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MICROBALANCE APPLICATION IN THE PRIMARY GRAVIMETRIC HYGROMETER OF THE UK NATIONAL HUMIDITY STANDARD

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ABSTRACT

In 1981 the decision was taken to establish a National Standard for humidity measurement at the National Physical Laboratory, England. The instrument system consists of two major parts, the Precision Humidity Generator and the Primary Gravimetric Hygrometer (PGH). The latter has been developed by Sira Ltd under a contract from NPL (ref.1). In this paper, following a concise description of the principles of the Primary Gravimetric Hygrometer, aspects of the vacuum microbalance system are discussed.

Key words: Humidity Standard, Gravimetric Hygrometer, Vacuum microbalance, Calibration.

INTRODUCTION

The Primary Gravimetric Hygrometer (PGH) being the ultimate humidity standard of the UK has the function of the initial and periodic calibration of the Precision Humidity Generator, which provides the test gas for the calibration of hygrometers of transfer standard quality.

The PGH accepts a sample flow of test gas and determines its humidity in base units in terms of the mixing ratio

$$r = \frac{\text{mass of water}}{\text{mass of dry gas}}$$

This is achieved by separating the water vapour and dry gas components of the sample stream and determining their ratio by direct mass measurement.

In the classical method of gravimetric hygrometry the wet gas is passed through U-tubes filled with desiccant. The mass of the moisture absorbed is determined by differential weighings. The dry gas is collected and its mass is determined usually volumetrically.

The design objectives of the instrument included the maximisation of the operating range in terms of humidity and the minimisation of measurement time. These requirements are to some extent conflicting since at the low humidity of interest the amount of water in the gas is extremely small. Consequently long periods are required to collect a sufficient amount of water whose mass can be determined with the required precision.

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In an attempt to overcome some of the limitations of the classical gravimetric hygrometer the present instrument system incorporates several novel ideas.

Instead of U-tubes with their inherent large "dead weight", a smaller amount of desiccant is contained in a package of minimum weight and the mass determination is carried out by a microbalance in a vacuum system.

THE PRINCIPLE OF THE PRIMARY GRAVIMETRIC HYGROMETER

The principle of the instrument is shown in the schematic diagram, Figure 1. Figure 2 illustrates the simplified front elevation of the complete system.

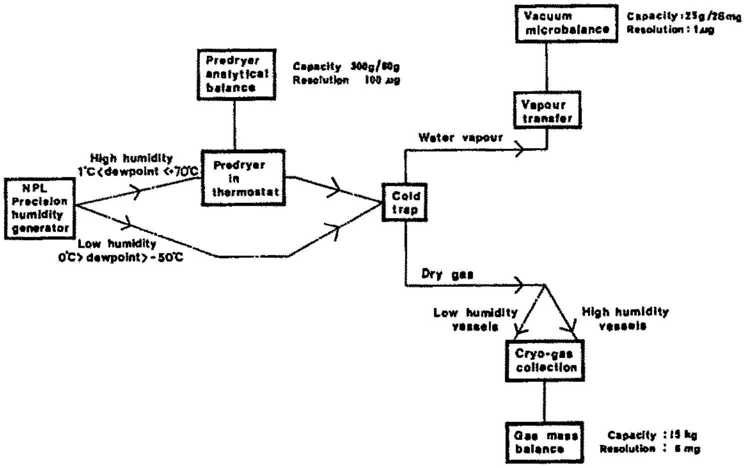

Figure 1. Schematic diagram of the Primary Gravimetric Hygrometer

Two paths are provided for the inlet gas: low humidity gas (dew point <-0 °C) is fed directly into a high efficiency cold trap; high humidity gas (dew point >+1 °C) enters the pre-dryer first, where the bulk of the moisture is condensed out. The exit gas from the predryer is fed into the cold trap, where the remaining water is separated. The dry gas emerging from the cold trap is liquefied and collected in a pressure vessel assembly placed in a specially-developed cryostat. The liquification of the gas provides the suction to move the gas through the system. The mass of the dry gas in the vessel is determined by differential weighing on a 15 kg capacity equal arm balance. On the reference side of the balance an identical empty vessel is suspended for automatic buoyancy correction. The potential accuracy of the gas measurements is 0.01%.

For high humidity measurements, the mass of the water collected in the predryer, is determined on an electronic analytical balance, by differential weighing using an identical empty unit as the reference for buoyancy correction.

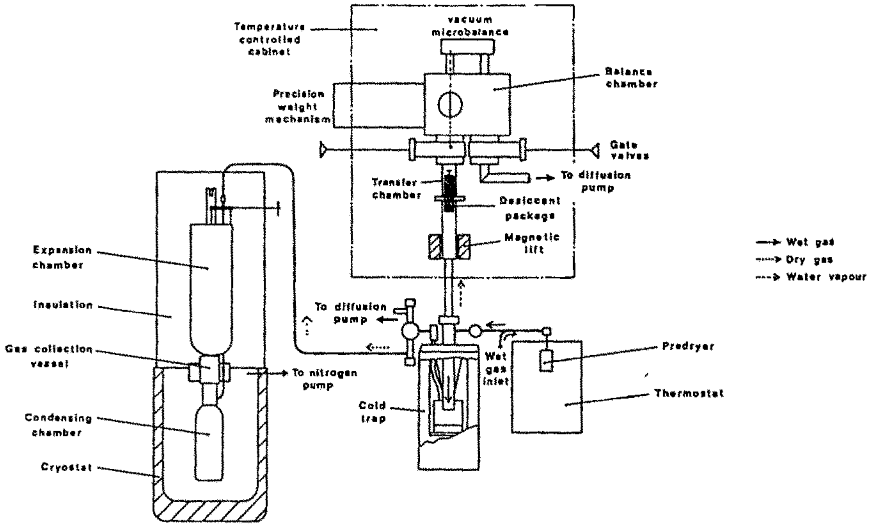

Figure 2. Schematic front elevation

The cold trap described in reference 1 is a specially-developed component. It is an efficient trap of water vapour operating at cryogenic temperatures and also allows, when heated, the relatively unrestricted release of the trapped water into the desiccant. The desiccant is placed in the transfer chamber from where it can be lifted on to the microbalance hook by the lift mechanism. The transfer chamber can be isolated from the cold trap by the transfer valve and from the balance chamber by a gate valve. The balance chamber supports the microbalance and contains the weight mechanism.

On completion of the collection period the water contained in the cold trap is heated and vapourised. It then quickly diffuses into the dessicant under vacuum where it is absorbed. Its mass is determined by differential substitution weighing by the microbalance.

In the following sections, this process and the associated mechanism which forms the main subject of this paper are discussed in some detail.

The measurement task

The specified humidity range of the PGH is from -35 °C to +35 °C dew point (or in terms of mixing ratio 0.14 to 37.8 g/kg). The useful range however extends from -50 °C dp (0.025 g/kg) to +70 °C dp (285 g/kg) although with decreasing accuracy for the lower humidities.

The target performance is ±0.2% uncertainty over the specified range.

The nominal mass of dry gas collected above -25 °C dp humidity is 400 g and below this level 1200 g. At the nominal 1 l/min gas flow rate the collection time is 6 and 18 hours respectively.

The amount of water collected in the cold trap at 0 °C dp is 1.56 g and at -50 °C dp 30 mg. This amount of water is transferred into the desiccant and is the normal working range of the the microbalance. Above +1 °C dp the predryer comes into action, and the cold trap only receives the breakthrough from the predryer which, over a six hour period, amounts to about 0.3 mg. At +1 °C dp this represents only 0.005% of the total water mass collected and becomes progressively less at higher humidities. At these levels the role of the microbalance system is only a check of the proper functioning of the predryer.

The vapour transfer system

The water collection, transfer and mass determination takes place in a high quality stainless steel vacuum system, shown on the photograph (Figure 3).

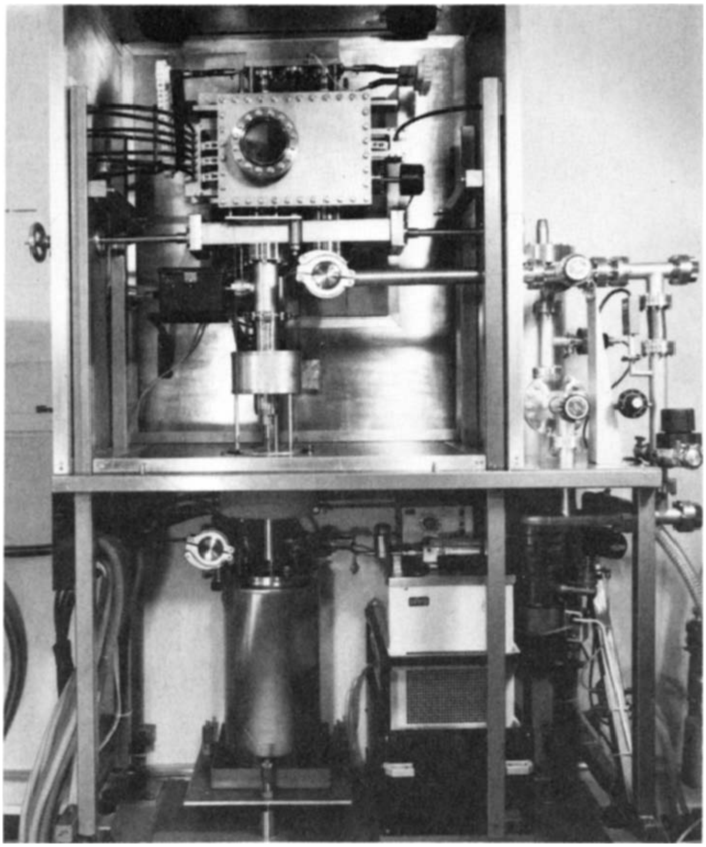

Figure 3.
The vacuum microbalance system

The function of the vapour transfer system is to provide a means of applying the water collected in the cold trap to the microbalance.

The water is transferred in vacuum by controlled heating into specially activated magnesium perchlorate which is initially situated in the small transfer chamber. During the initial experiments it became apparent that the components of the microbalance interact with water vapour and if the transfer took place with the balance exposed to it, significant measurement errors would result. Also, it was found that drying the balance took very long periods after each time it was opened to place the desiccant in the system. For this reason the desiccant is first placed into the lift chamber which can be attached to the transfer chamber in a matter of seconds, and evacuated without disturbing the balance environment. The resulting volume functions as a lock between the cold trap and the balance system. Figure 4 shows the design features. The lift chamber contains a cage on which the desiccant is suspended. On completion of the vapour transfer, this cage is lifted by the external magnetic yoke sliding on the tube through a large orifice gate valve into the balance chamber. The moving mechanism has both longitudinal and rotational movement and the package can be suspended on the microbalance hook with a bayonet-lock action. This way the desiccant can be weighed in the sealed vacuum system before and following the vapour transfer, by manipulation from outside the temperature-controlled enclosure. The high precision lift mechanism is made of composite stainless steels of carefully controlled magnetic properties. The arrangement permits the use of the same desiccant package for several low humidity measurements.

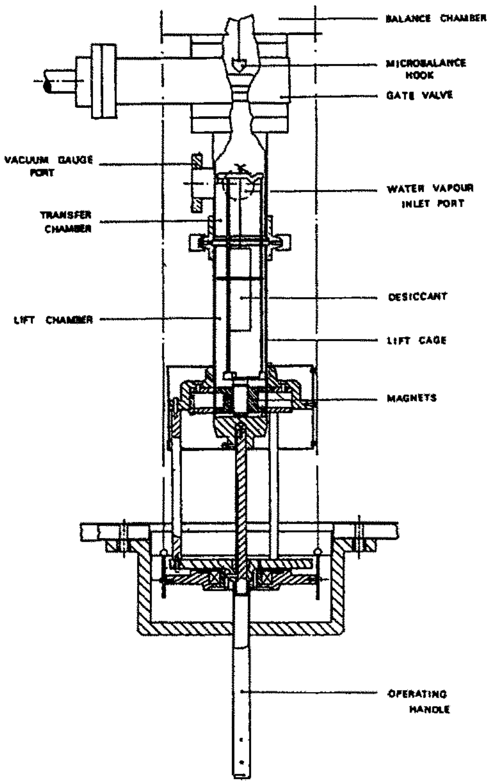

Figure 4. Lift chamber

The microbalance system

The Sartorius 4410 symmetrical double beam vacuum microbalance was selected for the instrument. It has a total capacity of 25 g and a fine electronic range of 28 mg with 1 µg resolution.

The total mass of the hangdown is 23 g. This includes the dry desiccant package and support members. The maximum amount of water to be weighed is an additional 1.5 g.

The adopted method of differential substitution weighing requires the counter-balancing of the 23 g "dead weight". For this purpose a fixed tare weight can be applied to the reference side of the balance.

In order to meet the specification, it was also necessary to extend mechanically the 28 mg electronic range to provide a floating 1 µg resolution range over 1.5 g total span.

This has been achieved by the provision of a range of mechanical precision weights. A photograph of the hangdown assembled outside the system for illustration, is shown in Figure 5 with one weight in position.

Figure 5 also shows the desiccant package suspended on the hangdown which is made of very fine stainless steel mesh.

Figure 6 shows a photograph of the balance chamber interior, with the hangdown in position.

Seven calibrated precision platinum wire weights sit in the elongated slots of the perforated tube. These can be placed on and off the balance by forks mounted on wobble sticks which have flexible extensions to outside the temperature-controlled enclosure. The tare weight, also shown, has a similar actuating mechanism.

The balance has remote actuated arrest mechanisms on both sides. The sample is hooked on the balance in the arrested state.

Figure 5. Hangdown with desiccant package

The mechanism allows "zero" readings to be taken with both the hangdown and tare weight removed. This is particularly important in this application since the interval between the differential weighings can be several days.

Combinations of applied weights can be used directly for the calibration of the microprocessor-based electronic display.

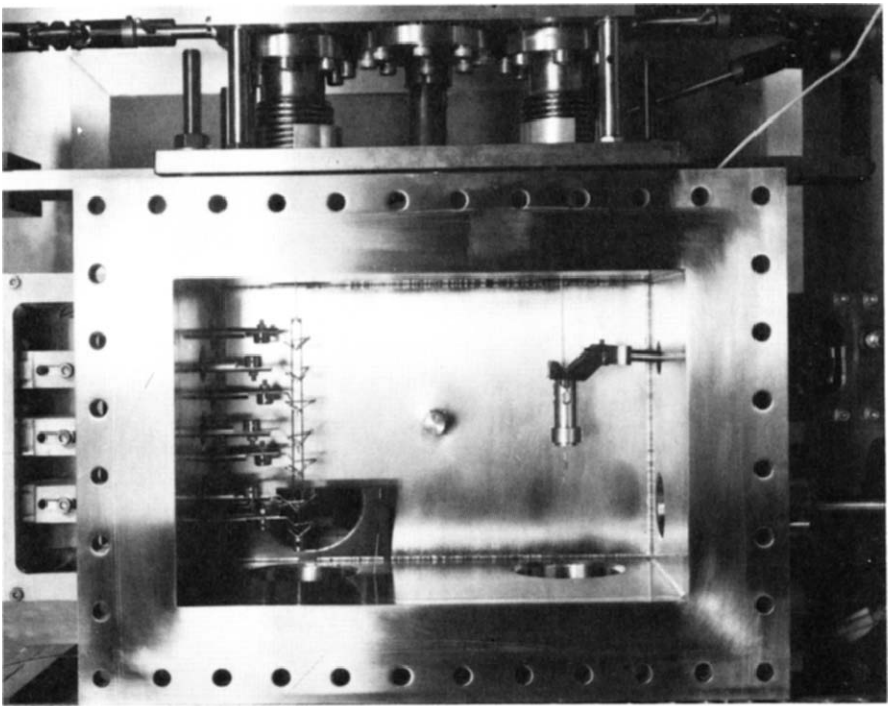

Figure 6. Balance chamber with cover removed

Operational features and initial results

The whole of the vacuum system is normally operated at 30 °C in a closely temperature-controlled enclosure. The temperature gradients are of the order of 0.2 °C and consequently thermal forces are negligible.

All the stainless steel components of the hangdown assembly have been vacuum annealed to reduce residual magnetic properties. Measurements indicate that the effect of the lift magnets is negligible.

The mass determinations are normally carried out at static pressures in the region of 3×10^{-3} mb. Errors of the order of 3 µg were experienced for pressure variations of 10^{-3} mb at the above level. This can be reduced if the pressure of the balance chamber is controlled by the admission of specially dried nitrogen. During the collection and transfer periods the balance chamber is isolated and continuously pumped.

The operational sequences of the instrument system have been carefully optimised. By adhering to a fixed routine, the standard deviation of single mass determinations is 5 µg.

The rigorous acceptance tests carried out at Sira Ltd proved that the assembled instrument system functions properly and that no major sources of errors are present which would prevent it from performing to specification. Final validation of the instrument involving the quantification of all the measurement uncertainties will take place when it is fully commissioned and integrated with the Precision Humidity Generator at the National Physical Laboratory.

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REFERENCES

1 Forton A G, Pragnell R F. Development of the Primary Gravimetric Hygrometer for the UK National Humidity Standard Facility. Moisture & Humidity, Proceedings of 1985 International Symposium, Washington, ISA 1985, p 79-89.
2 Poulter K F, Hales J L, Forton A G, Pragnell R F. The UK National Humidity Standard - Justification and Concept. Moisture & Humidity, Proceedings of 1985 International Symposium, Washington, ISA 1985, p 7-13.
3 Hales J L. The two-temperature generator in the UK Humidity Standard. Moisture & Humidity, Proceedings of 1985 International Symposium, ISA 1985, Washington, p 229-231.
4 Wexler A, Hyland R W. The NBS Standard Hygrometer (Gravimetric Chain). NBS Monograph 73, US Dept of Commerce, National Bureau of Standards, May 1964. Lib of Congress, Cat Card No 64-60005.
5 Wexler A et al. Chapter 19, Humidity and Moisture Vol III, Rheinhold, NY, 1965, p 389-432.
6 Kostyrko K. A two balance direct method of mixing ratio determination. J of Phys E, Scientific Instruments, Bristol, England, v 10, 1977, p 802-807.
7 Kostyrko K. A direct two-balance method for the high-value mixing ratio determination. Report on the 9th Intl Conference on the Properties of Steam, Intl Assoc for the Properties of Steam, Muenchen, W Germany, Sept 1979.
8 Merigoux J, Cretinon B. Le centre d'etalonnage des hygrometres. Bulletin BNM, France, No 42, Oct 1980.
9 Still J E, Cluley H J. A new method for the measurement of extremely low humidities and its application to the testing of desiccants. The Analyst, London, v 97, n 1150, Jan 1972.
10 Besley L M, Bottomley G A. The water vapour equilibria over magnesium perchlorate hydrates. J Chemical Thermodynamics, London n 1, p 13-19.
11 Robens E. The effect of thermal gas motion on microbalance measurements. Vacuum Microbalance Techniques, v 8, Plenum, NY, 1971.
12 Massen C H, Poulis J A. Sources of errors in microweighing in controlled environments. Microweighing in vacuum and controlled environments, Volume 4, Chapter 3, Methods and Phenomena. Ed. A W Czanderna & S P Wolsky, Elsevier 1980.