GRAVIMETRIC MEASUREMENT OF WATER VAPOUR SORPTION, MOISTURE AND DRY MASS

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Abstract

The gravimetric measurement of the moisture content of solids is discussed in comparison to other usual methods. Results of measurements of silica gel are reported. Furthermore, we inform on standardisation work.

Keywords: adsorption, gravimetry, humidity, moisture content, water vapour

Introduction

The knowledge and control of water content and humidity are necessary in many industrial processes e.g. in corrosion protection, refrigeration and air-conditioning, generation of pure materials [1], protection of buildings [2]. In commerce it is necessary to know the dry mass of materials like food and textiles [3] as a basic parameter for its price.

In the gaseous phase, water is present as a dimeric complex along with single atoms [4]. In air, concentrations vary from near zero up to the saturation value. Liquid water consists mostly of differently arranged aggregates of several molecules.

The water molecule is angled (Fig. 1), its shape determining its polarity. Therefore, in comparison with other liquids it has anomalous features and this facilitates its analytical detection. In the measurement of water uptake, humidity, water content or dry mass of solids, different methods can be applied. These parameters, however, are not well defined and cannot be determined exactly. The commonly used term, 'humidity', includes also liquid contents other than water, e.g. solvents and monomers [5]. Indeed, gravimetric methods merely measure the sum of volatile substances within a solid, whereas, in general, the task is often to determine the water content only. Therefore, standardisation of measuring methods and procedures is required.

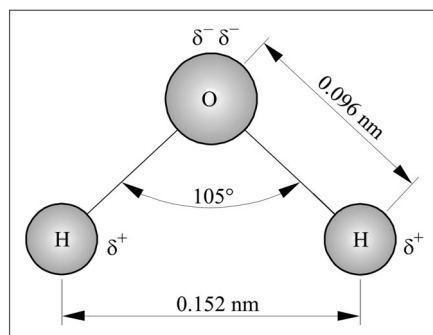*   Author for correspondence: E-mail: erich.robens@t-online.de

Fig. 1 Schematic structure of a water molecule

The system solid/water

Also in contact with solid surfaces water behaves differently in comparison to other liquids or sorbates. On account of its polar molecules it is attracted or repelled. Down to very low temperatures two to three molecule layers remain liquid like. Nevertheless, highly ordered, ice-like structures are observed occasionally extending through several layers above the surface. Water is bound to solids in different ways:

Absorptive bonds of water of hydration and crystallisation

In aqueous solution ions are surrounded by a hydrate shell which may be kept as crystal water when the salt is crystallised. The binding is stronger than in physisorption. Nevertheless, water of crystallisation may be released at low temperatures.

Chemisorption: dissociative, stoichiometric bond with 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.

Physisorption

The maximum physisorption enthalpy of water was measured as 57 kJ mol^{-1} [6]. The physisorbed water is in equilibrium with the ambient water vapour. Physisorption is reversible: The adsorbate vaporises if the vapour pressure decreases or the temperature increases and a new equilibrium responds to the new ambient state. To remove physisorbed water completely within a reasonable time, a temperature increase is often required, in addition to vacuum conditions.

Solution

Water adsorbed at surfaces is mostly contaminated. Impurities of the surface are rarely avoidable. They may be dissolved or emulsified, for example, as ionic salt solutions.

Swelling

Swelling changes the structure of some materials by the impact of water. For example, the small surface area of dry clay minerals increases by water uptake up to 2200 $m^2 g^{-1}$.

Methods of moisture measurements

The peculiar characteristics of the water molecule allow the application of very different methods to determine moisture of materials depending on the ambient conditions. Only a few methods permit the determination of reliable values of the water content of solids [7, 8] and allow to distinguish between free bulk water, adsorbed vicinal water, absorbed and chemisorbed water. Some of the methods used as routine tests are summarised in Table 1.

Table 1 Methods for the measurement of moisture content of solids

Method	Principle of measurement
Oven-drying; Moisture balance	Heating of sample and gravimetric measurement of mass loss
Thermogravimetry	Mass loss under controlled temperature programme
Sorptometry; 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	Capacity measurement with a condenser taking advantage of the high dielectric constant of water
Electrical 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 ^1H nucleus of water of a sample which is in a strong homogeneous magnetic field
Activation analysis	Measurement of absorption of fast neutrons or -rays
Calorimetric method	Measurement of heat capacity
Karl Fischer	Titration using Karl Fischer reagent
Phosphorus(V) oxide	Thermal activation of the sample, absorption of water
Moisture indicator	Qualitative test observing colour change

Gravimetric moisture measurement

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. 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 be removed too. The mass decrease of the solid sample is measured gravimetrically.

Gravimetric measurements are strongly influenced by the pressure dependent buoyancy of the sample. The buoyancy of the adsorbate should also be taken into account for sensitive measurements. Measurements are affected by convection and, at low pressures, by thermal gas flow effects. During the drying of large samples, shrinking of porous materials or caking of fine materials result in encrustation. This obstructs evaporation from the interior of the sample and distorts the kinetics of drying.

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 constant mass. Such measurements give reliable 'true' results only when the drying characteristics of the material are well known. 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 water content is continuously registered mostly as a percentage. The humidity balance is a simplified model of a thermogravimetric apparatus but used at constant temperature. 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].

A thermogravimetric apparatus consists of a balance and a heating unit to adjust the sample temperature at a constant value or to control the defined temperature increase (usually linear with time) [11]. Measurements are made either in air, in an inert flowing gas or in vacuum. The resulting TG curves, which depend on the operating conditions, show the degradation of the sample. They can be a 'fingerprint' of the material and may permit an identification of its composition [12]. Prerequisite for a successful application of that method is that at given temperatures a sudden gas evolution takes place due to a sharp activation temperature of the decomposition process or a sudden increase of the vapour pressure of a volatile compound e.g. at its boiling point.

To investigate the water content, measurements are performed at low temperatures. At temperatures up to 100°C, mainly physisorbed water and condensed pore water vaporise. At higher temperatures chemisorbed components, for example, water of crystallisation, are liberated. Thermal curves (Fig. 2) cannot be evaluated in detail, however the course of the curve above 100°C allows for the identification of stronger bond water or volatiles.

Paulik and Paulik [13] used a special type of sample vessel in which the sample at ambient pressure is held always at saturation pressure of water. Such curves measured at quasi-isothermal conditions represent equilibrium values of isobars and it is possible to assign the deliberated water to the special binding types.
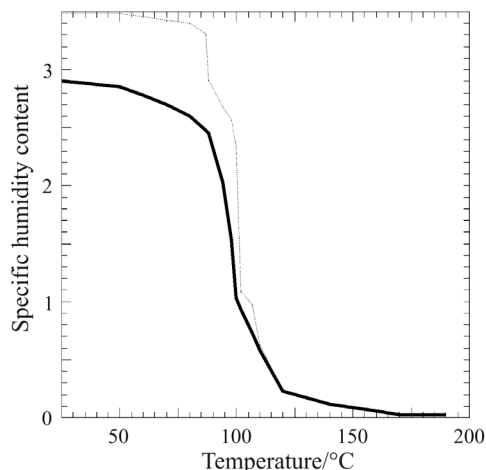
Fig. 2 — Thermogravimetric water desorption from Silicagel Si-60 (Merck) and
— quasi-isothermic [1] water desorption according to Staszczuk [20]

By observing the mass loss of a heated sample one cannot distribute between the release of water and other volatile species. The water alone can be determined by means of a balance loaded with a water specific hygroscopic siccative, e.g. phosphorus(V)oxide.

Measurement of sorption isotherms

To measure adsorption isotherms of water vapour the mass is usually determined gravimetrically as a function of pressure varied stepwise. Whereas the adsorption measurement is started from a dry sample in vacuum or dry atmosphere, the desorption is commenced from a defined humidity, if possible from saturation pressure.

Sorption isotherms may be measured simply by placing the samples in a desiccator at constant temperature. Different humidities are obtained using salt solutions [14]. In the integral sorption method one sample is exposed to one defined humidity; alternately, in the interval method the humidity around one sample is varied stepwise. To reach equilibrium may take days or even weeks. Measurements can be shortened by intermediate evacuation or motion of the gas atmosphere.

An apparatus for investigating gravimetric water sorption consists of a microbalance and a thermostat. Water vapour pressure is adjusted and varied by means of a carrier gas mixed with water vapour. Alternatively, using a vacuum balance, controlled amounts of water vapour are added or the pressure is adjusted by means of a thermostated water reservoir.

Standard contact porometry was developed by Volfkovich, Bagotzky, Sosenkin and Shkolnikov [15]. Here the sample is brought in contact with a porous standard sample having defined water content. In thermodynamic equilibrium, the liquid in the whole pore system has the same chemical potential. From the water mass in the

standard the humidity of the sample can be derived. A set of standards allow the determination of an isotherm.

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

$$m_a = f \left(\frac{p}{p_0} \right)_T \tag{1}$$

In hygrometry, the relative humidity is expressed as a percentage; this is the ratio of current air humidity to the saturation value at the actual temperature. The values differ slightly from relative pressure near the saturation point [16].

With hydrophilic surfaces, isotherms of types I, II, IV and VI according to IUPAC classification [17] are observed (Fig. 3). Hysteresis may be voluminous and may cover the whole region of relative pressure. On hydrophobic materials adsorption starts only at elevated pressures; that means there is hardly any adsorption at the surface but condensation in pores. Isotherms correspond to type III and V. However, water sorption isotherms often cannot be assigned to the IUPAC classification. From type I, II, IV and VI isotherms the specific surface area [18] and from II and IV the pore size distribution can be calculated. In general, the results deviate from those obtained from nitrogen and noble gas isotherms.

Extrapolation of kinetic curves

Very often sorption or drying processes are of inadmissible long duration. In many cases, the kinetic drying curve at constant temperature as well as the adsorption/desorption kinetics at constant temperature and pressure follows an exponential law:

$$m(t) = m_s (1 - e^{-t/\tau}) \tag{2}$$

where $m(t)$ is the sample mass as function of time t, m_s is the asymptotical equilibrium value and τ is the so-called characteristic time of the system solid/water [19, 20]. Application of this equation may be used to shorten the experimental measurement [21].

Standardisation

Several working groups of national and international standardisation committees are developing standards for humidity measurements. One reason is that new measuring instruments are available, which are not consistent with older standardised methods. In addition, manufacturers as well as trade organisations and scientific societies, have developed specialised testing specifications. Because the adsorption of water depends largely on the nature of the solid adsorbent, the measuring procedures are often specialised. There are more than 200 standards for the investigation of about 70 different materials, for example, building materials, soil, paint, ceramics, coal, ores, plastics, food, leather, stone, paper and paperboard. More than 50 standards are already harmonised in international ISO standards. A working committee of the German standardisation organisation, DIN, is currently developing basic standards on gravimetric humidity

measurements. Certified methods of the measurement of air humidity are compiled in a German vademecum [22].

Table 2 Parameters used

Symbol	Parameter	unit	SI unit
m	Sample mass (dry mass+adsorbed mass)	g	kg
m_a	Adsorbed mass	g	kg
	Specific adsorbed mass (adsorbed mass/dry sample mass)		
m_s	Asymptotical equilibrium value	g	kg
	Specific humidity content (water content/dry sample mass)		
p	Vapour pressure	Pa	Pa
p_0	Saturation vapour pressure	Pa	Pa
p/p_0	Relative pressure	1	1
t	Time	s	s
τ	Characteristic time of the system solid/water	s	s
T	Temperature	°C	K

Experimental

A Linseis thermogravimetric apparatus was used with balance pan on the side. To obtain comparable results a 175 mg sample of silica gel Si-60 (Merck) was prepared at similar conditions as published by Staszczuk *et al.* [23]: wetted with water and stored in a vacuum dessicator at relative pressure p/p_0=1. That measurement was carried out using a MOM Derivatograph. Results are plotted in Fig. 2. The water sorption isotherm was measured by means of a DVS sorption measuring apparatus [24].
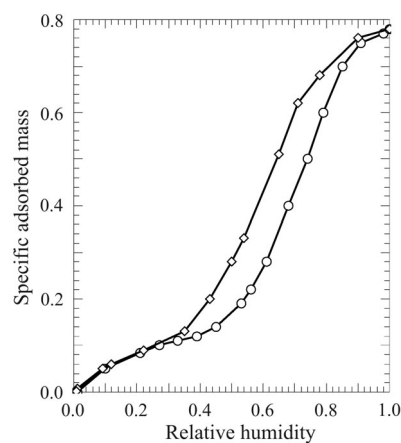

Fig. 3 Water vapour isotherm at 298 K on Silicagel Si-60 (Merck). ○ – adsorption, ◇ – desorption

Conclusions

Gravimetric methods measure the sum of volatile substances within a solid. The portion of water may be obtained by a dessicative on a balance. To distinguish between different binding types special thermogravimetric techniques are required. Standardised procedures are required for routine tests of similar materials. Additional information on moistening/drying processes can be derived from adsorption isotherms.

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