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THE DESIGN OF AN AUTOMATIC SYSTEM FOR THE GRAVIMETRIC MEASUREMENT OF WATER SORPTION

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Abstract

An understanding of the mechanisms by which water molecules are held within a substance or at its surface, either by physical or chemical processes, is of importance in the formulation, preparation and storage of a wide variety of substances. The traditional experimental techniques which have been used to make measurements on samples exposed to specific levels of relative humidity, (e.g. using desiccators containing saturated salt solutions), are slow, laborious, inaccurate, and provide a limited amount of data. This paper describes the conception, operation, and facilities of a new system which by employing recently developed electronic components and transducers, significantly advances the performance capability for moisture sorption analysis.

Keywords: relative humidity, sorption kinetic, water sorption

Introduction

A knowledge and understanding of the ways in which water molecules are held within a substance, either by physical or chemical processes, is of importance in the formulation, preparation and storage of a wide variety of materials.

By the traditional experimental method a sample is exposed for a sufficient time within a desiccator containing a saturated salt solution which provides a known level of relative humidity. It is then removed, weighed, and replaced in the desiccator with another salt solution to provide the next value of relative humidity. This technique is necessarily slow, laborious, and inaccurate.

The availability of electronic transducers capable of measuring either dew point or relative humidity, has facilitated the development of automatic systems capable of performing water sorption analysis much more rapidly and in greater detail.

In recent years systems have been constructed for individual use in universities and research establishments and there are now several commercial systems on the market.

This paper describes the design of such as system aimed at accuracy and ease of use.

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Design objective

The objective is to design a microbalance system in which the weight of a sample is monitored while it is suspended in an enclosed chamber, and exposed to accurately controlled values of temperature and relative humidity. Each of these parameters is to be rapidly set and precisely held over a wide range of levels, with continuous monitoring. Loading of the samples and calibration of the microbalance should be simple, and the system should operate over an indefinite time without any attention.

Design considerations

These were to provide:

1. Easy access for balance calibration and for the loading and unloading of samples.
2. Precise control of the environment surrounding the sample – in temperature, air flow and relative humidity.
3. Sufficient isolation of the weighing head mechanism from the sample environment to avoid weighing errors due to fluctuations in temperature, air flow and relative humidity, (R.H.).

Weighing accuracy requires that the weighing mechanism is subject to a constant environment, whereas an experiment exposes a sample to a sequence of precisely defined conditions varied in steps over a wide range in temperature and relative humidity.

Thus it was necessary to consider means:

1. To provide isolation between balance head and sample.
2. To maintain constant temperature and R.H. for the Head.
3. To add and remove heat from the sample and its surroundings.
4. To rapidly change the R.H. at the sample, (without overshoot), and hold it constant.

The principal elements in the system are shown in the block diagram, Fig. 1.

The microbalance

The microbalance is a beam balance with the sample and tare weights suspended from opposite ends of the beam. For this application the sample is suspended by a fine stainless steel wire in a weighing chamber below the weighing head, while the tare weight is attached by a short suspension within the head enclosure. In practice it is rarely necessary to change the tare weight as there is sufficient dynamic weighing range to cover the change in sample weight during the experiment.

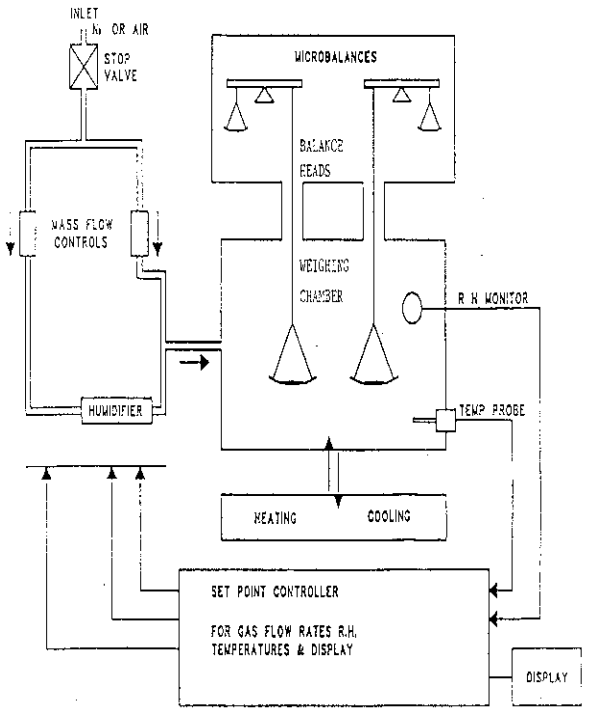

Fig. 1

The balance head should not be subjected to variations in temperature or R.H. during an experiment, and should be allowed to acclimatise initially for thirty minutes.

Acceptable isolation between the weighing head and the sample was achieved by:

1. The use of an extended narrow bore tube around the sample pan suspension.
2. Separate temperature control for the weighing head.
3. Provision for the head to be head continuously flushed with dry air.

Temperature control

There are three locations at which precise temperature control is required. These are the weighing head, the Sample Chamber and the Humidifier. The latter generates a stream of near 100% humid air, which mixed in proportion with dry air, provides the controlled conditions for the sample environment.

The design specification requires the sample temperature to cover a range between 5 and 65 degrees centigrade. The humidifier should also cover this range,

while the range of the weighing head is normally set between room ambient, (20°C and the maximum for the sample, i.e. up to 65°C).

In practice the majority of experiments are made under isothermal conditions so that the only temperature change in a particular experiment may be an initial sample 'purge' at elevated temperature and near zero humidity. In this case it is usual to set the balance head at about two degrees above the 'isothermal' temperature selected for the experiment, to prevent any possibility of condensation occurring in the balance head enclosure.

Maintenance of a precise temperature around the sample is particularly important due to the very large effect of a temperature change on relative humidity in an enclosed volume of air. This varies across the R.H. and ambient temperature ranges and in the extreme situation a 1°C change can alter the R.H. by as much as 6%, (e. g. below 20°C and at 90% R.H.). On average 2% to 3% errors are typical over the R.H. range.

The specification requires set temperatures both below and above the room ambient. In addition to the use of heaters, which present no problem, a means of fast controlled cooling is required.

Conventional refrigeration is cumbersome and slow for this purpose, and a decision was made to control each module independently, by the use of peltier cells. In recent years peltier cells matrices have been developed, using semiconductor P N junction technology, with power levels of 70 W or more. A typical format comprises a ceramic sided wafer of 40 mm square and 3 mm thickness in which heat is transferred from one face to the other in a direction depending on the polarity of an applied dc voltage.

Each of the system modules is mounted on the upper face of a group of these cells, with the lower faces of the cells in contact with a heatsink. The available heating/cooling power for each module is about 200 W. The temperature of each module is accurately measured by a platinum resistance thermometer, coupled in a closed loop servo system which controls the applied electrical power. Each module weighs 2 kg or less and can be heated or cooled between the extremes of its range in a few minutes without overshoot. At equilibrium the module temperatures remain constant within ±0.1°C

Measurement and control of relative humidity

Relative humidity may either be measured directly, using one of several recently developed devices, or by calculation from a measurement of the dewpoint, using a Dewpoint Analyser, (DPA).

The traditional dewpoint instrument, (suitable only for manual operation), uses a wet and dry bulb thermometer combination and a conversion chart. Most electronic DPAs operate by cooling a mirror surface until it just forms a dew, thus causing a reduction in a reflected light beam. An electronic servo circuit holds

the temperature of the mirror at this level and, indicates the dewpoint. These systems have the disadvantage of being rather bulky and are usually slow in response.

Typical direct reading R.H. transducers make use of changes in either the conductivity or the capacitance of a polymer membrane. These devices can be very compact and have a rapid response but they require initial and periodic calibration, response linearisation, and they may be damaged by contaminants.

For this system a very compact direct reading R.H. probe was selected. Its dimensions are 3 mm diameter by 50 mm in length and its time constant is less than 20 s.

The sample is suspended in a flow of gas, either air or nitrogen, of controlled R.H. The flow rate is kept low, to avoid affecting the balance reading, and after R.H. stability is achieved may be close to zero. Precise R.H. control is effected by dividing the source air stream into two, one dry and one of high humidity, and then recombining the two streams in appropriate proportions. The flow rate of each stream is accurately controlled within 1% by mass flow control valves.

Water vapour is taken up by the 'wet' gas stream by passing it through a humidifier. A variety of types of 'humidifier' have been used. The simplest method is to use a bubbler, passing the gas through a flask of water. While this is effective and quite suitable for a system which is unlikely to be moved, it was considered undesirable to locate an open water vessel within an enclosed electronic instrument, because of the difficulty of providing easy access for re-filling and also the possibility of water spillage within the unit.

The wick material selected was a glass fibre possessing very high water retaining capacity with no tendency to drip. This material is widely used to hold the electrolyte in car batteries.A stream of air passed over this wick material readily achieves almost 100% relative humidity. This 'wet' air is then mixed with a proportion of dry gas to provide the desired level of relative humidity. During operation very little water is used and in practice it is only necessary to top up the system after several weeks running.

Overall control of the system

Control of the system operates at several levels:

- Lower level: Individual feedback control of the various parameters (heating/cooling, gas flow, balance control).
- Intermediate level: Real time supervision of the experiment sequence.
- Upper level: Specification of experiment, data recording, display of results, data analysis, printout and archival.

Control is simplified by the separation of the 'real time' software from the data associated with the experimental parameters, displays and information stor-

age. The lowest level accepts 'set point' inputs to control temperature, gas flows and balance operation, and these are handled by a microprocessor within the instrument. Supervision of the experiment, its defining parameters, and all aspects of data handling take place within a separate 'state of the art' personal computer.

Table 1 Example of the Table of Data used to define the course of an experiment

Experiment sequence step No.	Relative humidity R.H.%	Min. step duration/ min	Weight stability for step endpoint		Sample temperature/ °C
			Wt.A%	Wt.B%	
1	0	60	0.005	0.005	60
2	0	30	0.005	0.005	25
3	5	10	0.005	0.005	25
4	10	10	0.005	0.005	25
5	15	10	0.005	0.005	25
6	20	10	0.005	0.005	25
7	30	10	0.005	0.005	25
8	40	10	0.005	0.005	25
9	41	10	0.005	0.005	25
10	42	10	0.005	0.005	25
11	43	10	0.005	0.005	25
12	50	10	0.005	0.005	25
17	41	10	0.005	0.005	25
18	42	10	0.005	0.005	25
19	43	10	0.005	0.005	25
20	50	10	0.005	0.005	25
23	85	10	0.005	0.005	25
24	90	10	0.005	0.005	25
26	85	10	0.005	0.005	25
27	80	10	0.005	0.005	25
32	25	10	0.005	0.005	25
33	20	10	0.005	0.005	25
34	15	10	0.005	0.005	25
35	10	10	0.005	0.005	25
36	0	10	0.005	0.005	25

Modern PCs are ephemeral, becoming out of date in a matter of months, and without technical support in a very few years, so that it is unwise to incorporate them too uniquely into a product intended for a rather longer active life.

All designs involve compromise, and can appear less than perfect in hindsight in the light of subsequent technological developments. In this design the low level control has the advantage of simplicity in its interface with the external PC, by the use of a very concise command protocol which for most purposes comprises only a single ASCII character.

These include:

- The range of control functions for the microbalance.
- Set point commands for temperature for each module.
- Set points for the mass flow meters.
- Operation of solenoid flow valves.

A well-designed instrument should be easy to use and it should provide flexibility to the operator in the configuration of an experimental procedure. With this instrument experiments may take a week or more to complete so that the ability to change some of the experimental parameters while it is running is very beneficial.

System operation

Typical moisture sorption experiments provide static records of adsorption and desorption, under isothermal conditions, or a kinetic record of the moisture uptake or loss with time, following a specific change in relative humidity.

For the static isothermal test to be meaningful, it is necessary for the sample weight to reach a defined equilibrium condition at each successive step in the level of R.H. A concurrent kinetic test can clearly indicate the degree to which equilibrium has been reached *vs.* elapsed time at each step.

The Operator is able to define the course of an experiment in the form of a table as shown in Table 1.The experiment proceeds stepwise as the conditions in each sequential step are met. The Operator is also able to modify, add or delete any steps beyond that currently in operation, or to move on to the 'next step'.

An indefinite number of steps can be accommodated in any experiment. With reference to the table the end point for a step is reached when the logical conditions in columns 2 to 5 are all satisfied within defined tolerance limits. The weight stability endpoints refer to a percentage weight change within a unit time interval, this unit being separately specified. Throughout the course of an experiment data is recorded including: elapsed time – sample weight – R.H. – sample temperature – wet and dry gas flow.

During an experiment the isothermal and kinetic records can be displayed, enabling the operator to make changes in the step parameters if necessary, as for

example to provide smaller increments in R.H. or to alter the equilibrium condition specified for weight stability.

The tabular data may be arranged to define a wide range of experiments.

The 'elapsed time' column normally sets the minimum time for a step, with the weight stability figure setting the actual time. However, if the latter is set very high so that its logical condition is always met, then the experiment proceeds in time intervals established by column 3.

For isothermal experiments column 6 is constant for all steps, apart from a possible purge of the sample at an elevated temperature at the beginning. The effect on the sample of a temperature ramp may be investigated by setting small incremental values in this column with a very small elapsed time in column 3 and high weight stability set in columns 4 and 5. A sample may be tested over a series of adsorption/desorption sequences by repeating the data steps in the table.

Conclusions

An automatic moisture sorption system has been developed using the principles outlined here. This system, identified as the CISORP Monitor, incorporates two microbalances, to permit two samples to be analysed under identical conditions simultaneously. Thus the isotherm plot for an unknown sample may be compared against a standard sample, or a small and a large sample of the same material may be examined together to provide an indication of homogeneity.

The design had to overcome some demanding technical problems, in order to achieve both accurate control and uniformity of the relative humidity within the weighing chamber at quite low air flow rates. This required that temperature gradients in this chamber be held within very close limits.

The approach adopted proved capable of meeting the target specifications and providing substantial benefits to the user in terms of accessibility, fast and accurate response and ease of use.

Equipment with the described design features has been used and its application described in the paper in these proceedings entitled 'Investigating a Range of Solid Samples by Automatic Water Sorption' by Astrid Mangel.