Thermochimica Acta, 235 (1994) 125–133
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01533-9

Studies on historical gravimetric hygrometers

E. Robens [a,*], C.H. Massen [b] and J.J. Hardon [c]

[a] *Institut für Anorganische und Analytische Chemie der Johannes-Gutenberg-Universität, D-55099 Mainz (Germany)*

[b] *Department of Physics, Technical University, Postbus 513, NL-5600 MB Eindhoven (The Netherlands)*

[c] *Department of Building Engineering, Technical University, Postbus 513, NL-5600 MB Eindhoven (The Netherlands)*

(Received 23 June 1993; accepted 21 July 1993)

Abstract

The German cardinal Nicolaus Cusanus (1401–1463) proposed the determination of the humidity of air using a balance loaded with wool. Several years later the Italian architect and painter Leo Battista Alberti (1404–1472) recommended a sponge as the absorbing material. From Leonardo da Vinci (1452–1519), we have drawings of gravimetric hygrometers, equipped with either a sponge or cotton.

Using an electromagnetic vacuum microbalance, we measured water vapour absorption and desorption isotherms in order to estimate whether these instruments could be used as hygrometers. Our investigations include measurements with human hair for comparison of the mass effect of the water absorption with the length variation, as used in de Saussure's hair hygrometer.

INTRODUCTION

Hygrometers were described as early as the 15th century. These instruments that measure the humidity of the air consisted of balances loaded with a hygroscopic material. The aim of the present investigation was to discover whether only ideas were reported or whether the descriptions are based on practical experience.

Sorption measurements using such gravimetric hygrometers result in the relative humidity. The amount sorbed m^a (related to the sample mass m) plotted versus the relative humidity p/p^0 gives isotherms which, over a wide range, are independent of temperature and, therefore, are suitable for climatic observations. Other prerequisites for a gravimetric hygrometer are that the adsorbed amount of water must be large enough with respect to the ratio of sensitivity to load of the balance; the isotherm is reproducible;

---

* Corresponding author.

there is a definite curve with negligible hysteresis between absorption and desorption; and the response time is short in comparison with the periods of humidity variations in the air.

Using an electromagnetic vacuum microbalance, we measured water vapour absorption and desorption isotherms at ambient temperature using a sponge, cotton, and wool as hygroscopic materials. The investigation also included measurements with human hair for comparison of the mass effect with the length variation, as applied in the hair hygrometer.

HISTORICAL

The 15th century marks the beginning of scientific investigations in the West. The systematic observation of climate using objective methods also started at that time. Several hygrometers were invented. The first description of hygrometers involved balances loaded with water-absorbing substances. Probably the very first to describe such an instrument was the German cardinal Nicolaus Cusanus (1401–1463) [1]. In his book published in 1450, "Idiota de Staticis Experimentis" which means "The non-professional conducts experiments with a balance" [2], he lets this amateur, probably his assistant, suppose: "If someone hangs dry wool on one side of a balance and loads the other side with stones until equilibrium is reached, at any place and in air of moderate temperature, it can be observed that with increasing humidity the weight of the wool increases, and with increasing dryness of the air it decreases. From these differences, it is possible to weigh the air and possibly one might perform weather forecasting."

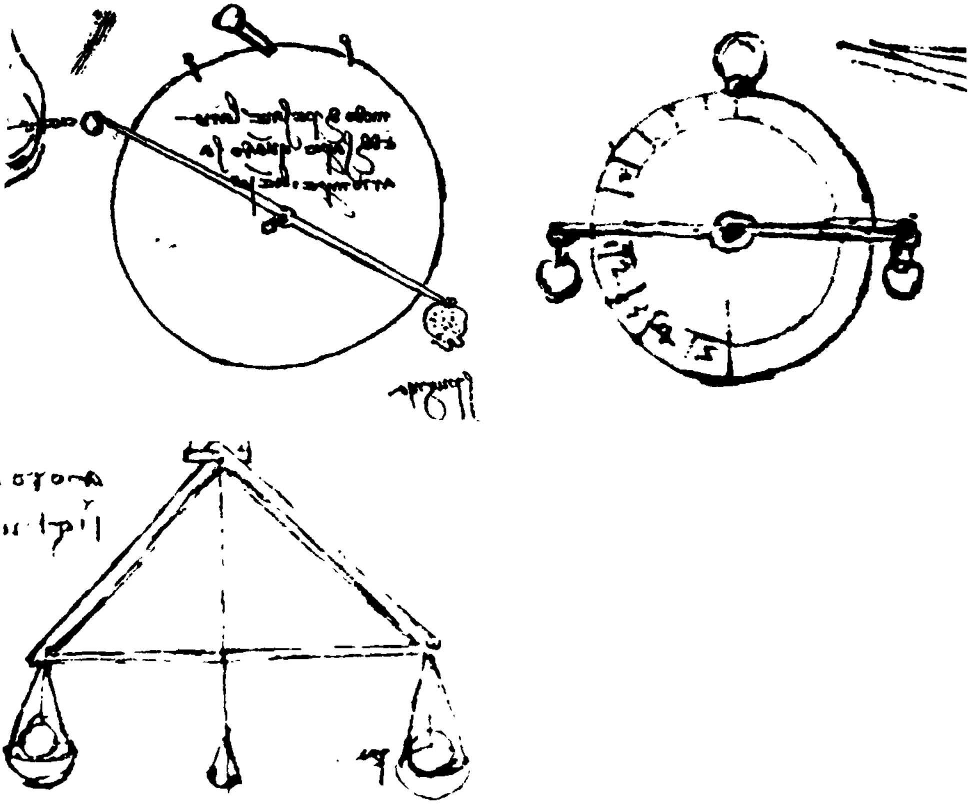
About 20 years later, the Italian architect and painter Leon Battista Alberti (1404–1472) recommended a balance with a sponge: "We know that a sponge becomes wet from the humidity of the air and using this fact we make a balance with which we weigh the weight of the air and the dryness of the winds" [3].

Leonardo da Vinci (1452–1519) made three drawings of gravimetric hygrometers [4], equipped with a sponge or cotton. One of these (Fig. 2) is found on a sheet of paper also showing sketches for the Last Supper (Fig. 1) [5], which was painted between 1495 and 1497. The balance consists of a short rod suspended from a nail as an axis in its centre, loaded on one side with a sponge and on the other with a counterweight made of wax [6]. The use of wax as a counterweight is a good means of accounting for buoyancy effects. In mirror writing, he has written: "To detect the quality and density of the air and when it will rain". Another sketch (Fig. 3), which is very similar, is loaded with cotton. The scale indicates that it would be an inclination balance, which might be very sensitive. A third instrument (Fig. 4) shows a strange type of inclination balance, which would be very insensitive. Models of these instruments can be seen in the London Science Museum.

Fig. 1. Sheet of paper with sketches by Leonardo da Vinci.

It is not clear whether Leonardo's drawings represent hasty sketches of apparatus he saw elsewhere or proposals of his own ideas and it seems somewhat doubtful whether he made experiments with such imperfect instruments [7, 8].

More than two hundred years later, in the 17th and 18th centuries, the first accurate hygrometers were invented. A large variety of hygrometers based on very different principles were tested. Modifications of these principles are still used today [9, 10]. The only hygrometer of that time still in use is the hair hygrometer of Horace Benedict de Saussure (Fig. 5) [11]. This simple



Figs. 2–4. Sketches of hygrometers by Leonardo da Vinci.

instrument consists of stretched, fat-free women's hair connected via a roller to a pointer [12].

EXPERIMENTAL

We used an apparatus (Fig. 6) comprising an electromagnetic vacuum microbalance, as described by Gast [13], with a sensitivity of 1 μg and a maximum load of 25 g. The balance and the water thermostat are mounted in a thermostable case. We used, however, a room thermostat (± 1°C). The water vapour pressure was controlled by a volume of distilled, degassed water in a small bulb suspended in a Dewar vessel filled with a mixture of methanol and dry ice. The absorption measurements were made continuously with increasing temperature; the desorption measurements were recorded discontinuously [14]. A vacuum was generated by means of an oil diffusion pump and measured using Pirani and ionization gauges.

The wool sample (0.250 g) consisted of washed yellowish raw sheep wool, which was cleaned at 30°C in distilled water with detergent and rinsed with distilled water. In production, sponges are prepared by beating, bleaching,

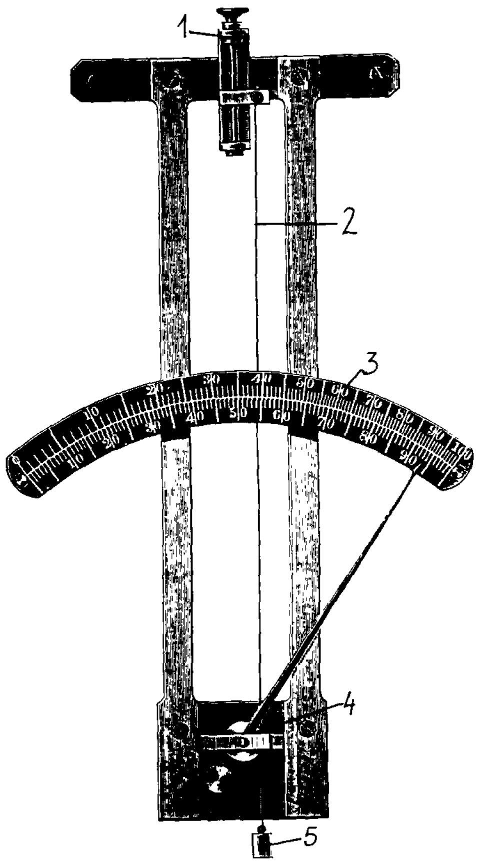


Fig. 5. Hair hygrometer devised by de Saussure: 1, zero adjustment; 2, hair; 3, non-linear graduation in relative humidity; 4, roller with pointer; 5, pre-stressing weight.

washing and possibly cooking in soda. Only the skeleton remains. The sponge used was a small cleaning sponge, 4.3 g in mass, with predominantly small pores and a few wide pores. Inspection under the magnifying glass showed mostly pores of about 1 mm in diameter. A sponge sample of 0.132 g was heated in distilled water and used as a sample. Chemically clean 100% cotton, according to Dr. von Bruns (Franz Kalff GmbH, D-5350 Euskirchen), has been treated in its production with 4% soda solution and washed. The sample (0.410 g) was used without any further cleaning process. The hair sample (1.072 g) was obtained from a light-brown-haired woman (Head Hunters, Friedrichsdorf). It was degreased in the same way as the wool.

RESULTS

Using reference samples, nitrogen isotherms were recorded at 77 K [15]. With regard to the detection limit of the arrangement, the specific surface area was below the detection limit of the apparatus, i.e. lower than 0.1 m^2 g^{-1}.

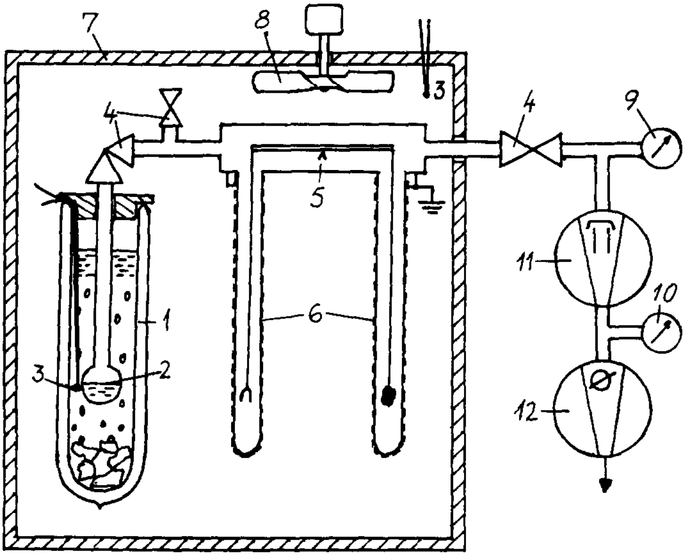
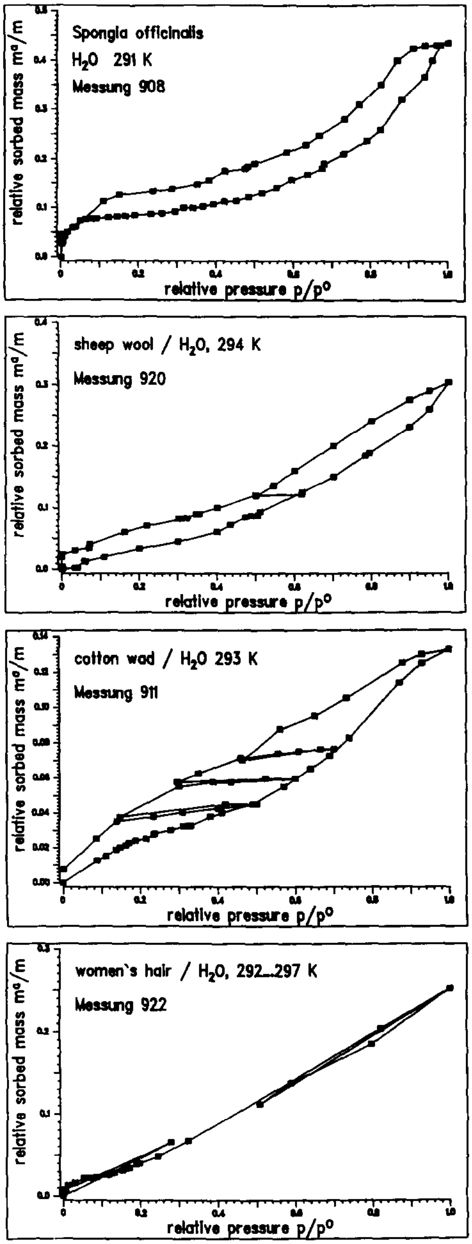


Fig. 6. Gravimetric apparatus: 1, Dewar vessel with methanol/dry ice; 2, bulb with water; 3, semiconductor thermometers; 4, valves; 5, electromagnetic balance; 6, balance tubes covered with metal stockings; 7, heat insulated case; 8, fan; 9, ionization vacuum gauge; 10, Pirani gauge; 11, oil diffusion pump; 12, rotary vane pump.

All measurements on water isotherms (Figs. 7-10) were started at high vacuum and at ambient temperature without pre-heating treatment. Despite the very different chemical structures of the materials, all the isotherms appeared to be reproducible. Reaching the zero point by pumping down after desorption proved that it was not necessary to use additional heating. The isotherms of sponge, wool and cotton wad show a pronounced hysteresis between adsorption and desorption, covering the whole region between saturation and the zero point [16]. On decreasing the pressure during the adsorption process, the adsorbed mass remains constant until the desorption curve is reached. The same happens on increasing the pressure during the desorption process: the adsorbed amount remains constant until the adsorption curve is reached. At each measuring point, the time required to reach equilibrium was between a quarter of an hour and more than a day. The water isotherm on the sponge begins with a steep increase followed by a more flat rise, which is typical for hydrophilic materials. In contrast, cotton and wool show a nearly straight ascending slope and should, therefore, be more hydrophobic [17].

Qualitatively, the sorption isotherms measured agree with those in the literature [18-20]. Quantitative differences are to be expected with this large variety of natural materials.

Regarding the isotherms shown in Figs. 7-9, it is rather surprising to see that the isotherm of human hair (Fig. 10) results in a nearly straight line without noticeable hysteresis.



Figs. 7–10. Experimental isotherms.

DISCUSSION AND CONCLUSIONS

To assess the sensitivity of Leonardo's balances shown in Figs. 2 and 3, we applied the following data: mass of the beam M, 5 g; length of the beam $2l = 1$ span, ≈ 0.24 m; distance from centre of gravity/fulcrum H, 2 mm;

resolving deflection Δh, 2 mm; sample mass m, 5 g; resolution Δm; factor (friction, etc.) k, 1.

If the fulcrum and suspension points of the sample and counterweight are on one line and for small deflections, we can use the equation [21]

$$\frac{\Delta m}{m} = \frac{HM\Delta h}{kl^2 m} \tag{1}$$

and we obtain 3×10^{-4}. This suggests that balances of the 15th century achieved a relative sensitivity of 10^{-3} to 10^{-4}. The balance shown in Fig. 4 is likely to be based on a bricklayer's tiltometer. Because of its low centre of gravity, it would be very insensitive.

Our measurements resulted in mass effects of sorption which could easily have been observed using sensitive balances of that period. In our experience, equilibrium values were reached in reasonable times when humidity values fell between 10% and 80%. All isotherms were reproducible. The hysteresis loops, though reproducible, could lead to serious problems when applied to the determination of humidity. Here, an exception is the isotherm of hair which shows no hysteresis.

No mention of the choice and the pre-treatment of the samples has been found in the descriptions of the hygrometers. Treatment with 4% soda solution to make cotton absorbent was first applied during the French/German war of 1870/71. The cotton used by Leonardo must have been much more hydrophobic. In control measurements, we did not find any significant influence on the isotherms resulting from contamination by fingerprints [22–24].

In principle, the hygrometers described in 15th century literature could have been used, although hair would have been a much better material as absorbent. With respect to the sketches of Leonardo da Vinci, because of low sensitivity or instability, it seems unlikely that he realized those instruments.

The measurement of mass changes is more reliable than measurement of length changes of the hair. The latter method, however, is much easier and cheaper, and is therefore used in all hair hygrometers.

ACKNOWLEDGEMENTS

We are indebted to H.R. Jenemann for valuable discussions, procurement of literature and providing photos. The apparatus used was part of the equipment described by Dr. Willems [25]. The authors acknowledge their lively discussions with Professor J.A. Poulis (Technical University, Eindhoven).

REFERENCES

1 E. Gerland and F. Traumüller, Geschichte der physikalischen Experimentierkunst, Leipzig, 1899. Reprint: Olms, Hildesheim 1965, pp. 83–84.

2 Nicolaus Cusanus, Idiota de Staticis Experimentis, Dialogus, Straßburg, 1450. German transl.: H. Menzel-Rogner, Der Laie über Versuche mit der Waage, Philosophische Bibliothek, Vol. 220, Meitner, Leipzig, 1942.
3 L.B. Alberti, L'architettura, Padua 1483/Firenze 1485, Zehn Bücher über die Baukunst. Translated by M. Theurer. Wissenschaftliche Buchgesellschaft, Darmstadt 1975. (Reprint of the 1st edn., Heller, Wien 1912, p. 357.)
4 Leonardo da Vinci, Das Lebensbild eines Genies. Vollmer, Wiesbaden, 1955, p. 211.
5 Léonard da Vinci, Catalogue "Les Mots dans le Dessin", Cabinet des Dessin, Louvre, Paris, 1986, pp. 68–69.
6 Codex atlanticus, fol. 8 verso-b. Saggio del Codice atlantico, Milano, 1872, cited in refs. 1 and 5.
7 loc. cit 1, pp. 107–108.
8 Codex atlanticus, Milano 1872, fol. 249 verso-a, cited in refs. 1 and 5.
9 W. Lück, Feuchtigkeit: Grundlagen, Messen, Regeln, Oldenbourg, München, 1964.
10 D. Sonntag, Hygrometrie, Akademie-Verlag, Berlin, 1967.
11 H.B. de Saussure, Essais sur l'hygrométrie, Neuchâtel, 1783. Ostwald's Klassiker der exakten Wissenschaften, No. 115/119, Engelmann, Leipzig, 1900.
12 L. Pfaundler (Ed.), Müller-Pouillet, Lehrbuch der Physik, Vol. III, Vieweg, Braunschweig, 1907, p. 832–833.
13 Th. Gast, J. Phys. E, Scientific Instruments, 7 (1974) 865.
14 S. Gá, Die Methodik der von Wasserdampf-Sorptionsmessung, Springer, Berlin, 1967.
15 R.Sh. Mikhail and E. Robens, Microstructure and Thermal Analysis of Solid Surfaces, Wiley, Chichester, 1983.
16 F. Kneule, Das Trocknen, Sauerländer, Aarau, 1959, p. 29.
17 A.J. Juhola, Manufacture, pore structure and application of activated carbons, Parts I and II, Kem. Kemi, (11) (1977) 543–551; (12) (1977) 653–661.
18 F. Kneule, Sorptions- und Desorptionsisothermen, Maschinenbau-Verlag, Frankfurt am Main, 1964.
19 Landolt-Börnstein, Zahlenwerte und Funktionen, Vol. IV, Springer, Heidelberg, 1955, Part 1, pp. 367–368.
20 J.G. Wiegerink, Moisture relations of textile fibres at elevated temperatures, J. Res. Nat. Bur. Standards, 24 (1940) 645–664.
21 H.R. Jenemann, Die Entwicklung der mechanischen Präzisionswaage, in M. Kochsiek (Ed.), Handbuch des Wägens. Vieweg, 1985, p. 549–551, 570, 572.
22 E. Robens, G. Robens and G. Sandstede, Measurement of sorption, vaporization and decomposition of materials used in vacuum technology by means of an electromagnetic microbalance, Vacuum, 13 (1963) 303–307.
23 E. Robens, Wägefehler durch Adsorption an Gewichten, Wägen + Dosieren, 5 (1981) 188–194.
24 C.H. Massen, E. Robens, J.A. Poulis and Th. Gast, Disturbances in weighing. Part II, Thermochim. Acta, 103 (1986) 39–44.
25 H.H. Willems, Creep Behaviour and Microstructure of Hardened Cement Pastes, Proefschrift, Eindhoven, 1985, p. 21.