials

Moisture is responsible for various kinds of damage in buildings and construction materials. The effects range from cracking of bricks during kiln firing, through efflorescence (build-up of salt deposits) on walls and failures of coverings laid on floor screeds, to loss in strength of reinforced concrete. Bituminous materials need to contain less than 0.1% moisture in their raw state. If moisture content is incorrect, coatings can fail to bond, or can strip away some time after application.

2.2.6 Foodstuffs

Moisture content of foodstuffs can range naturally from 0.01% (in granulated sugar) to 80% or 90% (in freshly harvested forages). This is one of the most critical applications because of exacting consumer demands for product quality, and also for reasons of health and safety. Spoilage (mould and infestation, as well as less serious “staleing”), texture and handling properties, value by weight, cooking properties and many other issues hinge on moisture content.

2.2.7 Agricultural produce

The moisture content of grain and other agricultural produce needs to be monitored at harvest, during storage and when bought and sold. A threshold for spoilage in grain is said to be about 14% or 15% moisture content, subject also to prevailing humidity. The sale of grain by weight also requires measurement of the moisture content.

2.2.8 Other sectors

Drying and baking processes in all industries can benefit from optimisation to the exact level of dryness required. This can allow savings in energy and in handling emissions from these processes. Sometimes monitoring of the humidity of oven gases allows effective control, but in other cases the moisture content of the product is the most useful indicator.

2.3 METHODS OF MOISTURE MEASUREMENT IN COMMON USE

Techniques of measuring moisture in solids may be divided into "absolute" (direct) and "inferential" (indirect) - the latter utilising attributes such as electrical properties which are influenced by water content. The main approaches to moisture measurement, and their applicabilities are shown in Table 1. (Surveys by Slight, 1991; Maley, 1985; and others).

Table 1. Methods of moisture measurement

Method	Range of moisture content ("wet basis")	Uses, restrictions and sampling requirements
Electrical condnctance Current (DC or AC) is passed between electrodes. Pure water and most solids do not conduct - actually measures presence of aqueous solutions.	0 - 25%	Affected by other conductive substances in the material (eg salts, wood preservatives). Surface effects may dominate the results. Accuracy affected by inhomogeneities in the material.
Electrical capacitance between plates or electrodes. (Dielectric permittivity)	0 - 30% (beyond which most materials are conductors)	Conductivity and density of the material affect the measurements. Geometry-sensitive. Particular surface characteristics may affect readings. (Some instruments use insulated electrodes and high frequencies (>10 GHz) to deal with this). Dielectric spectroscopy a developing extension of this field.
Near infrared reflection (or rarely transmission) at "absorbed" and "reference" wavelengths.	0 - 95%	A surface measurement (or with very limited penetration of 2-3 mm). Not generally colour sensitive, but reflective surfaces and very dark materials may be hard to measure. Mainly designed for granular or particulate material.
Microwave absorption	0 - 100% (laboratory) 3 - 45% (on-line)	Sensitive to changes in density and temperature of material.
Radio frequency	0 - 100%	Sensitive measurement. Affected by density and position.
Nentron moderation	0 - 100%	Detects all hydrogen, not just water.
Nuclear magnetic resonance	0 - 100%	Affected by hydrogen present in the sample other than in water (eg in oils). "Pulsed" NMR can be water-specific. Ground-up samples or solid plugs of material.
"Wet chemistry" methods Karl Fischer titration	0 - 100%	Ground material mixed with solvents or reagents for laboratory chemical analysis. Karl Fischer method regarded as "absolute" but there are other chemical methods (eg carbide reaction) which do not have the same standing.
Thermogravimetric analysis by weighing before and after moisture is driven off using conventional oven or microwave heating.	0 - 100%	Measures total volatile content, not only water, so may read falsely high. Oven drying may drive off an unspecified amount of bound water as well as free water. Nonetheless regarded as an "absolute" reference measurement. Normally need ground-up samples.
Distillation	0-100%	Water (and perhaps other volatiles) are driven off and measured by volume, and compared to weight of original substance. Used for materials such as bitumen.

2.4 AIR HUMIDITY MEASUREMENTS RELATING TO SOLID MATERIALS

As an alternative to measuring the moisture content of materials, measurements of equilibrium relative humidity (ERH) or water activity (A_w) are sometimes used. These are effectively the same measurement; a relative humidity recorded when the solid material is in equilibrium with the surrounding air. Sometimes this is carried out by introducing samples (in ground form) to a small test chamber with an integral relative humidity sensor. Otherwise, a relative humidity sensor is simply immersed in an environment whose temperature and humidity are dominated by the material of interest (eg deep in a hopper of grain, or interleaved in a stack of paper.) The humidity of the surroundings may reflect the moisture content, or may affect it, but these methods do not in general indicate the moisture content directly. In some cases it possible to draw an empirical relationship between moisture content and ERH or A_w.

2.5 TYPICAL STATED UNCERTAINTIES OF MEASUREMENTS

Measurement uncertainties vary from method to method and are often highly dependent on the material being measured. It is widely perceived that inhomogeneity of samples is the main limitation in many cases. This view may be influenced by the fact that brochures for moisture content instruments rarely carry any statement of uncertainty or "accuracy" - other than figures for resolution, and sometimes repeatability.

For some instrument types (but not specific to materials), some typical figures quoted by manufacturers are:

Infrared (on-line)	-	"accuracy" 0.5% of instrument full scale.
Infrared (bench-top)	-	repeatability 0.02% to 0.2% moisture content
Karl Fischer	-	" accuracy" 0.3% moisture content

The cheapest instruments (for example those for conductivity-based measurements) tend to carry the least information. On the other hand, perhaps the most detailed and realistic statement was found in a manual for one of the more sophisticated "loss on drying" analysers, which referred to an estimate of errors as "generally less than 10%" [of result].

In most cases, manufacturers' claims are clearly a limited guide to overall performance.

Required levels of performance for measurements are specified to some extent in a few published standard specifications, but generally only the repeatability of replicate measurements is specified, and this is little indication of the overall uncertainty of measurement. Some examples are discussed in Section 4.3.

Intercomparisons, where they are undertaken, can show the reproducibility of measurements, which may be a better indication of overall uncertainty. The results of industry-specific intercomparisons found in the survey are mentioned in Section 5 and beyond.

2.6 OTHER MEASUREMENT CONSIDERATIONS

In almost any manufacturing situation, rapid "real-time" measurements are needed. In aggressive environments, non-contact measurements may be essential. For routine "on-line" monitoring, the possibilities differ from those under laboratory conditions.

Surface moisture content and bulk moisture content are each detected differently. Unless the material is in moisture equilibrium (which is rarely the case) the moisture content will not be uniform. This makes reliable measurement difficult.

There is an important distinction between "free" water present in materials and water which is physically or chemically "bound". Many methods of measuring moisture content cannot distinguish between the two forms. Some recent research has made progress on this distinction, using dielectric spectroscopy, which uses the response in different frequency regions (Gerhardt and Cao, 1996).

Sampling and sample preparation are critical to good measurement. Some measurement methods require ground samples of material. The process of grinding normally heats the material, and also maximises the surface area exposed to the air. Both of these encourage sample moisture losses or gains, and so can lead to unrepresentative measurement results.

3 CALIBRATION

There is little or nothing world-wide in the way of a national measurement standard which can provide conventional traceability for measurements of moisture in solids. Therefore confidence in moisture measurements cannot be simply obtained by traceable calibration in terms of this quantity as would be the case in other fields of measurement.

Instead, heavy reliance is placed on standardised methods in this field. Two main methods recognised as "absolute" are "loss on drying" methods or related "thermogravimetric analysis" (weighing substances before and after drying), and electrochemical determination known as "Karl Fischer titration". These are detailed in the sections below. Instruments can be purchased "off the shelf" for both these types of measurement. Other methods are then calibrated by comparison with these.

3.1 OVEN DRYING METHODS

3.1.1 Traditional "loss on drying" method

A sample is weighed, dried in a separate oven and weighed afterwards. Protocols vary for the drying temperature, duration, sample preparation, detection of the "end point" of moisture loss, and for how the result is calculated. These are specified for individual materials in published standard specifications. (See Section 4.2 below).

Users widely consider this method to be "fundamental" and thus to need no calibration or validation, except for replicate testing in some cases. However it is still susceptible to various kinds of errors as discussed in section 3.1.3 below. The supporting measurements of mass and temperature are easily calibrated in general.

Traditional "loss on drying" measurements generally take many hours, in some cases days, to complete.

3.1.2 Thermogravimetric analysis

A sample is dried in an oven with an integral balance for weighing beforehand and afterwards (sometimes referred to simply as a "moisture balance"). Integral data processing is usually provided which allows monitoring of the process and automation of drying cycles which may be programmed to end after a given time, or when the rate of weight loss reduces to a given low value. Automation aids the consistency of performance of these instruments. However, exact choice of time and temperature profiles, and sample presentation, are said to lead to variations of at least 1% of result.

Calibration of these instruments is normally by measuring substances of "known" moisture content. Sodium tartrate dihydrate (with a nominal moisture content of 15.61%) is one "reference material" used, but it is not clear what degree of recognition it has as a reference material (See Section 3.3, below). Broadly speaking, for samples weighing more than 1 g, manufacturers claim resolution and repeatability of results of several hundredths of a percent (ie several tenths of a percent of result for a sample containing 10% water). The actual uncertainty in measurements would be substantially larger, depending on calibration and on sample handling. Certain instruments of this kind also can be calibrated by dispensing a measured volume of liquid water into the sample chamber.

In general, these commercial instruments are not viewed with the same authority as traditional "loss on drying" methods, but are nonetheless regarded by many users as unquestioned reference methods.

Typically, these measurements take some minutes and perhaps up to an hour or two to complete.

3.1.3 Comments on "loss on drying" methods

Gravimetric analysis is not specific to water. Other volatiles (eg oils) may be included in any measured weight loss, or may interfere with driving off the moisture. Some "bound" water may be driven off with the "free" water, also leading to uncertainty in the result.

Some practical issues affecting the uncertainties involved are (Maley, 1985):- oven temperature; time in oven; size of sample (small samples dry faster); pressure; air velocity in oven; sample distribution; ambient relative humidity; time sample exposed to atmosphere; loss or gain of sample moisture during preparation; possible spillage in oven; balance uncertainty and sensitivity; scorching or chemical decomposition; sample dust "blown away".

3.2 ELECTROCHEMICAL DETERMINATION: KARL FISCHER TITRATION

This method 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 pre-weighing and grinding of samples and, as for gravimetric analysis, these potentially carry uncertainties which must be borne in mind. It is also important to consider the effectiveness of transfer of moisture 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 water, 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, noted above. Some suppliers offer reference (liquid) samples for calibration purposes.

Some materials are incompatible with this type of analysis, for example strong oxidising or reducing agents, or chemicals which react with the Karl Fischer reagent. (Makers' literature gives details.)

The chemical reagents can be purchased ready for use and are generally well enclosed by the instrument assembly when in operation. However, careful handling and disposal are necessary. Traditional Karl Fischer reagent is toxic and highly flammable (flash point 20 °C) and gives off noxious fumes. Modern pyridine-free alternative reagents are available, which are less hazardous.

Measurements of this type may take an hour or two to complete.

3.3 REFERENCE MATERIALS

Certified reference materials offer a method of checking or calibrating moisture measuring instruments. They are particularly valuable where users are unwilling to take their instruments out of service for calibration.

The COMAR international reference materials database lists a limited number of certified reference materials for moisture, which can be obtained from the Laboratory of the Government Chemist Office of Reference Materials, and other chemical suppliers. They are all foodstuffs: four meat products at particular values of moisture content between 60% and 70% (wet basis), and one biscuit product near 3%. They are all available for sale at under £100. Very roughly 50 to 100 of these references are sold per year. At least one other certified reference material is available which was not listed in this database - a flour (approximately 14% moisture) developed under the EC Community Bureau of Reference (BCR) Programme. For the meat and biscuit reference materials, the certificates supplied with them show how the values of moisture content were assigned (from measurements by a large number of laboratories) and estimates of uncertainty are given.

A chemical salt, sodium tartrate ($[CH(OH).COONa]_2.2H_2O$), with a nominal moisture content of 15.61%, is used and recommended as a calibrant by suppliers of commercial moisture balances. Analytical Reagent grade chemical is used, apparently with no particular preparation. Although it is reported to be an effective calibrant, it is not offered as a certified reference material by LGC, and the detailed analysis supplied for the material does not specify the water content, except in the formula. It could therefore depend on the conditions of use as to whether the material was entirely in the form of the first hydrate ($.2H_2O$) or partly in a higher or lower state of hydration - and hence at a different average moisture content. This material also offers only a single value check which is outside the range of interest for some users, and completely outside the range of certain moisture instruments.

Reference samples for Karl Fischer measurements are available from instrument suppliers. However, many users treat this method as fundamental and beyond question. On the other hand, there is some disagreement among authorities in this field about the sources and extent of the uncertainties involved in these measurements.

3.4 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 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”.

3.5 SAMPLE PREPARATION AND HANDLING

Sample preparation and handling may be the greatest source of uncertainty in using the “reference methods” for moisture content. 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 and oven 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). 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%. However the use of a comparative method, using the same balance for weighing before and after drying, greatly reduces the error. 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.

3.6 OTHER CALIBRATION ISSUES

The most obvious way to transfer a calibration from a reference instrument to another instrument would be to replicate measurements of the same sample using different methods. However, attempts to compare one method against another may be intrinsically flawed. This is because absolute methods tend to register other volatiles as well as water, or to measure some or all of the bound water as well as the free water. Some inferential methods may be more specific to free water but need calibration against the absolute methods.

Calibration of surface measurements (such as infrared methods) relies on establishing that the surface and bulk moisture content of the measured sample are equal, before using the sample to compare the readings on two different types of instrument. Infrared measurements may also be specific to a particular colour or range of colours (frequency signature) as well as being material-specific for the usual reasons (volatiles).

It is perhaps because of such difficulties that much reliance has been placed on standardisation of procedures rather than of outcomes. The International Organization for Legal Metrology (OIML) publishes protocols which "standardise" the calibration of wood and grain moisture meters for trading purposes. In other cases, "standard" data, such as tabulated values of moisture content for different wood species (U.S. Department of Agriculture, 1974; 1975), are used for calibration purposes. However, instrument suppliers often give their own preferred values for these data.

4 LITERATURE SURVEY OF MOISTURE MEASUREMENT REQUIREMENTS

Some general information available in the literature is given below.

4.1 MAIN SECTORS REQUIRING MEASUREMENTS OF MOISTURE

Some major industries requiring moisture measurements are given below, in Table 2, together with the estimated value of goods they produced in the UK (variously in 1995 or 1996) (Office for National Statistics, 1998). The relative importance of moisture measurement to each sector is discussed further below.

Sector	Total UK production (£billion) 1995/6
Construction	79
Food and drink	64
Pulp and paper products (excluding printing)	13
Pharmaceuticals	6
Wood and wood products	5
Cereals and grains	3
Tobacco products	2.5
Horticulture	2.0

Table 2. Major industries requiring moisture measurements, and value of goods produced annually.

4.2 MARKET FOR SALES OF MOISTURE MEASUREMENT INSTRUMENTATION

Markets for moisture instruments in the UK are small in comparison to the total size of the markets which depend on the measurements. Nonetheless, the value of the sector is worth noting (and in addition to the UK market, the typical manufacturer exports 60-70% of instrument sales.) Unfortunately, no reliable overall estimate of the market for this specific instrument range is available, except as given by individual companies supplying these instruments. Based on this, rough conservative estimates of some of the UK markets (p/a) are:

Conductivity instruments - (surveying and wood moisture meters) - approx. £2M (but may be falling due to saturation of market)
Grain moisture meters (dielectric type) approx. £3M (falling due to disappearance of the "small farm" in favour of large farms or cooperatives - so fewer units sold)
Near infrared - approx. £1.2M to £3M.

In addition the markets would be considerable for oven-drying instruments and Karl Fischer instruments, although no estimate for these was available. It seems likely that the overall market in the UK for instruments for moisture in materials is of the order of £10M, and that UK exports of these instruments might be twice that figure.

Also, consultancy on moisture-related problems in timber (for example) has an estimated value of about £0.5-1M.

4.3 PUBLISHED STANDARD SPECIFICATIONS

Published standards relating to moisture content are of two kinds. Some standards specify values of moisture content to be achieved in particular materials or processes. For example, BS 5248 Part 2: 1996, states that the moisture content of structural timber must be not above 20% on average, with no single reading above 24%. (This is said to be a fairly challenging specification, not so much because of the difficulty in making the measurements, but because wood does not always easily dry to the required level.). There are a very large number of such specifications covering all types of materials. These originate with standards bodies such as BSI (British Standards Institution), or with bodies representing certain sectors, for example the Building Research Establishment.

More relevant to the subject of calibration and measurement traceability are the published BS and international standards specifying reference methods for measuring moisture. Such standards are widely followed among the industries that make these measurements. A few of the specifications are for instrument designs (for example, OIML R92, for wood moisture meters). However the majority relate to "loss on drying" reference methods and their application to particular materials. For any given material, the ISO and counterpart standards (BS, ANSI, etc.) are often equivalent. However the differences in protocol from material to material are quite marked. Some examples of British and ISO standards for "loss on drying" methods, selected arbitrarily, are outlined below, in Table 3.

It can be seen from the Table that there appear to be arbitrary differences in some of the conventions. There would almost certainly be good technical reasons underlying the exact procedures adopted. The details as shown are concise summaries and therefore cannot give a full picture. However, there are two possible conclusions that could be drawn.

It appears that definitions, at least, vary from application to application. It is therefore important that users and suppliers of instruments using principles other then loss on drying have a clear understanding of what is being measured - moisture content on wet basis, or dry basis, or some other quantity.

Alternatively, the divergences may be taken to mean that measurements in different materials need to be treated as separate techniques. The tests as recommended will have been designed to suit the properties of the particular materials. It might therefore be unnecessary and unhelpful to try to harmonise practices across the different fields.

Table 3. Examples of various protocols for "loss on drying" measurements as given in published standards.

Temperature °C	Dwell time (hours)	Definition of moisture content *	Other points
BS 5752 : Part 2 : 1984 / ISO 1477-1978 Methods of test for coffee and coffee products Part 2. Green coffee : determination of moisture content (routine method)			
130 °C	6 hours drying, wait 15 hours, 4 hours drying	Initial loss plus half second loss, expressed as wet basis	Replicate measurement to agree within 0.3 g per 100 g of product
BS 1715 : Section 2.6 : 1989 / ISO 672 - 1978 Analysis of soaps Part 2. Quantitative test methods Section 2.6 Method for determination of moisture and volatile matter content			
103 °C	Periods of 1 hour repeated until end point when change is <0.01 g in 10 g	Dry basis. "Moisture content" taken to mean water only, not other volatiles.	Replicate measurement to agree within 0.25% of result.
BS 5663 : Part 1 : 1987 / ISO 3087 - 1987 Methods of testing iron ores Part 1. Determination of moisture content			
105 °C	4 hours, followed by periods of 1 hour repeated until end point when change is < 0.05% of initial mass	Dry basis - unless material is initially too wet to sieve, in which case wet basis is used	Instructions are given to correct for rain water (for either case - wet basis or dry basis).
BS 6870 : Section 2.2 : 1987 / ISO 8557 - 1985 Analysis of aluminium ores Part 2. Chemical methods Section 2.2 Method for determination of hygroscopic moisture in analytical samples: gravimetric method			
105 °C	Periods of 1 hour, repeated until end point when change is <0.02% of mass	Wet basis	—

*See Section 2.1 for general definitions.

4.4 LABORATORIES IN THE UK ACCREDITED BY UKAS

There are presently no laboratories accredited by UKAS for calibration of instruments for measurement of moisture in solid materials.

In the fields of testing where moisture measurements are performed, there are many accredited laboratories (UKAS, 1998). For example, there are some 152 organisations accredited for testing of food and food products, 66 for constructional materials directly (plus a similar number in other construction-related testing), 20 for wood, timber and products, 16 for paper and board, and 9 for tobacco.

This is not an exhaustive list, and moisture measurement is in many cases a very small part of their activity. However these would all be users who should be seeking quality assured and traceable measurements, in line with the general requirements of UKAS.

4.5 PROVISION OVERSEAS

Outside the UK, there are two notable examples of countries whose national measurement infrastructure addresses traceability of measurements of moisture content.

In the USA, there are some 12 000 licensed grain merchants making moisture measurements to meet trading standards requirements. By far the majority of these use dielectric methods (radiofrequency or microwave). The United States Department of Agriculture (USDA) maintains national reference standards for grain moisture, using "loss on drying" as the primary measurement. They also run a National Type Evaluation Programme for grain moisture meters. Although in principle this covers many types of measuring instrument, in effect it leads to usage of a very limited set of "approved" instruments. The "working standard" for the Evaluation Programme service is about to be replaced with a different instrument for the first time in 35 years. A representative of the USDA freely admitted that there is "no commonality between the technologies involved" (ie they do not achieve consistent results.) Because of this they find it necessary to implement traceability to the new instrument in stages, staggered for different grain types at different times.

In Germany the system of pattern approval for instruments is more strongly established than in most other countries. This covers moisture meters, and effectively controls which devices can be sold into Germany. Perhaps because of this, a moisture content measurement service for grain at least is offered at national standard level. However this may not practically be any different from measurements carried out at non-national level in other countries, for example in bodies such as the Campden and Chorleywood Food Research Association, in the UK.

Neither of these examples gives a strong model for how traceability of measurements of moisture content might be set up in the UK.

4.6 ACADEMIC RESEARCH

The database of the publication "Current Research in Britain 1998" lists some 83 research projects in UK universities looking into the significance of moisture content in solid substances for various applications. Based on figures for 1996 (65 projects) there is sustained and growing interest in these measurements. It is interesting to note the bodies which fund this work. They are:

Bakery Packaging Service
BBSRC (14 projects)
BNSC
BRE Strategic Research Programme Directorate
British Aerospace Sowerby Research Centre
British Coal Utilisation Research Association
British Concrete Association
British Council
Building Research Establishment (3 projects)
Carnegie Trust
Commonwealth Scholarship Office
Imperial Chemical Industries plc
Khakian and Company, Khakian, Iran
Leica Ltd
Leverhulme Trust
MAFF
Ministry of Agriculture and Agricultural Research Organisation, Iran
MOD (2 projects)
Motor industry
NERC (4 projects)
NORAD/SUA Framework Agreement
Nuclear Installations Inspectorate

Construction Industry (3 projects)
Defence Clothing and Textiles Agency
Defence Research Agency
DOE (2 projects)
DOE Construction Sponsorship Directorate (2 projects)
ECC Ltd
Edward Hall Ltd
Endress & Hauser
EPSRC (6 projects)
European Community
European Union
HEFC
HEFCE (2 projects)
Icelandic Government
ODA
Office of Naval Research
Pakistan Agricultural Research Council
PCFC
Perry Foundation
Rentokil Research and Development Ltd
Rhone-Poulenc Rorer
SERC
Technical Research Centre of Finlaud
The British Library
The Royal Society
United States Golf Association
World Bank

Only one of these projects explicitly addresses standardisation, but the list shows a level of interest across a wide variety of industries, and suggests that there is a degree of technical innovation in this field.

5 SURVEY OF USERS OF MOISTURE MEASUREMENTS

5.1 SELECTION OF INTERVIEWEES

Users of moisture measurements were identified from leads given by instrument suppliers, trade and research associations, UKAS, from the NPL Humidity Club, and other contacts. Some instrument suppliers, and some trade and research bodies themselves participated as interviewees, where they were practically involved in making moisture measurements. Others of these were consulted for general information, but were not surveyed as they were not making measurements. A list of the organisations that were surveyed and those that contributed in other ways is given in Appendix 1.

5.2 INTERVIEW PROCESS

Interviewees were contacted initially by telephone. Some were interviewed fully in telephone conversation. Others were interviewed in person by visiting them at their organisations. An initial checklist was used during the first telephone contact to establish their interest in the subject. Full interviews (whether by telephone or face to face) were carried out using a detailed questionnaire, covering company details, applications, measurement requirements (ranges and uncertainties), reasons behind the requirements, instruments used, sample preparation, arrangements for calibration and any shortcomings found in calibration arrangements, and any savings or commercial benefits in improving these. Notes were also made of any recent and anticipated changes in each sector and its requirement for moisture measurement.

5.3 OVERVIEW OF THE SURVEY

A simple summary of the findings is given in the pie charts in Figures 1-3, below. Some 24 organisations concerned with moisture measurement were consulted, of whom 13 organisations were surveyed in detail selected from sectors as follows:

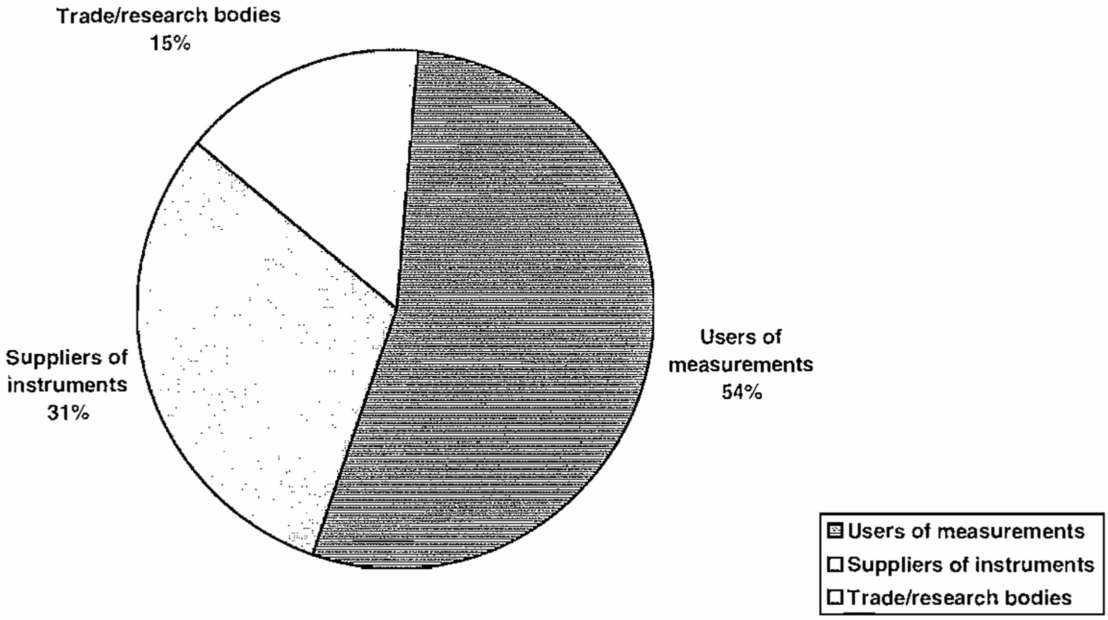

Figure 1. Pie chart showing the different categories of respondents to the survey

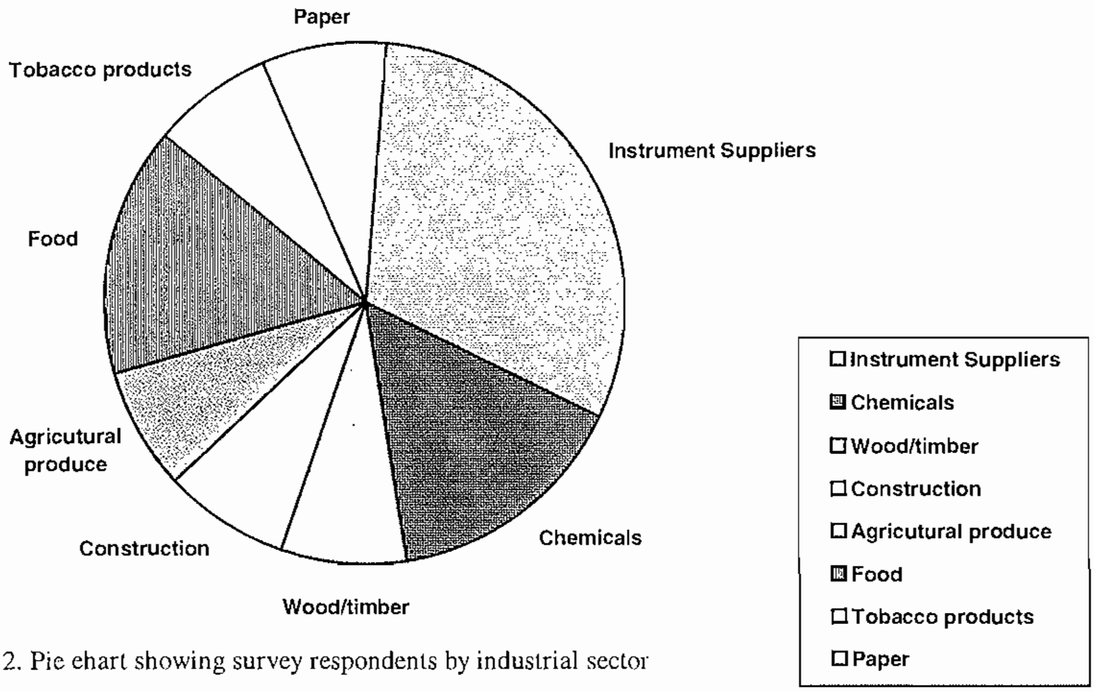

Figure 2. Pie chart showing survey respondents by industrial sector

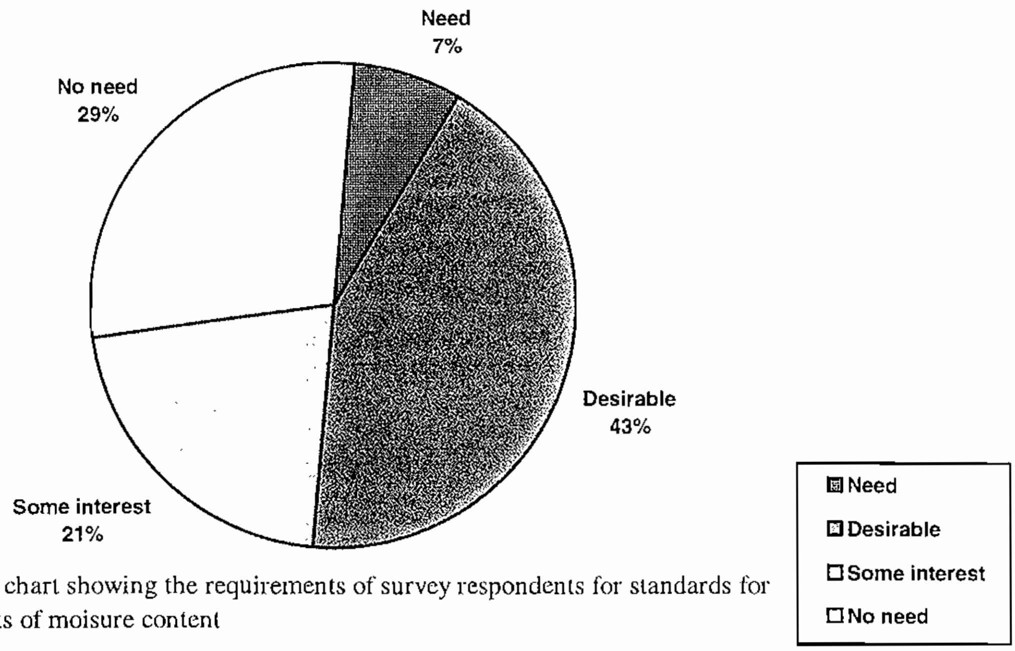

Figure 3. Pie chart showing the requirements of survey respondents for standards for measurements of moisture content

5.4 SURVEY FINDINGS ON TECHNICAL ISSUES

The main technical issues highlighted by responses to the survey were as follows.

The conventional definition of moisture content has an ambiguity which is unhelpful, but the meaning of the term as it is used is generally well understood. Many users are satisfied to have a measure of total volatile content. Others would ideally prefer to identify water content separately.

Most - if not all - methods of moisture measurement need material-specific calibration. In a few cases, (mainly food) certified reference materials are available. In some applications (such as measurements of wood) published data of varying authority are available. In other cases, a few users make their own "relative scales" for materials for which data are not readily available.

The disparity between what is measured by different techniques (eg pure water content versus total volatile content) leads to some doubt about all chains of calibration in this field.

Sampling is widely quoted to be the main difficulty in achieving reliable measurements. In some cases, the problem is said to be that the bulk material is inhomogeneous. In other cases, it is sample handling that introduces errors, although this may be less widely acknowledged.

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 little concern over absolute accuracy (ie achieving the "true value"). Most of those consulted were more interested in consistency of measurement for the purpose of product consistency.

More than one user of commercial "moisture balances" complained of scorching, which was said to lead to unreliable results. In most other cases users did not complain about the limitations of their instruments, except the slowness of laboratory measurements.

Measurements of equilibrium relative humidity (ERH) or water activity (A_w) are widely used where they can give some information about the moisture condition of materials. These measurements have a bearing on moisture content of materials, but do not give this information directly.

5.5 SURVEY FINDINGS ON ISSUES SPECIFIC TO PARTICULAR SECTORS

The degree of satisfaction, and the kinds of problems varied from application to application. For each area, some of the main conclusions are summarised below.

5.5.1 Construction

In some parts of the construction industry, for example in the application of floor screeds, it was reported that only humidity measurements (not measurements of moisture content) were required and used.

In general, monitoring of concrete is undertaken via the air humidity at the surface. However, one report says that actual moisture content of concrete is more important. Differences in moisture content in the range 2-6% while curing can make a difference in compression strength of about 25%. An estimate for the construction industry in Germany showed that the extra quantities of cement used to allow for potential losses in strength had an equivalent cost of almost £100M annually (Kupfer 1997).

Users of moisture testing of bituminous materials by distillation were happy with what they could achieve. In branches of construction where calcium carbide testing methods were used for "field" testing, these were not highly regarded.

5.5.2 Food

Manufacture of foods appeared to be one of the most intensive applications of moisture content measurements, with well informed users. In finished products, the main issues are mould growth and infestation, and shelf life in general. Raw ingredients such as flour arrive with varying moisture content and the ingredient mix needs to be adjusted accordingly.

Near infrared methods of measurement were much used in this sector. Respondents were aware of the limitations, and used reference "loss on drying" and other methods.

The few certified reference materials in existence are for foodstuffs. However interviewees were not fully aware of what was available, or else were working with foodstuffs for which there were no certified references.

One user said that UK/European published standards documents were not really available for finished food products, and they had to follow US standards. The disadvantage in this is not clear, except that the UK has limited influence over US documents.

Possible savings on baking efficiency were apparent although no respondent from the food industry quantified these.

5.5.3 Paper

Equilibrium relative humidity and water activity measurement are widely used in this industry, in line with the requirements in the published standards for paper and paper products. Measurement traceability of ERH and A_w is achieved in terms of relative humidity, not moisture content. Where near infrared methods are used, this is on manufacturing process lines, and the situation is much as it is for the food industry (above).

5.5.4 Chemicals and pharmaceuticals

One company making drying agents and other specialist chemicals reported a need for moisture measurements in their drying process, which they were not yet able to make sufficiently well. While unwilling to reveal exact figures, they said that improvement in the accuracy of measurement by 1% moisture content would save several tens of thousands of pounds per dryer annually, for a large number of dryers, each drying 2 tonnes of product per hour. The savings would come from reduced material and energy costs, and from reduced treatments of flue gas emissions. They had already fruitlessly spent many tens of thousands of pounds on trying to solve the problem in other ways. Humidity measurements in the flue gas were not found to be an effective solution.

It seems reasonable to suppose that energy savings in drying processes are often as great as in this case. Wherever there are associated chemical emissions, then minimising drying processes would also minimise the cost of "gas scrubbing" and minimise the environmental impact of the residual emissions.

5.5.5 Wood and wood products

The timber supply industry is a low-technology area where quality control is not intensively practised. More could be done by raising awareness than by improving measurement techniques. Users of timber have somewhat stricter requirements than suppliers. UK production of wood is growing relative to imports.

In measurements using wood moisture meters, disparities of 2%-5% moisture content do occur, but financial consequences are not clear. Any disputes are usually clear-cut and not due to questions over calibration.

Wood moisture meters must be referred to data for particular wood species. However, there are no authoritative "wood species tables", each country or instrument maker using their own version. In surveying, 60-80 percent of the time the wood species is unknown and can't cheaply be identified (hence the measurement must have an increased uncertainty). Even timber yard designations include several types of wood in a single name.

Standards specifying the required moisture content for constructional wood, and the expected building environment, are not realistic (eg humidity levels are actually lower than those for which moisture content recommendations are valid). This may be partly due to gradual changes in heating and glazing practices, and partly due to formulation of standards so as to ensure they are easy to meet.

The dimensional changes of wood with moisture content are documented (eg U.S. Dept of Agriculture, 1974). Species vary, but a typical equilibrium moisture content of wood indoors at

20 °C and 45 %rh could be 8.5 percent (ASHRAE, 1993). At 24 °C and 70 %rh it might be 13 percent. This should be viewed in the light of the typical shrinkage which can occur - in the above case of 4.5% variation in moisture content a change in volume of some 2.5% would occur for white oak.

The resistance of wood is said to vary with temperature as well as moisture. There is said to be a need for authoritative data for this relationship.

Wood moisture content seems (as far as is understood) to be intrinsically hysteretic: structures in the material hold water differently depending on whether the moisture content is rising or falling. The difference is said to be a fraction of a percent in moisture content.

5.5.6 Cereals and grain

Spoilage is related to equilibrium relative humidity, but the grain market works in terms of moisture content (because this also relates to sale by weight). Moisture content is regarded as an easier measurement. However calibrations of moisture content instruments are material-specific.

The data for particular grains originate with instrument suppliers as well as trade research bodies, and need to be re-evaluated for every harvest. All this lays the authority of the information open to question. However, in an intercomparison of measurements among a number of agricultural users (Brown, 1994), disparities did not generally exceed 1% - but this was not considered a particularly good result by those reporting it.

The moisture profile in grain is different at harvest than later in the laboratory. (While growing, plants supply moisture to the grain from the inside.) One respondent took some measures towards simulating this.

Producers of grain have an interest in selling it as wet as possible (to minimise drying cost and maximise weight sold). Grain merchants have an interest in buying the grain as dry as possible while remaining within specified limits.

A current initiative by the National Farmers' Union to encourage traceability of measurements may soon lead to a stronger interest in this among users.

5.5.7 Tobacco products

There seemed to be few unresolved problems in moisture measurement in this industry. This may be partly as a result of using specialised ovens (developed for this sector by British American Tobacco) for "loss on drying" measurements, together with analytical spectrophotometry where needed. Although tightly regulated by HM Customs and Excise, the requirements for moisture measurements were met through a careful approach to measurements and sample handling. There was a feeling that availability of additional aids such as certified reference materials would not improve much upon the other checks they make using "in-house" reference materials. It was reported that uncertainties were estimated, and were satisfactory. ERH measurements were also used.

The actual values of moisture content found may vary according to exactly which measurement protocol is used: shorter tests result in a different cut-off point and thus show materials to be dryer than a longer similar test. Historically, if not now, tobacco producers felt they could influence the outcome of measurement by their choice of which published standard to follow.

5.6 COMMERCIAL ISSUES FROM SURVEY RESPONSES

It was generally difficult to find clear commercial benefits to improving calibrations of moisture instrumentation. Drying processes were the single notable example, and it is arguable that even this could often be addressed using air humidity measurements.

Industrial users of moisture measurements had either moderate or slight interest in traceability via certified reference materials. They were in general not willing for moisture monitoring equipment to be taken out of service for calibration. They also reported that, for process measurements, waiting times of hours for checks by "loss on drying" methods were much too long.

Those in high-value or high-technology manufacturing processes (such as foodstuffs and specialist chemicals) were more interested in access to better calibrations than those in traditional or low value production (such as timber).

Most suppliers of "high cost" measuring systems felt that recognised calibration certificates would be beneficial. Suppliers of "low cost" instruments in general did not.

Certain respondents cited "sale of goods by weight" as a reason for needing the best moisture measurements. It is true that errors could favour the buyer or the seller, but there would be no net benefit.

Grain moisture meters are subject to pattern approval in Germany and (effectively) in the US. This was felt by some instrument suppliers to amount to a "restrictive practice", or protectionism.

5.7 QUALITY AND CONFIDENCE ISSUES FROM SURVEY RESPONSES

Industrial users of moisture measurements had either moderate or slight interest in traceability for measurement of moisture content. The generally preferred mechanism was through the use of certified reference materials.

Those respondents with experience of measurement traceability in other fields (eg humidity and temperature) particularly felt that it would be beneficial to extend this infrastructure to moisture content measurements. This was sought for quality assurance and customer confidence, though not necessarily on technical grounds.

Laboratories accredited by UKAS reported that the area of moisture content measurement is almost unique in not having any direct route of traceability.

Laboratories accredited for tests including moisture measurement did not find that assessors or customers demanded anything particularly stringent in terms of calibration practices, or as an alternative to measurement traceability.

UKAS technical officers in several fields, including construction materials testing and food testing, felt that existing provisions for moisture content traceability were adequate. However, UKAS points of contact were not fully aware of the availability of certified reference materials for moisture content. Increasing enforcement by UKAS of the requirements of their publication M 3003 (requiring statements of measurement uncertainty for testing laboratories) was reported by laboratories to lead to a requirement for standards for moisture content. Traceable calibrations give laboratories reliable information on which to base estimates of uncertainty.

In general, few users of moisture content instruments had made any estimate of measurement uncertainty in moisture measurements. Most instruments for measuring moisture content were supplied with incomplete information about their uncertainty of measurement, or with no such information. It seems unlikely that most users are aware of the real extent of uncertainties in their measurements.

Suppliers of moisture instruments reported that they were rarely asked for measurement traceability, or for quality assurance recognised though UKAS or similar calibration certificates.

Some instrument suppliers and research bodies felt that standardisation, and the focus it provides, are good mainly because they improve awareness and practices of users of instruments, and so stimulate the business (of instrument supply and measurement) generally.

Where the sale of goods by weight in the UK is the reason for moisture measurement, accurate measurement may add no value but it ensures fair trade.

6 SUMMARY OF REQUIREMENT FOUND

There seems to be a number of technical problems in the field of moisture content measurement. However the commercial implications are hard to identify, other than for instrument suppliers and those others involved in the moisture measurement business itself.

Among those asked, certified reference materials and user education were felt to be the measures which would have most benefit.

A calibration service for instruments does not seem to be feasible technically, due to the fact that calibrations are in most cases material-specific.

A number of those consulted felt that focus groups would be of interest to them.

7 RECOMMENDATIONS

The availability of certified reference materials for moisture should be more fully publicised, for example among the laboratories accredited by UKAS for relevant tests.

The provision of further certified reference materials should be considered, for the main industries which could benefit.

Where purely water content is of interest, approaches to validating or calibrating reference instruments should include calibration with material which has no "bound" water, and also calibration with material which has no "other volatiles". Some practical investigation of suitable substances in these two categories would be useful. This might show a way of providing calibrations without relying on "material-specific" references. Investigation of the properties of sodium tartrate as a reference material might form part of this work.

Instrument suppliers should be encouraged to supply realistic statements of the estimated uncertainties in using their instruments.

A short programme of awareness should be directed at standards committees, to draw attention to conventions in defining moisture content, and to press for realistic acknowledgement of measurement uncertainties. However, it would be unnecessary and unhelpful to force the harmonisation of moisture measurement practices across different fields.

A technical meeting or workshop on uncertainty in measurements of moisture content would be valuable to some users of the measurements. Such a meeting might aim to stimulate awareness of all the practical issues in moisture content measurement, and might help accredited laboratories across a number of fields and other users who need to formulate estimates of uncertainty. It might also aim to bring uncertainty issues out into the open among suppliers of instruments.

8 ACKNOWLEDGEMENTS

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APPENDIX 1. LIST OF INTERVIEWEES

A2.1 SURVEYED IN DETAIL

Able Instruments and Controls Ltd
Allied Colliods
British American Tobacco
Campden and Chorleywood Food Research Association
Central Science Laboratory (formerly MAFF)
Kelloggs
Moisture Systems Ltd
NDC Infrared Engineering
Pira International
Protimeter plc
Raychem
Surrey County Council Engineering Materials Group
Timber Research and Development Association (TRADA)

A2.2 CONSULTED BUT NOT FULLY SURVEYED

AEA Technology
British Leather Centre
Building Research Establishment
Laboratory of the Government Chemist
Maurice Levitt
Ove Arup
The Home Grown Cereals Authority
UKAS (United Kingdom Accreditation Service)
The Textile Institute
Thames Water
The Concrete Society