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METHODS OF HUMIDITY DETERMINATION
Part II: Determination of material humidity

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Part II covers the most common methods of measuring the humidity of solid material. State of water near solid surfaces, gravimetric measurement of material humidity, measurement of water sorption isotherms, chemical methods for determination of water content, measurement of material humidity via the gas phase, standardisation, cosmonautical observations are reviewed.

Keywords: *adsorption, humidity, material humidity, water*

Introduction

Water is present everywhere in nature; this could be advantageous or disadvantageous. Handling of a variety of materials includes often the use of water, as solvent or dispersion medium, adsorptive, reacting agent, for cleaning and as lubricant. Many processes require identification, knowledge and control of the water content. The very different applications of humidity measurements are made under very different circumstances within a wide measuring range from nearly zero up to saturation and sometimes with high sensitivity. So a great variety of measuring methods are applied [1–4]. Because the term ‘humidity’ is not well defined and because the different measuring methods deliver not always comparable results standardisation of measuring methods and procedures is required.

Water near solid surfaces

Under global environmental conditions water exists in all three classical states of matter: solid, liquid and gas [5]. Water molecules are non-linear and therefore polar. At ambient temperatures up to about 35°C free bulk water consists of unstable and quickly varying aggregates of several molecules; single molecules are seldom (Fig. 1).

As shown in Table 1 water is bound at a solid differently. Interpacked water filling larger pores and spaces between grains has the similar structure as free bulk water. Likewise capillary water fills capillaries (macropores) and nanopores (mesopores). Due to water uptake the structure of some materials can store large amounts and/or undergo swelling. A solid surface exposed to the atmosphere is more or less covered with physisorbed water molecules attracted by van der Waals forces (London dispersion forces). These are induced, fluctuating dipoles. Whilst their temporary mean value is zero the binding energy per atom is of the order of 0.5 eV. Down to temperatures of –50°C liquid water layers have been observed in fissures of permafrost structures. About two layers of physisorbed water molecules at a solid surface or at the surface of ice behave in a quasi-liquid state down to a temperature of 33 K. Such quasi-liquid layers behave like free water; however in addition the surface will influence the structures within about eight layers. Thus, bound water has properties different from those of free water [6]. Physisorption is reversible because

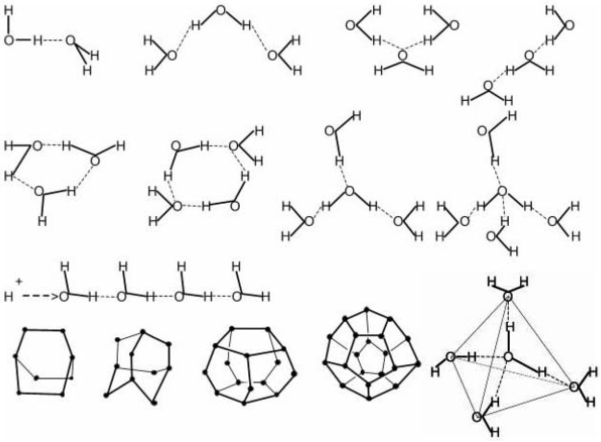

Fig. 1 Molecular structures in liquid water

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the electron orbital structure is not influenced and only weak deformation of the molecular grid occurs. Parts of the adsorbate vaporise with decreasing vapour pressure or increasing temperature and a new equilibrium responds to the new ambient state. Nevertheless, to remove physisorbed water completely in a reasonable time warming up is often required in addition to vacuum.

Much stronger are binding forces at polar surfaces and induced electrostatic dipoles at metallic surfaces, which are of the order of 0.1 kJ mol^{-1}. Still there is no chemical bond and thus such bindings should be classified as physisorption.

Chemisorption is dissociative stoichiometric bonding at surface molecules of the solid. Binding enthalpies range between 100 and 500 kJ mol^{-1}. Chemisorption is irreversible. Energy is required to release molecules whereby hydroxyl groups may recombine to form water molecules.

Absorptive binding of water is associated with diffusion of water molecules first physisorbed at the surface into free molecular sites in the interior of a material.

The formation of a hydrate and binding as water of crystallisation are chemical reactions. Binding enthalpies are stronger than in physisorption. Nevertheless such reactions may be completely reversible and may take place even at low temperature.

Natural and technical surfaces are always contaminated. Impurities at the surface are hardly avoidable. Water may emulsify or dissolve such species by forming, for example, an ionic salt solution.

A typical effect accompanying water sorption is swelling. By expanding the matrix of dry material additional volume is available for water molecules. For example, the small specific surface area of dry clay minerals increases by water uptake to values between 10 and 2200 m^2 g^{-1} as determined by the BET method.

Material humidity measuring methods

There are indeed two types of humidity: Air humidity which is independent from the other components of the air and the humidity of materials which is influenced or even dependent on the material in question; it may be a solid, a liquid or a gas. The common term humidity also comprises liquid contents other than water, e.g. solvents [7]. In the following we restrict ourselves to the content of water generally expressed as the amount of water in relation to unit mass or unit volume of the sample.

The peculiar characteristic of the water molecule facilitates its identification and allows the application of very different methods to determine water content and humidity depending on the ambient conditions. However, only a few methods provide reliable values [8] of the water content of solids and enable to distinguish between free bulk water, adsorbed vicinal water, absorbed and chemisorbed water. Indeed, just the gravimetric methods measure the sum of volatile substances within a solid, whereas, in general, the task is to determine the water content only.

Gravimetric measurement of material humidity

Gravimetric measurements to determine the humidity or dry mass of a solid material are based on the removal of water by reducing the partial pressure of water vapour of the gaseous phase above the sample.

Table 1 Water near solid surfaces

Type of water	Formation process
Free bulk water	
– volume water	Filling of volumes
– interpacked water	Filling of macropores and interspaces between particles
Water bound physically at the solid surface	
– physisorbed water layers	Adsorption (physisorption) at the outer surface and at pore walls and micropore filling
– capillary water in mesopores	Adsorption (physisorption) + condensation in mesopores (capillary condensation)
Water bound chemically at the surface	
– chemisorbed water	Adsorption + chemisorption at the outer surface and at pore walls
Water bound in the solid bulk material	
– absorbed water	Adsorption + diffusion → absorption

Table 2 Usual methods for the measurement of moisture content

Method	Principle of measurement
Oven-drying Moisture balance	Thermal activation of the sample and gravimetric measurement of mass loss.
Thermogravimetry	
Sorption measurement Desiccator method	Variation of (partial) water vapour pressure and measurement of mass change.
Standard contact porometry	Contact with standard of defined humidity, measurement of mass change.
Dielectric measurement	Capacitive measurement with a condenser taking the advantage of the high dielectric constant of water.
Electric conductivity measurements	Electrochemical measurement of conductivity.
Microwave and infrared spectroscopy	Measurement of absorption of radiation.
Nuclear magnetic resonance spectroscopy	Measurement of resonance between a high-frequency electromagnetic field and ^{1}H nucleus of water of a sample which is arranged into a strong homogeneous magnetic field.
Activation analysis	Measurement of absorption of fast neutrons or γ-rays.
Calorimetric method	Measurement of heat capacity and conversion heat.
Karl Fischer	Titration using Karl Fischer reagent.
Phosphorus pentoxide	Thermal activation of the sample, absorption of water.
Moisture indicator	Qualitative test observing colour change.

This may be done with a vacuum pump, by a condensation process or by means of a dry gas flow. Controlled heating of the sample shortens the measuring time. In addition to physisorbed water chemically bound water may also be removed. The mass decrease of the solid sample is measured gravimetrically or the water mass removed is weighed.

Gravitational balances measure not the mass but the sum of mass plus buoyancy of the sample. The buoyancy of the adsorbate must also be taken into account in case water is predominant in spongy structures in comparison to the skeleton. Measurements are disturbed by convection and, at low pressures, by thermal gas flow. During the drying of large samples shrinkage of porous materials or agglomeration of fine materials result in encrustation. This obstructs evaporation from interior and distorts the drying process.

Oven-drying is a widely used method. Here the sample is dried at constant temperature. Humidity is removed by circulating air. The sample is weighed after reaching mass constancy. Such measurements give reliable ‘true’ results only in case of well known drying characteristics of the material. More information may be obtained by weighing at intermediate times and deriving a kinetic curve.

Humidity balances are equipped with an infrared or microwave heater and a device to remove the moistened air. The humidity balance is a simplified model of a thermogravimetric apparatus. It is based on so-called conditioning apparatus which was used for humidity control of silk shipped from China in the 19th century [9, 10].

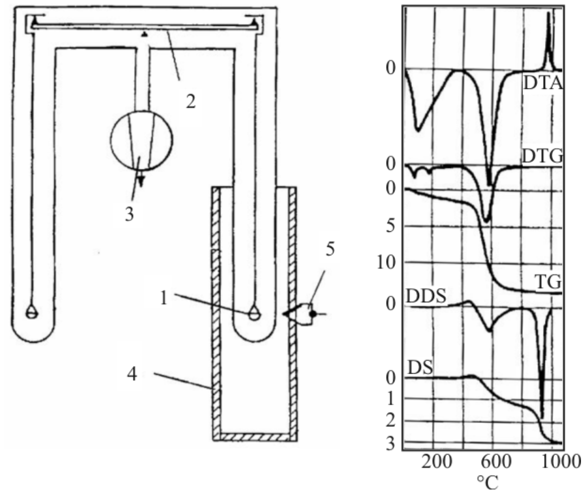

Fig. 2 Sketch of a thermogravimetric apparatus. 1 – sample pan, 2 – balance beam, 3 – vacuum pump, 4 – oven, 5 – temperature sensor, DTA differential thermal analysis, DTG differential thermogravimetry, TG thermogravimetry, DDS differential dilatometry, DS dilatometry

A thermogravimetric apparatus (Fig. 2) consists of a balance and a heating unit to adjust the sample temperature at a constant value or to control the defined temperature increase [11]. Measurements are made either in air, in an inert gas flow or in vacuum [12]. To investigate the water content measurements are performed at low temperatures. Up to 100°C, physisorbed water and condensed pore water vaporise mainly. At higher temperatures chemisorbed compo-

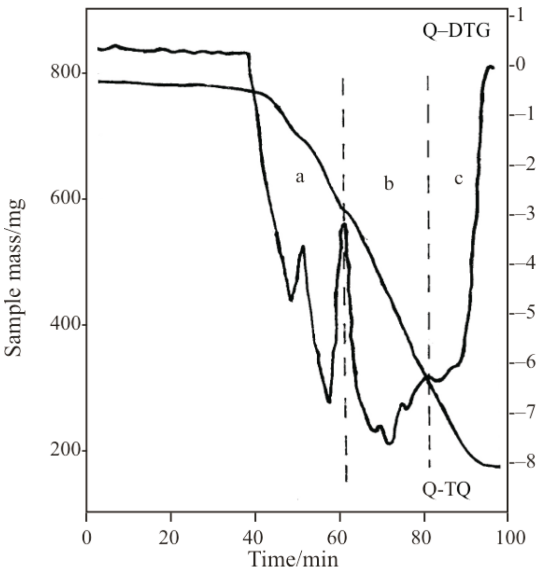

Fig. 3 Quasi-isotherm water desorption from activated carbon [11]. Mass loss (Q-TG) and its time derivative (Q-DTG) are plotted

nents and crystal water are liberated. Quasi-isothermal curves (QTGA) are measured at slow temperature increase whereby the sample is held under saturation vapour pressure using special sample containers (Fig. 3). QTGA can be evaluated for binding parameters and for pore size distribution.

Measurement of water sorption isotherms

To measure adsorption isotherms of water vapour the mass is usually determined gravimetrically as a function of stepwise varied pressure at constant temperature. Adsorption measurements are started from a dry sample state in vacuum or dry atmosphere as well as from a defined humidity. Desorption is started from a defined humidity, from saturation pressure if possible.

Sorption isotherms may be measured simply by placing the samples in a desiccator at constant temperature. Different humidities are adjusted by means of salt solutions [13]. By the integral sorption method one sample is exposed to a defined single humidity, whereas by the interval method the humidity around one sample is stepwise varied. Measurements can be speeded up by intermediate evacuation or movement of the gas atmosphere.

An apparatus of gravimetric water sorption consists of a microbalance and a thermostat. Water vapour pressure is adjusted and varied by means of a carrier gas flow loaded with water vapour (Fig. 4a). Alternatively, using a vacuum balance, either portions of water vapour are added or pressure is adjusted by means of a thermostated water reservoir (Fig. 4b).

Modified volumetric apparatus as widely used for the measurement of adsorption of permanent gases may also be applied for measurement of water sorption isotherms. Here condensation in the manifold must be avoided. Drying processes can be easily observed by stepwise pumping of water vapour developed from a sample in a calibrated volume.

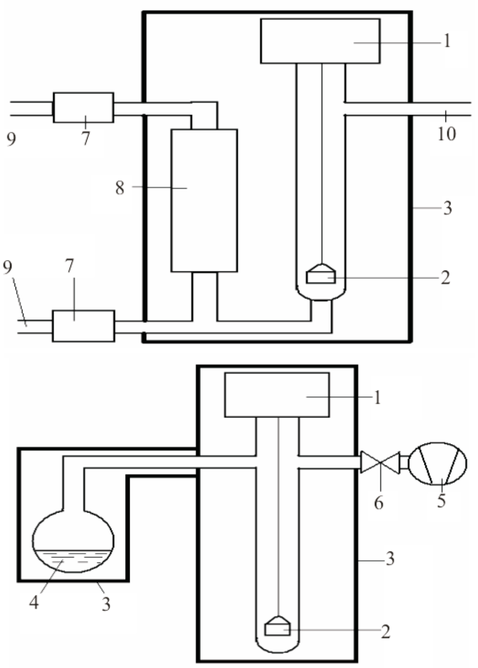

Fig. 4 Gravimetric apparatus for the measurement of water sorption isotherms. 1 – balance, 2 – sample, 3 – temperature controlled case, 4 – water reservoir, 5 – vacuum pump, 6 – valve, 7 – mass flow control, 8 – humidifier, 9 – carrier gas inlet, 10 – gas outlet

The standard contact porometry was developed by Volfkovich, Bagotzky, Sosenkin and Shkolnikov [14]. Here the sample is brought into contact with a porous standard sample with defined water content. In thermodynamic equilibrium the liquid into the whole pore system has an identical chemical potential. From the equilibrium water mass in the standard the humidity of the sample can be derived. A set of standards allow the determination of an isotherm even near saturation pressure.

Drying and adsorption at constant temperature generally are slow processes. Therefore often the measuring procedure will be shortened not waiting for equilibrium conditions. To speed up measurements and to avoid errors an extrapolation method should be applied as described in [15–17].

In water adsorption isotherms the adsorbed mass m_a is plotted as a function of the relative vapour pressure p/p_0:

$$m_a = f\left(\frac{p}{p_0}\right)_{T=\text{const}} \tag{1}$$

This corresponds to Eq. (2b) of Part I applied in hygrometry [18].

With hydrophilic surfaces isotherms of types I, II, IV and VI according to IUPAC classification [6, 19] are observed. Hysteresis may be voluminous and may cover the whole region of relative pressure [20, 21]. On hydrophobic materials adsorption starts only at elevated pressures; that means there is hardly adsorption at the surface but condensation in pores. Isotherms correspond to type II and V. However, often water sorption isotherms cannot be assigned to any type of the IUPAC classification. From types I, II, IV and VI isotherms the specific surface area [22, 23] can be calculated according to the BET method [24] and from types II and IV isotherms the pore size distribution can be determined according to the method of Barrett, Joyner and Halenda (BJH) [25].

Furthermore, the ESW theory by Adolphs [26–28] provides a modeless way of calculating surface energies and specific surfaces areas directly from sorption isotherms. Thermodynamically the excess surface work (ESW) is the sum of the surface free energy and the isobaric isothermal work of sorption.

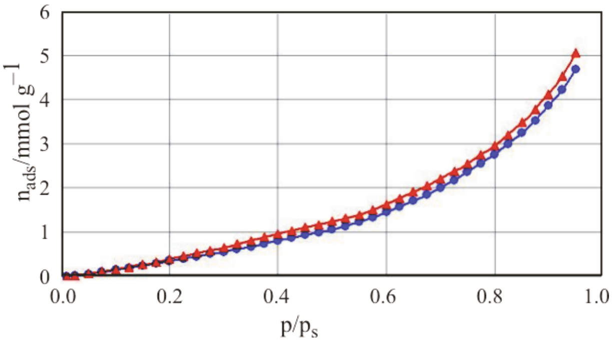

Fig. 5 Water vapour isotherms type III on hydrophobic materials (● – polyurethane and ▲ – silica/polyurethane nanocomposite)

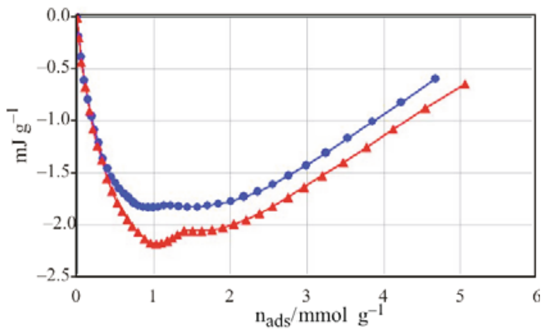

Fig. 6 Transformation of water vapour isotherms in Fig. 5 into ESW isotherms. The minimum of the ESW isotherms corresponds to a loss of degrees of freedom of ● – 1.6 for polyurethane and ▲ – 1.8 RT/2 for silica/polyurethane nanocomposite. The calculated specific surface areas are 5.9 (polyurethane) and 6.6 $m^2\ g^{-1}$ (nanocomposite), respectively

The measured isotherms are transformed into ESW isotherms by plotting the product of the adsorbed amount and the change in chemical potential *vs.* the adsorbed amount. The ESW isotherms show at least one minimum that yields a sorption energy, which corresponds approximately to the loss of degrees of freedom of the sorptive. Thus the binding strength of the adsorption layer can be estimated. From the mass adsorbed in the first minimum a specific surface area similar to the BET surface area can be obtained.

Figure 5 shows the water vapour isotherms on polyurethane and silica/polyurethane nanocomposite [29, 30]. These are type III isotherms that are characteristic for hydrophobic materials. According to the classical models of BET and BJH further evaluation of the isotherms is not possible. The transformation into ESW isotherms shows Fig. 6. The minimum of the ESW isotherms corresponds to a loss of degrees of freedom, which describe a medium strong physisorption of the water molecules on the surface. However, the deeper and sharper ESW minimum of the nanocomposite shows that the nanocomposite better adsorbs the water because of the silica additive slightly reduces the hydrophobic characteristics. Further evaluation of ESW isotherm yields a specific surface area of about 6 $m^2\ g^{-1}$.

Figure 7 shows the water vapour isotherm and the nitrogen isotherm on activated carbon [22]. The whole isotherms as well as the calculated specific surface areas and the pore size distributions are different. However, using the adsorbed volume as ordinate the nitrogen and water sorption curves meet each other at

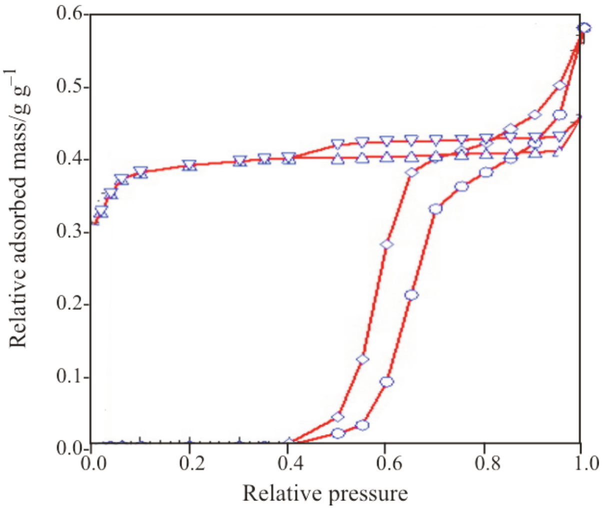

Fig. 7 △ – Nitrogen adsorption and ▽ – desorption isotherm at 77 K and ○ – water vapour adsorption and ◇ – desorption isotherm at 298 K on activated carbon according to Juhola. Note: using the adsorbed volume as ordinate the nitrogen and water sorption curves meet each other at the saturation point in accordance to Gurwitsch's rule

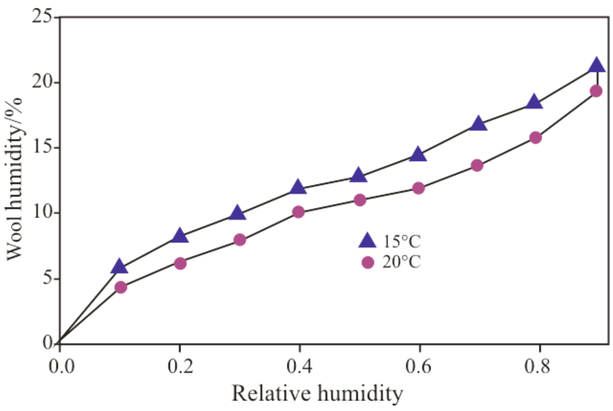

Fig. 8 Adsorption isotherm of water vapour on wool at ○ – 298 K and ▲ – 288 K

the saturation point in accordance to Gurwitsch's rule [31]. This demonstrates that parameters obtained by using inert gases can only be applied with restrictions to predict adsorption of water. If a material should be used in a humid environment water sorption measurement are unavoidable.

Measuring adsorbed water mass in a material can give the relative humidity of the air with which the material is in equilibrium. For example adsorption isotherm water vapour on wool in Fig. 8 can be used for air humidity measurement at 15 and 25°C [30].

Chemical methods for determination of water content

The most important method to determine the complete water content is Karl Fischer titration [32–36]. Water is titrated using Karl Fischer's reagent which consists of iodine, sulphur dioxide, a basic buffer and a solvent. The original composition was modified and adapted to the matter to be investigated. As solvent usually an alcohol, mostly methanol, is used. This is esterified by means of SO_2. To obtain a quantitative reaction the ester is preferably neutralised by imidazole to yield alkyl sulphite. In a second step alkyl sulphite is oxidised by iodine to give alkyl sulphate in a reaction that requires water. Simplified the reaction can be written as

$$SO_2+I_2+2H_2O \rightarrow H_2SO_4+2HI \qquad (2)$$

The consumption of iodine is measured either coulometrically or volumetrically. In the coulometric procedure iodine is formed from iodide by anodic oxidation. In the volumetric procedure a iodine solution is added and different techniques are applied for titration. Indication of the end-point is based on an electrochemical effect in both cases: Two platinum electrodes placed into the working medium are polarised either by constant current or by constant voltage.

Karl Fischer titration requires water to be in direct contact with the reagent. For insoluble or hardly soluble samples a special treatment is necessary; the water has to be released from the matrix first. Some materials may cause erroneous effects by side reactions.

Because many gases include amounts of water of only few μg dm^{-3} the admission of the gas sample should be made carefully in order to avoid contamination or adsorption of water by the tubing system [37]. Subsequently, the determination of humidity is made according to ISO 10101 [38–40].

Water vaporised from the sample by controlled increasing temperature can be analysed coulometrically. Parallel arranged electrodes, which are coated with thin layer of phosphorus pentoxide, may be used. At the cathode hydrogen ions are neutralised and hydrogen is set free whereas at the anode the reaction

$$P_4O_{12}^{4-} \rightarrow P_4O_{10}+O_2+4e^- \qquad (3)$$

takes place. The current is measured. Resolution of a commercially offered apparatus is 100 ng. Results should be comparable to thermogravimetric measurements. In contrast exclusively the water release is indicated. A typical device is the Keidel cell [5, 41, 42], a coulometric sensor with platinum electrodes on a substrate with a thin film of phosphorus pentoxide (Part I [5]).

Measurement of material humidity via the gas phase

Materials humidity can be measured by evaporation and condensation of sample water or by determination of vapour pressure or relative humidity, respectively, within the sample vessel or in a confined volume. This may be performed also stepwise in order to obtain a desorption isotherm. Such a procedure is applied in the phosphorus pentoxide method. Likewise other air humidity sensors can be used as described in Part I [5].

Standardisation

Several working groups of national and international standardisation committees develop standards of humidity measurements and related items. One reason is that new measuring instruments are offered which are in competition to standardised but obsolete methods. Because water adsorption largely depends on the solid partner often measuring procedures are specialised. More than 200 standards exist for the investigation of about 70 different materials, like building materials, soil, paint, ceramics, coal, ores, plastics, food, leather, stones, paper and paperboard. More than 50 standards are already harmonised in international ISO standards. In addition, manufacturers as well as vocational and scientific societies developed special testing specifications [43, 44]. A working committee of the German standardisation organisation DIN just prepared a basic standard on gravimetric humidity measurements [45]. Certified methods of the measurement of air humidity are compiled in a vademecum in Germany [46]. The principle of thermal analysis are described in DIN 51006/7 [47, 48].

Calibration of instruments is made e.g. in Germany by Physikalisch–Technische Bundesanstalt–Deutscher Kalibrierdienst, in UK by National Physical Laboratory–United Kingdom Accreditation Service.

Cosmonautical observations

At the Moon neutron radiation is observed as a reaction to the bombardment of cosmic radiation on the surface. Fast neutrons are slowed down by hydrogen and so the distribution of the neutron radiation gives some evidence for the presence of water distributed on the entire surface. However, recent comparative investigations showed similar effects by structured surfaces of dry stones. It has been hypothesized that significant traces of water remain on the Moon, either on the surface, or embedded within the crust. The results of the Clementine mission suggested that small, frozen pockets of water ice (remnants of water-rich comet impacts) may be embedded unmelted in the permanently shadowed regions near the poles [50]. Due to the very slight tilt of the Moon‘s axis, only 1.5°, some of these deep craters never receive any light from the Sun; they are permanently shadowed. Estimations amount to from about $6\cdot10^6$ up to 10^9 m^3 water in total – or nearly nothing, according to recent perceptions.

By the impact of a large object a lot of ice in a crater should be kicked up. Therefore after termination of its mission in 1999 the Lunar Explorer and 2006 Smart-1 were navigated into such craters. However, no ice dust could be detected in this way.

The water occurrence on Mars was investigated during several satellite missions, first by the Odyssey mission in 2002 [51, 52]. Galactic cosmic ray particles react with matter of the planets surface and are slowed by energy-loss. The spectra of the re-emitted neutron and gamma rays are evaluated with regard to H and O peaks, which can be attributed to water at the surface down to some depth. Recently by lowered echo from Mars' south-polar layered deposits large amounts of water ice could be identified which would cover – when melted – the planet with an 11 m thick water layer.

Conclusions

The survey demonstrates that due to the very different task~~s~~ of humidity measurements and due to the great number of materials to be tested different measuring methods must be applied. With regard to the disturbances, which are specific to each method, the measurements should be compared to standardised procedures. In many cases it is necessary to determine water within a mixture of different volatiles. In such cases as a reference, water should be identified by chemical methods.

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