Use of a gravimetric technique for humidity measurement
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THE USE OF A GRAVIMETRIC TECHNIQUE FOR

HUMIDITY MEASUREMENT

by

ANALYZED

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PREFACE

The Division has been much concerned with the calibration of humidity measuring devices since humidity is an important environmental factor entering into the performance of building materials and components. The devices which purport to measure directly some thermodynamic property of an air-vapour mixture from which relative humidity can be found are usually limited in accuracy and in adaptability to the range of situations under which measurements are desired. All devices which respond to relative humidity directly, require calibration. Some of the newer devices now available exhibit very satisfactory sensitivity but can be no more accurate than the accuracy with which their readings can be converted.

Unfortunately, the situation with respect to reference standards to be used in calibration is also far from satisfactory. Much attention has been given to this problem of a humidity standard and the Division has developed an "atmosphere producer" capable of producing atmospheres of known relative humidity to about 0.2 per cent.

The author, upon being awarded an Athlone fellowship, has recently left the Division to take up Ph.D studies at Imperial College, London. Before leaving, he completed a thesis based on this work, as yet unpublished, in which he discusses in detail the development of the atmosphere producer as a suitable calibration apparatus for most humidity-measuring devices.

The gravimetric method of determining humidity ratio from which relative humidity may be found is, in concept, one of the simplest and most direct. Careful consideration was given as to its suitability for standards purposes and it was tried out, in comparison with the atmosphere producer. The many sources of difficulty and error encountered with the gravimetric method which led to its rejection as a suitable "standard", in favour of the atmosphere producer, are now described.

Ottawa,
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N. B. Hutcheon,
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FOR HUMIDITY MEASUREMENT

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The humidity ratio W is defined in psychrometry as the weight of water vapour associated with a unit weight of dry air and is usually expressed in pounds or grains of water vapour per pound of dry air. A fundamental property of moist air, it is often quoted directly as an index of the moisture content of an atmosphere. Conversion to any other index of humidity may be made with the aid of accepted tables of the properties of moist air (1). The gravimetric technique involves a direct determination of the humidity ratio. Also, since the method involves a direct measurement of a fundamental property of moist air, it has often been accepted as a standard for humidity measurement against which other instruments may be calibrated. Unfortunately, although the method is simple and attractive in principle, it is awkward in application and investigators (2, 3, 4, 5) have stressed, or their results show, the great difficulty involved in obtaining reliable records of high accuracy.

The details of the gravimetric apparatus and the techniques used depend somewhat upon the desired accuracy of the results but in each case the principle is the same. The moist air sample to be analysed is passed through a series of tubes containing an absorbent. The dried air sample is then metered in some way to permit the calculation of the quantity of air involved. The measured quantities of major interest, therefore, are the increase in weight of the absorbent tubes and the metered quantity of air. Before these quantities can be used to give the humidity ratio of the sample, however, a large number of extraneous factors must be considered and their effects upon the records accurately evaluated.

I. EXPERIMENTAL CONSIDERATIONS

Conducting the Sample

The air sample must be clean initially or filtered so that the absorbent picks up nothing but water vapour. The filter and the tubing used to conduct the sample from the test space to the absorbent tubes must not alter the water-vapour content of the sample. The sorption of water on the walls of the tubing, for example, must not be significant. Weaver (6) found that rubber is unsuitable; even the small amounts of rubber used to connect glass or metal tubes introduced significant error at low temperatures where the concentrations of water vapour are very small.

The Absorbent

Magnesium perchlorate, phosphorous pentoxide and calcium chloride have each been used for the absorption of the water vapour. Phosphorous pentoxide, although very efficient, is more messy and difficult to handle than the other two desiccants. Calcium chloride has poor efficiency in comparison with the other two (7). Magnesium perchlorate has been widely used in quantitative microanalysis (8). The properties of magnesium perchlorate and its use as a drying agent have been investigated by Willard and Smith (9). The maximum rate of flow which will insure complete removal of the water from the air is less for magnesium perchlorate than for phosphorous pentoxide. This is expected since the mechanism of absorption is the formation of water of crystallization rather than that of true chemical combination, as in the case of phosphorous pentoxide. When the gas flow does not exceed this maximum, however, magnesium perchlorate has proved to be as efficient a drying agent as phosphorous pentoxide. Also, the weight of water absorbed per unit weight of desiccant is several times greater with anhydrous magnesium perchlorate than with phosphorous pentoxide. Nearly 60 per cent of its own weight of moisture can be absorbed before any trace of water vapour is detected in the effluent gas. In addition, it does not form channels and it contracts in volume after absorbing moisture.

Weighing the Absorbent Tubes

Certain problems arise in the actual weighing of the absorbent tubes. It is difficult to evaluate the error caused by the various influences on the absorbent tubes that affect their apparent weight. Humidity, changes in atmospheric pressure, changes in temperature, use of various types of bores, electrostatic charge, deposits on the surface of the tubes from handling, as well as other factors, may influence the accuracy of the weighing.

The absorption of water on the surface of the absorption tube and the deposition of other materials such as moisture from the hands on the tubes during handling will produce errors if the tubes are not wiped before weighing. However, all glassware develops an electrostatic charge when wiped with a chamois skin (the usual procedure), that is easily detectable on a microbalance. Styermark (10) states that if the static charge is not dissipated on the balance the object decreases in weight so rapidly that weighing is impossible. A rate of decrease of 0.3 mg in several minutes is not uncommon. Electrostatic charge is a particular problem on dry or cold days. To test for it, the absorption tube is held near a small piece of tissue paper suspended by a silk thread which, if an electrostatic charge is present, will be attracted or repelled. Lime glass is preferred to pyrex for the tubing as it does not hold a static charge as long. Almost all glass articles to be

weighed on a microbalance, therefore, are of lime glass.
At a relative humidity of 40 to 50 per cent, charge is
rapidly lost; fifteen minutes should be time enough for
the dissipation of the charge. The weighing process was
improved in one instance by the grounding of the balance
operator when he was wearing nylon apparel.

Since the tubes are weighed in air the buoyancy
effect must be considered, as changes in atmospheric tempera-
ture and pressure will introduce error. Also, if the tubes
are at a different temperature than their surroundings on
the balance, convection currents may cause trouble. The
absorption of water by the magnesium perchlorate releases
heat so the tubes should be allowed sufficient time to
approach temperature equilibrium with the surroundings after
removal from the gravimetric train. This will also allow
the electrostatic charge to be dissipated before the
weighing takes place.

A common method of minimizing these volume forces
on the absorbent tubes is the use, on a double-pan balance,
of a tare of identical dimensions and density to the tube
to be weighed. The tare is given, as closely as possible,
the same treatment as the weighed tube, insofar as wiping
and exposure to room conditions are concerned. In this way
it is hoped to cancel the effects of the factors just mentioned.
A standardized routine should be followed in the weighing of
the tubes. For example, the time lapse between the wiping
and the weighing of the tubes should be the same for weighing
the tubes before they are placed on the gravimetric train
as for weighing them after they have absorbed the moisture
from the sample. The more closely that conditions under
which the tube was initially weighed are approached in the
final weighing, the better the chance that the extraneous
factors will cancel out.

The Measurement of the Quantity of Air

In making a measurement of the quantity of air, it
is necessary to define not only the volume but also the
pressure, temperature and degree of saturation of the air.
The weight of the volume of air may then be taken from tables
prepared for this purpose.

The meter usually used in the laboratory for the
measurement of gas volumes is the wet-test gas meter. The
National Bureau of Standards has published an investigation
of the sources of error inherent in these meters. The errors
in the measurement caused by errors in levelling, in adjust-
ment of water level and in temperature, humidity and pressure
measurement were investigated. The reproducibility of
calibration, the variation in calibration with flow rate,
and the use of fractional revolutions were also investigated.

The meters tested were all in the one-tenth cubic foot per revolution range. A brief summary of the conclusions is now given.

(i) Levelling:- If the water level is adjusted when the meter is level, tilting the meter in various directions up to 1° of an arc produces changes exceeding 0.2 per cent in the calibration. However, readjusting the water level when the meter is tilted causes a change in calibration of about 1.6 per cent for an angle of 1°.

(ii) Adjustment of Water Level:- A change in water level of 1 mm produces a change in calibration of 0.5 to 0.8 per cent, the meters delivering a smaller volume of gas per revolution when the water level is high.

(iii) Temperature, Humidity and Pressure Measurement:- At reasonable flow rates (7 cu ft/hr with a 1/10-cu ft meter) the air is actually metered at the temperature of the water in the meter and becomes practically saturated at that temperature. The effective pressure of the gas when measured in the compartments of the meter drum is the pressure in the inlet chamber, and is almost equal to the pressure at the inlet of the meter.

(iv) Variation in Calibration with Rate:- The volume of gas delivered per revolution, at rates between two and ten cubic feet per hour, is constant to within 0.1 per cent.

(v) Reproducibility of Calibration:- The order of reproducibility may be put at about 0.2 per cent, although the error may reach almost 0.5 per cent, even if the water-level adjustment is correctly made. The presence of any leakage, through stuffing boxes for example, of course voids the accuracy of the meter.

(vi) Fractional Revolutions:- The procedure is not recommended as it may lead to very significant error.

The accuracy of the wet-test meter is thus shown to be subject to considerable uncertainty, although with careful adjustment and calibration against a standard volume before use it may be used to an accuracy of about 0.2 per cent provided the meter has suffered no mechanical injury.

Laboratory meters are often calibrated by the water displacement method using an aspirator bottle, a simple, inexpensive and potentially accurate method of obtaining a known volume of air. The volume is simply calculated from the volume of water displaced from the bottle. Here again, the temperature, pressure and degree of saturation must be known in order to calculate the weight of air involved. The temperature of the air in the bottle is easily determined since the gas passes through a heat-exchange coil in the large mass of water and the water temperature is relatively simple to measure. Also, by using some form of a pre-saturator, complete saturation may be ensured.

Other methods of measuring air volume have also been used. Amdur (4) describes the use of a partially evacuated tank as a volumetric flask for the air sample. In each method, however, assumptions must be made with regard to the average temperature, the degree of saturation and the pressure of the volume of air.

Leakage

It is important to eliminate any possibility of leakage. Each connection should be checked for tightness before each run. Although most connections are not disturbed, those connecting the absorbent tubes to the remainder of the train are removed each time a run is made. Discussions on quantitative microanalysis (10) state that atmospheric pressure should be maintained at the connections between absorbent tubes to reduce the possibility of moisture gain or loss at this point.

II. EXPERIMENTAL WORK

The experimental work on the gravimetric technique was done in five phases. Modifications and refinements to the apparatus and to the technique were made after each phase in an attempt to obtain more consistent records and also to check whether the results previously obtained were dependent upon the particular experimental arrangement used. In all work the air sample was taken from and the results checked against, the two-temperature recirculation-type atmosphere producer developed at the Prairie Regional Station of the Division (11). This machine supplies a stream of moist air of known and constant humidity. While the atmosphere producer was still under development during much of the work and the gravimetric work was taking place in an attempt to verify its accuracy, all evidence showed that the atmosphere producer was much more consistent and reliable than the (gravimetric) method used to check it.

The results obtained and the various forms of the gravimetric hygrometer that were used will be set down in chronological order. Many of the records will be useful only to show the sort of values that might be expected from equipment and techniques similar to those used here. It was believed that the reliability of the records was improved with each succeeding phase, but at no time could the success of a particular trial be predicted with any confidence. When, at any time it appeared that the results were consistent and reproducible, a divergent run or series of divergent runs would occur.

The First Phase

The initial work took place in August, 1955 and the arrangement of equipment is shown in Fig. 1. Flow rates of 1 to 4 litre/min. were used with 100 to 300 mg of moisture being picked up in the absorbent tubes. Two U-tubes, 0.7 inches in diameter and about 11 inches in total length, were used as the absorbent tubes. The desiccant was magnesium perchlorate which occupied about 7 inches of the tube. Glass wool plugs were inserted on top of the desiccant in each arm of the U-tube to keep it in place and to prevent it from being blown around by the flow of air through it. It was expected that the bulk of the moisture would be absorbed in the first tube. The second tube was used as a check on the efficiency of the first tube and to indicate when the desiccant was exhausted.

The dried air from the absorbent tubes was passed through a pre-saturator before reaching the wet-test meter. In the pre-saturator the air was bubbled through a mixture of vermiculite and water. The purpose of this component was to bring the air sample to a known condition of saturation for calculation purposes and to prevent the evaporation of water from the wet-test meter, which would mar the calibration of the meter. The difficulty of attaining complete saturation of an air stream with the bubbling technique was recognized but it was believed that the saturating efficiency was sufficient for this purpose. A "precision" wet-test laboratory gas-flow meter was used for the measurement of the volume of air. It measured three litres per revolution, with a maximum capacity of 550 litres per hour. The manufacturer lists its "normal accuracy" at one-half of one per cent. Pressure and temperature measurements were made at the meter. The air was then dried and returned to the atmosphere producer.

The U-tubes were weighed to one-tenth of a milligram on a two-pan balance against standard metal weights. The tubes were handled carefully but were not wiped or brushed before weighing. No special effort was made to cancel or reduce the volume forces on the tubes. In most cases the weight of the second tube stayed fairly constant but sometimes

it lost appreciable weight between the initial and final weighings. At the faster flow rates at high moisture contents, the first tube became quite warm from the heat liberated in the absorption of the water. Twenty minutes were allowed before weighing for the tubes to come to temperature equilibrium with the surroundings. The weighing room was apart from the remainder of the equipment and while neither room was air-conditioned, the weighing room temperature stayed fairly constant at about 70°F while the temperature in the main room fluctuated as much as 20°F above this figure, depending on the time of day.

Calculation Procedure

In essence, the calculation procedure consisted of the comparison of the known vapour pressure of the air stream in the atmosphere producer with the calculated vapour pressure as determined by the gravimetric hygrometer. The temperature and total pressure of the moist air in the saturator of the atmosphere producer were measured and the corresponding vapour pressure was taken from the existing tables(1), to give the vapour pressure value against which the gravimetric result was compared. The measured quantities were:

(i) Atmosphere producer saturator temperature. (A thermo-couple mounted in the saturator in conjunction with a precision potentiometer)

(ii) Atmosphere producer saturator pressure. (A mercury manometer to a pressure tap to the interior of the saturator)

(iii) Barometric pressure. (A mercury laboratory barometer, the vernier read to 0.01 in. Hg)

(iv) Wet-Test meter: Pressure (Mercury manometer at inlet)
                      Temperature (Mercury-in-glass thermometer)
                      Volume (From integrating dial, in litres)

(v) Weight of moisture absorbed in U-tubes.

The calculations were made on the following basis:

(i) The Weight of Air:- The air was assumed to be saturated at the temperature of the wet-test meter, as measured by the mercury-in-glass thermometer. The thermometer is graduated to 1/10°C. The specific volume V_s of saturated air at the inlet pressure of the test meter was taken from existing tables prepared for this purpose (unpublished thesis). Then if V_a is the volume of air in litres, as measured by the wet-test meter, the weight of dry air W_a is:

$$W_a \text{ (lb)} = \frac{V_a \text{(litres)} \times 1/28.32 \text{ (cu ft/litre)}}{V_s \text{(cu ft/lb)}}$$

(ii) <u>The Humidity Ratio W</u>:- The weight of moisture associated with the calculated weight of air was determined from the weighing of the absorbent tubes. This figure was converted to pounds and divided by the weight of air to give the desired quantity, the humidity ratio. Ordinarily this figure would be the end result of the absolute humidity determination, but in order to compare the result with the values given by the atmosphere producer, it was converted to the equivalent vapour pressure at the existing total pressure. The reverse procedure could have been used instead, that is, the conversion of the vapour pressure value given by the atmosphere producer to its equivalent humidity ratio at the existing total pressure. Either procedure would show the same percentage difference when the two values are compared and in either case the following procedure (or its equivalent) must be used to make the conversion.

(iii) <u>The Vapour Pressure p_w</u>:- The conversion from humidity ratio to vapour pressure was accomplished through the relation:

$$p_w = \frac{P/1.004}{0.62197/W + 1} \tag{1}$$

where p_w is the partial pressure exerted by the vapour associated with the given humidity ratio W at the total pressure P. This relationship is derived from the several considerations. Firstly, by definition,

$$W = \frac{18.016 \; n_w}{28.966 \; n_a}$$

where n_w = number of mols of water vapour

n_a = number of mols of dry air

18.016 = molecular weight of water

28.966 = molecular weight of dry air

But from Dalton's rule,

$$\frac{n_a RT}{p_a} = \frac{n_w RT}{p_w} = \frac{(n_a + n_w)RT}{P}$$

where the undefined symbols

R = universal gas constant

T = absolute temperature

p_w = partial pressure exerted by the water vapour

p_a = partial pressure exerted by the dry air

Therefore, within the accuracy of Dalton's rule,

$$\frac{n_w}{n_a} = \frac{p_w}{p_a}$$

or

$$W = \frac{18.016}{28.966}\frac{p_w}{p_a} = .62197\frac{p_w}{P-p_w}$$

Dalton's rule gives a fairly close approximation to the actual behaviour of moist air at common atmospheric pressures. However, the departure of the actual gas from ideal behaviour may be taken into account by the introduction of a coefficient f_s (P,T) into the above equation,

$$W = .62197\frac{f_s p_w}{P-f_s p_w} \tag{2}$$

The variation of f_s with pressure and temperature is given by Goff (12). For the range of temperatures and pressures encountered in this work, f_s may be considered a constant with the value 1.004. Substitution of this value into equation 2 and rearrangement gives the desired relation, equation 1.

The results of this work are listed in Table I.

The Second Phase

The second phase of the gravimetric work took place February 5th to 20th, 1957. The unsatisfactory results obtained in the first phase of this work led to a number of changes in both equipment and method. Instead of using large absorbent tubes, flow rates high enough to yield weighable amounts of moisture in the tubes and a wet-test meter to measure the comparably large volumes of air, the apparatus was arranged on a much smaller scale. Microanalytical absorption tubes were used in place of the much larger U-tubes.

These are about $\frac{1}{4}$-inch in diameter and about 3 inches long. The entrance and exit are through a coarse capillary. Magnesium perchlorate was again used as the desiccant.

Copper tubing was used for all piping to which the air sample was exposed before reaching the desiccant tubes. All connections were made metal-to-metal, metal-to-glass, or glass-to-glass and were formed with polyethylene tubing, except those at the desiccant tubes, where aged (8) rubber was used. The flow rates were only a fraction of those employed in the first phase of this work. In place of the wet-test meter, a 20-litre aspirator bottle was used to measure the volume of air. A saturator of vermiculite and water was placed in the line between the desiccant tubes and the aspirator bottle. A copper coil heat exchanger in the water mass in the aspirator bottle was employed to bring the air temperature to that of the water mass. The water temperature was measured with a mercury-in-glass thermometer, graduated to 0.1°C. A schematic diagram of the apparatus is given in Fig. 2.

The procedure is now discussed. The copper tubing from the atmosphere producer to the absorbent tubes was first purged with a small diaphragm pump drawing the air through stopcock A. After a purging period of ten minutes, stopcock A was closed. Stopcock C was then opened and water was allowed to flow into the weigh pail, the weight of which had been previously recorded. When a certain amount of negative pressure had built up in the bottle, stopcock A was opened to the absorbent tubes and the run was started. The following measurements were made:

(i) Initial and final barometric pressures (mercury barometer, the vernier read to 0.01 in. Hg).

(ii) Initial and final aspirator bottle pressures (oil manometer, read to 0.1 in. oil).

(iii) Initial and final aspirator bottle temperatures (mercury-in-glass thermometer, graduated to 0.1°C).

(iv) Atmosphere producer saturator temperature (Leeds and Northrup platinum resistance thermometer and Mueller bridge, the temperature read to 0.01°F).

(v) Evaporation from the weigh pail (estimated by allowing a second pail containing a comparable amount of water to stand on the balance during the run and measuring the loss of weight).

(vi) Weight of water displaced (20 kg single pan balance sensitive to 1 gm).

(vii) Gain in weight of absorbent tubes.

The weighing of the absorbent tubes was done on a two-pan micro-balance which had a maximum capacity of 20 grams. The tare used for rough balancing was a small flask containing copper shot. The weighing procedure was standardized in the time between successive steps but no other attempt was made to cancel or lessen the volume forces on the absorbent tubes during weighing. A repeated, apparent weight loss in the second tube was noted in these runs. This could have been due to the adsorption of water or the accumulation of dust on the surface of the tare, or the inadequate cancellation of the effect of buoyancy or electrostatic charge. The weight of moisture was taken as the gain in weight of the first tube. The weight change in the second tube was not used in the calculations but was taken merely as an indication of the reliability of the particular run.

Various alterations in method were tried in this series. Calcium chloride was used as the absorbent tube desiccant in two runs. It did not remove entirely the water vapour in the stream passing through it and both times substantial gains in weight were noted in the second tube. Flow rates of 1 and 3 litres per hour were used. The lower rates did appear to yield the best results, and at low temperatures they led to prohibitively long runs. Some uncertainty came into these runs when it was found that, although the 20 kg balance had been calibrated, its indications were dependent to some degree upon the position on the pan of the object that was to be weighed.

The method of calculation that was employed is substantially similar to those of the previous section, differing mainly in that the volume of air was determined by the displacement of a weighed quantity of water rather than the wet-test meter. The changes are now described.

(i) <u>Weight of Air</u>:- First, a buoyancy correction due to the difference in density between the water and the iron weights was applied. This was derived in the following manner. It was assumed that the weight of water on the balance was equal to the weight of the steel weights needed to balance it, with both at the same lever arm. This may be seen by considering the effect on the moment of the buoyant force of the air on a), a 1-gram steel weight with a lever arm of 10 cm and b), a 10-gram steel weight with a lever arm of 1 cm. It is obvious that the effect on the moment will be the same in both cases for in a), while the lever arm is ten times that in b), the volume is only one-tenth. Therefore, providing the weights are of the same material (density), the above assumption will be true. Thus, if W is the measured weight of water, V_w and V_s are the volumes of the water and the steel weights respectively, and d_w, d_s and d_a are the densities of water, steel and air respectively, then for balance

$$V_w d_w = V_s d_s \tag{1}$$

But the difference in the amount of air displaced multiplied by the density of air is the added weight of water needed to cancel the buoyancy effect, i.e.

$$B = (V_w - V_s)\, d_a$$

Then substituting from 1

$$B = (V_w - \frac{V_w d_w}{d_s})\, d_a$$

$$= \frac{W}{d_w}\, (1 - \frac{d_w}{d_s})\, d_a$$

$$= W d_a\, (\frac{d_s - d_w}{d_s d_w})$$

and the true weight of water,

$$W_T = W(1 + d_a \left[\frac{d_s - d_w}{d_s d_w} \right])$$

The volume of water was then calculated by dividing the true weight of water by the density of water at the bottle temperature, i.e.

$$V = W_T / d_w$$

and this is equal to the volume of air that displaced it providing the initial and final bottle pressures are equal. Finally, the weight of air is given by multiplying the volume V by the density of air at the temperature and final pressure of the bottle.

(ii) **Weight of Moisture**:- The quantity was taken directly from the weighing with only a buoyancy correction, similar to that described, applied to it.

The remainder of the calculations were identical to those in the previous series. The results are listed in Table II.

The Third Phase

The third test series took place with substantially the same experimental arrangement as that used in the second series. Although the modifications mainly concerned the procedure for weighing the absorbent tubes, a third absorbent tube was also added, in series, downstream of the first two tubes. It was not weighed as its purpose was merely that of a guard tube to protect against the back diffusion of moisture from the air-metering bottle and pre-saturator.

The weighing was done against tares that were identical to the tubes being weighed. The tares were also filled with magnesium perchlorate in an attempt to duplicate exactly the density of the weighed tubes. They were subjected to the same conditions and pretreatment as the weighed tubes in a further attempt to nullify the effect of volume forces. The weighing procedure was again standardized in the time taken between successive steps. After removal from the gravimetric train, the tubes were allowed 10 minutes to approach equilibrium with the weighing room conditions; they were then wiped with a dry chamois and allowed to stand for precisely 10 minutes. After wiping, they were not touched by the hands in the weighing procedure. After ten minutes, an attempt was made to dissipate any remaining charge by shorting the ends of the tube with a metal conductor (8). The tares were given identical treatment. The tubes were then transferred to the balance using chamois "gloves" to cover the fingers and the weighing was completed.

The calculation procedure was identical to that used in the preceding series. The results are given in Table III.

The Fourth Phase

The fourth test series saw two major changes in the gravimetric apparatus and technique. The gravimetric apparatus was moved to an air-conditioned room in which the ambient temperature was controlled at 70°F ± 1°. The rather wide fluctuations in the ambient temperature that occurred in the room where the apparatus had been housed caused some uncertainty in the measurement of the air temperature in the aspirator bottle, and thus in the accuracy of the calculated weight of air. The installation of the apparatus in the air-conditioned space removed this doubt. The second change was that the system of weighing the displaced water to give the weight of air was discarded. Instead, the volume of displaced water was measured directly with calibrated volumetric flasks. The method of calculation was similar to that used in the previous work. The results are given in Table IV.

The Fifth Phase

The fifth and final series of runs were done after the final testing of the atmosphere producer. The purpose was to determine just how closely the values given by the gravimetric apparatus would correspond to the known values produced by the atmosphere producer. There were two alterations in the apparatus and technique. First, although it was believed that the air sample drawn from the atmosphere producer was essentially clean, a sintered glass filter was added to the entrance of the gravimetric train to ensure the stoppage of any possible solid matter in the air sample before it could be carried into the absorption tubes. Secondly, to standardize further the weighing technique and make the treatment more nearly identical between initial and final weighings, the tubes were placed on the gravimetric train before the initial weighing, and moist air identical to the sample to be drawn was allowed to flow through them for about 20 minutes. They were then put through the same weighing procedure as that used in the final weighing. As in the previous runs, considerable care was taken in all techniques and measurements. The results are given in Table V.

III. DISCUSSION

It is difficult to evaluate precisely the accuracy of the results listed in this report. Certainly, the earlier phases suffered from some now obvious faults in technique that undoubtedly affected the reliability of the results. Further, two decided faults in equipment were subsequently discovered that affected the results in Phases I, II and III. After the work in Phase I had been discontinued it was discovered that the wet-test meter leaked around the packing glands, which affected the accuracy of its calibration to an unknown degree. It is known that the meter indication was low. Also, in Phases II and III, it was found that the indications of the 20-kg scale, on which the displaced water was weighed, were dependent to some degree on the position of the object to be weighed upon the pan of the balance. The error due to this, however, is known to be less than one-half of one per cent. Although the final runs suffered from no faults in technique known to the writer, their consistency is not much greater than that of the previous runs.

It should be mentioned that, although the atmosphere producer is an excellent calibration apparatus for most humidity-measuring devices, it is not ideally suited to an

application where a stream of moist air is being continuously drawn from it and a stream of different humidity is being supplied to take its place. The continuous exchange of the air streams of different humidities upsets the equilibrium condition upon which the principle of the recirculation system of the atmosphere producer is based. If the quantity of moist air being drawn from it is known, however, it is possible to evaluate quantitatively the effect on the properties of the atmosphere produced. The method of calculation is outlined in the writer's unpublished thesis. At the flow rates used in the final four phases, it can be shown that the effect of the withdrawal of the sample is considerably less than 0.1 per cent and is, therefore, negligible. In the first phase, however, it is possible that the values set up by the atmosphere producer were as much as 1 to 2 per cent in error.

It is difficult to exaggerate the exasperation of the experimenter who wishes to use the gravimetric method to a reasonable accuracy. The writer found that extreme care is necessary to obtain results of the order of accuracy reported here. Some trials were thought to be more reliable than others, but always when it was believed that reproducible results were finally being attained, a divergent run or a series of divergent runs would appear.

The writer believes that while the gravimetric method can be considered a potential primary standard of humidity, it is extremely difficult to accept it as such in practice. The method is so subject to error and so awkward in application that it is almost impossible to obtain reliable, accurate results from it. It also requires a constant atmosphere for its application and essentially destroys the sample in evaluating it.

IV. CONCLUSIONS

1. As the gravimetric method involves a direct measurement of a fundamental property of moist air, it has often been accepted as a primary standard of humidity measurement.

2. There are a large number of extraneous factors that affect the accuracy of the experimental results. It is difficult to evaluate accurately or to cancel effectively the influence of all factors.

3. Considerable time was spent, great care was taken, and a number of modifications and refinements were made to the equipment, in an attempt to obtain reliable records. At no time were the results entirely satisfactory; they were still not satisfactory when the work was discontinued.

4. The gravimetric hygrometer, although potentially a fundamental standard, is of negligible use as a practical standard as it is subject to error and awkward in application.

TABLE I

RESULTS OF TEST SERIES I (1955)

Date	Flow	Saturator Temperature	Vapor Pressure (corres. to saturator temperature)	Weight Gain		Gravimetric Vapour Pressure	Difference
				Tube 1 (gm)	Tube 2 (gm)		
24-8-55	1	63.8	0.5966	.3277	+.0001	0.5744	-3.7
	1	63.8	0.5966	.3366	+.0004	0.5705	-4.4
26-8-55	2.9	63.9	0.5987	.3119	-.0017	0.5844	-2.4
	2.1	63.9	0.5987	.3000	+.0004	0.5533	-7.6
	0.5	63.6	0.5925	.3151	+.0017	0.5763	-2.7
	1.6	63.3	0.5862	.3008	+.0012	0.5612	-4.3
	3.4	63.3	0.5862	.2992	+.0005	0.5540	-5.5
28-8-55	2.3	53.6	0.4140	.2833	-.0013	0.4150	+0.2
	2.5	53.6	0.4140	.2815	-.0014	0.4122	-0.4
	3.0	53.8	0.4170	.2853	-.0006	0.4196	+0.6
	2.7	53.9	0.4185	.2839	-.0007	0.4189	+0.1
	3.0	53.9	0.4185	.2842	-.0013	0.4189	+0.1
29-8-55	2.7	44.8	0.2980	.2035	-.0010	0.3038	+2.0
	2.7	44.6	0.2957	.2050	-.0015	0.3053	+3.2
	2.7	44.6	0.2957	.2048	+.0003	0.3070	+3.8
	2.7	32.6	0.1848	.1284	+.0005	0.1939	+4.9
	1.3	32.6	0.1848	.1307	-.0011	0.1898	+2.7
	3.2	32.6	0.1848	.1732	+.0023	0.1936	+4.8
30-8-55	2.7	30.2	0.1661	.1177	+.0015	0.1772	+6.7
	2.7	30.2	0.1661	.1164	+.0003	0.1748	+5.2
	3.3	30.2	0.1661	.1169	+.0009	0.1753	+5.7
	2.8	18.0	0.09327	.0924	+.0009	0.1001	+7.3
	2.2	18.0	0.09327	.0891	-.0008	0.0965	+2.4
	3.0	18.0	0.09327	.0870	-.0006	0.0942	+0.9
31-8-55	2.5	7.7	0.05599	.0870	-.0015	0.0599	+6.9
	2.7	7.6	0.05571	.1694	+.0023	0.0597	+7.2
1-9-55	2.7	7.6	0.05571	.1001	-.0022	0.0610	+9.5
8-9-55	2.7	62.4	0.5680	.2785	-.0001	0.5730	+0.9
	2.7	62.4	0.5680	.2786	+.0003	0.5744	+1.1
9-9-55	2.7	54.3	0.4247	.2063	-.0006	0.4315	+1.6
	2.7	48.4	0.3414	.1662	+.0010	0.3480	+1.9
	2.7	42.6	0.2739	.1317	-.0010	0.2762	+0.9
	2.7	38.8	0.2364	.1585	.0000	0.2340	-0.9
	2.7	33.0	0.1878	.1538	-.0001	0.1895	+0.9
12-9-55	2.7	26.2	0.1379	.1371	-.0005	0.1376	-0.2
	2.7	2.13	0.1094	.1125	-.0020	0.1064	-2.7
13-9-55	2.7	14.9	0.08947	.1113	+.0012	0.0821	-1.9

TABLE II

RESULTS OF TEST SERIES II (1957)

Date	Flow	Saturator Temperature (°F)	Corresponding Vapour Pressure ("Hg)	Weight Gain Tube 1 (mg)	Tube 2 (mg)	Measured Air Vol. (cu ft)	Gravimetric Vapour Pressure ("Hg)	Difference (%)	Comments
5-2-57	3	-13.42	0.01825	3.588	-0.097	0.2950	0.01782	-2.4	
6-2-57	3	+35.60	0.2083	18.539	-0.666	0.1256	0.2154	+3.4	Very appreciable weight loss in 2nd tube
7-2-57	3	+35.66	0.2088	11.610		0.08245	0.2049	-1.9	New desiccant
7-2-57	3	+35.64	0.2086	13.770	-0.059	0.09833	0.2065	-0.9	
8-2-57	3	+35.64	0.2086	10.374	-0.255	0.07650	0.1975	-5.3	
11-2-57	1	+35.74	0.2094	6.441	-0.077	0.04506	0.2049	-2.1	Smaller flow rate
12-2-57	1	+35.74	0.2094	39.058	-0.115	0.2765	0.2056	-1.8	8-hour run
13-2-57	1	+35.74	0.2094	23.167	-0.124	0.1652	0.2056	-1.8	
14-2-57	3	+35.77	0.2097	12.284	-0.004	0.09004	0.1991	-5.1	Greater flow rate
14-2-57	3	+35.70	0.2091	21.053	+0.233	0.1521	0.2024	-3.2	CaCl used as desiccant
15-2-57	3	+35.70	0.2091	14.608	+0.257	0.1060	0.2013	-3.7	CaCl desiccant
18-2-57	3	+55.00	0.4356	13.962	-0.145	0.04784	0.4221	-3.1	Magnesium perchlorate desiccant
18-2-57	3	+55.00	0.4356	20.455	+0.010	0.06857	0.4317	-0.9	
19-2-57	3	+57.55	0.4778	26.467	-0.066	0.08130	0.4699	-1.5	

TABLE III

RESULTS OF TEST SERIES III

Date	Flow	Saturator Temperature (°F)	Corresponding Vapour Pressure ("Hg)	Weight Gain Tube 1 (mg)	Tube 2 (mg)	Weight Air (mg)	Gravimetric Vapour Pressure ("Hg)	Difference (%)
13-3-57	3.2	40.17	0.2494	60.415	+0.008	1104.2	0.2467	-1.1
14-3-57	4.0	40.17	0.2494	63.748	-0.013	1177.1	0.2458	-1.4
18-3-57	4.0	40.14	0.2491	49.754	-0.008	896.4	0.2491	0
20-3-57	5.0	40.15	0.2492	69.057	-0.020	1244.3	0.2468	-1.0
21-3-57	4.1	61.38	0.5479	64.285	-0.020	519.0	0.5417	-1.1
21-3-57	3.6	61.38	0.5479	76.962	-0.014	623.3	0.5396	-1.5
21-3-57	4.6	70.64	0.7555	147.356	-0.039	873.7	0.7389	-2.2
22-3-57	2.5	70.64	0.7555	33.848	-0.034	199.78	0.7423	-1.7
22-3-57	3.3	70.64	0.7555	104.453	+0.389	610.9	0.7495	-0.8
25-3-57	2.1	70.64	0.7555	59.000	-0.043	371.9	0.7012	-7.2
26-3-57	3.3	70.64	0.7555	59.996	-0.149	387.6	0.6832	-9.6
26-3-57	4.0	70.64	0.7555	77.974	-0.051	464.1	0.7480	-1.0
28-3-57	4.0	70.64	0.7555	75.308	-0.045	435.7	0.7481	-1.0
29-3-57	2.5	70.64	0.7555	90.000	0.000	532.0	0.7500	-0.7
29-3-57	1.9	60.19	0.5251	23.517	-0.008	204.8	0.5167	-1.6
30-3-57	2.3	53.66	0.4149	29.929	-0.010	328.9	0.4056	-2.2
1-5-57	3.6	33.71	0.1932	25.955	-0.014	619.6	0.1881	-2.6
2-5-57	2.7	33.73	0.1933	22.018	-0.051	519.9	0.1897	-1.9
3-5-57	3.4	27.57	0.1470	35.400	-0.015	1094.7	0.1464	-0.4
7-5-57	4.3	21.64	0.1111	34.046	-0.008	1386.3	0.1101	-0.9

TABLE IV

RESULTS OF TEST SERIES IV

Date	Flow (litre /hr)	Saturator Temperature (°F)	Corresponding Vapour Pressure ("Hg)	Weight Gain Tube 1 (mg)	Tube 2 (mg)	Weight Air (mg)	Gravimetric Vapour Pressure ("Hg)	Difference (%)
15-5-57	2	51.96	0.3891	37.562	+0.034	4422	0.3825	-1.7
15-5-57	3.4	51.96	0.3891	37.592	-0.013	4416	0.3828	-1.6
16-5-57	3.4	29.22	0.1589	31.078	-0.078	8851	0.1859	0
17-5-57	3.4	8.36	0.0578	13.984	-0.061	11005	0.0575	-0.5
21-5-57	6.0	-10.40	0.02156	5.342	-0.027	10952	0.02193	+1.7
22-5-57	6.0	-10.32	0.02168	8.637	-0.001	18633	0.02085	-3.9
24-5-57	3.6	-10.28	0.02169	10.762	+0.004	21786	0.02216	+2.1
27-5-57	4.0	+25.03	0.1305	25.158	-0.005	8793	0.1287	-1.4
28-5-57	4.0	+25.03	0.1305	25.219	-0.003	8837	0.1286	-1.4
29-5-57	4.0	+25.13	0.1309	25.571	-0.004	8834	0.1304	-0.4
30-5-57	4.0	+60.33	0.5277	77.241	+0.007	6621	0.5184	-1.7
31-5-57	4.0	+34.60	0.2002	38.310	-0.002	8873	0.1958	-2.2
4-6-57	2.7	+32.57	0.1845	35.131	-0.071	8711	0.1815	-1.7
4-6-57	4.0	+29.98	0.1643	31.112	-0.064	8656	0.1636	-0.4

TABLE V

RESULTS OF TEST SERIES V

Date	Flow	Saturator Temperature (°F)	Corresponding Vapour Pressure ("Hg)	Weight Gain Tube 1 (mg)	Tube 2 (mg)	Weight Air (mg)	Difference (%)
19-6-58	4	40.32	0.2508	24.545	-0.006	4403	-0.1
23-6-58	4	40.32	0.2508	24.952	+0.002	4372	+0.2
23-6-58	4	40.32	0.2508	20.941	-0.014	3739	-0.6
24-6-58	4	28.35	0.1525	24.536	+0.008	7028	+3.3
24-6-58	4	28.35	0.1525	21.957	-0.020	6309	+2.9
30-6-58	4	40.20	0.2496	29.070	-0.007	5146	+0.7

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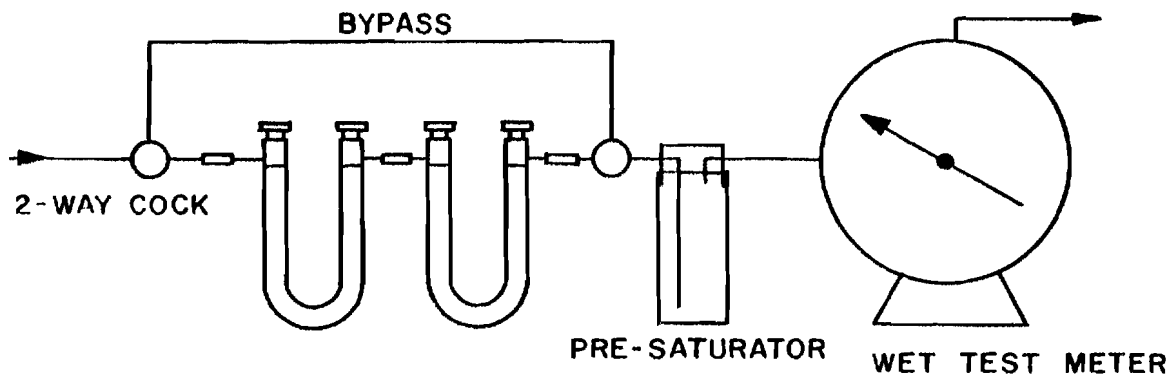   Heating, Piping and Air Conditioning, November 1949.

BYPASS

2-WAY COCK

PRE-SATURATOR

WET TEST METER

FIGURE I

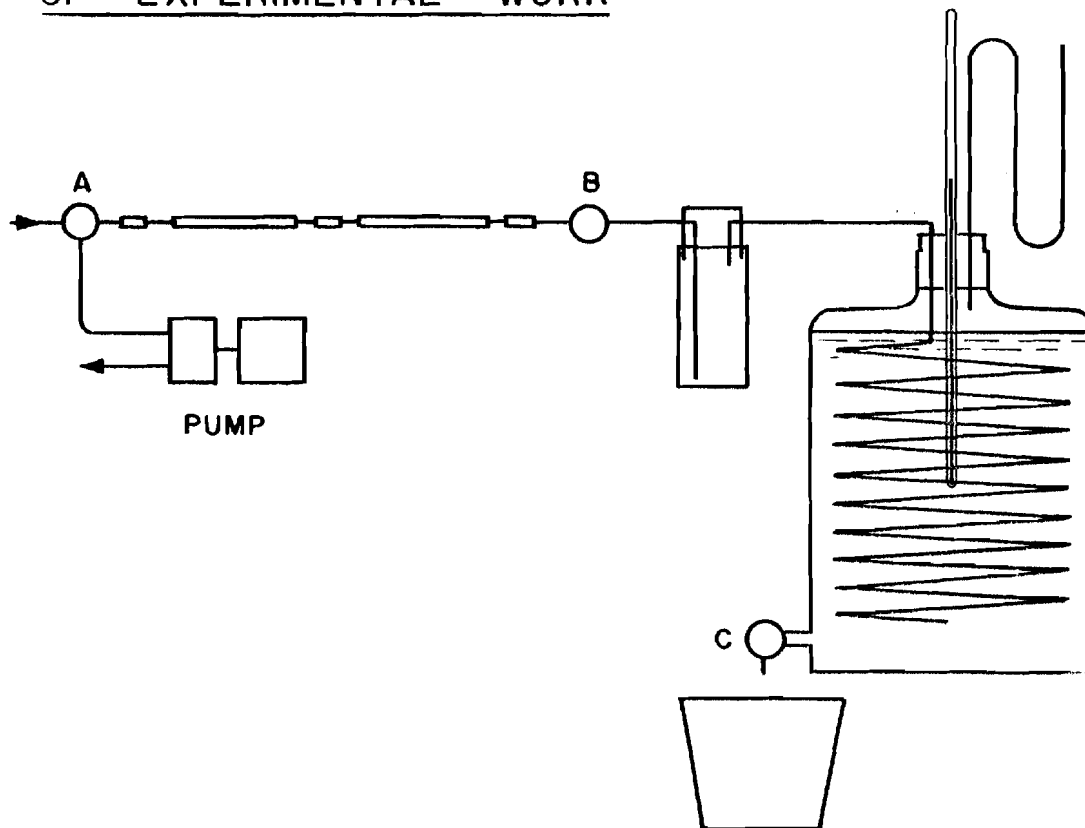ARRANGEMENT OF EQUIPMENT USED IN FIRST PHASE
OF EXPERIMENTAL WORK

A

B

PUMP

C

FIGURE 2

APPARATUS USED IN SECOND PHASE OF EXPERIMENTAL
WORK