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INVESTIGATING A RANGE OF SOLID SAMPLES BY AUTOMATIC WATER SORPTION

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Abstract

The CISORP Water Sorption Analyser has been used to characterise a selection of solid samples at relative humidities from 0 to 100% and at ambient pressure. The analysis reveals many interesting features about the samples and shows the scope of the equipment.

Hysteresis due to porosity and differences in the physical properties of similar chemical samples show up clearly in isotherm curves. Kinetic curves reveal features such as the level of stability of dehydrated food products, changes in the hydration states of salts, and the effect of adding powdered excipient on the water sorption behaviour of a pharmaceutical compound. Kinetic curves were also used to compare the water sorption behaviour of two types of wood found inside a pine cone, and to determine equilibrium moisture sorption by calculation.

It was shown that many samples take up moisture irreversibly under the experimental conditions such as amorphous sucrose and other freeze-dried samples, as well as unstable crystalline forms of compounds. Wet samples such as soaked brick and archaeological wood from a well dry out irreversibly even at 100% RH.

Recording isotherms at different temperatures allows the calculation of enthalpies of water sorption. If these are compared with the enthalpy of water condensation the two processes can be compared quantitatively.

Keywords: adsorption, desorption, humidity, hysteresis, isotherm, kinetic curve, temperature test

Introduction

Water sorption analysis is an important tool which increases the understanding of solid samples and thereby helps in fields as diverse as research and development, quality control, packaging and storage of products, the understanding of natural and man-made materials, and the conservation of archaeological samples.

The CISORP Water Sorption Analyser [1] was used to characterise a selection of solid samples ranging from finely powdered pharmaceutical compounds to natural materials, and at relative humidities from 0 to 100% at ambient pressure. Water uptake and release was determined gravimetrically, i.e. by weighing the sample during the process. The results reveal many interesting features and principles.

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Properties of water

Water is an unusual substance with unique properties. Thus, despite the small size of its particles (molecules) its 'stickiness' is unusually large. Water therefore freezes and boils at the relatively high temperatures of 0 and 100°C respectively. This is due to the polar nature of the water molecules which each act as tiny magnets, attracting each other to form liquid water or aligning themselves into the regular arrays found in ice.

The extent to which water molecules can escape from the surface of ice or the liquid to form vapour depends crucially (and non-linearly) on the temperature. Hence at 100°C the maximum (saturated) vapour pressure of water is 1 atmosphere (approx. 101 kPa), at 50°C it is 0.12 atm (12.3 kPa), and at 0°C it is 0.006 atm (0.6 kPa) [2]. For this reason it is more useful to quote the amount of water present as its relative pressure for a vacuum environment which contains water vapour only, or as the relative humidity (RH) for a mixed atmosphere. The relative pressure or humidity is then the pressure of water as a fraction or percentage of the saturated vapour pressure at that temperature.

Since water is ubiquitous and life on this planet depends on it, its characteristics and behaviour are crucially important. The condensation of water molecules onto solid surfaces is one phenomenon which occurs in many contexts and is worthy of systematic study. This is the type of analysis which can be undertaken with the CISORP.

The phenomenon of water sorption

The sorption of water vapour onto solid surfaces is comparable, in the first instance, to its condensation. This is a purely physical phenomenon which is often reversible. Some samples, on the other hand, interact more strongly with water and may swell, change colour, or dissolve. In most cases these changes are also physical but are often difficult to reverse. In rare cases chemical changes occur as a result of changes in the relative water pressure or humidity, but none of our samples behaved in this way.

Specifications of the CISORP Water Sorption Analyser

The CISORP records the uptake (adsorption) and release (desorption) of water onto or from a sample gravimetrically, i.e. by weighing. The resolution of the balances is 0.1 μg. However, for practical considerations, the realistic resolution of the equipment is nearer 1 μg. A typical sample mass could be 100 mg. Water uptake or release of as little as 0.001% of the sample mass is therefore easily detectable with the equipment. In addition the CISORP has two balances. This enables the simultaneous investigation or comparison of two samples.

The relative humidity can be changed from 0 to 100%, and the equipment operates at ambient pressures. Operating temperatures can be set between 5 and 65°C. The experimental parameters of RH, temperature, and equilibration criteria are pre-programmed by the user for each test and can be changed during an investigation. Data are recorded and saved automatically during an experiment. The results can be viewed during or following an investigation using dedicated software or exported to other packages. Sample masses can be as little as 5 mg or as much as 1.5 g.

Types of investigations and applicability to different samples

Three basic types of investigation can be carried out with the CISORP:

1. In an isotherm test the user is interested mainly in the amount of water ad-/desorbed by/from the sample at different relative humidities. This provides valuable information about the surface properties of a sample.
2. In a kinetic test the user observes continuous changes in the sample masses as a result of one or more step changes in the relative humidity. This type of information is useful to a kineticist who may derive mechanistic information about the process of water sorption.
3. A temperature test is an isotherm (or kinetic) test carried out at different temperatures. The information gained can allow the physical chemist to calculate thermodynamic properties of the sample surface.

The type of investigation chosen depends on the type of sample and the information sought. Usually it is useful to collect kinetic data, i.e. changes in the sample masses and the RH with time, alongside an isotherm test as a diagnostic tool and to reveal additional features.

Using the CISORP to investigate a range of samples

We used the CISORP on a large variety of samples to illustrate its usefulness and versatility.

Isotherms

Probably the most widely used type of water sorption test is an isotherm. It reveals interesting and useful information about a host of samples.

The isotherm curve of Avicel (microcrystalline cellulose) (Fig. 1) is a typical Type IV (Fig. 2) [3]. It has a distinct 'knee' at low RH, i.e. water adsorption is enhanced at low RH as a result of the polar nature of the surfaces. The sample also shows hysteresis, i.e. there is a discrepancy between the ad- and desorption branches at high humidities. This points to the presence of mesopores (pore diameters 2 to 50 nm [4]) open to the surfaces which cause capillary condensation, i.e. water readily condenses into the pores but only desorbs from them at lower

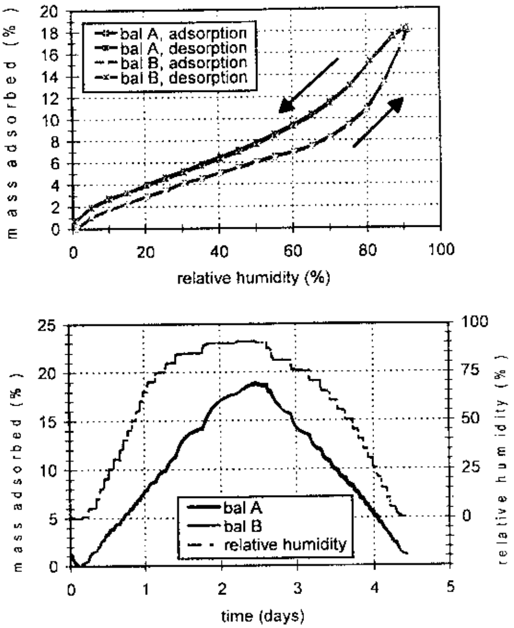

Fig. 1 Water sorption of Avicel at 12°C

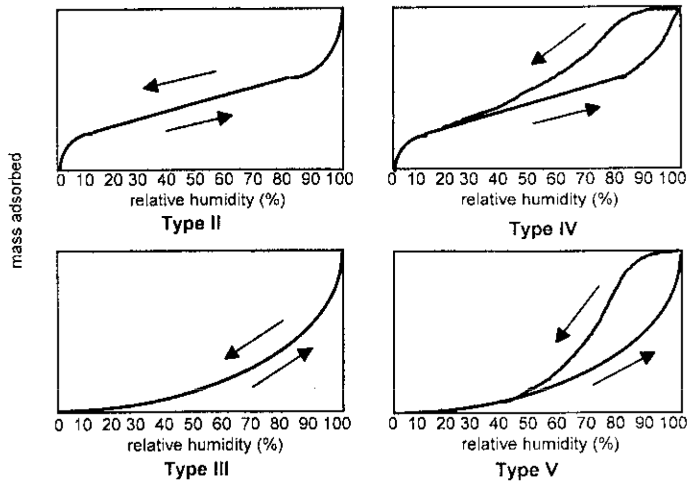

Fig. 2 Some types of isotherms in the BDDT classification

humidities than those required for condensation [5]. The fact that the sample masses during desorption at low humidities do not return to the original values is, by contrast, an experimental characteristic: as is evident from the corresponding kinetic curve, weight equilibration was incomplete at each RH leading to cumulative errors.

The isotherm of graphite (Fig. 3a) [6] is intermediate between Type IV and Type V: it also shows hysteresis at high RH but at low RH the 'knee' is rather flat. This points to a largely non-polar surface, as would be expected for this type of sample. The isotherm of activated charcoal [6], by contrast, is a classical Type V (Fig. 3b). The interpretation is that the surfaces of this sample are less polar than the water molecules, resulting in decreased water sorption onto the clean compared with the water-covered surfaces. The opposite is the case in samples which give Type II or IV isotherms [4].

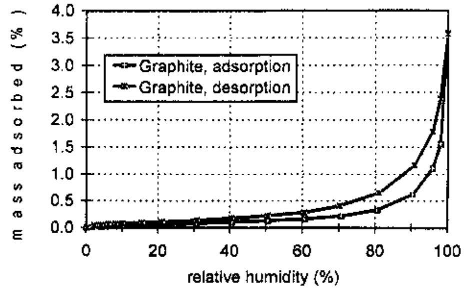

Fig. 3a Water sorption isotherm of graphite

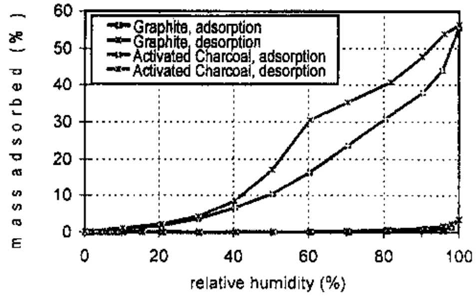

Fig. 3b Water sorption isotherm of graphite and activated charcoal

Figures 3b also shows that samples which are almost identical chemically can nevertheless give very different isotherms. This is understandable in the light of the highly polar nature of the water molecules and the fact that water sorption is usually a purely physical process. The simple tool of water sorption can therefore be used to distinguish between apparently identical samples [6]. This point is again confirmed in Fig. 4 which shows the isotherms of a series of silicas. These consist of the same bulk compound which is surface-modified with different organic groups of more or less polar nature [8]. Although in this case water sorption

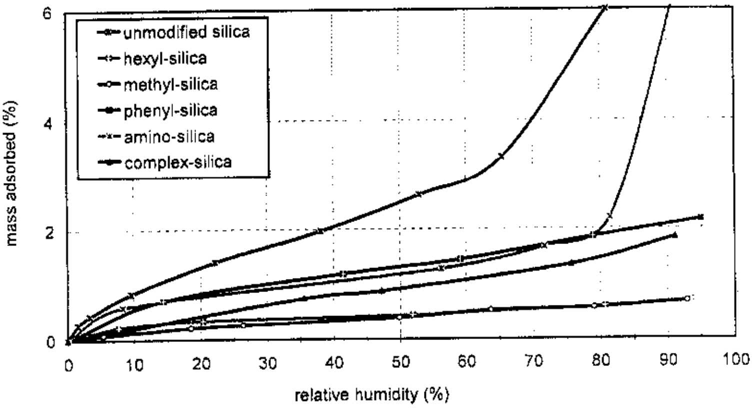

Fig. 4 Water isotherms of surface-modified silicas at 30°C

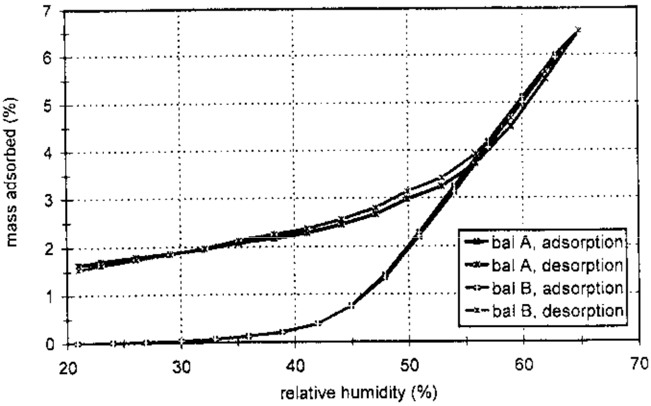

Fig. 5 Water sorption isotherm of an unknown sample

was carried out using a vacuum system, the results are unlikely to differ from those of an ambient system since competing gases (mostly nitrogen and oxygen) do not adsorb to any measurable extent at the temperature used (30°C).

Figure 5 shows an irreversible isotherm. This behaviour indicates that the sample undergoes a physical or even chemical change as a result of water sorption.

Kinetic curves

Kinetic curves can be used as a diagnostic tool alongside isotherm curves, or in their own right. Figures 6a and b show examples of the former. They reveal clearly that equilibration was close to completion at most relative humidities.

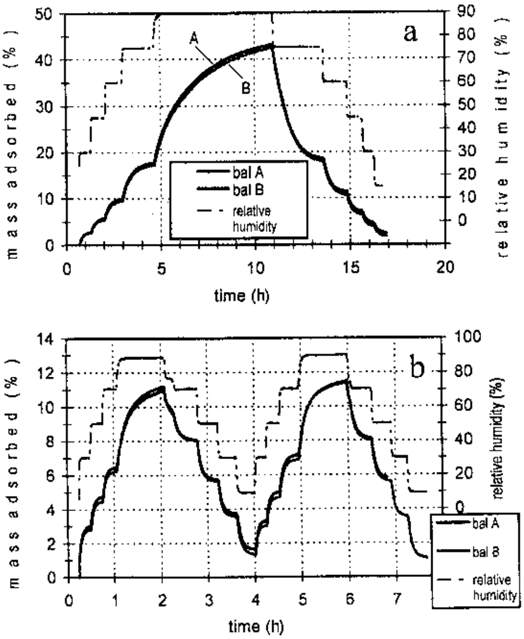

Fig. 6 Water sorption kinetics of two powders

This is not the case in Fig. 7 where the sample is slow to equilibrate especially at high humidities.

In some cases changes in a sample resulting from water sorption are revealed equally dramatically in the kinetic and the corresponding isotherm curves. This is the case for many salts which have one or more sharp transitions as their hydration states change (Fig. 8).

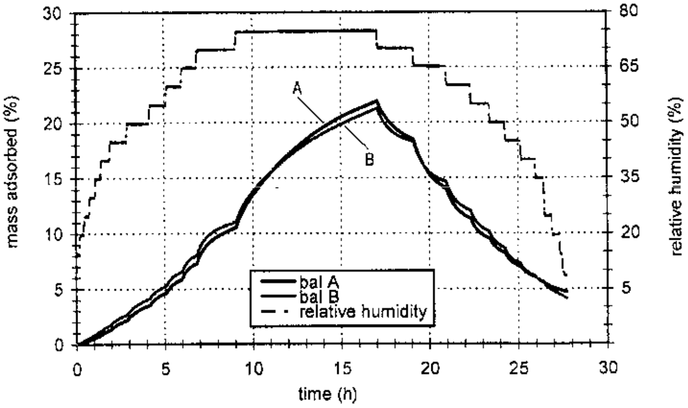

Fig. 7 Water sorption kinetics of soup powder (tomato flavour!)

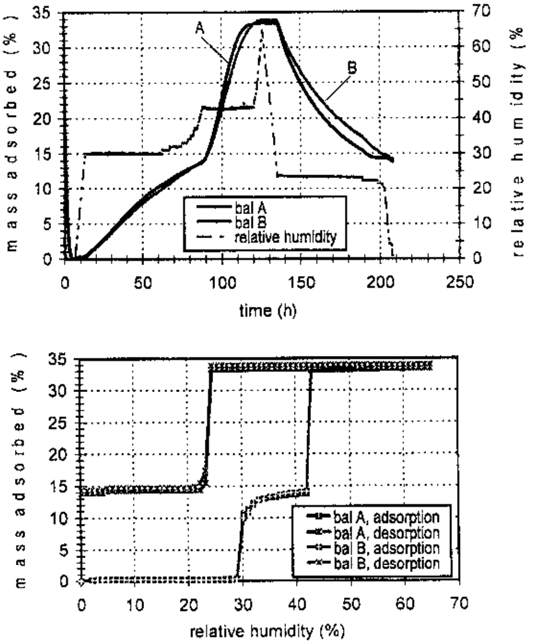

Fig. 8 Water sorption of copper sulphate

When faced with a totally unknown sample it may be useful to run a quick water sorption test to get a rough 'feel' for it. This can be done by using a 'ramp' test where the RH is in- and decreased in small and rapid steps. This can reveal whether a sample is likely to take up water evenly across the RH band or has sharp transitions (Fig. 9).

Another useful application of a kinetic test is the single kinetic where the RH is changed in one or two large steps. 'Normal' water sorption behaviour shows exponential water uptake or release (Fig. 10). This can be used for example to show the effect of mixing two samples: Fig. 11 shows the water sorption kinetics of a pure pharmaceutical sample and of the same sample mixed with 50% excipient (filler). It reveals that the excipient does not adsorb water to any significant extent compared with the sample.

A comparison of the water sorption behaviour of the two types of wood found inside a pine cone show clear differences (Fig. 12). These are again seen in the multiple kinetic and isotherm curves of the same sample (Fig. 13). They explain the fascinating behaviour of pine cones which open only during dry conditions to release their seeds, allowing these to be blown further from the tree than they would in damp conditions.

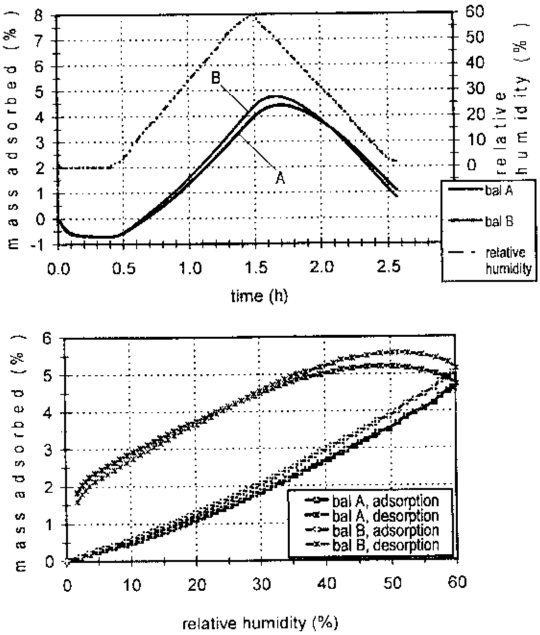

Fig. 9 'Ramp' test

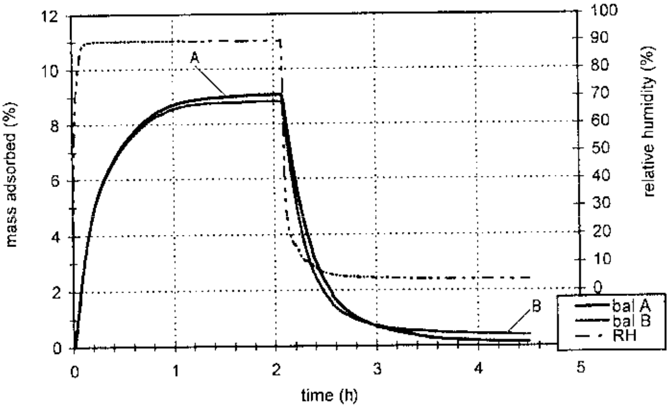

Fig. 10 Single-step water sorption kinetics of a powdered sample

Calculating the equilibrium moisture sorption from a kinetic test

Some samples equilibrate very slowly when exposed to changes in RH. One of these is 'MB Carbon', a polymer-treated carbon black. Even a very slow test does not give a satisfactory isotherm as can be seen in Fig. 14. The cumulative er-

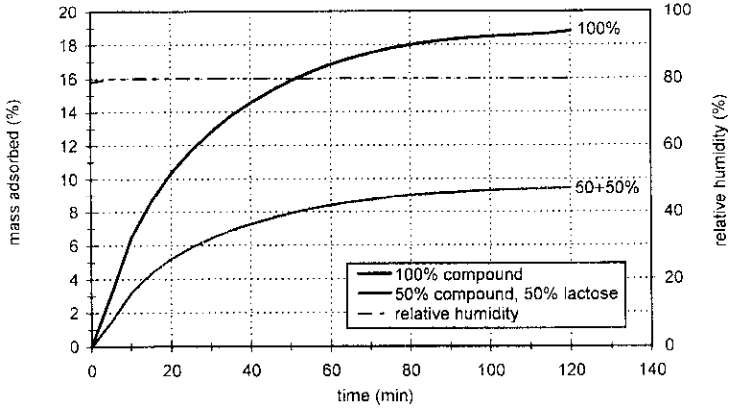

Fig. 11 Water sorption kinetics of a pharmaceutical compound

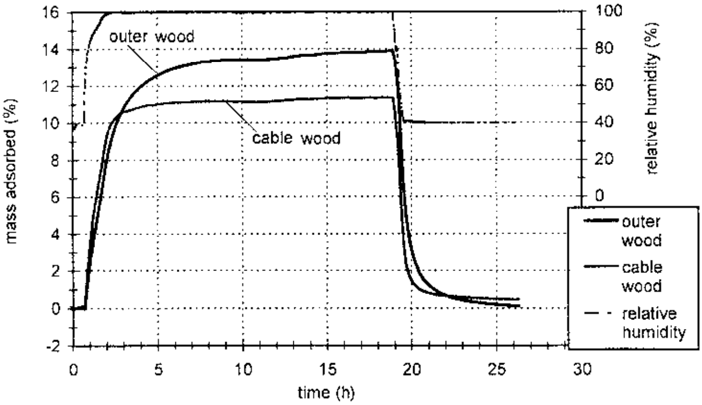

Fig. 12 Water sorption kinetics of wood from a pine cone

rors are enormous as a result of totally inadequate equilibration at each step. This type of behaviour lends itself well to the determination of the equilibrium moisture sorption by calculation. This is done by replotting a single-kinetic step as time per unit mass of water adsorbed as a function of time. The equilibrium moisture sorption in the linear section of the curve, i.e. after initial adsorption, is then given from the reciprocal slope. This was done for two samples from single-kinetic data in Fig. 15.

Irreversible water sorption behaviour

Many samples undergo physical or chemical changes during water sorption which are irreversible under the experimental conditions. This constitutes a use-

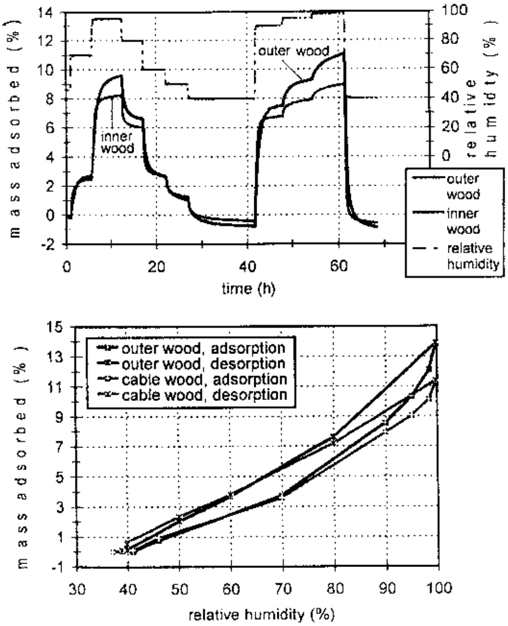

Fig. 13 Water sorption of wood from a pine cone

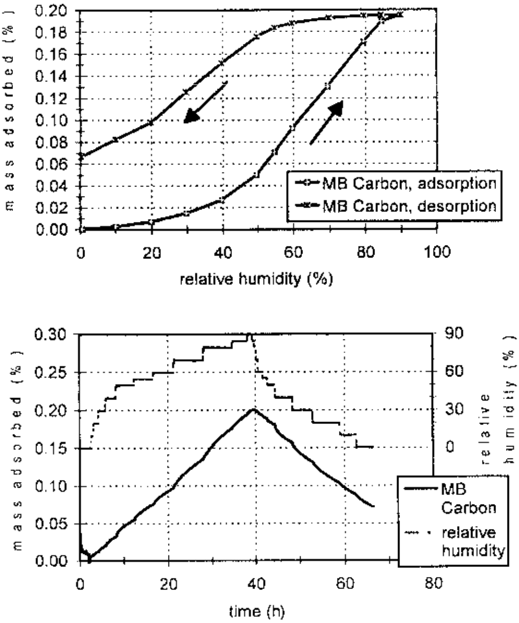

Fig. 14 Water sorption of MB carbon ('quick test')

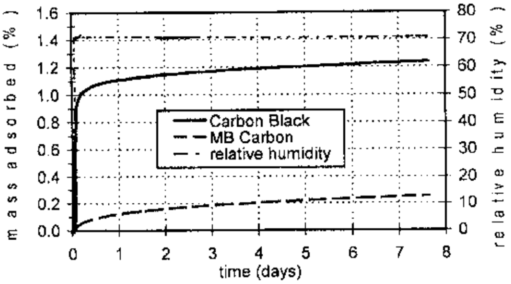

Fig. 15a Water sorption kinetics of carbon black and MB carbon

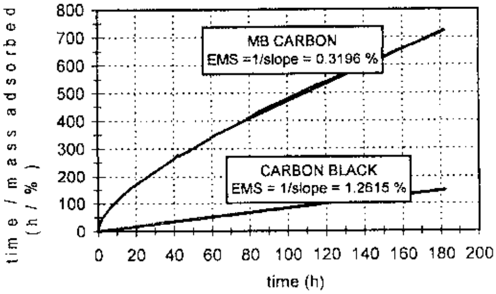

Fig. 15b Calculating the equilibrium moisture sorption (EMS) from a kinetic curve

ful diagnostic tool. For example, amorphous sucrose, which has been prepared by an elaborate method of freeze-drying, dissolves and subsequently crystallises even at moderate RH. The dissolution results in the uptake of moisture while subsequent spontaneous recrystallisation expels around 80% of this water (Fig. 16).

A similar change is observed in Fig. 17. This shows the water sorption behaviour of a novel pharmaceutical compound. The initial substance has a relatively unstable crystalline structure which gives a particular first adsorption isotherm but destroys the structure. On desorbing the water, the substance recrystallises in a different form giving a totally different first desorption isotherm (black line). The adsorption properties of this crystal are very different from those of the original form (grey line).

Irreversible sorption behaviour can also be demonstrated using wet and dry fragments of brick (Fig. 18). Once the water has been driven off from the wet brick by a reduction in the RH it cannot be re-wetter by increasing the RH alone.

Such behaviour is also observed in archaeological wood from a Roman well which had been immersed in water for hundreds of years (Fig. 19). As the wood dries out its cells collapse and cannot be refilled with water. This is evident not only from the enormous initial loss in the sample mass during drying (65% at

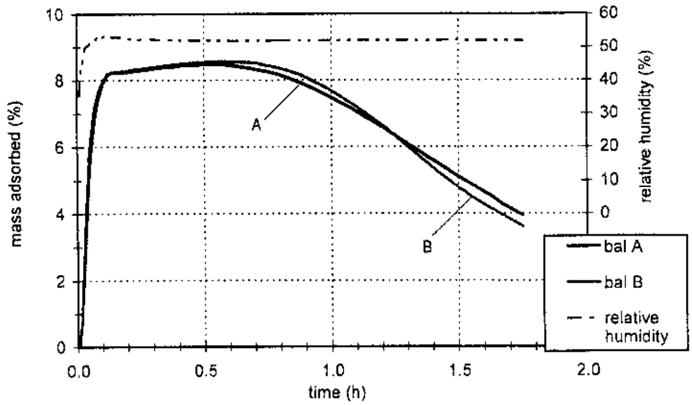

Fig. 16 Water sorption kinetics of amorphous sucrose

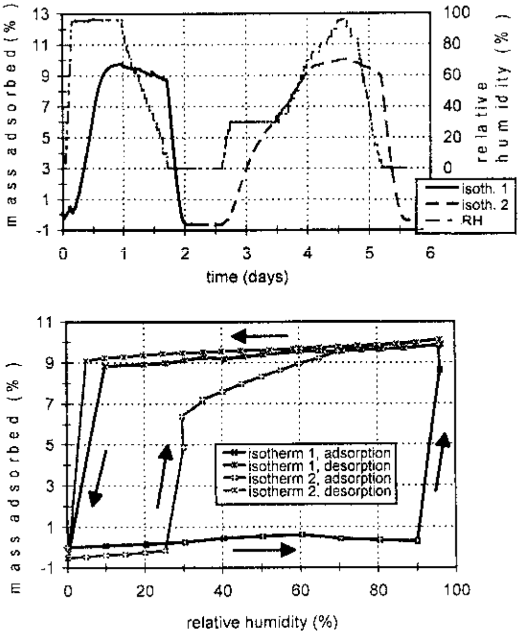

Fig. 17 Successive water sorptions of a crystalline compound

100%RH, and over 80% at 0% RH), but also from the appearance of the sample: the wood shrivels up and crumbles. This obviously has serious implications for the conservation of archaeological samples.

Irreversible water sorption is also observed in other freeze-dried samples. Figures 20a to c show the single- and multiple-step kinetics and isotherms of a

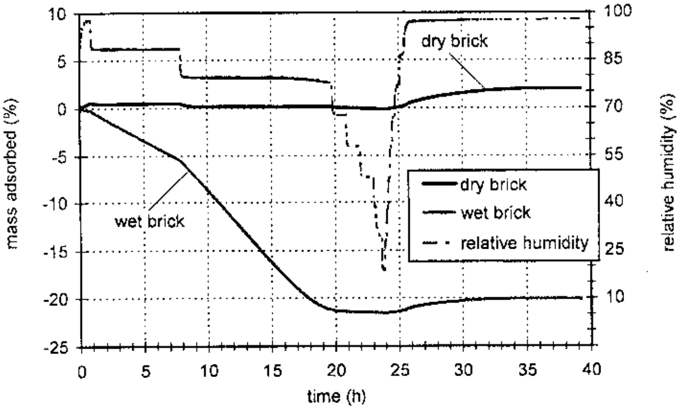

Fig. 18 Water sorption kinetics of wet and dry brick

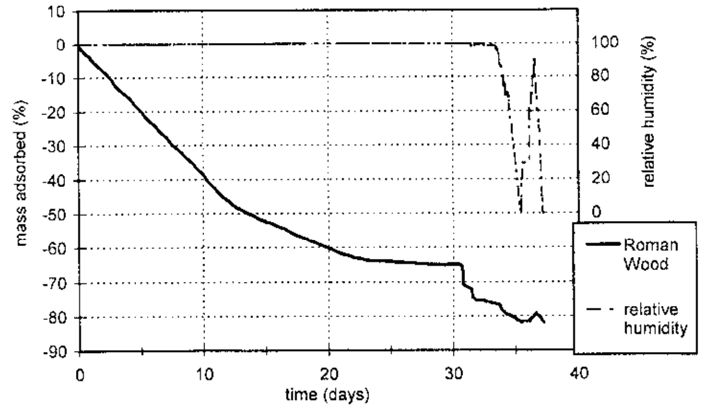

Fig. 19 Drying of archaeological wood at 100% RH (followed by isotherms)

freeze-dried pharmaceutical filler. Again sorption behaviour is very different for the first (black) and second (grey) cycle. We therefore ran a series of ad- and desorption cycles for a fresh sample whereby we increased the maximum RH for each cycle (Fig. 21). The purpose was to find out at which point irreversible behaviour sets in. It appears that up to quite large RH (80%), water sorption is largely reversible. Beyond that point the sample dissolves rapidly and irreversibly.

Temperature tests

As mentioned earlier, the recording and study of water sorption isotherms at different temperatures can yield useful thermodynamic information. However, this is meaningful only if the isotherm is reversible, i.e. indicative of weak and purely physical interaction between the surfaces and the water molecules This is the case with Avicel. Figures 22a and b show isotherms of Avicel recorded in separate experiments at different temperatures.

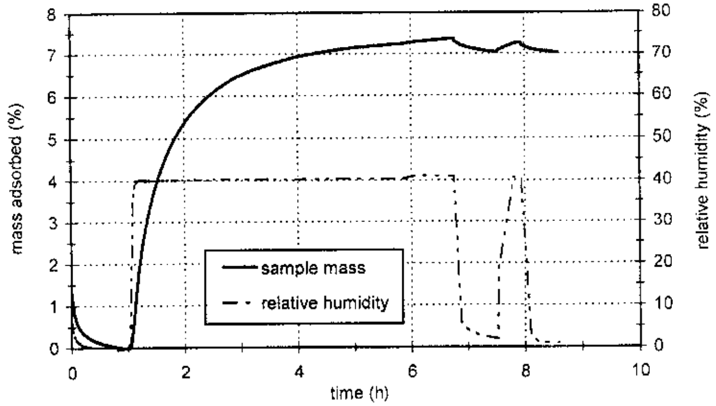

Fig. 20a Water sorption kinetics of a freeze-dried sample

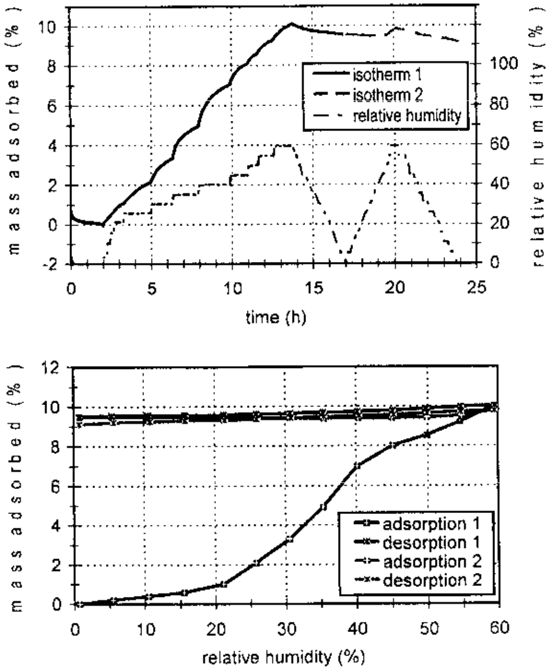

Fig. 20b Water sorption of a freeze-dried sample

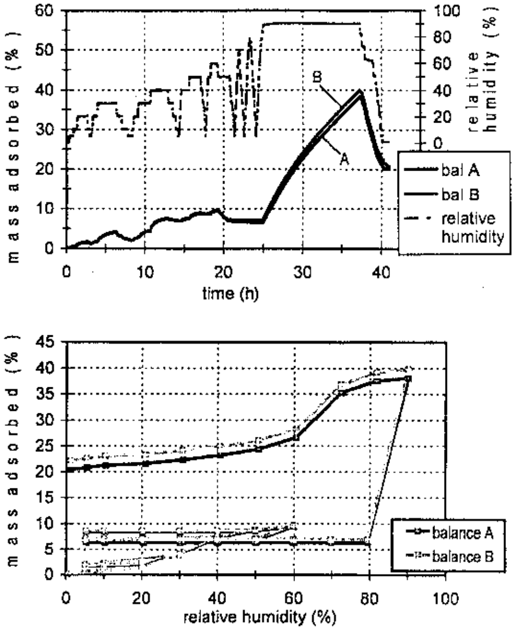

Fig. 21 Water sorption of a freeze-dried sample

However, a main feature of the CISORP is that the experimental temperature can be changed easily during an investigation. Figure 23a therefore shows isotherms of another sample (γ-alumina) recorded at different temperatures in one continuous experiment. For practical reasons the temperature was increased at one RH level and decreased at the next, etc. The original data were then separated into individual isotherms (Fig. 23b).

The relative humidities at the three experimental temperatures were recalculated into absolute pressures and the isotherms replotted (Fig. 23c). From the isosteres, i.e. figures of ln(pressure) at fixed amounts of water adsorbed *vs*. recip-

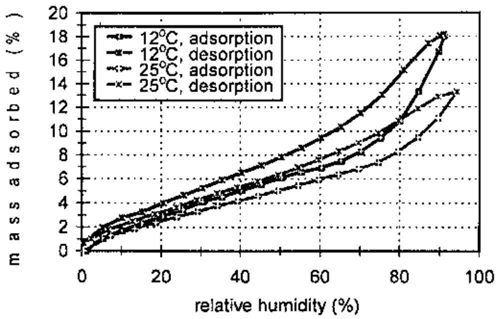

Fig. 22a Water sorption of Avicel at 12 and 25°C

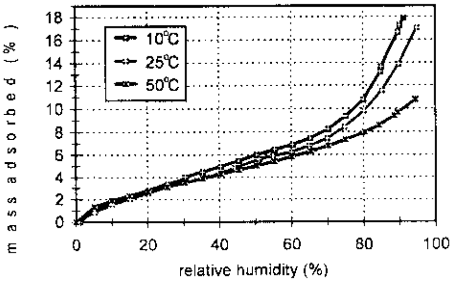

Fig. 22b Water sorption isotherms of Avicel at different temperatures

rocal absolute temperature, the so-called isosteric enthalpies of water sorption can be calculated (Fig. 23d) [5]. It is often useful to plot these as a function of the coverage, i.e. of the number of water layers on the surface of the sample, whereby it is assumed that the 'knee' in a Type II/IV isotherm corresponds to the monolayer water coverage (Fig. 23e) [8]. Type II and Type IV isotherms, i.e. those with a sharp 'knee' at low RH indicative of highly polar sample surfaces, should give isosteric enthalpies of water sorption which are highest at low RH, i.e. at low coverage, and higher than the modulus of the enthalpy of the condensation of

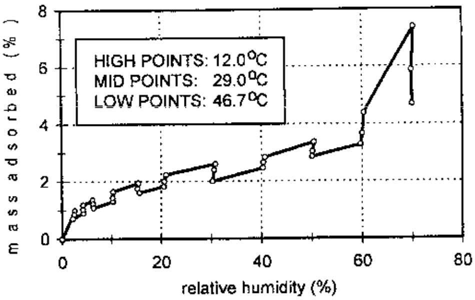

Fig. 23a Water adsorption of gamma-alumina at three temperatures recorded in one test

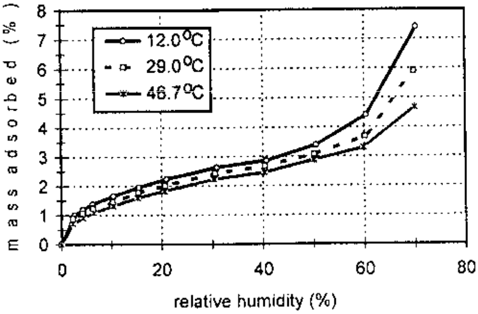

Fig. 23b Above isotherms replotted separately

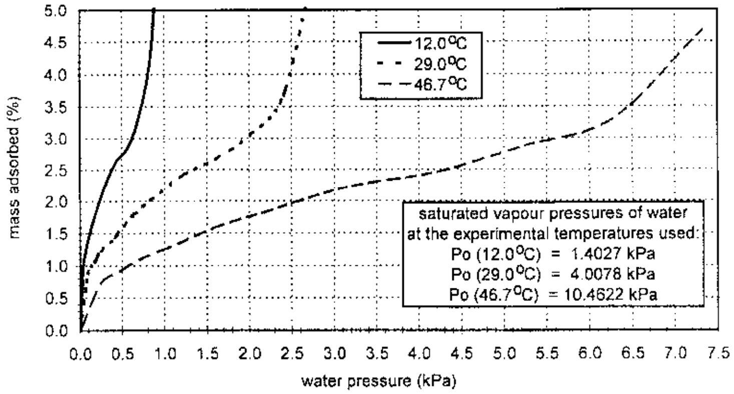

Fig. 23c Isotherms of gamma-alumina replotted as absolute pressures

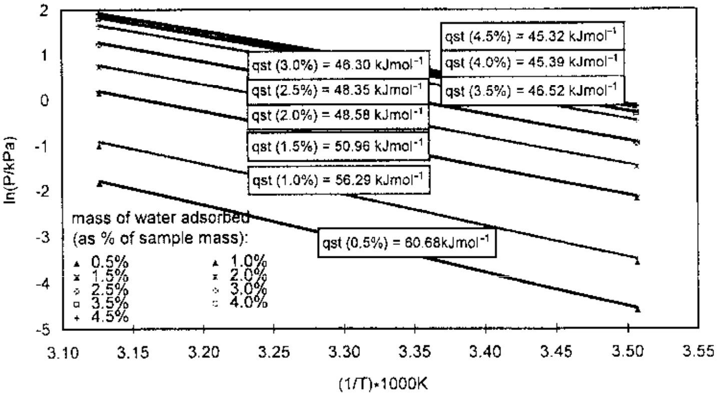

Fig. 23d Isosteres of gamma-alumina

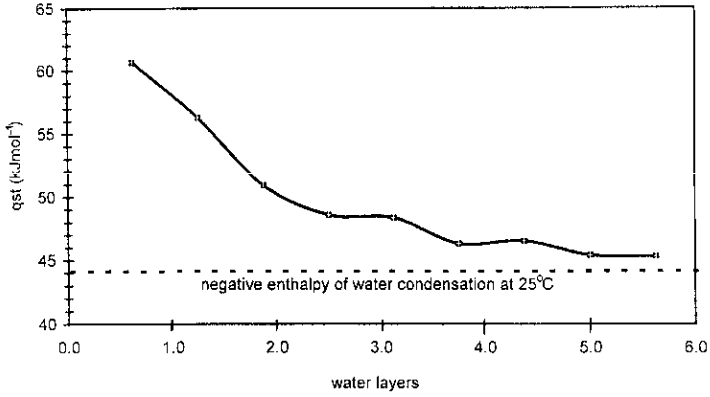

Fig. 23e Variation of qst with water coverage

water at that temperature (approx. 44 kJ mol^{-1} at 25°C). At larger coverages the adsorption of water onto the surface resembles its condensation and the isosteric enthalpies should be similar to those of (negative) water condensation, i.e. of water evaporation. In the above example, precisely this behaviour is observed.

Conclusions

The intention of this summary was to demonstrate some ways in which water sorption analysis can be used as an analytical tool, in order to investigate different aspects of physical and chemical sample properties and behaviour.

* * *

I would like to thank all those who have made samples available to us for investigation and given their permission to cite the results, and my colleagues for their invaluable support.

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