

Rainer Herrmann
Udo Schlemm
TEWS-Elektronik
Abt. F+E

Guidelines for reference measurement techniques in the laboratory for the purpose of calibrating microwave moisture measuring devices

The classic moisture content measurement techniques, used for many years in many areas of manufacturing, are direct measurement techniques. Besides gravimetric techniques (drying oven, loss on drying techniques), these include the chemical techniques (Karl Fisher titration, gas chromatography, etc) as well. All of these techniques work on the principles of **directly** measuring the presence and quantity of water, as opposed to **indirect** procedures (microwave, resonator, and near-infrared measuring methods) where moisture is that which is measured directly. Generally, direct procedures take more time to yield a result (many hours, sometimes even days), and can only be performed on samples in the laboratory, and not "online". By contrast, indirect methods produce very quick results and microwave measurements can also often be carried out "online".

As a rule, microwave measurement as an indirect method is used in the laboratory as well as in quality control, and is calibrated with respect to well tested direct methods, so that the measurement it produces is that which is normally supplied by direct methods. This means that the quality and the accuracy of the microwave measurement technique is mainly judged on the basis of its ability to reproduce values given by the direct reference method. The advantages of the technique, its relative independence of the type of material it is used on to measure, can only be fully utilised if, besides those concerning the handling of microwave measurement devices, some guidelines regarding direct methods are also adhered to. Contrary to the widely held view, the direct methods are by no means simple to control --- important experiences in connection with these methods will be discussed in the following.

Loss on drying methods:

Loss on drying techniques are gravimetric methods, and are used in manufacturing as the classic methods for determining moisture content. A sample is obtained from the product, it is weighed in the laboratory, dried in a drying cabinet, then weighed again. The difference in mass gives the moisture content of the sample. The gravimetric dry-and-weigh method mainly uses one drying cabinet for the drying and heating of the sample.

The drying is done at a temperature at which no chemically bound water is released. For most materials, this is at 100°C (for natural products between 80°C and 120°C, depending on measurement method); for some with a marked tendency to release crystallised water (for example gypsum at 40°C), for materials with volatile components (silage, 40°C, or filtering materials with volatile softener 20°C in a desiccator) or for materials that would undergo chemical reaction during the drying process, the temperature is lower. Some products of pasty consistency, in order to increase the surface area, are roughened with dried sand (for marzipan, it is 103°C).

The vacuum drying method involves placing the sample in a desiccator, and the drying is carried out by decreasing the ambient air humidity at a low temperature, in order to prevent the sample from undergoing a chemical reaction (i.e. sandstone, using pre-dried air and convection). Drying of samples in a frozen state is also possible, which will also prevent any distribution of salts during the drying process.

As a rule, the higher the temperature, the shorter the drying period is. Thus, it can vary from 1 week (desiccator method), through a few hours at around 100°C, to 5 minutes at temperatures over 110°C. As an example, different samples of the same cut tobacco will show similar moisture content through shortening the drying time and raising the temperature from, respectively, 3 hours at 80°C, to 2 hours at 100°C, 1.5 hours at 103°C, and 0.5 hour at 106°C. At the same time, this also illustrates the need to maintain a stable temperature. Short drying periods lead to clear influences of moisture and of surface structure on the drying results: samples with higher moisture content and smaller surfaces need longer to reach the drying temperature.

Often, drying period and temperatures specific to a company have been established and used within a given manufacturing process for decades. Yet, mistakes can only be avoided by eliminating a series of potential sources of error:

- With sample sizes of 5g, an error by 5mg in weighing before or after drying results in a moisture content measurement that is out by 0.1%. Possible causes may be care-

lessness in taring, a carelessly cleaned sample container, or loss of the smallest bits of sample due to the movement of air inside the drying cabinet.

- Some drying cabinets channel the airstream through the sample container with a fine mesh bottom (i.e. the Beaudesson method). The danger of losing some part of the sample during drying is especially great with samples of high dust content, which swell considerably as a result of even small amounts of moisture.
- Often the sample container is still warm or quite hot as the sample is weighed before or after drying. The resulting upswing of the scales can lead to an error in measurement whose severity is dependent on the container's temperature. Even with scales integrated into the drying equipment (infrared lamps or special drying cabinets) this effect can only be roughly compensated for. In addition, if the pre-drying sample is weighed in a hot container, the sample may start losing moisture before it is weighed.
- Especially at low moisture content under 1%, the position and placement of the scales must be taken into account: movements of air, air conditioners, will influence the measurement if it is carried out in an open room.
- As the sample is cooling down, its container must be covered airtight, preferably with the lid that covered it while in the drying cabinet. If this is not done, and the environment is even slightly humid, the dry and highly hygroscopic sample may start re-absorbing moisture.
- The actual drying procedure is critical: since the drying period is often short, the quality of the ventilation in the drying cabinet has an effect on the result of the measurement. The way the cabinet is loaded, the way the sample is positioned within, and the individual differences between different cabinets can have manifold influence on the outcome. Care must be taken that the ventilation is optimal, the humidity is transported out of the cabinet, and that there is a uniform temperature and humidity distribution inside the drying cabinet. The relative air humidity in the cabinet must be kept very low.
- The consistency of temperature regulation also contributes to the outcome of the measurement. For this reason, it is important to ensure that the temperature consistently stays at the previously determined and noted level.
- Different parts of the product may require their own particular drying time. Often, however, the same times are used for samples with more moisture content. Evaporative cooling prevents samples with high moisture content and short drying time from heating up to the drying temperature, with the result that, at high moisture content,

there is too little evaporation, and, as a result, the moisture content measurement will be too low. This kind of deviation is also connected with the type and size of surface area, that is, in the case of a sample that was obtained by cutting, the result also in part depends on the size of the surface area of the cut.

- The sampling method itself is a possible source for error: since there may be a considerable time difference between the time the sample is obtained, and when it is weighed prior to drying, it is important to ensure that the sample does not lose moisture during this time, that is, the sample container is kept hermetically sealed and, if possible, filled as full as possible. This is because, if evaporation takes place inside the container, the fuller the container, the less danger there is of condensation building on the walls inside the container. If condensation does build up, the sample must be given time to reabsorb the water before the sample container is opened again.
- Ultimately it is the extent of uniformity of moisture content in the product that determines the reachable precision of the moisture measurement. That is why always at least three samples must be obtained for each measurement that employs a loss on drying method, in order to determine the average moisture distribution in the product. If the difference between moisture content measurements for distinct samples is greater than 0.5%, the number of samples taken should be increased to up to 10, or if higher than 1.5%, up to 20, in order to obtain a reasonable average. The standard deviation within a sample group then delivers the theoretically determinable agreement between reference equipment and the indirect measuring method or device which is being tested; as the case may be, the microwave device.
- The comparative measurements between that using microwave device for laboratory use and the one using the loss on drying method should be carried out so that the pre-drying weighing for the loss on drying method first weighing takes place about the same time as the microwave measurement, and using the same sample.
- The comparative measurement with the microwave device should be carried out so that the sample is obtained at the location of the microwave sensor, and during the interval in which the microwave device delivers the result. Only in this way can the strongly varying moisture values that change according to time and place allow the microwave values and reference value from the laboratory to be meaningfully compared. For this purpose, there is a reference measurement switch on the microwave device, which should be pressed twice, once when the sampling begins, and the second time when the averaging following successive samplings is finished. For extremely inhomogeneous products, in order to improve the correlation between device

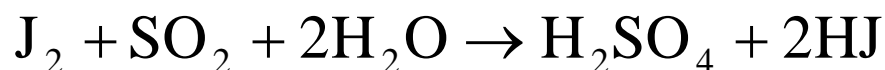
and control measurements, it is sometimes sensible to keep the averaging time as short as possible - corresponding to the shortest possible sampling time.

- In order to ensure the quality of the loss on drying reference measurement method, it is imperative that, from time to time, a comparison test is made with different drying cabinets using homogeneous samples in the same sample receptacles. The reachable precision of the loss on drying technique will then be determined by the standard deviation of the individual values from the same homogeneous sample group.

The Karl Fischer titration technique:

The Karl Fischer titration technique is one of the chemical moisture measurement methods. It involves observing and analysing the chemical reaction of a titrant solution with water. The sample can only be used once. For subsequent measurements, for instance, at a later time, different samples must be obtained.

The Karl Fischer technique involves weighing a given amount of a sample product; the water contained in the sample is then through stirring made into solution, and then, with the addition of a solution containing iodine and sulphur dioxide content, is titrated:



The iodine, sulphur dioxide and water combine to form sulphuric acid and hydrogen iodide, which process also leads to the loss of the brown colour of the iodine. At the end point, the

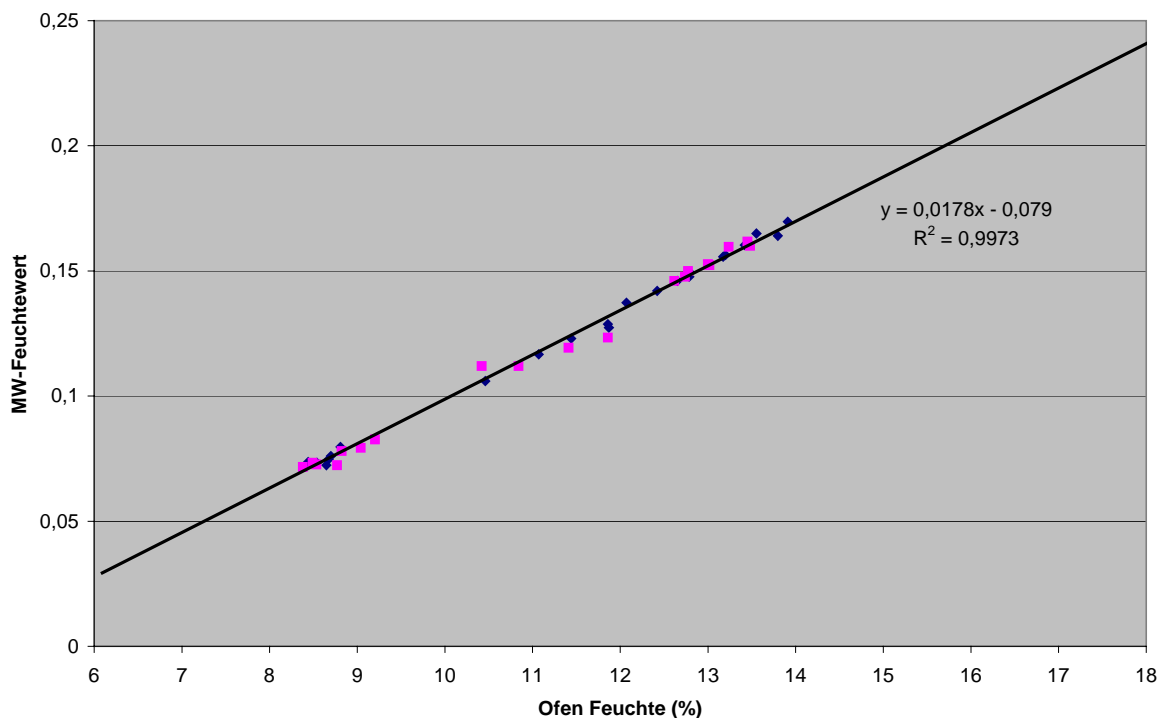
sample regains a brownish colour, which means that this point can be determined either visually or with modern potentiometers. The moisture content of the sample is determined from the amount of the Karl Fisher solution needed. With this technique, already traces of water can be detected. Samples of solid materials must be pulverised, which may result in a loss of water, and thus, in a measurement error.

Since this technique also requires a carefully weighed sample, all the sources of error identified for the loss on drying method that have to do with the weighing procedure, the loss of moisture, and the obtaining of the sample, apply here too. Beyond these, other sources of error can be avoided through care, especially because the materials are used in very small quantities:

- The water content in the sample must be brought into solution. This can happen through a hygroscopic liquid, such as methanol, which should however contain no, or very little, water. This initial water content must be separately determined.
- The chemical reaction needs a little time, during which more water must not get into the solution. Only the water which is in the solution can be chemically converted and determined. That's why the solution must be continuously stirred for a long time, which is determined according to the product (about an hour, as a rule).
- Here also, it is recommended that multiple measurements be carried out on inhomogeneous products, since a single sample of 5g will represent a very small percentage of the product, driving up the overhead costs in materials.

Ground rules for the calibration of microwave resonator measuring devices

The figure below shows a typical linear calibration curve with a correlation coefficient of 0.997 (for different kinds of tobacco and tobacco mixtures). The creation of this kind of accurate calibration curve requires not only taking into account the above rules for the use of reference measurements, but also the ones for using of the microwave resonance method:



- The samples used for calibration must lie with respect to their moisture content over the measurement range in which these are to be measured later - or better yet, further. So, if for example, only a measuring range of between 5-15% should be given if the samples too were between 5-15%. Admittedly, the device will also perform outside this range, but only by mathematical extrapolation, i.e. with diminished precision.
- The mean spread range of the samples at the calibration must exceed by the factor of 5 the measurement uncertainty of the reference measurements. For instance, if the standard deviation of the error margin of a given oven measurements is 0.25%, then the mean spread range of the samples should be at least 1.25%.
- To calibrate a tube resonator, the applicator **tube must be filled up until it is full**. With planar sensors, care must be taken that the sensor is covered evenly.

- The samples used for calibration should be available **in the same condition in which they are at the time of measurement**. For measurements at any stage of production, samples from the same process must be used for calibration. Sometimes the moisture content in the product is not yet in balance. Then the product, which comes directly from the process, must also be calibrated, as later the measurement will follow (that is, also with samples in moisture imbalance).
- The **laboratory comparison measurement** with a direct method must be carried out on the same samples, which were measured with the microwave device. Especially with sample temperatures over room temperature, with hygroscopic materials or ones that easily lose moisture, care must be taken that the material between the time of microwave measurement and the laboratory test (the time of weighing for loss on drying methods) does not change through evaporation, or loss or gain of moisture for other reasons. If the sample is hot, it is important to wait until it cools down before weighing it before the reference measurement. Additionally, the sample can be kept, packed tightly, in a watertight closed container.
- Two factors determine the necessary **calibration points**.
 1. The accuracy of the laboratory reference measurements. The more uncertain the result, the more calibration points are necessary to compensate for the resulting statistical errors.
 2. The kind of calibration curve required by the product to be measured. When this is a straight line, the comparative laboratory measurements are very precise, and the determined moisture content of the given samples are far enough, already two calibration points fulfil the requirements of a good calibration. However, as a rule, at least five points are necessary.
- For considering **the temperature of the sample**: the temperature of the samples must be in the same range as it is for the measurement.
- When the spread of temperatures for calibration and of those for the measurement lie within a margin of $\pm 3^{\circ}\text{C}$, no compensation for temperature is necessary. For a larger spread, the temperature dependence of the microwave signals must be calibrated for.