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METTLER TOLEDO moisture content determination

Methods of moisture content determination

Halogen Moisture Analyzer from METTLER TOLEDO

Layout and contents of this brochure

This brochure is aimed at people who are concerned with the determination of the moisture content of substances. It supports the reader in the selection of the most suitable measurement method.

The brochure contains easily surveyed tables which can be used to quickly find solutions with the HR73 or HG53 Halogen Moisture Analyzer from METTLER TOLEDO.

The first part of the brochure describes the principles of common moisture determination methods. The description of the strengths and weaknesses of the individual methods will support you in your evaluation of a suitable method.

The second part is specially concerned with applications for the Halogen Moisture Analyzers from METTLER TOLEDO. Sampling, the sample preparation and optimum adaptation of the drying parameters to different types of problems are discussed. A number of examples show how to find optimal settings for the instrument. It is also explained how the moisture content measurement for a sample which has been determined by a reference method drying oven can be repeated much more quickly with a Halogen Moisture Analyzer. This chapter also contains several examples of applications developed at METTLER TOLEDO, as well as instructions for integrating the Halogen Moisture Analyzer into a computer environment.

This second part deals particularly with the applicational aspects of the Halogen Moisture Analyzers from METTLER TOLEDO. Your local METTLER TOLEDO dealer will be pleased to advise you of other methods of determination.

Contents

1. Introduction

What is moisture? There is no definition of general validity for the concept of moisture. In many cases, the physical measurement principle used for the moisture determination influences the definition. The following section describes moisture of the type occurring in connection with thermal (dry) determination methods.

Definition The moisture contained in a material comprises all those substances which vaporize on heating and lead to weight loss of the sample. The weight is determined by a balance and interpreted as the moisture content. According to this definition, moisture content includes not only water but also other mass losses such as evaporating organic solvents, alcohols, greases, oils, aromatic components, as well as decomposition and combustion products.

Types of bonding of moisture In moisture determination it is important to note that water can be bonded differently in solids: With increasing bond strength as

– free water on the surface of the test substance
– water in large pores, cavities or capillaries of the test substance
– water adhering to the surface of polar macromolecules
– occluded in lattice ions or water of crystallization coordinately bonded to ions.

Water on the surface

Substance particle
Water
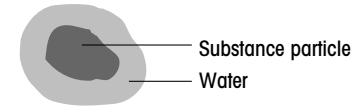
Water in pores or capillaries

Substance particle
Water

Substance particle
Water
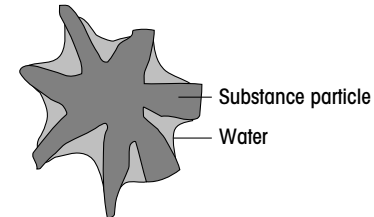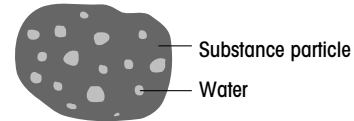
Water of crystallization

Gypsum: $Ca\ SO_4 \cdot 2H_2O$

The separation of water of crystallization and adhesively bound water by thermal methods is occasionally accompanied by unavoidable, simultaneous product decomposition.

Selection of the suitable measurement method

The selection of a suitable measurement method essentially depends on the following quantities:
– Requirements regarding accuracy, measurement range, repeatability, sensitivity
– Type of bonding of the water
– Desired information: water or moisture content
– Measurement speed
– Amount of sample
– Physical properties of the sample
  (e.g. decomposition temperature)
– Budget
– Simplicity (operation or functionality)
– Statutory regulations (reference methods)
– Automation capability
– Calibration capability

Why measure water or moisture content?

Most natural products contain moisture.

The water content per se is seldom of interest. Rather, it shows whether a product intended for trade and production has standard properties such as
– Storability
– Agglomeration in the case of powders
– Microbiolgical stability
– Flow properties, viscosity
– Dry substance content
– Concentration or purity
– Commercial grade (compliance with quality agreements)
– Nutritional value of the product
– Legal conformity (statutory regulations governing food)

Trade and industry are interested in the dry substance content of commercial goods. The water present in the product is taken into account when the product is priced. Legal regulations and product declarations define the difference between natural moisture and moisture added to the product.

Moisture determinations must be capable of being carried out quickly and dependably to allow possible action to be taken rapidly in the production process and avoid lengthy breaks in production. Many producers today thus determine the moisture content of raw materials, intermediates and finished products directly at the production line, exactly as defined by quality assurance.
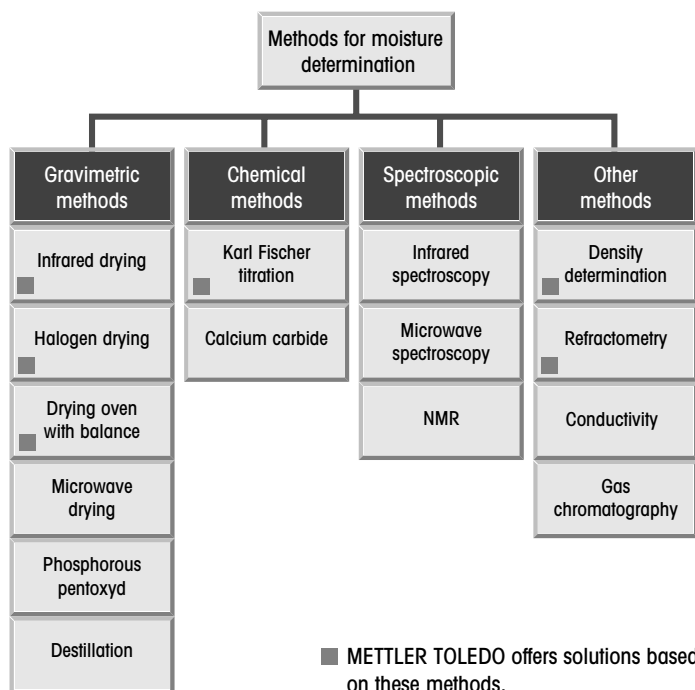
2. Methods of moisture content determination

The moisture content influences the physical properties of a substance such as weight, density, viscosity, refractive index, electrical conductivity and many more.
Over the years, a wide range of methods has been developed to measure these physical quantities and express them in the form of the moisture content.

The measurement methods can logically be divided in the following procedures:
– thermogravimetric
– chemical
– spectroscopic
– others.

METTLER TOLEDO offers solutions based on these methods.
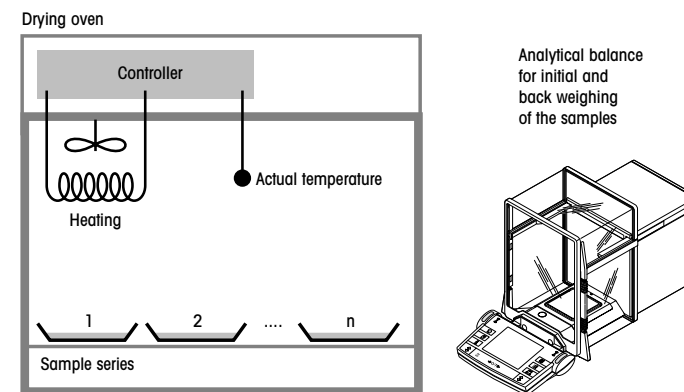
Method	Strengths	Weaknesses
Drying oven	Reference method Several samples can be determined simultaneously Weighing-in of large amounts of samples possible	Typical determination time in the region of hours Decomposition of sample possible Substances which vaporize in addition to water Time consuming handling with possibility of mistakes
Infrared drying	Typical measurement time 5…15 min. Weighing-in of large amounts of samples possible Simple handling, simplicity of method Compact problem solution	Decomposition of sample possible Substances which vaporize in addition to water
Halogen drying	Fast, typical measurement time 2…10 min. Weighing-in of large amounts of samples possible Simple handling, simplicity of method Wide range of applications, compact problem solution	Decomposition of sample possible Substances which vaporize in addition to water
Microwave drying	Fast, typical determination time 2…5 min. Weighing-in of large amounts of samples possible	Decomposition of sample possible Problematic for substances with low moisture content Average temperature control
Distillation	Favorably priced	Solvents often needed (ecology) Average result accuracy
Karl Fischer titrations: coulometric	Accurate reference method Suitable for trace analysis, water detection	Work technique must be matched to the sample at hand
volumetric	Accurate reference method, water detection	Work technique must be matched to the sample at hand
Ca carbide method	Favorably priced	Formation of explosive materials Trained personnel required
Infrared spectroscopy	Extremely short measurement time, continuous measurements Also for multicomponent analysis (proteins)	Calibration specific to substance required Only for measurement of surface moisture Dependent on material properties Dependent on temperature, particle size
Microwave spectroscopy	Extremely short measurement time Continuous measurements possible	Calibration specific to substance required Disturbing influences are bulk density, particle size
NMR spectroscopy	Short measurement time Multicomponent analysis possible Structure determination	Calibration required Extensive apparatus required, trained personnel, expensive Only small amounts of samples measurable Hydrogen atoms not associated with moisture also determined
Gas chromatography	Suitable for multicomponent analysis	Trained personnel required, expensive
Conductometry	Fast method, mobile use	Calibration specific to substance required
Refractometry	Fast method, little effort required, mobile	Suitable only for clearly defined samples
Density measurement	Fast method, little effort required, mobile	Suitable only for clearly defined samples

2.1 Thermogravimetric methods

Principle Thermogravimetric methods are weighing-drying methods in which the samples are dried until their mass is constant. The mass change is interpreted as the evolved moisture.

Drying ends with attainment of an equilibrium state, i.e. when the vapor pressure of the moist substance is equal to the vapor pressure of the surroundings. The lower the vapor pressure of the surroundings, the lower the residual moisture in the substance when equilibrium is reached. Reducing the pressure lowers the vapor pressure of the surroundings and hence results in stricter drying conditions.

Influence For reproducible thermogravimetric moisture determinations, the drying temperature and the drying time are of great importance. These influence the measurement result. The influence of atmospheric pressure and atmospheric humidity is of secondary importance. However, these must be taken into account for highly precise analyses.

Importance The thermogravimetic methods are the classical methods. For historical reasons, they are often part of the relevant legislation (regulations governing food etc.).

Restriction In the thermogravimetric method, moisture is always separated as defined in the introduction. There is thus no distinction made between water and other readily volatile product components.

Application Thermogravimetric methods are suitable for practically all thermally stable substances with a moisture content >0.1%.

2.1.1 Drying oven

Principle A sample is dried by means of hot circulating air. To tighten up the drying conditions or to protect thermally unstable substances, drying is frequently performed under vacuum. The moisture content is determined by a differential weighing before and after drying.

Importance For many substances the drying oven method is a mandatory reference method with good reproducibility. This method is frequently cited in laws governing food.

Advantage The advantage of the classical drying oven method lies in the number of samples which can be investigated simultaneously. Moreover, it offers the possibility of analyzing large amounts of samples, which can be a particular advantage with inhomogeneous samples.

Disadvantages A disadvantage of this method is the large amount of manual effort involved and the long measurement time in the region of hours. To shorten the measurement time, infrared or microwave dryers are thus often used today.

Considerable systematic errors arise if the sample is hygroscopic and absorbs moisture from the air after drying before it can be weighed. This can be eliminated by use of modern dryers with an integrated balance since weighing and drying are performed simultaneously.

Applications   Check on substances for legal conformity (food).
Reference method for the calibration of other methods.
For these methods METTLER TOLEDO offers a complete range of analytical and precision balances as well as software and sample identification systems to simplify processes.

2.1.2 Infrared drying

Principle   This method uses direct infrared radiation instead of hot circulating air to dry the sample. The infrared rays are absorbed by the sample and the absorbed energy causes the desired heating of the substance.

IR heating

Test substance

7.385 g   Balance
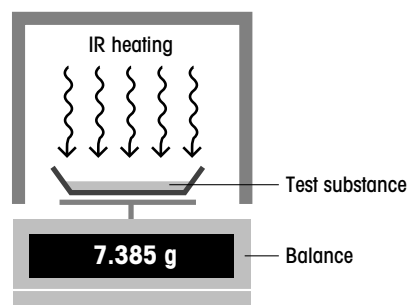
Advantage   Important advantages of this method are the simple operating principle and the short drying time. Measurement results are available after a few minutes. Infrared dryers are supplied with an integrated balance and have a very compact and rugged construction.

Disadvantage   In addition to water, other substances can vaporize.

2.1.3 Halogen drying

Principle   This method is a further development of infrared drying. The radiator technology is based on the new halogen radiator principle.

Advantage   Thanks to the compact construction of the halogen radiator, this reaches the desired operating temperature very quickly and can be precisely controlled. The result is usually a shorter measurement time compared with the traditional methods and better heat distribution throughout the sample.
Even radiation of heat onto the sample, combined with fine regulation of the temperature, give measuring results with outstandingly good reproducibility.
This technology is used for the radiator in the METTLER TOLEDO Halogen Moisture Analyzers. Depending on the sample and moisture content, it produces accurate measurement results within 3-10 minutes.

Temperature of the radiator

Halogen technology

Traditional IR technology

Time
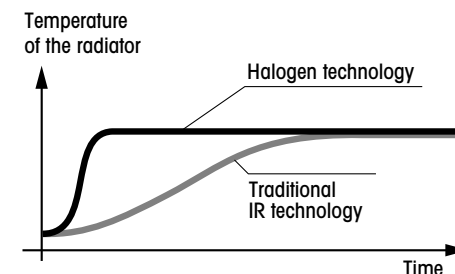
Disadvantage   As with all thermal methods, decomposition of the sample is possible.
In addition to water, other substances can vaporize.

2.1.4 Microwave drying

Principle
This method is based on the absorption of microwave radiation by the water molecules of the sample. This absorption generates heat and leads to vaporization of the volatile components. Measured variable is here also the total amount of volatile components. This is determined by weighing before and after drying.
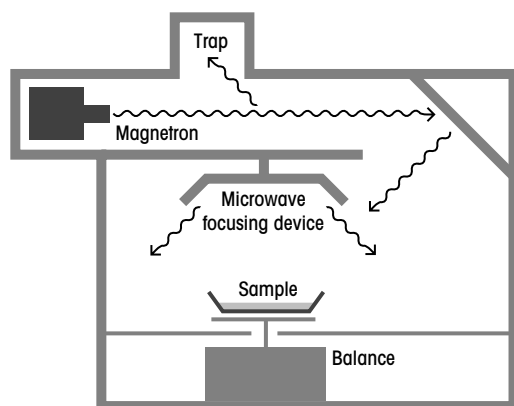
Restrictions
In contrast to the favorably priced microwave household devices, much higher demands are placed on professional instruments. The uniform distribution of the microwaves and the power regulation are important as imprecise control can lead to uncontrollable over-heating of the sample. This method is not suitable for apolar substances with a low water content (<2%) as these samples have no substances which absorb microwaves and hence lack the driving force for the heat generation.

Advantages
Rapid measurement method.
Weighing-in of large amounts of samples is possible.

Disadvantages
A selective water determination is not possible as thermal conduction within the sample leads to other substances being heated and subsequently vaporized.

Average temperature control and danger of decomposition of the sample. Problematic for substances containing a small amount of moisture.

2.1.5 Phosphorous pentoxide method

Principle
The water-absorbing phosphorous pentoxide is placed in a closed system along with the moist sample. The water vapor which vaporizes through heating of the sample is immediately chemically bound by the pentoxide. The weight increase of the phosphorous pentoxide is the measure of the water content of the sample. Occasionally, the change in the electrical conductance of the phosphorous pentoxide is measured and represented as the moisture content. For these methods METTLER TOLEDO offers a complete range of analytical and precision balances, as well as an assortment of software and sample identification systems to simplify processes.

2.1.6 Distillation

Principle
The mass or volume fraction of the moisture thermally separated from a sample is measured.
An organic solvent insoluble in water (e.g. toluene, xylene) is frequently added to solid samples before the distillation and forms an azeotropic vapor phase with water in the distillation at a temperature <100 °C. After cooling, the two liquid components separate, the water fraction is determined volumetrically or – after prior separation of the solvent fraction in a separating funnel – by weighing.

Advantage
Favorably priced method

Disadvantages
Average accuracy.
In many cases, solvents which represent an environmental hazard are necessary.

2.2 Chemical methods

2.2.1 Karl Fischer titrations

Principle

The Karl Fischer method is used for many substances as a reference method. It is a chemical analysis procedure which is based on the oxidation of sulfur dioxide by iodine in a methanolic hydroxide solution. In principle, the following chemical reaction takes place:

$$H_2O + I_2 + SO_2 + CH_3OH + 3RN \rightarrow [RNH]SO_4CH_3 + 2[RNH]I$$

The titration can be performed volumetrically or coulometrically. In the volumetric method a Karl Fischer solution containing iodine is added until the first trace of excess iodine is present. The amount of iodine converted is determined from the burette volume of the iodine-containing Karl Fischer solution. In the coulometric procedure, the iodine participating in the reaction is generated directly in the titration cell by electrochemical oxidation of iodide until again a trace of unreacted iodine is detected. Faraday's law can be used to calculate the amount of iodine generated from the quantity of electricity required.

Application

The Karl Fischer titration is a moisture determination method specific for water and is suitable for samples with a high moisture content (titrimetry) and also for those with water contents in the ppm range (coulometry). It was originally developed for nonaqueous liquids, but is also suitable for solids if these are soluble or if the water they contain can be removed by heating in a stream of gas or by extraction.

Advantages

Accurate reference method, coulometry also suitable for trace analysis and water detection.

Restriction

The working method must be adapted to the specific sample. METTLER TOLEDO is a leading manufacturer of Karl Fischer titration instruments, and offers a comprehensive range of instruments, software, and accessories.

2.2.2 Calcium carbide method

Principle

In the calcium carbide method a sample of the moist substance is carefully mixed with excess calcium carbide resulting in the following reaction:

$$CaC_2 + 2H_2O \twoheadrightarrow Ca(OH)_2 + C_2H_2$$
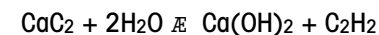
The amount of acetylene formed is determined either by measuring its volume or by the rise in pressure in a closed vessel.

Advantage

Favorably priced.

Disadvantages

A calibration is required for this procedure as not all the water contained in the sample participates in the reaction. The evolution of the explosive substances hydrogen or acetylene is probably the reason why this method of water determination is not in widespread use.

2.3 Spectroscopic methods

Principle

Spectroscopic moisture determination methods are indirect measurement methods. All these methods require calibration to determine the relation between the display of the spectrometer (primary measured variable) and the value determined by a reference method.

The variable measured by the spectrometer is never a function which is dependent solely on the moisture, but on other parameters such as the density, temperature and material properties.

Restriction

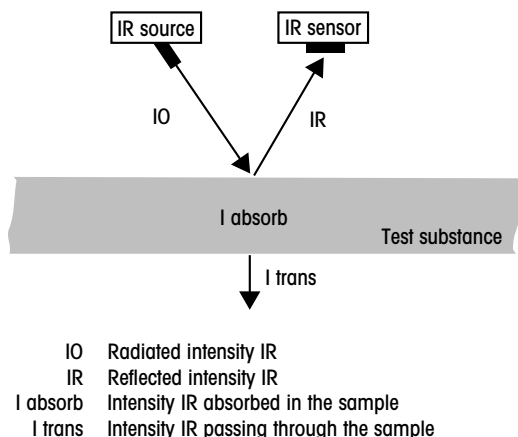To obtain an unambiguous relation between moisture and physical measured variable, all other parameters must be kept constant. However, as the material being measured is never completely homogeneous nor are its properties constant, all characteristic curves have a more or less marked scatter. It is thus necessary to use a large number of samples for the calibration which are representative of the planned application case.

2.3.1 Infrared spectroscopy for determination of the surface moisture

Principle

This moisture determination method is used solely to measure the surface moisture. A sample is irradiated with light (electromagnetic radiation). The intensity of the reflected spectrum forms the basis for determination of the moisture content. In the electromagnetic spectrum, the near infrared (NIR) region used comprises wavelengths between 800 nm and 2500 nm. In this region the three-atom water molecule (H_2O) has two prominent absorption bands at wavelengths 1.475 µm and 1.94 µm (harmonic vibrations and combination vibration).

If a moist sample is irradiated with light of these wavelengths, part of the light is absorbed, a second part diffusely reflected and a third part passes through the sample (transmission). The diffuse reflected intensity is measured (spectrum), which is proportional (in a non-linear relation) to the water concentration on the surface. With thin samples, the spectrum of the transmission is also evaluated on occasion.

IO	Radiated intensity IR
IR	Reflected intensity IR
I absorb	Intensity IR absorbed in the sample
I trans	Intensity IR passing through the sample

Advantages

Short measurement time within seconds and the possibility to perform multicomponent analyses and real-time measurements.

Restriction

A calibration for each particular substance must be performed beforehand.

2.3.2 Microwave spectroscopy for determination of the total moisture

Principle

Owing to the exceptionally high dielectric constant of water (DC = 81), microwaves are absorbed, reflected and scattered in moist substances. This allows measurement methods for the moisture to be derived which can be implemented as transmission, reflection or resonator methods (see NIR spectroscopy), depending on the measurement task.

The transmission and reflection methods will not be discussed further here as they involve a variation on the NIR moisture determination method and offer similar advantages and disadvantages. The resonator method is a discontinuous lab measurement method with a relatively high accuracy. In this method, the sample is placed in a cavity resonator which is made to "oscillate" by microwaves. Any polar water molecules present now absorb part of the energy and change the microwave field. A shift in the resonance frequency as well as an amplitude change of the oscillation can be measured. This shift shows nonlinear proportionality to the water content of the substance; the temperature and the sample weight must be known for purposes of compensation.

Restriction

A calibration of the measurement system for each specific substance is required for the transmission measurements and the resonator method. Continuous measurements can be performed with the transmission or reflection method.

2.3.3 NMR (nuclear magnetic resonance) spectroscopy

Principle

1H NMR spectroscopy determines the number of water nuclei in a substance. This can then be used to decide the amount of water in the sample. Two different types of 1H NMR spectroscopy are always used for the moisture content determination.

In the first type the substance under investigation is positioned in a high frequency alternating magnetic field. The resonance behavior of the water nuclei (spin of the protons) is a measure of the water content in the substance.

In the second type water nuclei (protons) are deflected by a magnetic pulse. The spin flip of the proton induces a voltage in the receiver coil. Mathematical processing of the experimental signal results in an NMR spectrum, which provides information on the hydrogen atoms in the sample.

Restrictions

It must be noted that NMR spectroscopy determines all H atoms present in the sample. The hydrogen atoms which are not part of a water molecule are also shown, although the bonding conditions are apparent from the spectrum.

NMR signals must therefore be calibrated for all components to be measured and matched to the structure of the substances. However, a calibration for each specific substance as in NIR spectroscopy is not necessary.

Advantage

An advantage of nuclear magnetic resonance spectroscopy is the high accuracy. It detects all forms of water, irrespective of the bonding strength.

Disadvantage

The main disadvantage is the considerable amount of apparatus required and the associated high costs. Even the small sample size can be disadvantageous in industry for quality assurance applications.

2.4 Other methods

Principle

The water determination methods described in this section mostly test physical product properties which depend solely on the water content, assuming the test substance has a simple composition.

Restriction

These methods frequently require a calibration and can be used only if a simple analysis matrix (number of components comprising a sample) is present and the components present in addition to water do not interfere with the measured variable.

2.4.1 Determination of the electrical conductivity, conductometry

Principle

The primary measured variable in conductivity is the electrical resistance. This is greater the fewer the number of charge carriers (dependent on the water content) available for charge transport. The electrical resistance is thus a measure of the water content of the sample.

Restriction

This method is suitable for substances which have a very low conductivity in the dry state. It exhibits an appreciable temperature dependence, but this can be corrected by a temperature measurement.

Discontinuous measuring cells in which the test substance must be introduced are available, as well as immersion electrodes and continuous measurement devices.

2.4.2 Refractometry

Principle   This involves an optical measurement method. The refractive index is measured which (e.g. with dissolved sugar in water) is a non-linear function of the sugar concentration. A direct water content determination as such is thus not performed. The measured value defines only the analysis matrix present in addition to sugar (in this case water).
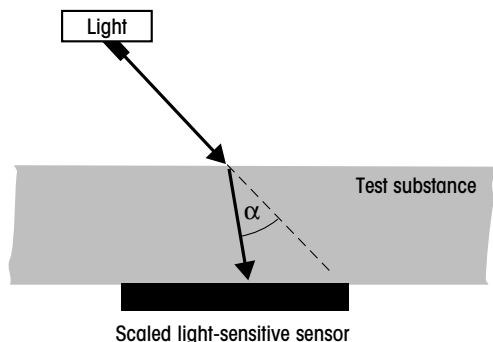
α depends on the substance (refractive index)

Application   This method of moisture determination is important primarily for products containing sugar.
Methods based on refractometry can also be used for the water determination of other pure substances such as glycol solutions.
METTLER TOLEDO offers a range of refractometers for this method.

2.4.3 Density determination

Principle   This analysis method is usually used only for pure solutions as the density is a measure of the concentration of a substance in an aqueous solution (e.g. NaOH, sugar solutions, alcohol-water mixture). This is another case where the residual matrix of the substance under investigation is interpreted as the water content.

Advantages   Simple method, results of binary mixtures can be read directly from a table.

Application   This method is normally very fast and the analysis can frequently be performed directly in the sample. It is thus primarily suitable for rapid sample checks and the analyses of trends. Its informative value regarding the water content depends essentially on the difference in density and the number of components in the substance. The density determination methods most widely used are
– Determination using areometer
– Determination using pycnometer
– Measurement of Archimedes' buoyancy force using a balance (dynamometer)
– Principle of the oscillating tuning fork.

A brief description of the operating principle of the tuning fork: The hollow arms of an oscillating body shaped like a tuning fork are filled with the test substance. The intrinsic frequency of the tuning fork depends on the density of the substance. METTLER TOLEDO offers a comprehensive range of density meters based on various different measuring principles.
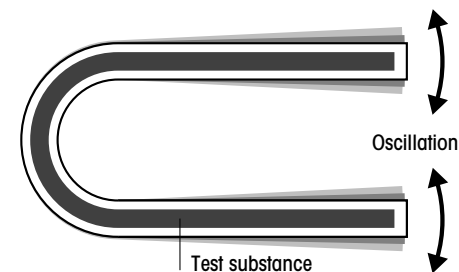
2.4.4 Gas chromatography

Principle

The sample mixture must first be capable of vaporization without undergoing decomposition so that it can then be transported in gaseous form by an inert carrier gas through a separating column. The individual sample components are separated by the column on the basis of their different boiling points and the intermolecular interactions between the liquid, stationary phase in the separating column and the sample components in the mobile gas phase. The individual gas fractions exiting the column are usually detected by thermal conductivity (TC).

Application

Gas chromatography is suitable for liquid samples with a moderate solids content and a water content greater than 5%, as well as for samples whose water can be removed by extraction.

Advantage

This analysis method allows several liquid sample components to be analyzed at the same time.

Restrictions

Owing to the extensive apparatus required, this method is normally used for water content determinations only if other sample components are of interest or if constituents lead to interfering side reactions in the Karl Fischer titration. A calibration is necessary.

2.4.5 Osmometry

Principle

Measurement of the vapor pressure supplies information on the moisture content of the sample.

2.5 Tabulated overview of the methods for moisture determination

Method	Method type	Measurement principle	Typical measuremnt range	Typical measuremnt accuracy	Water selective
Drying oven	TG	Heating by convection Mass determination before and after drying	0.5–100%	0.1–0.5%	no
Infrared drying	TG	Heating by absorption of IR radiation Continuous determination of the mass during drying	0.5–99%	0.1–0.5%	no
Halogen drying	TG	Heating by IR radiation with halogen radiator Continuous determination of the mass during drying	0.5–99%	0.1–0.5%	no
Microwave drying	TG	Heating by absorption of microwaves Mass determination before and after drying	2–99%	0.1–0.5%	no
Distillation	T	Usually azeotropic distillation with insoluble solvents Usually volumetric determination of the water content	3–70%	1%	yes
Karl Fischer titrations coulometric	EC	Electrochemical production of iodine, which reacts with an equivalent amount of water. Indication by voltage measurement at constant current		ppm	yes
volumetric	C	Titration of water with iodine solution. Indication by voltage measurement at constant current	1–100%	0.05–0.5%	yes
Ca carbide method	C	Volume/pressure measurement of acetylene formed	1–100%	0.1–0.5%	yes
Infrared spectroscopy	SP	Measurement of absorption/reflection of IR radiation	1–80%	0.3–1%	yes
Microwave spectroscopy	SP	Measurement of absorption/reflection of microwave radiation	2–70%	0.3–1%	yes
NMR spectroscopy	SP	Measurement of nuclear magnetic resonance (spin)	0–15%	0.1%	yes
Gas chromatography	CR	Separation on a gas chromatographic column Detection of the fractions using thermal conductivity	0.1–1% 1–5%	0.01% 0.1%	yes
Conductometry	EL	Measurement of the conductivity	>3%	0.5–1%	no
Refractometry	OP	Measurement of the refractive index	0–50%	0.5–1%	no
Dichtemessung	PH	Messung der Dichte	2–98%	0.5–1%	no

TG = Thermogravimetry
T = Thermal
EC = Electrochemical
C = Chemical
SP = Spectroscopic
CR = Chromatographic
OP = Optical

2.6 Metrological terms

Statistical considerations are also of relevance for determining certain physical dimensions. A number of important metrological terms are explained below by reference to the measurement error theory.

True value

The objective of most measurements of physical dimensions is to obtain the most accurate estimate possible of the "true" value of a dimension. However, for a number of reasons, it is impossible to determine the true value to any desired degree of accuracy. For example, the true value of the water content in a sample could only be found by counting the exact number of water molecules. Methods available today use physical effects such as moisture evaporation (thermogravimetric methods). The sample is heated, the moisture evaporates, and the weight loss is interpreted as the moisture content. This means that the moisture content includes water as well as other evaporated substances. With this method, measurement errors may be caused by the reduction in weight due to oxidation when organic substances are heated. This means there is often a slight discrepancy between the measured value and the true value.

If a measuring method delivers reproducible results, it is possible to correct the deviation between the true value and the estimated value by simple addition or subtraction of a constant.

To ensure that changes in the production process are rapidly and reliable detected, it is therefore critically important that the measuring method used delivers repeatable results.

Statistical error

Every measurement of a physical dimension is subject to a measurement error. If systematic errors are ignored, there always remain errors due to a large number of small disturbances. These errors are referred to as random, or statistical, errors. The objective is therefore to obtain a usable approximation for the value of the dimension being measured and its accuracy.

If a physical dimension is measured several times in succession, this produces a sample of measurement values $x_1, ..., x_n$. It can then be shown that in most cases the statistical error of a measurement dimension is derived from a normally distributed population with mean m and standard deviation s[1] s, and that

$$\overline{x} = \frac{1}{n}(x_1 + ... + x_n)$$

mean value
of the measurement values

and

$$s = \sqrt{\frac{1}{n-1} \sum_{i=1}^{n}(x_i - \overline{x})^2}$$

repeat standard deviation
of the measurement values

are good estimates of the unknown dimensions m and s. These assumptions can be used to make a number of statistical statements concerning the quality of the measurement results.

Repeatability

Repeatability describes the ability of a measuring instrument to deliver the same result for the same sample substance under identical ambient conditions at the same location (stated as the repeat standard deviation).

Reproducibility

Reproducibility describes the ability of a measuring instrument to deliver the same result for the same sample type under different ambient conditions (e.g. air humidity) at different locations (stated as the repeat standard deviation).

[1] The normal distribution is completely described by the two parameters m and s and is designated $N(m, s)$. The normal distribution (also known as the Gaussian distribution) is represented graphically by the familiar bell-shaped curve.

2.7 Comparability of the methods

Owing to the use of different physical principles, a comparison of the results obtained with different methods may show small differences. Even results obtained with the same method with instruments from different manufacturers can often show minimal differences. The measurement deviations are frequently very small and constant, they can be determined by running a measurement series with the two instruments. For instance, the traditional drying oven (slow, convective heating of the sample) supplies slightly different values than infrared or halogen drying (fast heating of the sample by direct infrared radiation) at the same temperature. One of the reasons is the different type of heating with the resultant dissimilar action of the associated side effects (e.g. oxidation of the sample). The results can usually be brought into line by changing the drying time, drying temperature or the switch-off criterion.

Example
An LP16 Infrared Dryer is already in successful use. The new HR73 Halogen Moisture Analyzer based on the halogen radiator principle is purchased from METTLER TOLEDO. With the same settings (temperature, drying time or switch-off criterion), the results may differ slightly. However, changing the settings can bring the values into line and ensure their coincidence. Each of the two methods *per se* supplies results with good repeatability.

The exact procedure by which results of a reference method can be transferred to the Halogen Moisture Analyzer is described in Chapter 5.6.

3. Solutions available from METTLER TOLEDO

3.1 The methods and the product line available from METTLER TOLEDO

METTLER TOLEDO offers products for the following measurement methods:
– Drying oven method
  (analytical balance with differential weighing software)
– Halogen drying method
– Karl Fischer titration (coulometric and volumetric)
– Density determination based on Archimedes' buoyancy principle employing an analytical balance
– Density determination using an oscillating tuning fork
– Refractometry

METTLER TOLEDO HR73 and HG53 Halogen Moisture Analyzers

METTLER TOLEDO HB43 Moisture Analyzer

**METTLER TOLEDO
Karl Fischer Titrators**

**AX analytical balance
with integrated differential
weighing software**

**AG analytical balance
with optional differential
weighing software**

**PR precision balance
with optional differential
weighing software**

4. Description of the Halogen Moisture Analyzer from METTLER TOLEDO

The Halogen Moisture Analyzer can be used to determine the moisture content of virtually any substance. The instrument operates on the thermogravimetric principle. A halogen radiator dries the test substance under investigation while the precision balance integrated in the instrument continuously measures the sample weight. The total weight loss is interpreted as moisture content. The main benefit of using a halogen radiator involves a shorter measurement time compared with traditional drying methods. In addition, the ring shape of the halogen radiator, and its position above the sample substance, result in very even heating of the sample, and therefore very good repeatability of the measurement result.

The basis for the calculation of the moisture content is the weight loss of the sample at the end of drying. Final results, intermediate results, procedures as well as method parameters are documented by the built-in printer available as an option. These analysis reports and calibration records satisfy the exacting demands of the standard quality systems (GLP, GMP, ISO 9000). In the Halogen Moisture Analyzer all system components (halogen radiator, balance, printer, display, data interface) are combined to form a compact instrument.

The Halogen Moisture Analyzer is available in three models: the HR73, HG53, and HB43.

The HR73 is a top-class instrument. Its measurement performance and functionality match up to the highest requirements. It can be adapted for a large number of different drying tasks and has a range of possibilities for evaluating measurement results. The HG53 is especially suitable for error-free routine operation. Its good measurement performance and simple operation guarantee reliable measurement results.

The HR73 and HG53 are designed for integration into networks (e.g. via FreeWeigh), and can both be optionally fitted with a built-in printer for measurement values. With its easy operation and rugged construction the HB43 basic model is designed for use in the production environment.

Key Characteristics of the Halogen Moisture Analyzers

Instrument model	HR73	HG53	HB43
Temperature range	50–200 °C	50–200 °C	50–200 °C
Temperature programs[1]	4	1	2
Minimum sample weight	0,1 g	0,1 g	0,5 g
Maximum sample weight	71 g	51 g	41 g
Readability of the result	0,01%	0,01%	0,01%
Repeatability (s) with 10 g sample	0,02%	0,02%	0,03%
Repeatability (s) with 2 g sample	±0,1%	±0,1%	±0,15%
Automatic switch-off	5levels, free	5 levels	5 levels
Adjustment	•	•	•
Add-on printer	•	•	
Methods database[2]	•		
Statistical analysis of results[3]	•		
Journal of the results[3]	•		

Notes on table
[1] Predefined drying programs allow optimum matching of the radiator power to the properties of the samples.
[2] Fail safe storage of settings specific to the substance for 20 different substances and other relevant drying parameters in a database.
[3] Measurement results are entered continuously in a journal and statistics database.

Operating principle and advantages of the halogen radiator

Drying with the halogen radiator is a further development of the infrared drying method. The heating element comprises a glass tube filled with inert halogen gas containing a tungsten wire heating element. The dimensions of the halogen radiator are so small that in contrast to conventional infrared radiators the full heating power is available within seconds. The halogen drying method is thus faster. Together with the large, gold-plated reflector, the shape of the halogen radiator guarantees an optimum, uniform distribution of the thermal radiation over the entire sample surface. This assures reproducible measurement results.

The sample pan handler

In the thermal drying method, the sample pan is frequently very hot at the end of heating. When removing the pan, the user may easily suffer burned fingers if he does not use a suitable implement such as tweezers. The Halogen Moisture Analyzer is supplied with a practical sample handler as standard, which allows simple and ergonomic installation and removal of the pan. At the same time, the sample pan handler also acts as a draft shield which reduces environmental effects such as air turbulence.
For the best results, we recommend this useful accessory be used all the time.
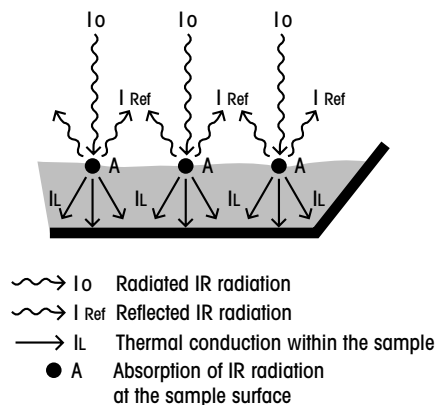
5. Moisture content determination with the METTLER TOLEDO Halogen Moisture Analyzer

5.1 The drying process

IR radiation (IR = infrared), often known as thermal radiation, is part of the electromagnetic spectrum. As this region is bordered by the red, visible region of the visual spectrum, it is often called the IR spectrum. Let us consider what happens when the IR radiation emitted by the halogen radiator falls on a substance undergoing drying.

The IR radiation is incident on the sample. Part of the radiation is absorbed by the test substance and converted to heat. As the absorptive capacity is not the same for all samples, different test substances may attain slightly different temperatures at the same instrument setting. If the transmission of the IR radiation is low, in the first instance only small mass particles on the sample surface heat up. These then transmit their heat via contact with neighboring molecules to lower-lying layers. The decisive factor for this heat transfer to the lower-lying layers is thus the thermal conductivity of the sample. The greater the thermal conductivity, the faster and more homogeneously the sample heats up.

I_o Radiated IR radiation
I_{Ref} Reflected IR radiation
I_L Thermal conduction within the sample
A   Absorption of IR radiation at the sample surface

On continuation of drying, the thermal conductivity of the sample changes with decreasing water content. Further, it must also be considered that the energy needed for vaporization of the moisture cools the sample at the start of drying (endothermic heat of vaporization). If the wrong temperature is chosen, both effects can lead to decomposition of the sample at the end of drying.

The surface properties and the "color" (IR absorptive power) of the sample have an influence on the heating and hence on the effective sample temperature. Smooth and bright surfaces usually reflect IR radiation more so that less absorbed energy is available for heating the sample.

5.2 Sampling and sample preparation

Introduction Sampling and the sample preparation have a great influence on the reproducibility of the measurement results. While crushing a sample, for example, care must be taken that the sample does not heat up and that the entire process is completed rapidly, since moisture will otherwise evaporate during the process. It is also important that the sample being investigated is a representative part of the total amount of the sample under test.
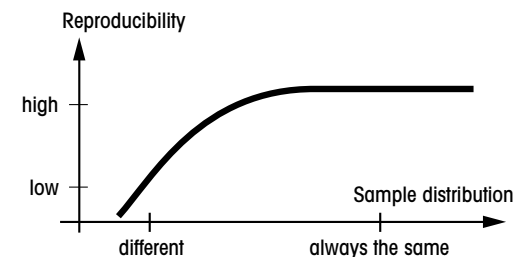
Sampling and sample preparation In the first instance, the result of a moisture determination depends on a carefully thought out sample preparation. The part of the sample used for analysis must always be representative of the total quantity. The sample preparation includes work processes such as

sampling, sample division, size reduction, homogenization and others. All these processes should be carried out as quickly as possible and without loss or uptake of moisture.

With most products, the lab samples, it can be assumed that they are not homogenous. As a result, random sampling will not lead to a representative analysis sample. To obtain a representative sample, the appropriate standards and directions must be consulted to determine the method of sampling as this is dependent on the product, consistency and the amount used.

Number of samples An increase in the number of samples always leads to an improvement in the statistical reliability of the analysis results. The size depends on the homogeneity of the test material, the accuracy of the measurement method and the desired accuracy of the measurement result.

Mechanical size reduction The comminution properties of the sample essentially influence the selection of the type of mill and its grinding implements. Hard, brittle samples are mainly reduced in size by pressure, impact or friction action, whereas soft and viscoplastic substances can be comminuted only by shearing or cutting action.

Whatever the operating principle of a mill may be, for the subsequent moisture determination there must be no loss of moisture from the sample during the milling operation. If this can not be avoided, for whatever reason, it should at least be calculable. The quantitative recovery of the milled sample from the mill chamber should also be simple and complete.

In practice, a wide range of kitchen mixer models are frequently still used to reduce the size of lab samples for moisture determination. While these units may produce a satisfactory performance in the kitchen, in the lab the standards are more exacting and can certainly not be met with such mixers.

You will find further information on the sample division, especially for moisture distribution, in other words on sampling and sample division as well as on different size reduction possibilities from the manufacturers of such units. e.g. RETSCH GmbH in Haan, Germany.

Sample pan The material and surface finish of the selected sample pan can have a significant effect on the quality of the measurement results. For example, scratched or smeared surfaces have different reflective properties than smooth, even ones.

Use of quartz sand To assure an optimum drying process, samples should always have as large an area as possible. Results of substances which form crusts (e.g. glucose syrup) or pasty substances (e.g. butter) can be considerably improved by mixing with quartz sand or covering with a glass-fiber filter.

Pasty, fat-containing and melting substances For pasty, fat-containing and melting substances, use of a glass fiber filter is advantageous to increase the surface area of the sample. The glass fiber filter is tared together with the sample pan. The liquid contained in the substance is uniformly and extensively distributed in the interstices between the fibers throughout the available area. The same also applies to melting fats and fat-containing samples. This increase in the surface area results in faster and complete vaporization of the moisture. Predrying of the glass fiber filter and its storage in a desiccator is necessary only for highly precise measurement results.

Otherwise it is sufficient to use strongly hydrophobic filters, such as those available in the METTLER TOLEDO range of accessories.

Liquid substances Liquid substances (e.g. dispersions) often tend to form drops on the sample pan owing to the surface tension of the liquid. This hinders rapid drying, because evaporation takes place only on a limited area of the liquid's surface. The use of a commercial glass fiber filter frequently shortens the drying time by a factor of 2 to 3. The glass fiber filter distributes the liquid sample over a wide area as a result of its absorbent action. Predrying of the glass fiber filter and its storage in a desiccator is necessary only for highly precise measurement results.

Skin-forming and temperature-sensitive substances

The use of a glass fiber filter can be useful for temperature-sensitive and skin-forming substances. In this case, the sample to be dried is covered by the filter and thus receives a "new surface". This shields the surface of the sample against the direct IR radiation and gentler heating of the sample based rather on convection than on IR radiation is achieved. Experience with this type of preparation has been good, particularly for products containing sugar. Further, the shielding of the sample against direct IR radiation by covering the test substance can make a considerable contribution to improving the reproducibility with temperature-sensitive samples.

This procedure is also useful for unevenly colored samples, since these heat unevenly due to the differing absorption of the heat radiation.

Sugar-containing substances

Samples containing a large amount of sugar tend to caramelize on the surface. In such cases, ensure a thin layer is applied. Also select a moderate temperature.
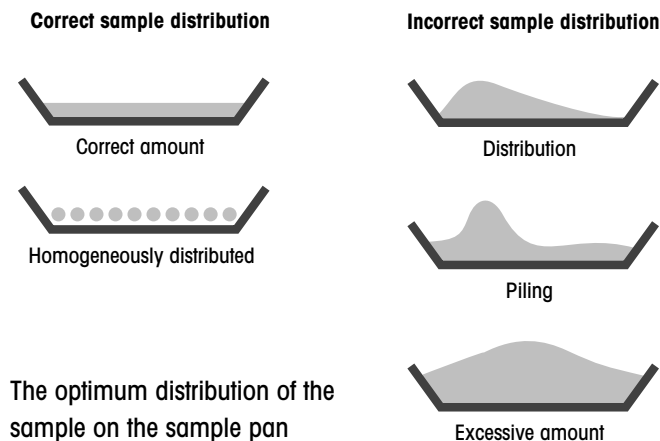
Bulky samples

Bulky or swelling samples can cause incorrect measurement results due to touching the protective glass in the Halogen Moisture Analyzer. To ensure even and mild drying, its is advisable to use a sample cage which is available as an accessory for the HG53 and HR73.

Sample application on the drying pan

To obtain reproducible results, it is essential to ensure uniform distribution of the sample on the pan. An uneven distribution can result in inhomogeneous heat distribution in the sample. As a consequence, the sample could be incompletely dried in the center owing to excessive piling. Thick layers have an adverse effect on the escape of moisture. The resulting lengthening of the measurement time promotes decomposition at the surface of the sample by prolonged heat action. Film formation on the sample can prevent complete escape of the moisture. With such samples, ensure application of a thin and uniform layer thickness.

With readily volatile samples, rapid application of the sample on the sample pan is advisable, otherwise moisture can escape before the initial weight is recorded; here, use of the "manual" operating mode is appropriate.

Correct sample distribution   **Incorrect sample distribution**

Correct amount

Distribution

Homogeneously distributed

Piling

The optimum distribution of the sample on the sample pan

Excessive amount

Treating the sample during drying

Occasionally, following recording of the initial weight of the sample and before the actual drying, the test substance is subjected to further treatment. The Halogen Moisture Analyzer from METTLER TOLEDO offers this possibility in the "manual" operating mode.

Applications for this could be:

– Mixing with quartz sand. Proceed as follows: tare the weighing pan, a small glass rod, and if necessary, a glass-fiber filter or quartz sand. Place the sample on the pan and start the drying process in operating mode "Manual". This records the starting weight of the sample, and includes any loss of mass due to evaporation in the result. Then use the glass rod to distribute the sample evenly on the weighing pan. Finally, start heating by closing the sample chamber (HR73, HG53) or heating unit (HB43), including the glass rod in the drying process.

– Coagulation of protein by dropwise addition of alcoholic solutions. This prevents skin formation during drying. Added solvent is not recorded in the final result.
– Formation of readily volatile azeotropes by addition of solvents insoluble in water (e.g. xylene, toluene).

Note that the addition of solvents can lead to the formation of flammable or even explosive mixtures. With applications of this type, you should thus work with extremely small amounts of samples and with the necessary care.

In cases of doubt, a careful risk analysis must be performed.

5.3   Development of a method
for the METTLER TOLEDO Moisture Analyzer

Statutory regulations, branch standards or in-house instructions which specify the method used for the moisture content determination are occasionally found for substances. The drying oven method or the Karl Fischer titration is frequently used as a reference method. In this case, when developing a method for the Halogen Moisture Analyzer from METTLER TOLEDO ensure that the measurement results of the reference method agree with the results of the Halogen Moisture Analyzer or that any discrepancy is known and can be reproduced. If no directions exist, moisture determination methods can be developed directly with the METTLER TOLEDO Moisture Analyzer. In such a case, interest is centered less on the true moisture content, but rather on the ability of the method to supply a measured value which can be correlated with the quality of the substance.

In what follows, matching of the drying parameters to the problem will be described.

Selection of the optimum sample weight

The sample weight has an influence on both the accuracy of the measurement results and the measurement time. With large amounts of samples, a great deal of water must vaporize and the moisture determination takes longer.

Also, if the sample is too large, this can cause the heat to be distributed unevenly and lead to poor analysis results. To keep the measurement time as short as possible, we advise you to choose a low weight for your sample, but not so low that attainment of the required measurement accuracy is no longer possible.
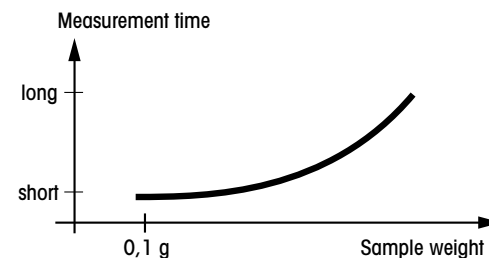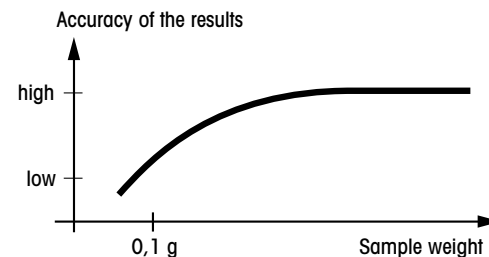
Influence of the sample weight on the repeatability of the results

In what follows we describe how the sample weight influences the repeatability of the Halogen Moisture Analyzer. As a general rule, a smaller sample weight gives lower repeatability.

With the Halogen Moisture Analyzer from METTLER TOLEDO, the relation between sample weight and repeat standard deviation (s) is shown in the following table:

Sample weight	Repeat standard deviation (s)	
	HG 53/HR73	HB43
0,2 g	1%	1,5%
0,5 g	0,4%	0,6%
1 g	0,2%	0,3%
2 g	0,1%	0,15%
5 g	0,04%	0,06%
10 g	0,02%	0,03%

Comments on the table

This table is based on the assumption that the sample is ideal, homogeneous and its moisture can always be separated completely and free from decomposition (e.g. moist sand). Deviations always comprise the uncertainty, which depends on the sample, and the repeatability of the instrument. In practice, measurement differences appearing within a measurement series can consequently be larger than the values of the Halogen Moisture Analyzer shown in the table.

The two examples below show how the sample weight is determined to keep the drying time to a minimum and meet the accuracy demands of the instrument.

Example 1

The repeatability should be better than ±0.1%. The accuracy table shows that this requires a minimum sample weight of 2 g for an HR/HG and 3 g for an HB43.

Example 2

Wet weight of sample:	10 g
Mean value of the results:	15.5%
Repeat standard deviation (s) from table:	±0.02%
Approx. 68% of measurement values are in the range:	15.48%–15.52%

Selection of the drying temperature The drying temperature exerts a controlling influence on the measurement time. It must be selected so that the sample neither decomposes nor changes its chemical structure. A drying temperature that is too low can unnecessarily prolong the drying time.

Note also that certain samples can give off different amounts of moisture at different drying temperatures. This is the case with substances in which the strength of the bonds binding the moisture varies or those which tend to show signs of decomposition. Minimum deviations from moisture content values of the reference method can be compensated by changing the drying temperature.

We suggest the following procedure for selecting the temperature.
– Estimate moisture content of the sample.
– Determine the decomposition temperature of the sample by experiments.
– Compare the measurement results with the reference method if one exists.
  If an excessive amount of moisture is evolved, lower the drying temperature. If the experimental results are too low, the drying temperature was possibly too low or the drying time too short.

With samples which have a high moisture content, it is possible to shorten the measurement time by selection of the step or rapid drying program. Here, the greatest part of the existing moisture is separated at an elevated temperature. The drying temperature is then lowered and kept constant until the end of drying. The excessive temperature is used for rapid vaporization of the moisture, but the effective sample temperature does not exceed the boiling temperature of the liquid (cooling effect through endothermic vaporization). In certain cases, local heating and decomposition could still occur at the sample surface (see also section 2.7).
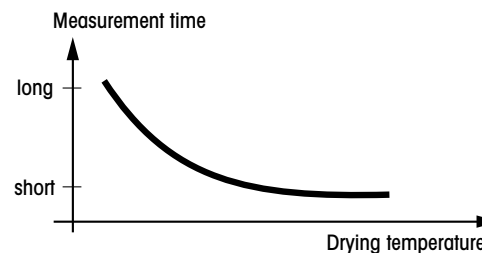
Selection or the drying program

Depending on the model of the Halogen Moisture Analyzer, various drying programs are available. Appropriate use of the different programs is described in what follows:

Instrument model	HR73	HG53	HB43
– Standard drying program	•	•	•
– Gentle drying program	•		
– Rapid drying program	•		•
– Step drying program	•		

Temperature profile

Standard

Gentle drying

Rapid drying

Step drying
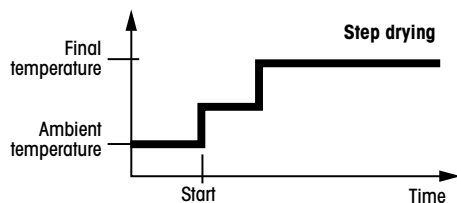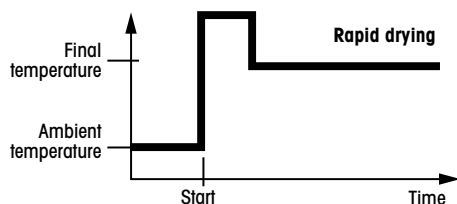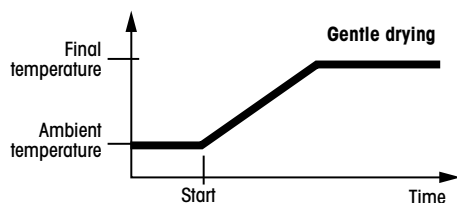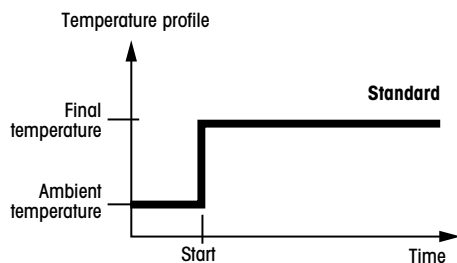
Brief description of standard drying

Standard drying is suitable for precise determination of the moisture content of most substances. For special cases or for time-optimized measurements, the selection of a more complex drying program may be advantageous.

Brief description of gentle drying

Gentle drying is selected if substances are not stable on exposure to the full heating power of the halogen radiator at the start.

In gentle drying, sensitive samples are preventing from decomposing by the gentle heating. Gentle drying can also be used successfully with substances which form a skin.

When mild drying is used, the sample heats up evenly from the outside to the inside by slow heat convection.

Brief description of rapid drying

The rapid drying program is suitable for samples with a moisture content between 5% and 15%.

With rapid drying, for three minutes after drying starts, the output from the radiator is 40% higher than for the set temperature value. This compensates the endothermic heat of vaporization and accelerates the drying process. Note that the sample must contain sufficient moisture during this first minute to cool it.

Brief description of step drying

The step drying program has a use similar to that of the rapid drying. The duration of the excessive temperature stage and the temperature value are freely selectable. It is used primarily with samples with a moisture content greater than 15%.

A second application possibility lies in the selective determination of the moisture at different temperatures. Gypsum, for example, evolves only its surface water at 50 °C, whereas the water of crystallization can not be separated until 168 °C. With this drying program it is thus possible to determine the surface water and the water of crystallization separately within the same measurement by a controlled temperature profile.

Selection of the drying time

The Halogen Moisture Analyzer offers two different types of switch-off criteria. A switch-off criterion is understood to mean the condition which must be met for the Halogen Moisture Analyzer to switch off automatically.

The first type is a timed switch-off. This is used primarily when the drying process does not attain a constant final value and the sample continuously loses mass over time through decomposition or the evolution of difficult to volatilize components.

The second type recognizes the end of drying automatically. The integrated balance continuously determines the weight loss of the sample during drying. It the weight loss per time unit is less than the set level, drying is stopped and the final result displayed.

The automatic switch-off criterion is divided into five selectable levels:

Level 1: For rapidly drying substances (e.g. paper)
Level 2: Intermediate level
Level 3: For standard samples (e.g. butter)
Level 4: Intermediate level
Level 5: For slow drying substances (e.g. plastics)
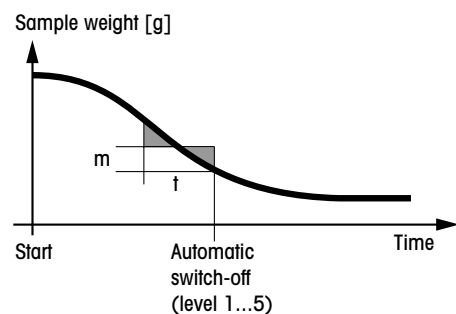
Switch-off criterion and sample weight

To ensure the Halogen Moisture Analyzer always recognizes the automatic switch-off criterion at the same extent of drying of the sample, the initial weight of the sample should always be around the same ($\pm 10\% \ldots \pm 20\%$).
When the timed switch-off is selected, the sample weight can also have an influence on the accuracy of the measurement result. This is the case when the moisture of a sample which is too large can not be separated completely within the selected drying time.
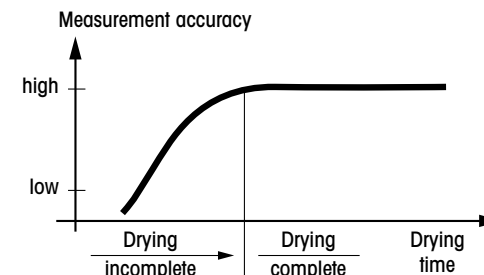
The influence of the switch-off criterion on the measurement time

The selection of the level (level 1…5) of the automatic switch-off criterion always has an influence on the measurement time.
The drying time is shorter when level 1 is selected. However, drying is often still incomplete. When selecting the switch-off criterion, the user must decide between a short measurement time or increased accuracy of the measurement result.

The test measurement to determine the optimum switch-off criterion

The test measurement function built into the HR73 and HG53 Halogen Moisture Analyzers provides a valuable aid for method development. During the test measurement a record is printed out with intermediate results. An analysis of these intermediate results provides the information needed for selection of the suitable switch-off level.

Analysis of the drying profile

The printer can be used to follow the drying profile thanks to the repetitive printout of intermediate values. The analysis of the drying profiles shows two types of curves.

In the first type the drying profile is asymptotic. The amount of moisture lost assumes a constant value and no longer changes even after long drying times. With this drying profile, repeatable determinations of the moisture content are always simple. The measurement result then corresponds exactly to the constant value of the asymptote. It is also correspondingly easy to find a suitable switch-off criterion.

In the second type drying runs quickly at the start and then flattens out. However, the moisture content never assumes a constant value. The causes of such a temperature profile can be as follows: The sample exhibits thermal decomposition, the decomposition products vaporize and the sample continuously loses weight. Fats, oils, plasticizers or other volatile components can lead to superimposed profiles owing to their slower vaporization than water. The difficult to volatilize components lead to a slow, continuous decrease in weight.
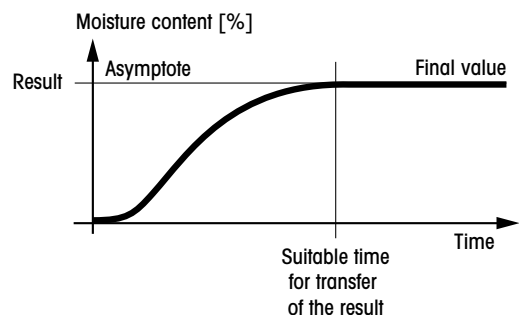
Measurement results of such a drying profile can be optimized:

– Lowering the temperature can slow down the decomposition reaction.
– The selection of a suitable switch-off criterion can allow recognition of the end of the analysis at the desired break point of the drying curve.

– The selection of a constant drying time often provides good measurement results.
– Keep the initial weight of the sample constant (±10%...±20%).

With coarse sample particles which toward the end of the drying diffuse only minimal moisture, the drying can already be terminated.
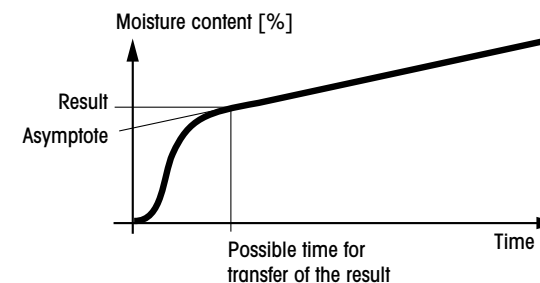
The method error

Considering the overall picture, a distinction is made between statistical and systematic errors.

Statistical errors are random deviations which can not be corrected. They essentially include the measurement deviations due to the instrument and those caused by different methods of preparation, procedures and handling of the sample.

Systematic errors are constant deviations and can frequently be corrected.
Such errors could include:

– Lengthy wait times between sampling and moisture determination
– Incomplete drying caused by too short a drying time.
– Decomposition of the samples at an excessive drying temperature
– Use of a moist glass fiber filter or moist quartz sand.
– Coarse samples

For further information, please see sections 2.6 and 2.7

5.4   Schematic procedure for developing a method

The scheme shows a possible systematic procedure to develop a method.

Scheme of the method development

Define requirements (expected reproducibility), collect information on the substance

Determine sampling and sample preparation. → section 5.2.

Does sample contain solvent? — yes → Perform risk analysis

no

Organic sample? — no / yes

Drying temperature is noncritical

Selection of the drying temperature → section 5.3

Selection of the drying program → section 5.3

Selection of the drying time or automatic switch-off criterion* → section 5.3

Are the results reproducible? — no → Improve sample preparation if possible

yes

Is agreement of the results with a reference method necessary? — yes

no

* The test function supports you here in determination of the optimum switch-off criterion

How is the measured moisture content related to the reference method? — higher / lower

Lowering of the temperature or automatic switch-off criterion*

Raising the temperature or automatic switch-off criterion*

Documentation of the method

Determination with the Halogen Moisture Analyzer

5.5   Case study

A case study will be used to show how a method was developed for butter.

Making preliminary assessment and collecting information

Analysis matrix
Butter contains mainly fat and water, as well as substances of high nutritional value.

Moisture content
Experience has shown that butter has a moisture content between 15 and 17%.

Legislation
Statutory food regulations.

Reference method
The statutory food regulations of most countries stipulate the drying oven method.
The Karl Fischer titration is also a method of determination in common use.

Amount of sample
An amount of sample of 3g assures results of sufficient accuracy. (instrument error is <0.1% according to accuracy table).

Possible complications
Organic substances: Decomposition possible.
Vaporization of readily volatile fat components at excessive drying temperature possible. Butter melts. Inhomogeneity of the samples. Contains frozen water droplets which could be squeezed out during the sample preparation on improper handling.

Consequences
Use glass fiber filter or quartz sand.

Determination of optimum drying parameters

The following measurements were performed in the test mode with a print interval of 10 seconds.

1st test run
Standard drying program with 150 °C.
Sample weight 3 g.

Result
Measured values are slightly too high.
Drying profile is asymptotic.
Fat odour and browning after drying (slight decomposition).

2nd test run
Standard drying program at lower temperature of 130 °C.
Sample weight 3 g.

Result
Good measurement results, drying profile is asymptotic.
After drying, no oxidation damage apparent.
Measurement time: 4 minutes (switch-off criterion level 3)

Determination of the drying parameters

Drying program
Step drying as moisture content above 15%.

Drying temperature
1st level   2 minutes, 150 °C
2nd level   0 minutes, 150 °C
3rd level   130 °C (duration determined empirically)

Sample weight
3 g (±10%)

Switch-off criterion
Level 3

Checking repeatability

Three measurements of the same batch were performed.

Tables of measurements
Measured values: 16.70%, 16.85%, 16.52%
n: 3
Mean value: 16.69%
Standard deviation (s):   0.17%

Comparison with the drying oven reference method

The measurement results of the METTLER TOLEDO Halogen Moisture Analyzer agree with the values determined by the drying oven method.

Comments on comparison of the measurement results.
If differences between the measurement results compared with the reference method are found, a series of experiments involving changing the temperature or the switch-off point can be performed to ensure agreement with the reference.

5.6   Obtaining results to match a reference method

When determining optimal drying parameters for a new moisture determination method, it is common to relate them to a reference method. This is often the traditional drying oven , but sometimes the LP16 or LJ16 infrared dryer, or Karl Fischer Titration.
In doing so, it is often assumed that the measurement result of a new method should match that of the reference method. However, for physical and technical reasons the drying temperature of the drying oven or infrared dryer cannot always be used without modification, and new settings must be found for the Halogen Moisture Analyzer.
The following procedure has proved itself in practice:

Test measurements After suitably preparing the sample (see Chapter 5.2) identical quantities of sample are measured at different temperatures using the test function of the HR73 or HG53 and the results shown graphically (see Fig. 1). To simplify this process, your Halogen Moisture Analyzer can be connected to a computer via the data interface

which is built in as standard. The measurement data can be read into a spreadsheet program by means of a suitable program (e.g. METTLER TOLEDO BalanceLink`). You will find further information in the "Reference Manual for METTLER TOLEDO Standard Interface Command Set (MT-SICS)" (order no. 11780409).

In a test measurement all five pre-programmed switch-off criteria (i.e. weight loss per unit of time) are measured in sequence and printed out on a printer (or the computer). In the present example, the test measurements were made on fine flour at 90, 110, 130, and 150 °C. The reference moisture content of the same sample, as determined by multiple measurements at 103 °C in a drying oven, serves as the basis for further evaluations and appears as a horizontal straight line on the graph. The temperature from the drying oven method is usually a good way of obtaining first information about the drying behavior of a sample. It will be seen immediately that with a drying temperature of 90 °C the moisture content which was determined with the drying oven is only reached after a very long time. This means that this temperature is too low. By contrast, at 150 °C the drying curve intersects the reference moisture content at a very obtuse angle (high weight loss per unit of time), which generally results in poor repeatability of the analysis results (sample not yet completely dry, or decomposes very quickly). This means that an ideal drying temperature would be lower.

The two other curves (110 °C and 130 °C) indicate good results and cut the line of the reference moisture content at a very acute angle, i.e. very low weight loss per unit of time.

Graphical data evaluation of the switch-off criteria

The results of the individual switch-off criteria are displayed graphically (Fig. 2). The moisture content of the sample is plotted against the drying temperature, and the results of the switch-off criteria appear as points on the graph. For example, point 110/2 indicates the moisture content of flour as determined at a drying temperature of 110 °C and with automatic switch-off criterion 2. The horizontal straight line on the graph again represents the result expected from the reference method. The points at which the five curves intersect the reference straight line indicate possible settings for the com-

bination of temperature and switch-off criterion. However, not all of them are realistic. Possible settings are, for example, 110/3 or 130/2. Needless to say, other settings between these are also possible (e.g. 120 °C and a free switch-off criterion) and have to be found out by experimentation.

Switch-off criteria 3 and 4 generally give well-repeatable results as well as short analysis times.

Fine tuning the method

To verify the repeat standard deviation of the results (mean and standard deviation) and attainment of the desired accuracy, several measurements based on the selected settings now have to be carried out. If time is more important than repeatability, a higher temperature can be selected. If a sample decomposes rapidly at higher temperatures, a lower temperature should be selected for reliable results.

Notes

Switch-off criteria 1 and 2 should only be used in exceptional cases, i.e. when speed is more important than repeatability.

The free switch-off criterion of the HR73 can also be used to select intermediate settings. This ensures more precise correlation of the result with that of the reference method. To measure a sample whose drying properties are completely unknown, it is advisable to start the determination of the curve values at 80, 100, 120, 140 and 160 °C. Approximating the results in the way described above is only necessary if the samples display thermal decomposition (especially substances with high grease or solvent content). With samples of this nature, after all the water has evaporated the weight continues to decrease due to the decomposition process (asymptotic drying, Chapter 5.3). In all other cases a high temperature guarantees fast, reliable results.
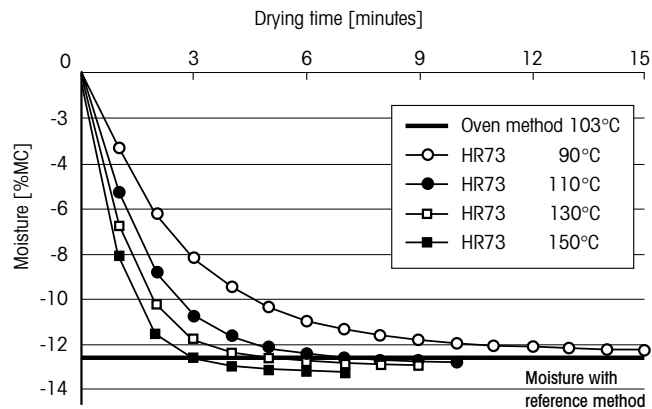
Figure 1: Moisture content determination of fine flour at various temperatures. Moisture content is plotted against drying time. The moisture content of the same sample analyzed using the reference method is plotted as a horizontal line and serves as the basis for the subsequent evaluations.
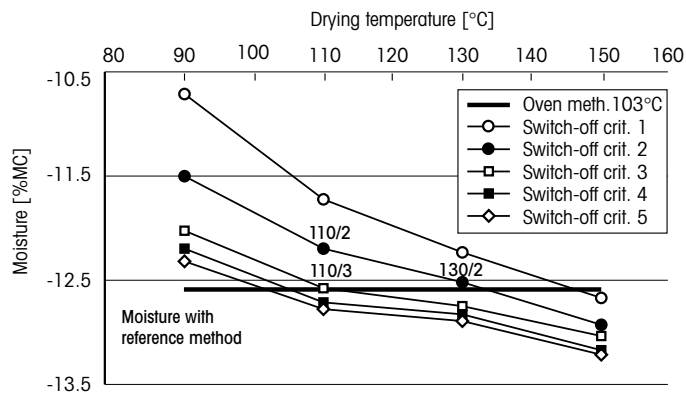
Figure 2: The results of the switch-off criteria are plotted against drying temperature. This makes it possible to find the ideal combination of switch-off criterion and temperature.

5.7   What if?

The table shows suggestions for solutions to various categories of problems

Problem	Possible solutions
Sample shows oxidation damage	Lower temperature. Try gentle drying program. Select rapid drying program to shorten the analysis time so that the extent of decomposition has no effect on the measurement result. Cover sample with glass fiber filter or Al foil during the measurement.
Analysis time is too long	Increase temperature, decrease switch-off criterion. Use rapid or step drying program (on moist samples). Reduce sample quantity. Increase sample surface by suitable sample preparation, use of quartz sand or glass-fiber filter.
Result accuracy is insufficient	Increase number of samples. Increase sample weight. Analyze drying profile. This often provides information on whether the end of drying has been reached or when the Halogen Moisture Analyzer has reach the automatic switch-off criterion.
Results are not reproducible	Select drying experiments with timed switch-off criterion. Optimize homogenization of the sample. Standardize handling of the sample, acclimatize sample. Glass-fiber filter for liquid samples. Grind sample and distribute evenly. Always dry identical quantity of sample.
Sample melts (high fat content), is liquid or pasty	Use glass fiber filter.
Sample has low moisture content	Increase amount of sample.
Sample contains sugar and caramelizes	Cover sample during drying with glass fiber filter.
Sample has moisture content between 5–15%	Try rapid drying program.
Sample has moisture content >15%	Try step drying.
Sample contains solvent	Follow safety directions at all costs.
Others	Coagulate protein. Dry on glass fiber filter. Cover caramelizing substances during drying with glass fiber filter.

5.8 Application examples

The table shows a range of application examples which have been worked out for the METTLER TOLEDO Halogen Moisture Analyzer. The data give a first indication of how the drying parameters can be set to rapidly obtain similar results to those measured in the drying oven. However, the settings must always be checked for the particular case, and adapted to the specific sample. Further examples and updates are available on the Internet at

http://www.mt.com.moisture.

Table

Compilation of applications with the METTLER TOLEDO Moisture Analyzer

	Reference Method Drying Oven					HR73 Halogen Moisture Analyzer							
	Sample preparation	Procedure	Sample weight (g)	Temperature °C	Mean value	Sample preparation	Sample weight (g)	Temperature program	Temperature °C	Switch-off criterion	Mean value (% moisture)	Repeat standard deviation (s)	Approx. drying time (min.)
Building materials													
Acrylic paint	16)	a)	5	103	66,91	10)	3	Standard	200	5	66,74	0,25%	19–21
Emulsion paint (black)	7)	f)	3	103	36,58	3)	2,5	Rapid	120	5	35,70	0,37%	11–16
Emulsion paint (yellow)	7)	f)	3	103	40,34	3)	2	Rapid	170	5	39,28	0,42%	7–10
Plaster	1)	a)	5	103	5,92	12)	5	Standard	180	4	5,97	0,15%	8–9
Foodstuffs													
Red kidney beans	5)	b)	5	130	14,36	13)	3	Standard	140	5	13,93	0,17%	9–12
Cannellini beans	5)	b)	5	130	13,59	13)	3	Standard	160	3	13,36	0,06%	8–11
Consommé (soup)	1)	d)	5	103	1,83	12)	3	Standard	120	3	1,55	0,09%	2–3
Meat (chicken)	17)	e)	5	102	74,89	18)	3	Mild	v)	5	74,38	0,27%	18–22

	Reference Method Drying Oven					HR73 Halogen Moisture Analyzer							
	Sample preparation	Procedure	Sample weight (g)	Temperature °C	Mean value	Sample preparation	Sample weight (g)	Temperature program	Temperature °C	Switch-off criterion	Mean value (% moisture)	Repeat standard deviation (s)	Approx. drying time (min.)
Foodstuffs (continued)													
Vegetable juice	2)	a)	10	103	93,24	3)	4	Rapid	140	4	93,50	0,06%	14–16
Hazelnuts (ground)	1)	d)	5	103	5,16	12)	5	Standard	130	3	4,91	0,07%	5–6
Millet	5)	b)	5	130	12,37	13)	3	Standard	160	3	12,09	0,23%	9–13
Yogurt	14)	c)	5	102	87,58	15)	3	Step	u)	5	87,92	0,06%	14–23
Coffee cream	7)	a)	4	103	77,67	8)	2,5	Step	s)	5	77,42	0,30%	14–17
Chocolate drink (instant)	1)	d)	5	103	2,10	12)	4,5	Standard	120	3	1,97	0,04%	2–3
Carrot juice	2)	a)	10	103	90,48	3)	4	Standard	140	3	90,49	0,05%	9–11
Potato flakes	1)	d)	4	103	7,71	12)	3	Standard	100	4	7,56	0,15%	11–13
Grated coconut	1)	d)	5	103	1,68	12)	3	Standard	110	3	1,50	0,05%	3–4
Condensed milk (sweetened)	11)	c)	2	102	25,91	10)	2,5	Mild	f)	4	25,98	0,29%	26–30
Condensed milk (unsweet.)	9)	c)	3	102	74,43	10)	3	Standard	130	4	74,23	0,14%	12–17
Salmon	17)	e)	5	102	67,70	18)	3	Rapid	120	5	67,51	0,34%	23–28
Lentils	5)	b)	5	130	11,43	13)	3	Standard	170	4	11,47	0,14%	5–8
Polenta	1)	d)	10	103	12,70	12)	4	Standard	120	3	12,28	0,41%	12–16
Corn starch	1)	d)	5	103	11,74	12)	3	Standard	90	3	11,14	0,13%	10–11
Almonds (ground)	1)	d)	5	103	4,32	12)	5	Standard	110	3	4,03	0,16%	8–9
Milk (skimmed)	1)	c)	5	102	88,51	3)	2,5	Step	u)	5	88,51	0,07%	7–9
Milk (whole)	1)	c)	5	102	87,45	3)	2,5	Step	u)	5	87,16	0,54%	7–9
Orange juice (from concentr.)	2)	a)	10	103	89,95	3)	4	Rapid	130	4	89,54	0,07%	15–19
Orange juice (fresh)	2)	a)	10	103	89,14	3)	4	Rapid	140	3	89,17	0,11%	10–14
Breadcrumbs	1)	d)	10	103	4,84	12)	2,5	Standard	100	4	4,16	0,10%	11–14
Pepper (black)	1)	d)	2	103	10,54	12)	2,5	Standard	90	3	9,54	0,28%	6–8
Cream	7)	c)	4	103	48,85	8)	2,5	Step	u)	3	49,11	0,36%	6–8
Rice	5)	b)	5	130	13,45	13)	3	Standard	165	5	13,06	0,23%	16–18
Cocoa powder	1)	a)	3	103	0,76	12)	6	Standard	80	3	0,71	0,02%	3–4
Syrup	4)	a)	5	103	27,10	3)	3	Rapid	80	3	26,85	0,25%	24–29
Tea (green)	1)	d)	2	103	6,24	12)	4	Standard	100	4	5,67	0,09%	15–18
Tea (black)	1)	d)	2	103	6,82	12)	3	Standard	100	4	6,33	0,08%	11–14
Raisins	20)	a)	4	103	16,97	21)	3	Standard	115	3	17,18	0,54%	27–32
Wheat	5)	b)	5	130	14,10	13)	3	Standard	175	4	13,88	0,23%	12–14
Garden and household													
Fertilizer (potash)	1)	a)	5	103	1,20	12)	3	Standard	140	5	1,13	0,05%	4–5
Lime	1)	d)	20	103	0,10	12)	20	Standard	200	4	0,11	0,00%	2–4
Bone meal	1)	a)	5	103	5,41	12)	3	Standard	140	3	5,52	0,08%	6–8
Detergent	1)	a)	5	103	10,81	12)	3	Standard	115	3	10,62	0,21%	17–20
Toiletries													
Hair gel	6)	a)	5	103	91,51	10)	3	Standard	120	5	91,35	0,08%	18–23
Bath foam	7)	f)	3	103	86,57	3)	3	Rapid	150	5	86,13	0,26%	6–8
Soap (liquid)	7)	f)	3	103	85,51	3)	3	Standard	170	5	85,56	0,10%	9–12
Shampoo	7)	f)	4	103	83,88	3)	3	Rapid	160	5	83,93	0,08%	9–12

Sample preparation:

Number	Description
1	Weigh (previously dried) weighing bottle. Distribute sample quantity of the respective product evenly in the bottle, then place in drying oven
2	Dry aluminum pan containing 10 g beach sand (or quartz sand) and glass stirring rod in drying oven (approx. 1 hour at 130 degrees) then weigh in. Use pipette to add sample and stir well. Ispissate for 45 min. on a heating plate or in a drying oven at 90 degrees, then place sample in a drying ofen at final temperature
3	Accessories: aluminum pan, glass-fiber filter, pipette. Use the pipette to distribute the liquid sample evenly in the pan, then cover with glass-fiber filter
4	Dry aluminum pan with 10 g beach sand (or quartz sand) and glass mixing rod in drying oven. Weigh. Use pipette to add sample liquid, weigh, then add 5 g clean water and mix. Inspissate for 30 min. in a water bath, on a heating plate or in a drying oven at 90 degrees before drying in drying oven
5	Grind sample in a water-cooled grinding mill (2 x 5 s, with interval of 20 s), then put 5 g the ground sample in a previously dried weighing bottle, and distribute evenly. Place in drying oven at 130 degrees
6	Dry aluminum pan with 20 g beach sand (or quartz sand) and glass stirring rod in drying oven. Weigh. Use pipette to add sample, then add 10 g clean water and mix. Inspissate for 30 min. in a water bath, on a heating plate or in a drying oven at 90 degrees before drying in drying oven
7	Dry aluminum pan with 20 g beach sand (or quartz sand) and glass stirring rod in drying oven (approx. 1 hour at 130 degrees) and weigh in. Use pipette to add sample and mix well with the sand. Weigh, then place in drying oven
8	Accessories: aluminum pan, glass-fiber filter, pipette. Use the pipette to distribute the liquid sample uniformly in the pan, then cover with glass-fiber filter. (Temp. 1: 180 degrees; time 1: 3 min.; temp. 2: 105 degrees, time 2: 2 mins.; final temperature: 77 degrees)
9	Weigh in aluminum pan with glass mixing rod. Add sample liquid and weigh, than add 5 g clean water and mix. Before the actual drying in the drying oven , allow to inspissate for 30 min. in a water bath, on a heating plate or in a drying oven at 90 degrees
10	Accessories: aluminum pan, glass-fiber filter, spoon. Use the spoon to distribute the viscous liquid sample evenly in the pan then cover with glass-fiber filter
11	Dry aluminum pan with 20 g beach sand (or quartz sand) and glass stirring rod in drying oven (approx. 1 hour at 130 degrees) and weigh in. Then add sample and stir well. Weigh in. Inspissate in a water bath, on a heating plate or in a drying oven for 30 min. at 90 degrees, then place in drying oven
12	Weigh in sample pan. Distribute sample material evenly in pan, start moisture measurement
13	Grind sample in a water-cooled grinding mill (2 x 5 s, with interval of 20 s), then evenly distribute 3 g of the ground sample in an aluminum pan
14	Dry aluminum pan with 20 g beach sand (or quartz sand) and glass mixing rod in drying oven for approximately 1 hour at 130 degrees. Weigh in. Then add sample and weigh. Then add 10 g clean water, mix well, inspissate for 30 min. in a water bath, on a heating plate or drying oven at 90 degrees, and then place in drying oven
15	Accessories: aluminum pan, glass-fiber filter, spoon. Use the spoon to distribute the sample evenly in the pan, then cover with a glass-fiber filter. Start moisture measurement program. (Temp. 1: 180 degrees, time 1: 3 min.; temp. 2: 105 degrees, time 2: 2 min.; final temperature 77 degrees)
16	Dry aluminum pan with 20 g beach sand (or quartz sand) and glass stirring rod in drying oven (approx. 1 hour at 130 degrees) and weigh in. Then add sample and weigh. Then add 5 g clean water, mix well, and allow to inspissate for 30 minutes in a water bath, on a heating plate or in a drying oven at 90 degrees, then place in drying oven
17	The meat was finely minced in a water-cooled grinding mill (2 x 5 s, with interval of 20 s), mixed well in an aluminum pan with 20 g quartz sand (and a glass mixing rod), then placed in the drying cabinet
18	The meat is prepared as for the drying oven method, except that the minced meat is then evenly distributed in the aluminum pan with a spoon
19	The pork was passed through the mincer twice, mixed well (using a glass rod) with 20 g quartz sand in an aluminum pan and then placed in the drying oven
20	Chop the raisins 3-4 times with a scalpel then distribute evenly in the aluminum pan
21	Remove the weighed-in aluminum pan from the balance, place the raisins in it, crush them with a pestle, and distribute evenly in the pan

Procedure:

a	Dry in drying oven for 3 hours, then cool in desiccator to room temperature, weigh out, then dry for 1 hour in drying oven, cool in desiccator, weigh out, then dry for a further 1 hour in drying oven, cool in desiccator, weigh out
b	Dry in drying oven for 1.5 hours, then cool in desiccator to room temperature, weigh out, then dry for 1 hour in drying oven, cool in desiccator, weigh out, then dry for a further 1 hour in drying oven, cool in desiccator, weigh out
c	Dry in drying oven for 2 hours, then cool in desiccator to room temperature, weigh out, then dry for 1 hour in drying oven, cool in desiccator, weigh out, then dry for a further 1 hour in drying oven, cool in desiccator, weigh out
d	Dry in drying oven for 3 hours, then cool in desiccator to room temperature, weigh out, then dry for 1 hour in drying oven, cool in desiccator, weigh out, then dry for a further 4.5 hours in drying oven, cool in desiccator, weigh out
e	Dry in drying oven for 4 hours, then cool in desiccator to room temperature, weigh out, then dry for 1 hour in drying oven, cool in desiccator, weigh out, then dry for a further 4.5 hours in drying oven, cool in desiccator, weigh out
f	Dry in drying oven for 3 hours, then cool in desiccator to room temperature, weigh out, then dry for 1 hour in drying oven, cool in desiccator, weigh out, then dry for a further 6 hours in drying oven, cool in desiccator, weigh out

Temperature Program:

s	Step drying (temp. 1: 180 degrees, time 1: 3 min.; temp. 2: 105 degrees, time 2: 2 min.; final temperature 77 degrees)
t	Mild drying (ramp 3 minutes), final temperature 155 degrees
u	Step drying (temp. 1: 180 degrees, time 1: 3 min.; temp. 2: 105 degrees, time 2: 2 mins; final temperature 77 degrees)
v	Mild drying (ramp 3 minutes), final temperature 160 degrees
w	Mild drying (ramp 3 minutes), final temperature 140 degrees

6. Safety

The safety aspects are treated in detail in the operating instructions of the Halogen Moisture Analyzer.

All information concerning applications and use contained in this brochure is given in good faith. However, any and all liability for damage resulting from use of this Applications Brochure is expressly excluded. This exclusion of liability also applies to any and all claims under industrial property rights of whatever nature. The brochure is included with the METTLER TOLEDO Halogen Moisture Analyzer when it is delivered.

7. Ecology

Energy consumption

A short measurement time reduces the power consumption. Hence ensure that your measurement time is always as short as possible for ecological and economical reasons.

Maintenance

Keep your instrument clean and comply with the maintenance directions. This prolongs the service life, reduces waste and minimizes repair costs.

Aluminum sample pans

Used aluminum sample pans should be disposed of in the proper manner. However, you always have the possibility to use reusable, washable sample pans.

8. Quality systems

International companies with different production sites and a high-profile quality image are dependent on measuring instruments which supply reproducible and dependable results irrespective of the location and time. At a local level, suppliers and customers are increasingly agreeing the product quality on a basis of trust.
Stricter regulations in the field of product liability and increasing competition are becoming apparent. The subject of quality management has thus today become important for survival for practically all companies. The functions of the METTLER TOLEDO Moisture Analyzer have been so designed that they can easily be integrated in modern quality assurance systems such as ISO 9000, GLP and GMP. These functions are described in what follows:

Instrument qualification

Measurement results must be comparable. This ensures consistent and manageable processes, and therefore consistent quality of the products. To fulfil this requirement, measuring instruments must be qualified for a specific task. As manufacturer of the Halogen Moisture Analyzer, METTLER TOLEDO undertakes the Specification Qualification (SQ) and the Construction Qualification (CQ). The four qualification steps which must be documented by the user (with local support from METTLER TOLEDO if required) are:
Design Qualification (D.Q.)   Definition of performance features
Installation Qualification (I.Q.)   On-site installation
Operational Qualification (O.Q.)   Calibration (certification)
Performance Qualification (P.Q.)   Tests with known standards

For documenting these qualification steps, it has proved helpful to use a logbook. If needed, you can obtain the "Logbook for Halo-

gen Dryers" from your local METTLER TOLEDO representative.

Adjustment

The balance component of the Halogen Moisture Analyzer can always be adjusted with a certified weight. On adjustment of the heating part, METTLER TOLEDO sets a completely new standard. The halogen radiator is adjusted by a reliable procedure at 100 °C and 160 °C. The adjustment can be performed at any time in a simple manner, i.e. without specialized knowledge using the separate precision thermometer. This thermometer is also available in a certified version, which thereby guarantees traceability to international standards. This ensures that the moisture content is determined under the same conditions whatever the location. Adjustment of the balance and the dryer unit can be traced through the records documented by the printer.

Documentation of the measured values

The built-in printer fully satisfies the principle of traceability of the measured values which forms the basis of all quality systems. The printed record includes all relevant supplementary information such as time, date, instrument number, sample number, instrument settings, raw data, results and the associated units.
The printout is chemically and thermally resistant and hence can be archived for a lengthy period.

Safety in operation

In the design of the user concept of the Halogen Moisture Analyzer, particular attention was paid to simplicity and clearness. To attain the greatest possible safety in operation, the keypad of the Halogen Moisture Analyzer can be protected against undesired adjustment. This is achieved by allowing partial blocking of the keypad. Essentially, in the protected case only the start, stop and tare keys are active. On the HR73 a compact database stores all the settings for the various different substances under a user-defined name. As a result, wrong adjustments when the substance is changed are practically impossible. The database keeps a chronological jour-

nal for each substance and this can be printed out.

LIMS

An increasing number of companies are choosing an LIMS (Laboratory Information and Management System) to improve the data quality in the lab. The powerful RS232C data interface allows bidirectional communication between the LIMS (computer, network, server, software) and the Halogen moisture Analyzer. All settings can be made via the interface. Results, daily journals and instrument settings can be read by the computer. The remote controlled closing and opening of the automatic sample chamber as well as the start and stop function are eminently suitable for use in automatic systems and robot applications.

You will find further information on these topics in the "Reference Manual for METTLER TOLEDO Standard Interface Command Set (MT-SICS)" which is enclosed with your Halogen Moisture Analyzer. Additional copies can be obtained from your METTLER TOLEDO representative.

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