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VALIDATION OF
THE NPL
GRAVIMETRIC HYGROMETER

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ABSTRACT

The gravimetric hygrometer of the UK National Physical Laboratory (NPL) provides a first-principles realisation of mixing ratio - the most fundamental measure of the humidity of a gas. The operation of the NPL gravimetric hygrometer has been validated to demonstrate its satisfactory performance as a primary standard for humidity within the UK national measurement system.

The measurement performance of the gravimetric hygrometer has been characterised for mixing ratios within the range 0.01 g kg^{-1} to 155 g kg^{-1} (equivalent at atmospheric pressure to a dew-point range of -60 °C to +60 °C). The significant aspects of the measurement have been assessed in detail; these being the balances and weighing processes, the efficiency of collecting water and dry gas, and the effects of stray water in the instrument. Sources of systematic error have been identified and their effects quantified. Wherever possible, such errors have been eliminated or reduced. Elsewhere, numerical corrections have been evaluated and applied to the results of measurements.

The overall uncertainty of measurement for the gravimetric hygrometer has been estimated by evaluating the uncertainties contributed by each aspect of the measurement, and combining these statistically to find the overall effect. The estimated uncertainty at a level of confidence of approximately 95% (a coverage factor of k=2) was found to range between 0.015 percent of value at the highest humidity considered, near 155 g kg^{-1}, and 1.27 percent of value at the lower limit of 0.01 g kg^{-1}.

The gravimetric hygrometer has been intercompared with the humidity generator which is the NPL standard for dew point, using nitrogen as the carrier gas in these measurements. For the conversion between values of dew point and mixing ratio, the uncertainties in the reference functions have been reviewed for the vapour pressure curve of water, and for the water vapour enhancement factor which accounts for the non-ideal behaviour of humid gases. A new calculation of the enhancement factor for nitrogen is presented. The uncertainties due to sampling were also evaluated. On average, the uncertainties due to the reference functions and those due to sampling were found to comparable with the uncertainty in the gravimetric measurements. Taking all these into account, the intercomparison measurements agreed to within the combined uncertainties of the two instruments.

CHAPTER 1

Introduction

Water is the principle, or the element, of things.
All things are water.

Thales of Miletus *circa* 640-546 BC
Plutarch *Placita Phosphorum i,* 3

CHAPTER 1. INTRODUCTION

1.0. Abstract

This chapter is an introduction to the work reported in this thesis; namely the validation of the operation of gravimetric hygrometer held by the National Physical Laboratory (NPL), to provide a primary realisation of mixing ratio for the UK National Standard of Humidity.

The aims and objectives of this work are first of all detailed, these being:- to characterise the performance of the gravimetric hygrometer; to consider uncertainties including those associated with sampling and with reference data for water vapour; and to use the instrument to carry out gravimetric measurements of humidity.

The subject of humidity is introduced, with a short discussion of the scientific and industrial importance of this field of measurement. General concepts relevant to humidity are outlined, with definitions of some terms and units of measurement. The physical theory relating to humid gases is introduced, starting with the Clausius-Clapeyron equation for vapour-liquid equilibria, and proceeding to the non-ideal behaviour of gas mixtures containing water.

Some commonly used methods of measurement and generation of humid gases are described, with comments on the applicability of the different approaches. Criteria are discussed for selecting a fundamental and practical method as the basis for a first-principles reference standard for providing calibrations for humidity. In this context, NPL's choice of a gravimetric hygrometer combined with a humidity generator is justified.

This chapter ends with a brief guide to the whole thesis document, outlining the structure of the text, with an indication of the content of each chapter.

1.1. Aims and objectives of this work

The primary aim of the work reported here has been to validate the operation of the NPL gravimetric hygrometer as a primary realisation of mixing ratio of humid gas, and hence to establish the authority of this instrument as the United Kingdom National Standard for humidity measurement.

The specific objectives to be met were as follows:

- To verify correct function of the individual aspects of the gravimetric hygrometer's operation, and to evaluate the contribution of each element to the overall uncertainty of measurement;
- To combine the individual components of uncertainty to give an estimate of overall uncertainty of measurement for the gravimetric hygrometer, aiming to meet the performance specification required to fulfil the calibration needs of the UK humidity industry;
- To consider the implications of the relationships between different units of humidity measurement, the documented reference data for water vapour, and the nature of the interface between this primary standard and any system which would be calibrated against it;
- To demonstrate satisfactory overall performance of the gravimetric hygrometer by carrying out gravimetric measurements of a repeatability consistent with the estimate of uncertainty.

1.2. Background - the importance of humidity measurement

The presence or absence of water vapour in air influences a vast range of physical, chemical and biological processes. The humidity of air affects its electrical, thermal, optical and transport properties. Additionally the moisture content of solids and liquids are influenced by water in the surrounding gaseous environment. For example the prevailing level of humidity can determine whether substances corrode, it can cause dimensional changes in materials, and can determine whether organisms thrive or die. Humidity is a condition which must be monitored and controlled in very many industrial processes. To list only a few examples; it is an important parameter in power generation, manufacture of electronic components, weather forecasting, food and pharmaceutical industries, and in environmental testing of a diversity of manufactured products.

As well as being highly industrially relevant, humidity is also a particularly difficult parameter to measure accurately. Whereas laboratory measurements of mass can be routinely accurate to one part in 10^6, and ambient pressure measurements to one part in 10^4, humidity can commonly only be measured to about three parts in 10^2.

Because of its ubiquitous importance and its relative difficulty, humidity measurement is a subject in which technical advances are always of practical and scientific interest. In the light of these considerations it is also clear that provision of a reference for measurements, in the form of a national humidity standard, is an important task. The work reported here addresses this task through the establishment of a gravimetric humidity standard which enhances an existing standard facility for humidity calibration.

1.3. General concepts relating to humidity measurement

"Humidity" can be broadly defined as the presence of water vapour in any gaseous environment. The single concept "humidity" is quantified in a number of ways, which are individually discussed below.

Figure 1 shows a hierarchy of the various parameters used for quantifying humidity.

Formal definitions - and measurements - of humidity fall superficially into two categories. One of these is relative humidity, which expresses the extent of saturation of a gas with water vapour, where 0 percent relative humidity (%rh) represents completely dry gas, while 100 %rh indicates gas which is fully saturated with water vapour. Relative humidity is a function of temperature, as well as of water vapour content. It is the measurand which is most commonly met in the context of human comfort applications, as well as in many cases where humidity measurements are of interest for their implications for moisture content of materials.

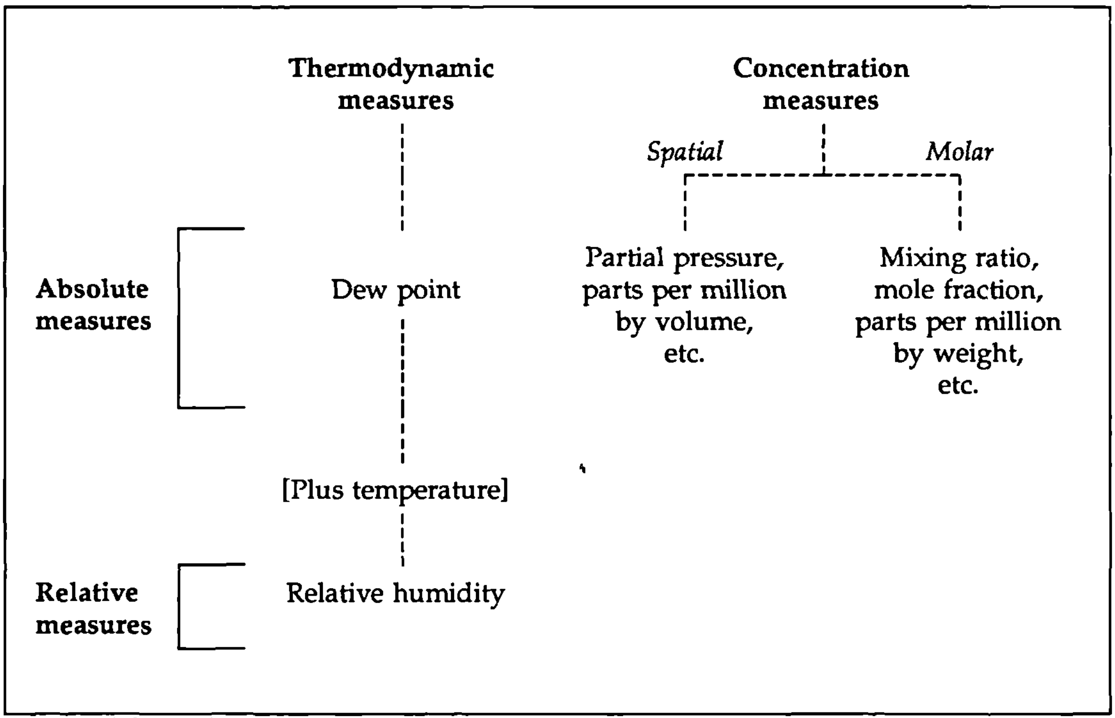

Figure 1 A hierarchy of the parameters relating to humidity measurement

Relative humidity is generally of interest wherever the influences of water vapour and temperature have a compounded effect.

The other category concerns absolute measurements. These can be sub-divided into two further categories. One of these sub-categories is the set of measurements which refer to the *concentration* of water vapour. This is expressed either in terms of spatial concentration (e.g. partial pressure of water vapour, parts per million by volume), or in units related to molar concentration relative to a carrier gas (e.g. mixing ratio, parts per million by mass). The second sub-category concerns measurement of *thermodynamic properties* uniquely characteristic of the composition of a gas, such as dew-point temperature. Dew point is the parameter of interest in applications where prevention of condensation is concerned. In other circumstances, units of either concentration or dew point are selected according to the intrinsic properties of sensors, or for convenience according to the magnitude of the numbers involved.

1.3.1. Some humidity terms and definitions

A wide variety of terms are in common use for discussing humidity. Not all of them are used consistently, and not all are detailed here. The following formal definitions relating to humidity measurement are taken from BS 1339: 1965 (confirmed 1981).

> *Dew point.* The temperature at which the vapour pressure of the water vapour in the air is equal to the saturation vapour pressure over water. If the ideal gas laws held, this would be equal to the temperature at which the mixing ratio had its saturation value. The latter temperature, which is the one measured in practice, is distinguished as the *thermodynamic dew point,* and is the temperature at which condensation begins to occur under normal conditions when the initial mixture is cooled at constant pressure.[1]
>
> *Hygrometer.* Any instrument used for the measurement of humidity.
>
> *Mixing ratio.* The ratio of the mass of water vapour to the mass of dry air with which the water vapour is associated.
>
> *Mole fraction.* The mole fraction of a component of a mixture is the ratio of the number of moles of that component to the total number of moles present. To every mixing ratio there is a corresponding mole fraction.
>
> *Relative humidity.* The ratio of the actual vapour pressure to the saturation vapour pressure over a plane liquid water surface at the same temperature, expressed as a percentage. This is commonly understood when the phrase 'X percent humidity' is used.
>
> *Saturation vapour pressure.* At a constant temperature free evaporation of water or ice from a plane surface into a space containing only

---

[1] Although this concept also applies to substances other than water, the term dew point, and the other terms defined here, such as vapour pressure, will be used to refer exclusively to water (or ice), unless otherwise specified.

water vapour ceases, and equilibrium is reached, when the pressure exerted by the water vapour attains a certain maximum value depending on the temperature. This pressure is known as the *saturation vapour pressure* and the space is said to be 'saturated'.

Vapour pressure. That part of the total pressure contributed by the water vapour.

In this account, certain conventions are followed for the expression of the quantities defined above. Mixing ratio, though technically a dimensionless quantity, is expressed in grams of water per kilogram of dry gas (abbreviated g kg^{-1}). This practice, routine in this field, leads to numerical values of a convenient magnitude; a factor 10^3 larger than if they were expressed as strict ratios. The term dew point is universally used here to include frost points (below 0 °C). It is assumed in the following discussions (and verified in the case of experiments) that dew points in the range below 0 °C relate to equilibrium with ice, not supercooled water. Throughout most of this account, values of humidity are expressed in terms of both mixing ratio and dew point, to aid clear identification of the different humidity regimes. Wherever mixing ratio and dew point are mentioned jointly or separately, a near-atmospheric pressure of 105 kPa is assumed unless otherwise specified. 105 kPa is the pressure at which the NPL humidity generator operates, and is the pressure at which the gravimetric measurements in this account were conducted.

1.3.2. Physical theory relating to humidity

Some aspects of the thermodynamical theory relating to humidity measurement are outlined below as a background to discussions later in this account, concerning the origins of reference formulae for the vapour pressure curve of water and the allowance for gas non-ideality.

Water vapour may be encountered as a pure single-phase system. However, in most practical contexts water is found in multiple phases. (For instance, liquid or solid water is normally accompanied by gaseous water or vapour in the nearby environment.) Consideration of the multi-phase system allows us to construct the thermodynamic parameters which are useful in discussing humidity.

Coexistent phases are in equilibrium if neither mass nor heat is being exchanged between the phases. The rate at which pressure must change with temperature for the two phases to remain in equilibrium is governed by the *Clausius-Clapeyron* equation

$$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{\Delta S}{\Delta V}=\frac{L}{T\Delta V} \ . \qquad (1)$$

where L, ΔS and ΔV are the latent heat, the change in entropy and the change in volume on passing from one phase to another. (A full derivation of this equation can be found in standard texts, such as Adkins (1983).)

To obtain an explicit equation for vapour pressure we can, with certain assumptions, integrate the Clausius-Clapeyron equation. We assume the system the gas behaves as a perfect gas (being at low pressure, away from the critical point), i.e.,

$$pV=RT \ , \qquad (2)$$

where R is the molar gas constant. If the specific volume of the liquid is negligible compared to that of the vapour then ΔV is simply equal to V. Under these conditions equation (1) becomes

$$\frac{\mathrm{d}p}{\mathrm{d}T}=\frac{Lp}{RT^2} \ . \qquad (3)$$

In the simplest approximation, L is taken to be constant. Integration of equation (3) then gives

$$\ln p=-\frac{L}{RT}+A \ , \qquad (4)$$

where A is a constant. This may be re-written

$$p=p_0\exp(-L/RT) \ . \qquad (5)$$

This reflects the approximately exponential form of the relationship which is found experimentally between equilibrium vapour pressure and temperature. Substituting a more realistic approximation for L, incorporating its temperature dependency (eg in the form $L = L_0 + L_1T$) provides values of vapour pressure which are closer to those found experimentally. Table I shows values of the saturation vapour pressure of water for a selection of temperatures in the range -60 °C to +60 °C.

In most practical circumstances, humidity measurement is concerned with water vapour mixed with another gas such as air. It is then necessary to consider the interaction between the two gaseous components.

The relation known as *Dalton's law of partial pressures,*

$$p=\sum p_i \,, \tag{6}$$

states that the total pressure exerted by a mixture of gases will be the sum of the pressures which each gas would exert individually. This is true for *ideal gases;* or for real gases where temperature and pressure are low enough that collisions between molecules are elastic and infrequent, with the gas or gas mixture obeying the relation

Table 1 Saturation vapour pressure over pure water (ice) for a selection of temperatures (Sonntag, 1990)

Temperature °C	Saturation vapour pressure Pa
60	19948
50	12353
40	7385
30	4247
20	2339
10	1228.2
0	611.2
-10	286.5
-20	125.6
-30	51.03
-40	19.03
-50	6.439
-60	1.948

$$pV \propto T\,. \qquad (7)$$

At atmospheric temperatures and pressures, air, water vapour and their mixture are close to behaving as an ideal gas - Dalton's law is obeyed to within 1 percent. However in this work, where uncertainty of much less than 1% is sought, the ideal gas approximation cannot be relied upon. Instead the value of the product pV is better characterised by a power series in p:

$$pV = A + Bp + Cp^2 + Dp^3 + \dots \qquad (8)$$

This is known as a *virial expansion,* and the *virial coefficients* A, B, C . . . are functions of temperature and of the gas species or mixture in question. Accordingly, real water vapour pressure e' in air is found from

$$e' = ef\,, \qquad (9)$$

where e is the partial pressure of pure water vapour (in the absence of other gas), and f is the correction for non-ideality known as the *water vapour enhancement factor* which has its origins in equation (8). At room temperature and atmospheric pressure, f is about 1.005, and the value varies with pressure, and slightly with temperature. This is discussed further in Chapter 5, where details are given of the water vapour enhancement factor applied in this work.

The relationship in equation (9) is important because the reference formulae for calculating the saturation vapour pressure over water as a function of temperature apply to pure-phase water vapour, in the absence of other gases. However in this work, and in most other cases, the formulae must be applied where other gases are present at or above atmospheric pressure.

Mixing ratio, r, the quantity of main interest in this work, is related to vapour pressure e and enhancement factor f by

$$r = C\frac{ef}{P - ef}\,, \qquad (10)$$

where C is the ratio between the average molar masses of water and the carrier gas.

1.3.3. Formulations for the saturation vapour pressure over water and ice

To inter-relate humidity measurements expressed in different units, the Clausius-Clapeyron equation (1), or some equivalent relation, must be used. A survey of the reference functions available for expressing vapour pressure of water has been conducted by Gibbins (1990). In his survey Gibbins cites more than 60 equations in common use to represent the vapour pressure curve of water, and more than 30 for ice. These equations vary somewhat in the values of vapour pressure they produce, and the implications of this are discussed later, in Chapter 5. However most practical purposes require only that users of these formulae agree in their choice of reference equations. In humidity metrology, the consensus favours the formulations by Wexler (1976, 1977), or alternatively that of Goff and Gratch (1946) later updated by Goff (1965). The formulations by Wexler, together with a selection of formulae an constants for humidity as well as other fields of measurement, have been converted by Sonntag (1990) into the terms of the International Temperature Scale of 1990 (ITS-90) (Preston-Thomas, 1990).

Values of the water vapour enhancement factor, *f*, have been established experimentally (Hyland and Wexler, 1973). However, experimental realisations have been rare, due to the difficulty of making these measurements. The equations given by Greenspan (1976) are widely favoured, being a simplification of the formula by Hyland (1975). Hyland's equation is a fitting of the values found experimentally by Hyland and Wexler to a physically meaningful formula based on the virial expansion of the equation of state.

Other approximations are also in widespread use, both for vapour pressure and enhancement factor.

1.4. Methods of humidity measurement in general use

It follows from the diverse range of phenomena which are susceptible to influence from humidity, that, conversely, there are many different effects which can be used to detect or measure humidity. An illustrative but not exhaustive list of hygrometric methods follows. (The list covers only methods of measuring humidity in gases:

The measurement of moisture in solids and liquids is considered to be a separate field.)

1.4.1. Methods considered to have a fundamental basis

Gravimetric hygrometer - Mass ratio of water to carrier gas is measured by separately collecting the water and dry gas and weighing each component. In general the water is collected by means of a desiccant, or by condensation. Gas mass is found by volume or flow measurement, or - more strictly - by weighing the dry gas, which may be collected by compression or liquefaction.

Other than for humidity measurement, some types of gravimetric analysis are quite commonly performed at low accuracies. For example thermogravimetry is used in finding the moisture (or other volatile) content of solids. However, since good alternative sensing methods are available for humidity, gravimetric hygrometry is almost never considered for low accuracy applications. Because it is only applied to humidity measurement when the highest accuracy is demanded, gravimetric hygrometry is mainly encountered in its most sophisticated form; as a complex analytical measurement.

Condensation dew-point hygrometer - Dew point is measured by cooling a surface until condensation occurs in the form of dew or frost. The sensing element normally consists of a mirror with a miniature temperature sensor embedded beneath the surface. This assembly is bonded to a peltier element, or thermoelectric cooler. An optical detection system is used to sense the change in reflectance of the mirror surface where the dew or frost forms, and the temperature is controlled at the temperature of formation. (Alternatively the temperature may be recorded at the instant of dew formation). Electrical methods of detection also exist, but are seldom capable of such high precision as the optical approach.

Wet- and dry-bulb hygrometer (psychrometer) - This instrument measures relative humidity in terms of humidity-dependent evaporative cooling. A psychrometer consists of a pair of thermometers, one of which is sheathed in a wet wick. The rate of evaporation from the wick varies with the humidity of the surrounding air. The cooling of the wet-bulb relative to the dry bulb temperature is recorded. Vapour pressure, e, is estimated (with at least nominal accuracy) by entering the wet-bulb and dry-bulb temperatures, t and t', in the *"psychrometer equation"* (variously attributed (Sonntag, 1967))

$$e = e' - AP(t - t') , \tag{11}$$

where A is a constant for any given instrument, and P is the total barometric pressure. An aspirated psychrometer with a fan for adequate air flow over the thermometers is the recommended basis for this measurement. Other approaches, such as non-aspirated psychrometers and whirling (hand aspirated) psychrometers, are less successful realisations of this principle and are more prone to errors.

1.4.2. Other methods

Mechanical hygrometer - the dimensions of many natural organic materials change on absorption of water vapour. Examples of those used for humidity sensing are hair, paper and animal membrane. The change in length of a sensing element is typically some 2%, in the range of response between about 20 %rh and 80 %rh. This is normally translated into displacement of a recorder pen, or a needle on a dial.

Resistive/capacitive sensor - employs a medium whose electrical impedance or dielectric constant changes with absorption of atmospheric water, so that a change in capacitance or resistance accompanies any change in prevailing humidity. Modern sensors are typically manufactured as a thin film for best response time, with interleaved comb-shaped electrodes for good sensitivity.

Aluminium oxide sensor - a specialised version of electrical type impedance sensor. Typically it consists of an aluminium electrode which has been anodised, providing a thin porous oxide layer where water can be adsorbed. This is coated with a further thin conducting layer which acts as a second electrode, while being thin enough to admit water molecules to the oxide layer. The electrical impedance is approximately proportional to the partial pressure of water vapour. Commonly the signal is linearised using a logarithmic amplifier to produce an output in units of dew point. These sensors can have a wide range of measurement, including very low humidities.

Lithium chloride sensor - an alternating voltage is applied to the sensing medium, which is a hygroscopic salt. Current passes according to the amount of water vapour that has been absorbed, and resistive heating takes place. Eventually a condition of both thermal and humidity equilibrium is achieved in the proximity of the sensor. The temperature at which this occurs is an indication of the dew point of the gas.

Electrolytic (phosphorous pentoxide) - The sensor consists of a film of powerful desiccant, which strongly absorbs water vapour from the surrounding gas. A voltage is applied across the P_2O_5, and electrolysis takes place, dissociating the water into hydrogen and oxygen. The current that flows is related, by Faraday's law, to the amount of water electrolysed, and hence to the vapour pressure.

Spectroscopic methods - Water vapour absorbs and emits radiation at characteristic frequencies. At high humidities absorbtion in the infrared region is used as a measure of the spatial concentration (or partial pressure) of water vapour. At low humidities excitation using ultraviolet radiation can be used to stimulate the hydrogen component of water vapour to emit in the ultraviolet. Fourier transform infrared mass spectroscopy (FT-IR) and atmospheric pressure ionisation mass spectrometry (APIMS) are also used.

Other methods - There are a host of other sensing principles in common use for humidity measurement, including: quartz oscillator frequency response; change in optical refractive index; acoustic attenuation; gas chromatography; heat of absorption or desorption from desiccant; pneumatic bridge (analogous to the electrical Wheatstone bridge); adiabatic expansion (mist forms on cooling to the dew point); and others. Some of the approaches listed here, e.g. infrared reflection, also lend themselves directly or indirectly to the measurement of water content in solids or liquids.

It can be seen from the paragraphs above that humidity measurement embraces a wide variety of techniques. Each is prone to different errors, which sometimes lead to marked disagreements between the results of the different techniques. Interpretation of such disagreements can be difficult, and this is a field where confusion is widespread among those who routinely make humidity measurements. These problems can be overcome by reference to a definitive standard for humidity which can provide authoritative measurements. The gravimetric hygrometer described in this account fulfils this role by its nature as a fundamental and precise measurement, by the authority which it gains from the validation reported here, and by virtue of the status assigned to it as the definitive humidity realisation for the UK.

1.5. Humidity generation

Calibration of hygrometers requires a supply of humid gas, either of a definitive humidity or of an approximate humidity to which a value can be assigned using a calibrated hygrometer. Various methods exist for humidity generation. Most rely on saturating gas by allowing it to traverse a water surface, or bubble through water, at the desired dew-point temperature. A number of national humidity standards are based on the following variants of this principle.

Two-temperature humidity generator - This description intrinsically denotes an instrument for generating humidity in terms of both dew point and relative humidity. Gas is humidified at the temperature required to define the dew point. It subsequently passes to a chamber at a higher temperature. In this chamber the relative humidity is defined by the gas temperature and dew point. The relative humidity can be varied by adjusting the temperature of saturation, or that of the chamber. This process can be employed in a simple flow-through system, or as a closed loop, or as a combination of partial recirculation with partial flow-through and top-up of gas.

Two-pressure humidity generator - This is an instrument where gas is humidified above (or at) atmospheric pressure, and can then be expanded to a lower pressure. With the pressure drop on expansion comes a (roughly) proportional drop in vapour pressure of the water present. A high degree of versatility arises from the possibility of varying both the temperature and the pressure settings. This technique is particularly well suited to generating very low humidities, and can be used with a further chamber to realise values of relative humidity, as in the two-temperature method.

Coulometric generator - This technique employs the recombination of hydrogen with oxygen in the presence of a catalyst to form water, This fundamental realisation of humidity is referred ultimately to the SI unit of current. It is mainly suited to low humidities (below a water content of around 100 parts per million).

With careful validation, any of the above methods is recognised as a sound basis for a first-principles realisation of dew point.

These methods can alternatively be employed in crude form to provide gas of nominal values of humidity. Other approaches are also used to provide approximate values of humidity. These include flow-mixing generators where humid and dry gases are mixed in selected proportions to achieve a desired value of humidity. Another practical but approximate method for low humidities is the use of diffusion or permeation of water through a porous barrier to release water vapour at a fixed rate into a flowing gas stream. For high humidities, temperature controlled cabinets or ovens with humidification (e.g. by steam injection) are widely used. Saturated solutions of various chemical salts are an interesting additional method, generating characteristic values of relative humidity according to the salt selected. There is some support for regarding this as a first-principles reference for "fixed points" for relative humidity, analogous to the use of triple points in thermometry. However, practical implementation of the salts method is too prone to errors to raise its standing much above other "approximate" methods.

As is the case for the variety of hygrometric methods, so the various approaches to humidity generation are each prone to systematic errors, principally due to the variations in efficiency of saturation, and due to sources or sinks of stray water in any apparatus. Such effects may be quantifiable by careful validation from first principles, or preferably by recourse to a definitive standard enabling consistency and harmonisation for measurements traceable to it.

1.6. Method of choice for a fundamental standard

Of the methods described above, only a few are suitable as a basis for a definitive standard. In selecting a method for the present work, first of all an absolute measurement is required, rather than one of relative humidity. The method must achieve accuracy, and traceability to an SI base unit. Definitions of these concepts are given in the publication of the International Organization for Standardization (ISO) *International vocabulary of basic and general terms in metrology* (known as "VIM, 1993"), as follows:

> *Traceability* - property of the result of a measurement or the value of a standard whereby it can be related to stated references, usually national or international standards, through an unbroken chain of comparisons all having stated uncertainties
>
> *Accuracy* - closeness of the agreement between the result of a measurement and the true value of the measurand (N.B. The International Organization for Standardization's *Guide to the Expression of Uncertainty in Measurement* (ISO, 1993) points out that "accuracy" is a qualitative concept only.)
>
> *Uncertainty* - parameter, associated with the result of a measurement, that characterises the dispersion of the values that could reasonably be attributed to the measurand (VIM, 1993)
> (or)
> - a measure of the possible error in the estimated value of the measurand as provided by the result of a measurement (VIM, First Edition, 1984)

The most accurate determination of humidity that can be achieved is by gravimetric measurement, with reference ultimately to the base unit of mass. (Details of the merits of the gravimetric method are given in Chapter 2.) However the gravimetric approach to humidity measurement has a number of limitations which make it an impractical basis for a calibration service: the measurements are normally time consuming, and acceptable uncertainties cannot normally be achieved for very low humidities.

On the other hand, a calibration facility for hygrometers can conveniently be provided using a humidity generator where a dew point is defined for water vapour in a carrier gas, with traceability to the base unit of temperature. However this method does not in practice offer such potentially high accuracy as gravimetric measurement. Dew point is also not regarded as an entirely authoritative reference definition because this property is somewhat dependent on the pressure of the carrier gas. This rules out from present consideration other realisations of dew point, such as condensation dew-point hygrometry (which in any case does not offer the possibility of such low uncertainty of measurement).

In some cases national standards of humidity have been established on the basis of a dew-point generator alone, such as the humidity standard of Italy (Crovini and Actis, 1989). However the approach more ideally adopted for national standard facilities is to use generators or transfer standard hygrometers as working standards, while placing ultimate reliance on a gravimetric primary standard such as the facility of the USA (Huang, 1985) or that of Germany (Scholz, 1984) or Japan (Takahashi and Inamatsu, 1985). Existing gravimetric hygrometers are reviewed in more depth in Chapter 2.

The NPL facility incorporates both a gravimetric hygrometer and a humidity generator which is a primary realisation of dew point. The generator supplies humid gas suitable for measurement using the gravimetric system. This has the benefit of realising humidity definitions in two fundamentally different ways. The generated dew-point temperature (in °C) can then be compared with the gravimetrically determined mixing ratio (in g kg^{-1}). The conversion between units is made using documented values of the saturation vapour pressure of pure water and water vapour enhancement factor. By this approach, the most accurate and fundamental gravimetric measurement capability is combined with dew point generation which provides a practical basis for the calibration of hygrometers.

1.7. Structure of thesis document

The account that follows is laid out in chapters as described below. Each chapter treats one broad aspect of the investigation, and incorporates an abstract and a short final summary, as well as a list of references.

Chapter 2 gives a description of the NPL gravimetric hygrometer, including an account of the extent of progress already achieved before the start of the work reported here. The NPL standard humidity generator, which complements the gravimetric hygrometer, is also described. The role of NPL in general, and in humidity measurement specifically are noted. The background to the present work is given, with a review of similar work, and an explanation of the starting point for this project.

Chapter 3 gives details of the investigative work carried out to evaluate all aspects of performance for the components of the gravimetric instrument, with results for each aspect.

Chapter 4 contains a summary of experimental results for the validation. The results are analysed using the conventions of the ISO *Guide to the Expression of Uncertainty in Measurement* (ISO, 1993) to provide an overall uncertainty statement for the performance for the gravimetric hygrometer. The implementation of the uncertainty analysis is considered for varying circumstances of measurement.

In Chapter 5 the measurements carried out on the NPL humidity generator using the gravimetric hygrometer during its validation period are reported, with a discussion of how the results are converted between the two different units of measurement: mixing ratio and dew point. At this point the use, in this conversion, of documented humidity data is reviewed, and a new calculation of the water vapour enhancement factor for nitrogen is presented. Other sampling uncertainties are also taken into account. The overall uncertainty in the intercomparison measurements is evaluated.

Chapter 6 is a discussion of the performance of the gravimetric hygrometer as revealed by the investigative work reported in Chapters 3 and 4. The uncertainty analysis is considered in overview and further interpretation and conclusions are discussed. The results for the comparison of the NPL humidity generator against the gravimetric hygrometer are reviewed, and their implications are considered.

Chapter 7 concludes the account with a summary and suggestions for further work.

1.8. Chapter summary

This introductory chapter has set the context for the scientific investigation documented in the rest of this thesis document - the validation of the NPL gravimetric hygrometer. Aims and objectives of the work have been established. The physical theory, terminology, definitions, industrial relevance, instrumentation and general nature of humidity have been surveyed. The arguments have been developed as to what type of measurement is suitable as a primary standard of humidity, and the fitness of the NPL gravimetric hygrometer to fulfil this role has been shown. A guide to structure and content has been given for the account ahead. The scene has been set for a closer look at the specific details of the gravimetric hygrometer which is the subject of the investigation reported here.

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CHAPTER 2

The gravimetric hygrometer

... hydrogen and oxygen aren't just transformed immediately in any old way into water. Water has its history too.

Mao Tse-tung 1893-1976
Mao Tse-tung Unrehearsed ed S Schram 1974 (London: Penguin) p 221

CHAPTER 2. THE GRAVIMETRIC HYGROMETER

2.0. Abstract

This chapter provides an overview of the NPL humidity standard facility in general, and a detailed description of the gravimetric hygrometer in particular.

Starting with a note on the general role of NPL, the history is told of NPL's involvement in humidity measurement, leading up to the present work. In establishing a humidity calibration facility, minimum performance targets were set for the facility overall, and for the gravimetric hygrometer. These specifications are listed, along with the more detailed predictions that were made for the performance of the gravimetric hygrometer at the design stage.

An overview description of the NPL gravimetric hygrometer is given, together with a general description of the NPL humidity generator. A full description of the gravimetric hygrometer then follows, giving details of the operation of all the important aspects of the system.

After a brief look at historical design of gravimetric hygrometers, the modern gravimetric hygrometers held by national measurement institutes worldwide are described. The differences in design among them are examined. From this survey it is concluded that the NPL gravimetric hygrometer combines many of the best features of other existing designs of gravimetric hygrometer. This offers unprecedented potential for the range and accuracy of gravimetric measurements.

The starting point for the present work is then defined, given the work previously carried out on the instrument, which included functional testing and feasibility studies to predict its performance.

2.1. History of the NPL humidity facility

NPL, as the national standards laboratory of the UK, maintains measurement standards for physical quantities of all kinds, and disseminates traceable measurements through calibration services to customers. In the field of humidity, NPL maintains standards for dew point and mixing ratio, with a dew point calibration service used by industrial customers from the UK and overseas. Other humidity activities at NPL include research and development of calibration techniques, and technology transfer through mechanisms such as accreditation of calibration laboratories, an advisory service, and an industrial awareness club (Bell, 1991).

There is a history of humidity work at NPL which extends back at least to the inter-war years. At that time, research in this subject was stimulated by the need for humidity control in the refrigerated shipping of food - the importance of which was particularly highlighted during war-time (see for example Griffiths (1927), Awbery and Griffiths (1935)). These early texts make reference to the gravimetric method - under the description "chemical hygrometry" - as the most accurate approach to humidity measurement, and it is clear that some use was made of gravimetric measurements at NPL at that time.

Over the intervening decades, the level of NPL's involvement in humidity measurement has risen and fallen in cycles; the latest of which started around 1980. At that time there was an up-turn in interest, highlighted in a survey conducted by Sira Limited on behalf of the Metrology and Standards Requirements Board of the Department of Trade and Industry. The survey showed a strong industry-wide need for primary standards of humidity to be established within the UK, and for calibrations to be made available to industrial users of humidity measurements. The specification which was established on the basis of the survey (and later published by Poulter et al (1985)) is summarised in Table II. [2]

The facility specification did not directly stipulate the performance of the gravimetric hygrometer. However performance at a certain level was implied by the requirement to underpin the dew-point realisation with a standard of lower

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[2] The term "accuracy" is reproduced in Table II as in the original publication. However the correct term in this context is "uncertainty".

Table II Specification for the UK national humidity standard facility (Poulter et. al., 1985)

Relative humidity range and accuracy	1.0 %rh to 98 %rh ±0.5 %rh over the above range
Dew-point range and accuracy	-70 °C to +90 °C ±0.1 °C at -70 °C to ±0.05 °C at +90 °C
Ambient temperature range in the test chamber	-30 °C to +100 °C controlled and measured to ±0.05 °C
Pressure range in the test chamber	0.1 bar to 10 bar controlled and measured to ±0.1%
Flow range of gas in the generator	Up to 15 l/min
Rate at which gas can be drawn off to an external device, e.g. a gravimetric hygrometer	Up to 1.5 l/min

uncertainty. In the light of this, a minimum specification was established (Forton and Pragnell, 1985). This is shown in Table III. Additionally, a feasibility study indicated that a gravimetric measurement would achieve a level of performance which would easily meet the specification. (Poulter et. al., 1985). A graph of the expected uncertainty is shown in Figure 2, with the target uncertainty of the standard facility as a whole (i.e. the calibration service) shown for comparison. It was also clear from this feasibility study that the range of operation could be much greater than the minimum stipulated in Table III. The account that follows therefore addresses a wide practical range of mixing ratios between about 0.01 g kg^{-1} and 155 g kg^{-1} (dew points from -60 °C to +60 °C), which spans almost twice the minimum specified range.

Table III Specification established for the gravimetric hygrometer (Forton and Pragnell, 1985)

Range	Mixing ratio 0.14 g.kg^{-1} to 38 g.kg^{-1} (Dew point equivalent -35 °C to +35 °C)
Uncertainty	Up to 0.2% of measured value (3 standard deviations)
Operating pressure	1 bar
Nominal sample flow rate	1 litre per minute
Maximum temperature of inlet gas	75 °C to 80 °C
Operating gases	Pure air, nitrogen

Following this justification, NPL designed and built a humidity generator (Hales, 1985) to function as a dew-point standard for the provision of a calibration service. The gravimetric hygrometer (Forton and Pragnell, 1985) was developed by Sira, under contract to the Department of Trade and Industry, and later installed and commissioned at NPL. The humidity generator was brought into service in 1985, well before the gravimetric hygrometer. Customer demand had expedited the start of the dew-point calibration service, albeit with a provisional uncertainty in dew point of ±0.1 °C at best, rising to ±0.15 °C and ±0.25 °C at the upper and lower extremes of the measurement range respectively. However, it was always intended that the outstanding requirements of the original specification would be met by quantifying the generator's uncertainty more accurately, through verification against the gravimetric standard.

A calibration service for relative humidity was also initiated to fulfil the specification. However the realisation of relative humidity was later devolved to secondary laboratories as a matter of policy. That aspect of the NPL facility then fell

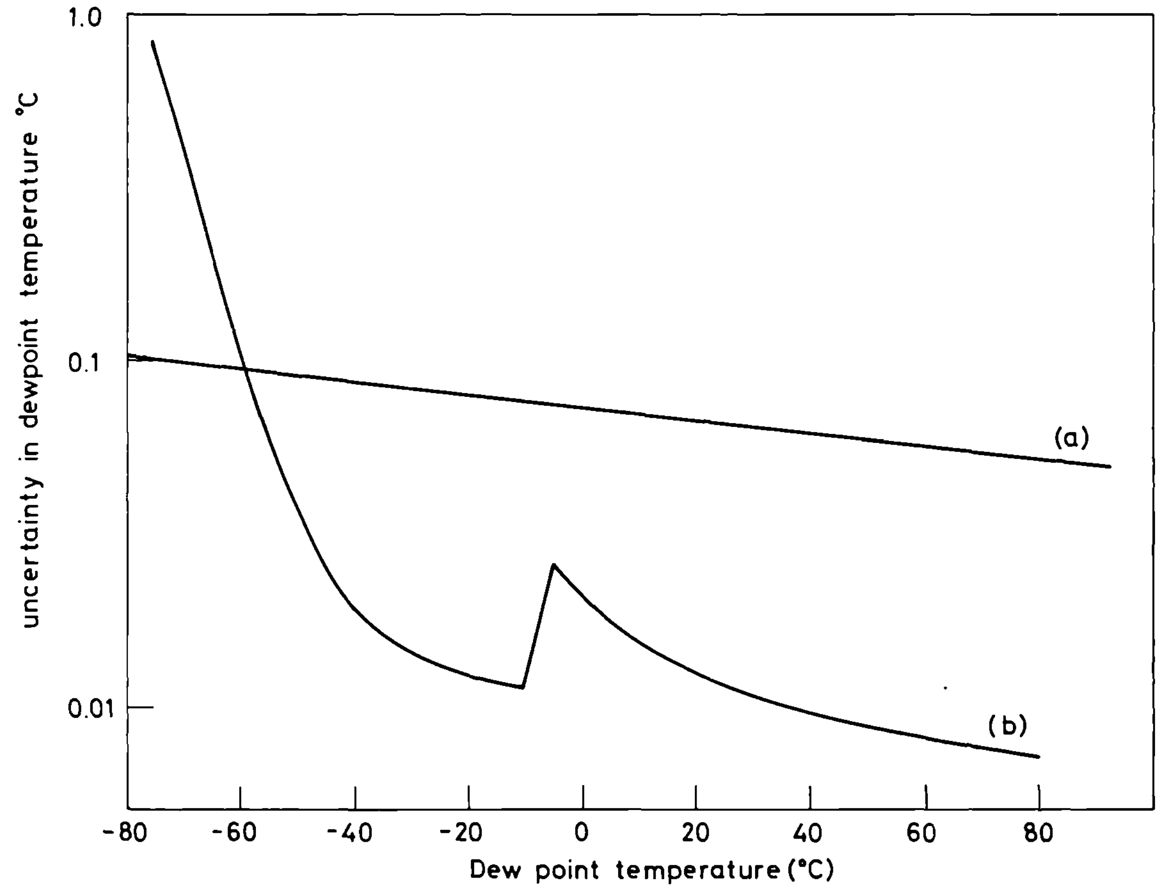


Figure 2 Comparison of the expected uncertainty for the humidity calibration facility (a) with the gravimetric hygrometer (b) at the 99% confidence ("3-sigma") level

into disuse, and has not been re-instated since, although there is continuing customer interest. Similarly, the facility to operate the generator at elevated or reduced pressures was not utilised beyond the development stage.

2.2. Overview of the NPL gravimetric hygrometer

Figure 3 shows a block diagram and Figure 4 a photograph of the NPL gravimetric hygrometer.

The gravimetric system is used to sample humid gas from the humidity generator at a rate of up to 1 litre/minute. In the case of high humidity measurement (dew points above about 0 °C) the gas passes initially through a predryer consisting of a steel can containing molecular sieve held at a temperature of 1 °C. This traps the majority of the water present in the gas. In the case of low humidity measurement the predryer stage is omitted. Next the gas flows through a specially designed cold trap which efficiently retains the residual water, freezing it as ice on the internal surface. The dry gas which emerges is collected by liquefying it in an aluminium cylinder which is externally cooled, creating a cryo-pumping action, which draws further gas through the system. After sufficient gas and water have been collected, all collection vessels are sealed by closing valves. Before and after the collection, the gas collection vessel is weighed against a reference copy on an equal-arm balance. The predryer, if used, is also weighed against a duplicate before and after the collection, on a top pan balance. The water trapped in the cold trap is evaporated onto a desiccant which is weighed beforehand and afterwards on a microbalance in vacuum. The overall result is obtained by dividing the change in mass of the desiccant (and of the predryer if used) by the change in mass of the gas collection vessel, to give a value of mixing ratio for the humid gas.

2.3. Overview of the NPL humidity generator

A block diagram of the NPL humidity generator is shown in Figure 5, and a photograph in Figure 6.

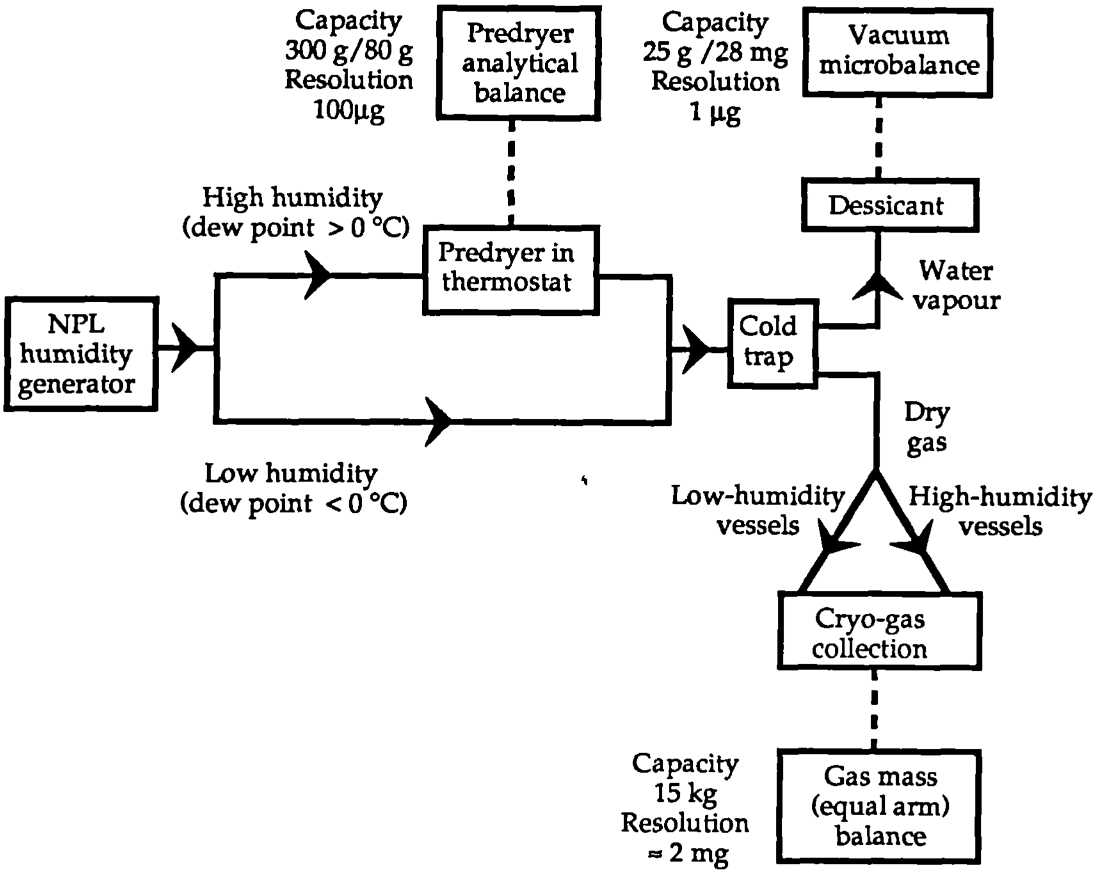


Figure 3 Block diagram of the gravimetric hygrometer

Figure 4 Photograph of the gravimetric hygrometer, showing (a) gas vessel in cryostat, (b) microbalance vacuum chamber, (c) cold trap, (d) predryer and thermostatted bath, and (e) gas vessel on equal-arm balance

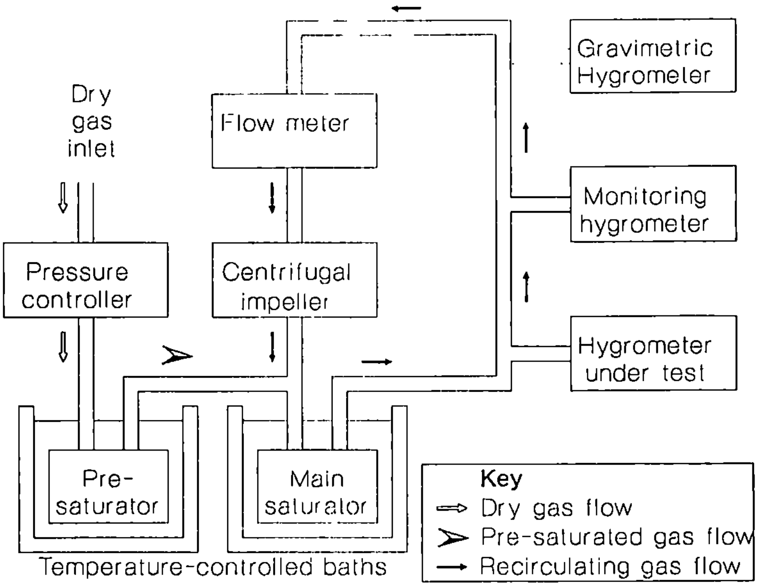


Figure 5 Block diagram of the NPL humidity generator

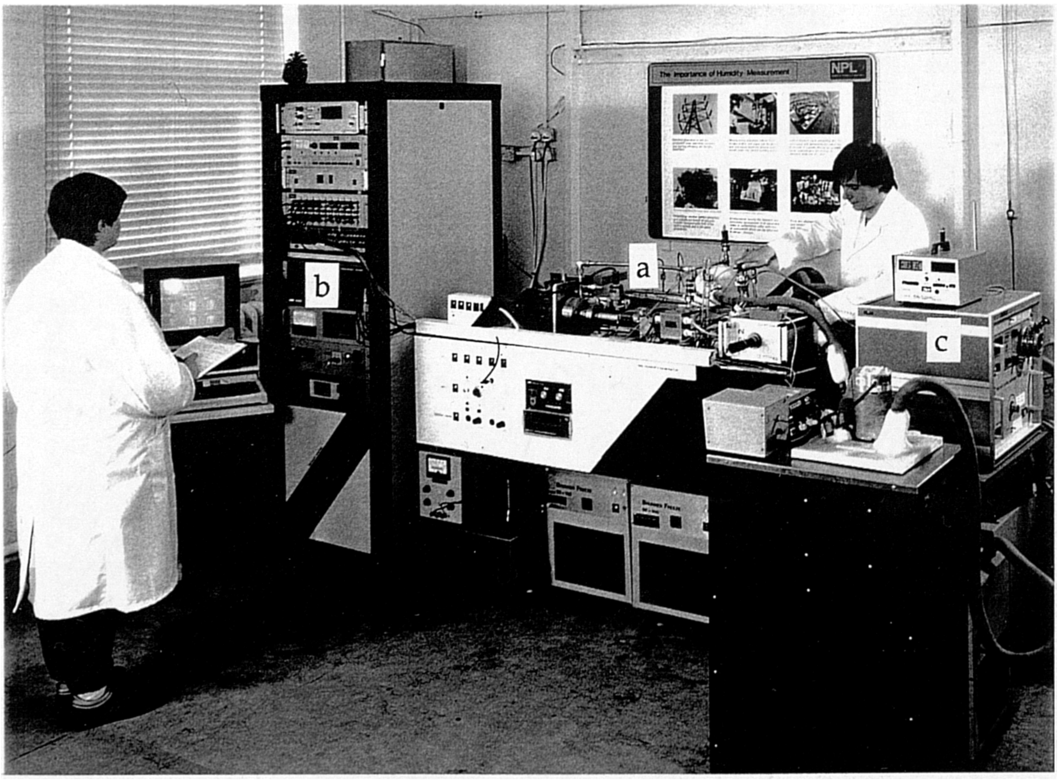


Figure 6 Photograph of the NPL humidity generator, showing (a) saturators and connecting pipework, (b) monitoring instrumentation, (c) hygrometers under calibration

The humidity generator consists of a recirculation system in which gas is saturated with water vapour by passage over a surface of water or ice at the desired dew-point temperature. A small proportion is then bled off to hygrometers under test or to the gravimetric hygrometer. Dew points in the range -75 °C to +80 °C are generated with an uncertainty of ±0.05 °C in dew point in the middle of the range, increasing to ±0.08 °C and ±0.15 °C at the upper and lower extremes respectively. These estimates of uncertainty were reached after validation of the operation of the humidity generator by assessing the performance of individual components of the system, such as efficiency of saturation, temperature conditioning, moisture conditioning of pipework, etc. (Stevens and Bell, 1993).

For the purpose of intercomparison of the two instruments, the full details of operation of the humidity generator are not of interest here. (Complete accounts of the design and operation of the humidity generator and of its performance are given in the paper by Hales (1985) and updated by Stevens and Bell (1993).) However a few particular aspects must be considered, as discussed below.

For the intercomparison results to be meaningful, the generator must be running under normal operating conditions while the output gas is sampled. In particular the sampling flow rate must place the system under a load which is typical of usual conditions of operation. The generator must be operating in a stable equilibrium as far as possible during intercomparison measurements. The pressure at which the generator is maintained - while not a sensitive influence on the dew point - must be known accurately in order to convert between units of dew point and mixing ratio (See the explanation of mixing ratio in Section 1.3.2.). Lastly it must be borne in mind that the result of a gravimetric measurement represents an integrated value of humidity over the duration of the gas sampling process.

2.4. Details of the operation of the NPL gravimetric hygrometer

The following sections describe in detail the key components of the gravimetric hygrometer. The drawing of the general assembly is shown in Figure 7, and the detailed schematic diagram in Figure 8.

2.4.1. Gas collection vessels and cryostat

Figure 7 shows a gas collection vessel positioned in the cryostat as normally arranged for collection of dry gas. Two pairs of vessels are available - one large and one small pair - enabling collection of up to 400 and 1100 grams of gas respectively. At low humidities, where water is an extremely small fraction of the gas to be measured, collection of the larger amount of gas is necessary so that the corresponding water collected is enough to be measured with reasonable precision. In the course of a measurement, the unused vessel of the pair serves as a counterpoise in the weighing process, and enables air buoyancy effects to be ignored, to a first approximation.

The vessels are made of aluminium alloy which has been anodised to inhibit corrosion. Each vessel consists of two connected chambers; the lower one where collection of liquefied gas takes place, and the larger upper volume which allows for expansion of the collected gas when raised to room temperature, while ensuring that the internal pressure stays below a safe limit. An integral valve enables each vessel to be sealed.

To collect gas, the lower part of the vessel is placed inside a cryostat as shown in the Figure 7. The cryostat is filled with liquid nitrogen, which is cooled to a temperature approximately 10 °C below the normal boiling point, by reducing the pressure above the surface, using a high capacity pump and a pressure controller. As long as this reduced temperature on the outside of the vessel is maintained, nitrogen gas in contact with the inner surface will be liquefied. As any contents become liquid, the consequent decrease in volume is accompanied by a decrease in pressure, creating a suction which draws further gas through. The rate of flow of gas is controlled upstream of the vessel using a needle valve. The upper part of the cylinder is thermally insulated during collection of gas, and the vessel is sealed into the cryostat at "waist level" by an ice seal. The cryostat is equipped with level control for the liquid nitrogen and with automatic filling via a reservoir.

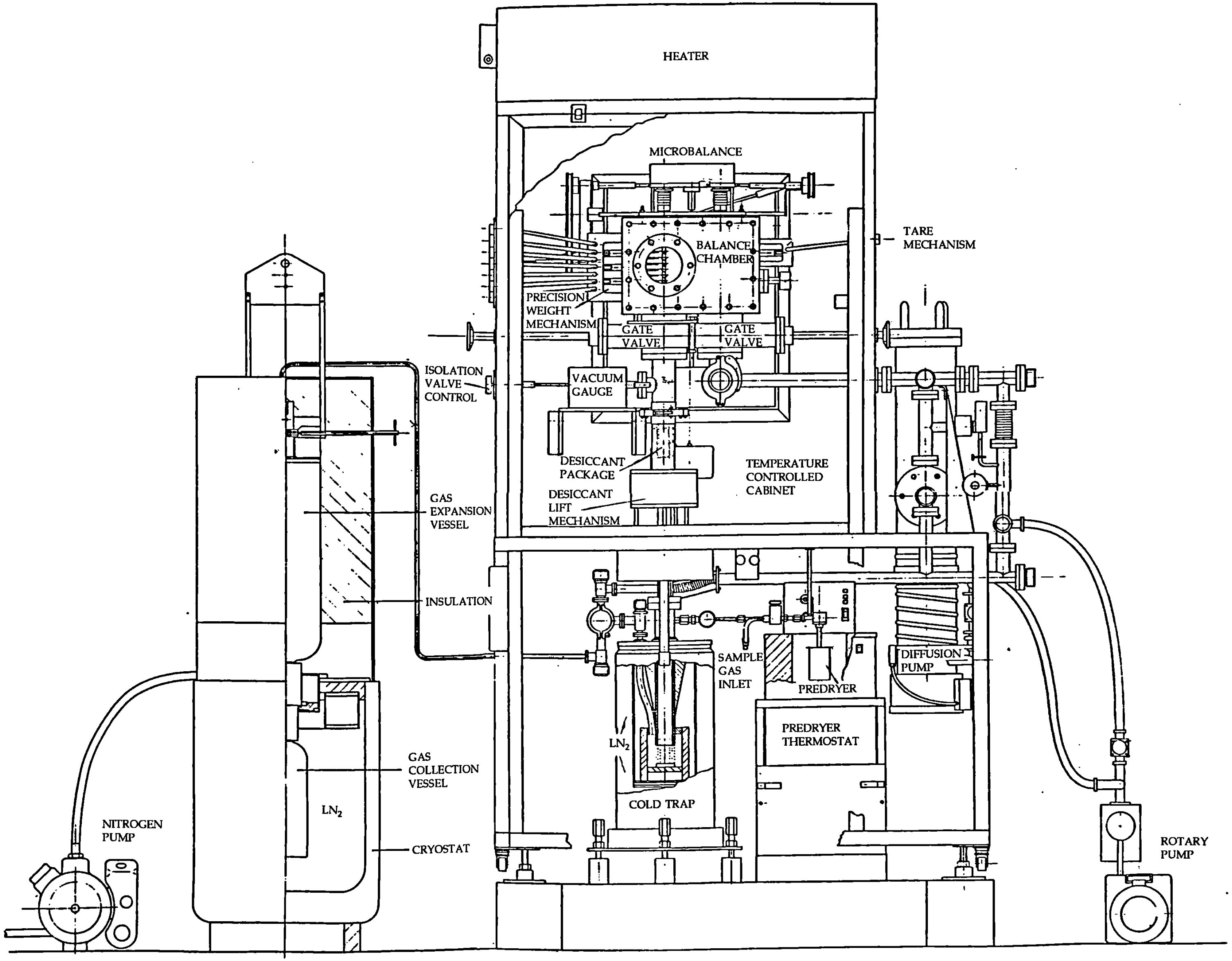


Figure 7 General assembly drawing of the gravimetric hygrometer (Forton and Pragnell, 1985)

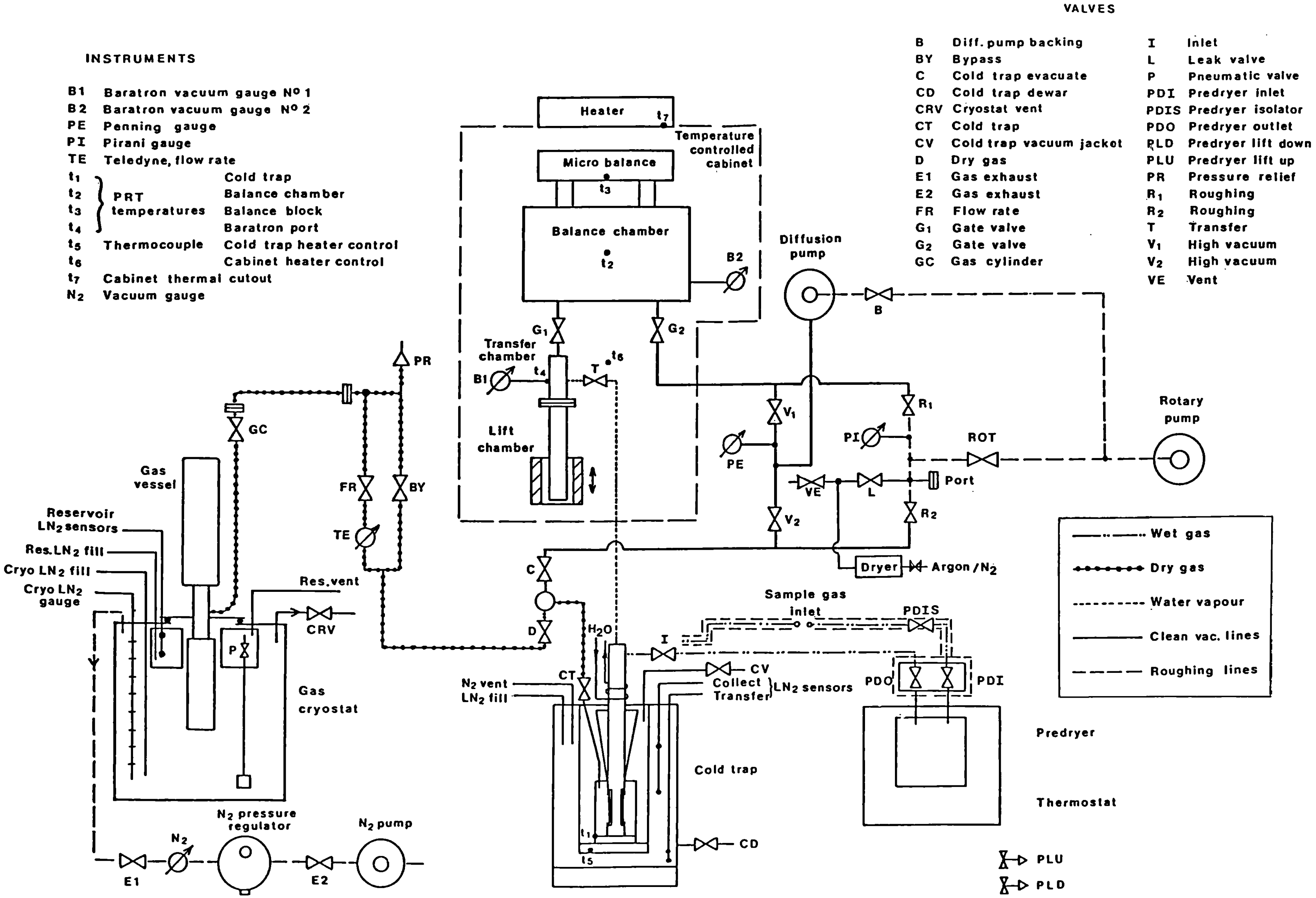


Figure 8 Detailed schematic diagram of the NPL gravimetric hygrometer (Sira Ltd, 1985)

2.4.2. Weighing of gas vessels

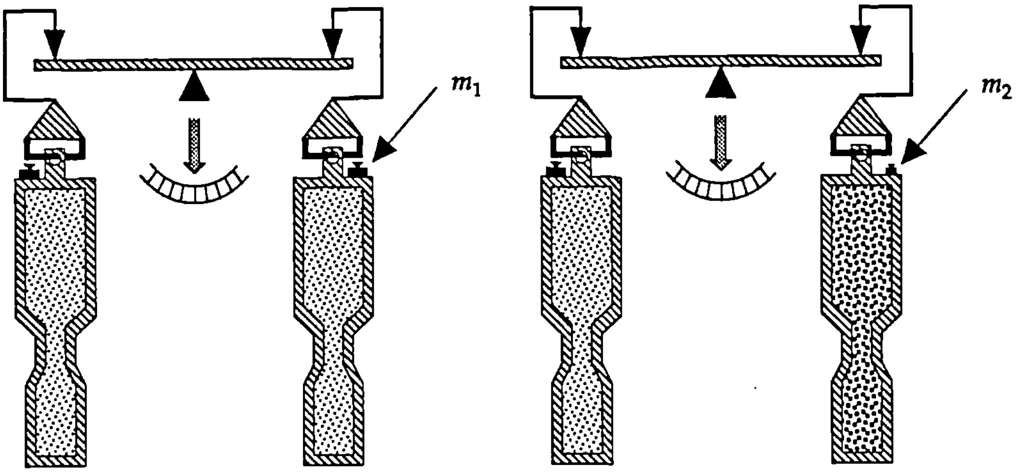
The gas vessels are transported between the cryostat and the balance using an overhead track and suspension system. The purpose built equal arm balance has a capacity of 15 kg and a resolution, by visual reading of the graticule, of approximately 2 mg. A photograph of the balance is shown in Figure 9. The empty masses of the small and large cylinders are approximately 7.5 kg and 13.5 kg

Figure 9 A photograph of the equal-arm balance used to determine the mass of collected gas, showing (a) large gas collection vessels, (b) suspension yokes, and (c) flat tops for accommodating weights (Forton and Pragnell 1985)

respectively. There are no scale pans - the cylinders being loaded directly onto hooks which are suspended from the arms of the balance by knife-edge bearings. The flat tops of the cylinders are used for accommodating weights.

The weighings are carried out by a "complementary" [3] method of weighing in which the empty vessel and the reference (counterpoise) vessel are first balanced using calibrated weights equivalent to (or exceeding) the mass of gas to be collected. After collection, fewer weights are applied; the difference corresponding to the mass of collected gas. This is illustrated in Figure 10.

This complementary method is analogous to the "substitution" method more conventionally used in weighing. A substitution weighing is one in which the object being weighed is first counterbalanced by some constant mass. Weights are then



Mass of collected gas ≈ $m_1 - m_2$

Figure 10 Illustration of complementary weighing of collected dry gas

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[3] BS 5233 : 1975 (Confirmed 1993) defines a "complementary method" of measurement as a "method of measurement by comparison in which the value of the quantity to be measured is combined with a known value of the same quantity so adjusted that the sum of these two values is equal to a predetermined comparison value".

substituted for the object, and are equal to it when they have been adjusted so that the first position of the balance beam has been regained (NPL, 1954).

2.4.3. Predryer vessels

Figure 11 shows a photograph of the pair of predryer vessels. These vessels are made of stainless steel and each incorporates a baffle and a basket of pellets of type

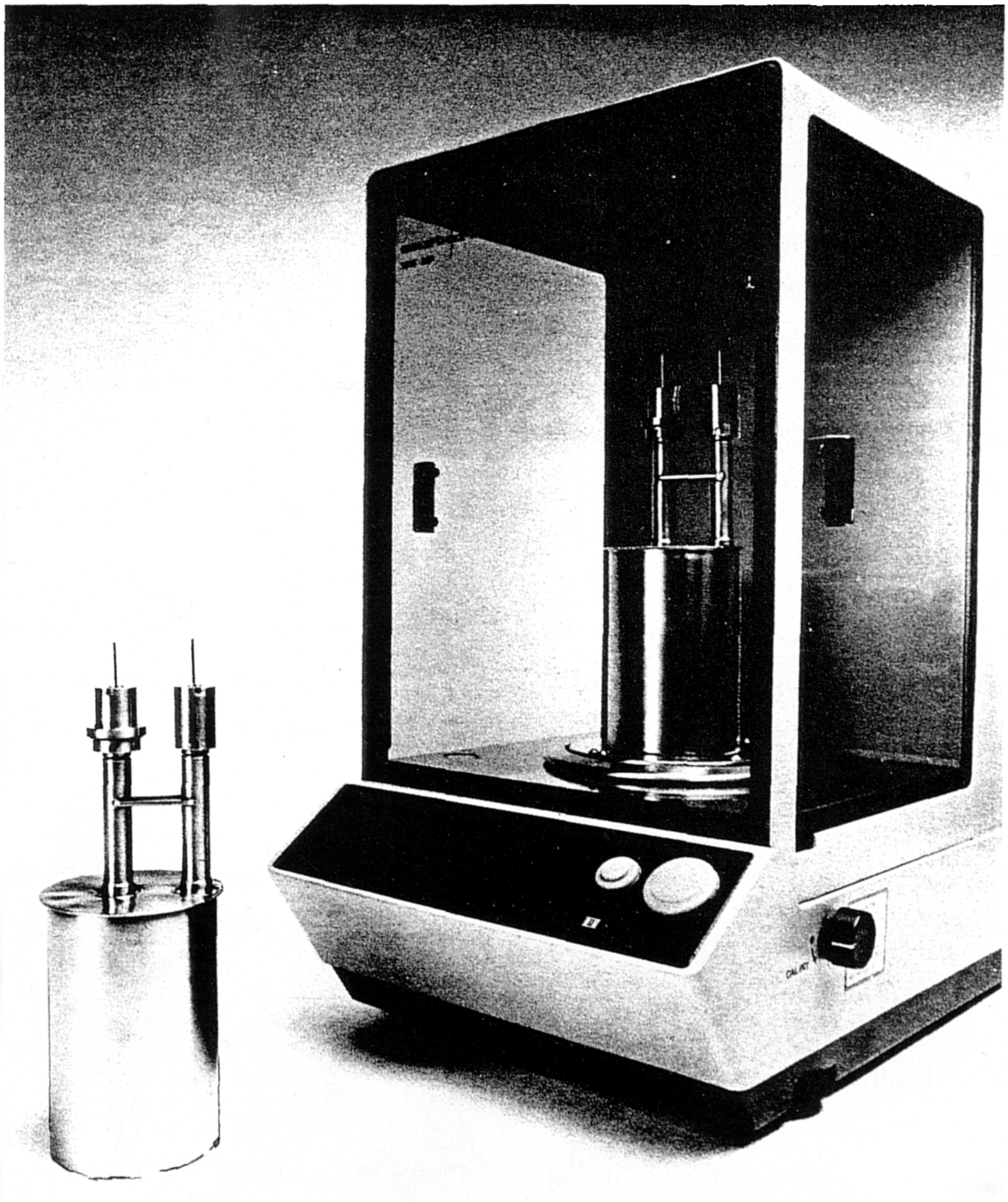

Figure 11 Photograph of the predryers and top-pan balance (Forton and Pragnell, 1985)

3A molecular sieve. Entry and exit tubes are sealed by sprung ball valves which automatically close when the unit is detached from the flow path. In use, the predryer sits in a bath thermostatically controlled at 1 °C. The pipework preceding the predryer is heated to approximately 10 °C above the dew point of the gas being measured, to prevent condensation. The humid gas enters the predryer downpipe, and water condenses and collects at the bottom of the vessel. The gas then passes upwards through the molecular sieve which extracts further water before the gas (now containing only a few parts per million of water vapour) exits the predryer and passes to the cold trap.

2.4.4. Weighing of predryers

The weight of the predryer before and after the collection of water, is compared with that of the unused duplicate predryer, using an electronic top-pan balance as a comparator. This procedure, like that for weighing the collected gas, eliminates the need to consider air buoyancy, to a first approximation. A Sartorius Model 1615 MP top pan balance is used, whose capacity is 300 g and whose resolution is 1 mg, with 0.1 mg resolution in a floating range of 80 g. The balance is shown in the photograph in Figure 11.

The vessels are compared by first placing the reference vessel on the scale pan, and taring the balance (i.e. offsetting the value of weight electronically so that the reading is zero at this load). The reference vessel is then replaced by the other one, and the displayed reading directly indicates the difference in mass (or, strictly, weight in air) between the two.

After each gravimetric measurement, the molecular sieve is regenerated by heating the predryer in an oven at approximately 150 °C while purging with dry nitrogen.

2.4.5. Cold trap

The general assembly drawing in Figure 7 shows the layout of the cold trap and vacuum system. The cold trap is designed to retrieve water vapour from the gas stream with maximum efficiency, and to release it efficiently later, to be absorbed by a desiccant.

Gas enters through a down pipe with baffles to create turbulence, next passing through a labyrinth of steel balls, before exiting the trap. The inlet is maintained near room temperature while the base of the assembly is cooled to approximately -150 °C using liquid nitrogen. The temperature gradient ensures that the gas passes over successively colder surfaces so that the water vapour is deposited evenly as ice along the flow path. The construction is in stainless steel with polished internal surfaces. High vacuum valves connect the assembly to the rest of the system. The base of the cold trap is also equipped with heaters which can be thermostatically controlled. An automatic filling system in conjunction with these heaters maintains the base of the assembly at an approximate temperature which may be set.

2.4.6. Vapour transfer and desiccant retrieval of residual water

At the conclusion of a measurement run, when sufficient gas and water have been collected, the gas flow is terminated by closing valves. The cold trap then contains ice plus a quantity of dry carrier gas. At this stage, the surplus gas is pumped away (and accounted for later) so that only the collected ice remains, and the cold trap is otherwise in vacuum. A valve is then opened to connect the cold trap to the transfer chamber, where the desiccant is located, and the cold trap is slowly heated to evaporate the water, which is then absorbed by the desiccant.

The desiccant used is granular magnesium perchlorate ($Mg(ClO_4)_2$) which has been previously sieved and dehydrated by heating at 150 °C under vacuum. Approximately 25 g of this material is suspended in a fine mesh steel basket lined with a vapour permeable membrane. The desiccant maintains a low equilibrium vapour pressure; approximately 1.2×10^{-4} mbar over the first hydrate (i.e. $Mg(ClO_4)_2.2H_2O$). Thus, if the water is driven off from the cold trap slowly so that no higher hydrates form, the vapour is efficiently collected by the desiccant.

During the transfer, the cold trap is heated to approximately 110 °C. When the transfer is complete a gate valve is opened, connecting the transfer chamber to the housing of the vacuum microbalance. The desiccant package, which is suspended by magnetic levitation, is hooked onto the microbalance for weighing.

2.4.7. Microbalance weighing of desiccant

The desiccant is weighed in vacuum before and after the collection of water. The microbalance used is a Sartorius model 4410 symmetrical double beam electronic balance with a capacity of 25 g and a resolution of 1 μg within a floating electronic range of ±12 mg. In use, the desiccant is approximately counterbalanced by a steel tare weight. Changes in the mass of the desiccant package are evaluated by offsetting the change approximately, using weights to bring the balance within ±12 mg of the equilibrium rest point. The residual mass difference is then counterbalanced electromagnetically, and the equivalent residual mass indicated on the display electronics. This process is therefore, like the other weighings, a complementary or quasi-substitution weighing against a counterpoise weight. On each occasion of use, the gain of the microbalance electronics is measured as a check of correct operation. The balance and nearby pipework are held at a constant temperature of 30 °C. The weights are manipulated from outside the thermostatically controlled enclosure via mechanical feedthroughs into the vacuum chamber, sealed with flexible bellows.

The desiccant is re-used, gaining mass successively with each measurement run, until it cannot absorb further without losing its efficiency (or until the range limit of the balance is reached). In principle the final weight figure for one measurement run may constitute the initial weight for the next measurement, but for best accuracy a fresh set of weighings is conducted on each occasion.

Once exhausted, the desiccant is not regenerated *in situ* but is replaced with fresh anhydrous material.

2.4.8. Other details of operation

In between measurements, the cold trap, balance chamber and all intervening pipework are kept under constant vacuum of less than 10^{-2} mbar. This ensures that the internal walls harbour only a minimum and consistent amount of adsorbed water vapour or other contamination which might influence the results of measurements.

Prior to measurement runs, the cold trap is baked and evacuated to ensure that it initially contains only a minimal amount of water. This baking process is designed to create an initial condition which is the same as the final condition of the apparatus after a measurement. This helps to ensure that the small amounts of water present initially and finally are similar, and therefore tend to cancel each other out, minimising the possible error in measurement results which could be caused by this.

During measurements, various parameters are monitored to ensure correct operation, including temperatures in the cold trap and cryostat, suction generated by the cryopumping action, rate of gas flow through the apparatus, and vacuum pressures in the balance chamber and desiccant chamber.

The entire process of preparing and conducting each measurement, including the weighings beforehand and afterwards, and the baking and cooling of components as required, occupies some 40 hours of operator effort spread over approximately two weeks. If two measurements are performed "back to back" so that the final microbalance weighings of the first run are also the initial weighings of the second run, then the two measurements can be completed within three weeks. For each measurement, the duration of actual sampling of gas to be measured is either approximately 6 hours or 20 hours (overnight), with the longer collection time being required at low humidities for best accuracy.

2.4.9. Magnitudes of water and gas collected

Table IV shows the nominal amounts of water and dry gas collected at different mixing ratios in the range of measurement of the gravimetric hygrometer. In parts of the range where use of the small (high humidity) vessels is recommended, 400 g is the maximum mass of gas collected. For the large (low humidity) vessels, up to 1100 g of gas can be collected (although a working upper limit of 1000 g has been adopted). The maximum amount of water collected in this range of measurement

Table IV Nominal amounts of water and dry gas collected in the NPL gravimetric hygrometer for a range of different values of mixing ratio

Mixing ratio $g\ kg^{-1}$	Dew point (nominal) at atmospheric pressure °C	Nominal mass of gas g	Nominal mass of water g
155	60	400	62
50	40	400	20
15	20	400	6.0
3.8	0	400	1.5
0.65	-20	400	0.26
0.080	-40	1000	0.08
0.007	-60	1000	0.007

is 62 g. This limit is dictated by the capacity for collecting the corresponding dry gas, although the predryers can in fact hold up to 0.1 litre (100 g).

2.5. Other gravimetric hygrometers

A number of countries have at some time developed gravimetric hygrometers as part of their national standard facilities. Apart from the UK, the list of current and recent gravimetric national humidity standards includes USA, Germany, Poland, Japan, France and (most recently) South Korea. These are described below, followed by some comments on the merits of the NPL instrument in comparison to the others.

First, though, it is interesting to note how these have their origins in the historic form of gravimetric hygrometer.

2.5.1. Historic design of gravimetric hygrometer

Early gravimetric or "chemical" hygrometers were built from laboratory glassware like any analytical chemical apparatus. Figure 12 shows a schematic diagram of this type of gravimetric hygrometer as described by Penman (1955). The water collection train consists of three u-tubes filled with desiccant, with valves to seal them from ambient air when detached from the assembly. A quantity of laboratory air is sampled by being drawn through the apparatus under the suction generated by a slowly emptying reservoir of water ("aspirator") beyond the u-tubes. The last of the three u-tubes is present to guard against measurement error due to the back-diffusion of water vapour from the aspirator. The first u-tube traps most of the water vapour in the air sample, and the second u-tube acts to trap any moisture breakthrough in case the desiccant in the first tube becomes exhausted, or in case of inefficiency due to excessively fast air flow. The mass of water collected is found by weighing the first and second u-tubes. The volume of the corresponding carrier gas is deduced from the volume or mass of water drained from the reservoir. The resulting value of humidity is given in terms of mass of water per unit volume of air (i.e. in terms of absolute humidity rather than mixing ratio). Penman (1955) quotes an uncertainty of 1% of value for this method under favourable conditions. The performance would be poorer than this at humidities below ambient values, because of the use of glass as the main material of construction, and because of the relatively small size of the gas sample.

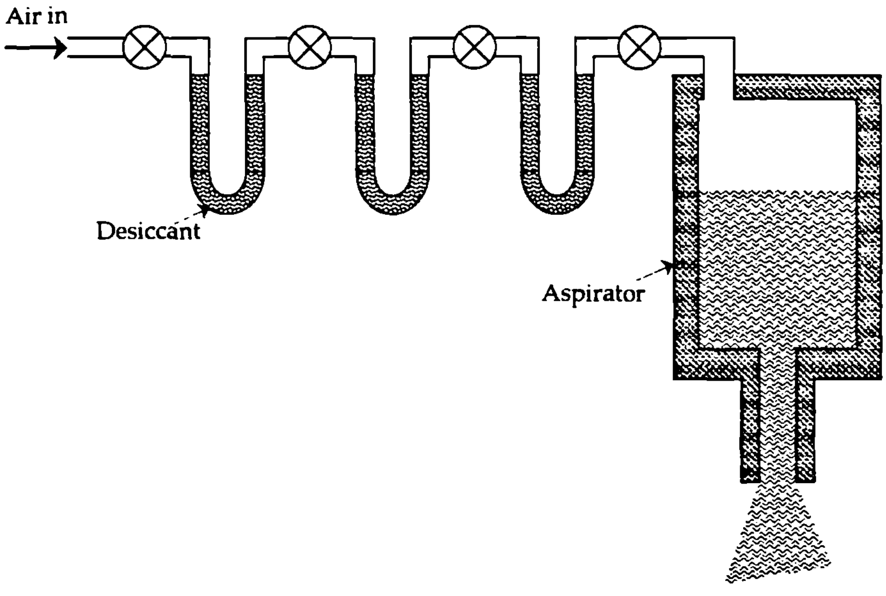

Figure 12 Principle of early gravimetric or "chemical" hygrometer

2.5.2. United States National Institute for Standards and Technology (Formerly National Bureau of Standards)

The gravimetric hygrometer built in the 1960s by the United States (then) National Bureau of Standards (NBS) - now National Institute of Standards and Technology (NIST) - is widely considered to have set the bench mark for gravimetric hygrometers (Wexler and Hyland, 1964). It was the first one to achieve the very low uncertainties that have come to be associated with the best of these standards. A block diagram of the NBS hygrometer is shown in Figure 13.

In concept, the NBS design is closer to the early chemical hygrometer than to the NPL instrument. Like the chemical hygrometer, the NBS gravimetric method does not involve literally weighing the gas component. Instead the gas is collected in cylinders of known volume (of approximately 30 litres), at defined pressure and temperature (both near ambient values). The gas collection process employs a pair of cylinders, used in continuous alternation. While one is filling, the other (full) cylinder is equilibrating in temperature and pressure, which are then measured, prior to evacuation ready for re-filling. The mass of the gas is then deduced from a calculation of its density, with an accuracy determined by the uncertainties in pressure, temperature, volume and in the equation of state for air.

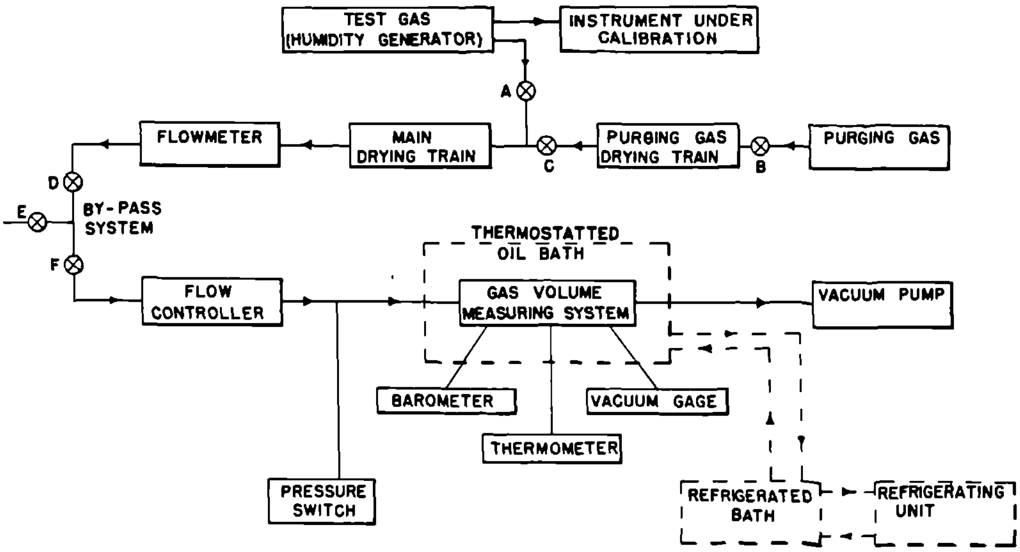

Figure 13 Block diagram of the NBS gravimetric hygrometer (Wexler and Hyland, 1964)

In the NBS design, water is extracted from the sample gas stream by passing it through a drying train consisting of three glass u-tubes containing desiccant. The first u-tube, which is filled with anhydrous magnesium perchlorate ($Mg(ClO_4)_2$), and backed with a plug of anhydrous potassium pentoxide (P_2O_5), absorbs all - or almost all - of the water vapour. The second tube traps any moisture which escapes the first u-tube. The third u-tube, as in the chemical hygrometer, acts to prevent back-diffusion of any water vapour which might unintentionally be present downstream of the assembly.[4] After the collection, the u-tubes are weighed in air. Gains in mass of about 0.6 g of water are measured in vessels whose overall mass is about 80 g.

The range of measurement of this gravimetric hygrometer as realised by the NBS is dictated by the maximum tolerable ambient temperature (at the upper limit) and by sources of error which become significant at the lower limit, due to inefficient trapping of water and to the unfavourable ratio between the mass of water and the mass of the u-tubes. This leads to a mixing ratio range from 0.19 g kg^{-1} to 27 g kg^{-1} (equivalent at atmospheric pressure to a dew-point range of -32 °C to +30 °C). The uncertainties at the lower and upper extremes of this measurement range are respectively ±0.09% and 0.07% of value, at the 95 percent level of confidence[5].

In fact, the original hygrometer of the NBS (now NIST) has not been in active service for some time, and workers at NIST are now developing a new gravimetric instrument (Huang, 1993). This will operate on the same principles as the original, but with a higher degree of automation to enable longer measurements and therefore better uncertainties, since large quantities of water and gas will be collected. This may provide significant improvement at low humidities, where substantial amounts of gas would normally need to be processed in order to collect enough water for precise measurement.

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[4] Use of a third u-tube in this case is more as a precaution than a necessity, since in the modern design the gas is drawn through the instrument by means other than a water-driven aspirator.

[5] Unless otherwise specified, the uncertainties of these instruments are quoted here at the 95 percent (or "two-sigma") level of confidence, i.e. for an approximate coverage factor of k=2. Where the original reports are expressed at other levels of confidence, these values have been converted to 95 percent for the present account. Statistical terms and definitions are discussed in Chapters 3 and 4 ahead, and in the ISO *Guide to the expression of Uncertainty in Measurement* (ISO, 1993).

2.5.3. Physikalisch-Technische Bundesanstalt, Germany, (formerly Amt für Standardiserung, Messwesen und Warenprüfung, East Germany)

The Physikalisch-Technische Bundesanstalt (PTB) maintains a gravimetric facility (Scholz, 1984) which was developed by the ASMW (Office for Standardization, Metrology and Quality Control), which later amalgamated with PTB as a result of German re-unification.

The design of the hygrometer is essentially identical to the NBS design. There are some small differences, such as the use of identical desiccant in all u-tubes; namely a mixture of potassium pentoxide and magnesium perchlorate. The documented range of measurement of the instrument is 1 g kg^{-1} to 30 g kg^{-1} (equivalent to a dew-point range of -16 °C to +32 °C). The uncertainty of measurement is conservatively documented as ±0.24% of result throughout this range, provided at least 400 mg of water is collected. Otherwise larger (unspecified) uncertainties are reported to apply.

The hygrometer is in occasional use to monitor the performance of the PTB dew-point generator, but normally only for the range of dew points between 0 °C and 25 °C, avoiding the difficult humidity range below 0 °C (Scholz, 1994). (In the ten or twenty degrees below 0 °C, humidity measurements are generally complicated by the occurrence of both ice and supercooled water, which give rise to differing equilibrium water vapour pressures).

2.5.4. Central Office of Measures (Glowny Urzad Miar), Poland

The design of the Polish gravimetric hygrometer (Kostyrko and Kacprzak, 1977; Kostyrko 1979) shares some of the features of both the NPL and NBS hygrometers. Its performance has been reported as equal to or better than that of the NBS instrument. However, it has never achieved as much international recognition, though this may be as a result of international isolation within the Eastern Bloc prior to the 1990s, rather than any lack of technical merit.

The Polish design constitutes a true gravimetric determination, where the mass of the dry gas is found by weighing (like the NPL hygrometer) not volumetrically (like

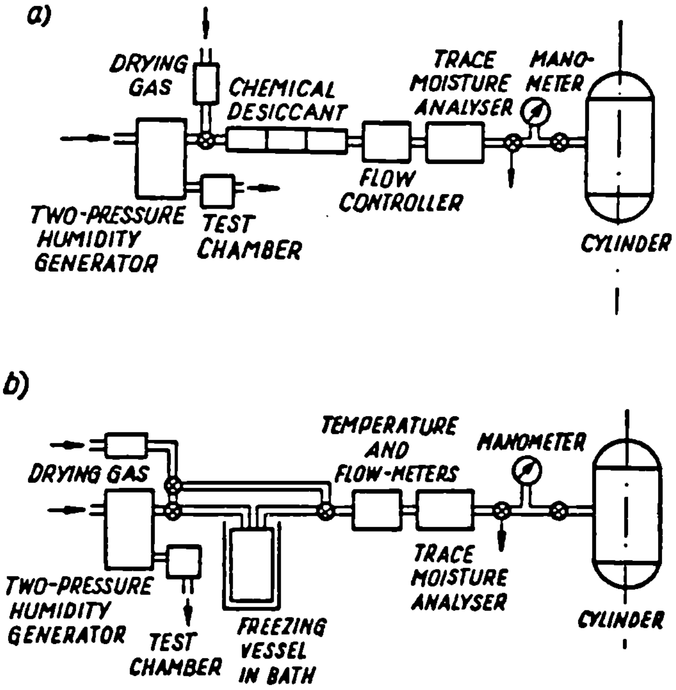

Figure 14 Block diagram of the gravimetric hygrometer of Poland (a) with chemical desiccant and (b) with cold trap (Kostyrko, 1979)

the NBS approach). A block diagram of the hygrometer is shown in Figure 14. Gas is collected in one 400 litre vessel whose empty mass is 70 kg. The vessel is first partially evacuated to an absolute pressure of 10 kPa, then filled to a pressure of 90 kPa, resulting in collection of up to some 400 g of gas. The vessel is weighed against a duplicate on an equal arm balance, by a substitution-type method.

In the design reported in 1977, the water is collected in a series of three u-tubes - made in this case from austenitic stainless steel - the first two filled with magnesium perchlorate and the last with potassium pentoxide. Located downstream of this drying train is a humidity sensor to monitor the residual water vapour left in the "dry" gas stream, enabling a correction to be made for this.

The water collection stage of the hygrometer was later re-designed to allow collection of larger quantities of water for measurements of high humidities up to 200 g $\mathrm{kg^{-1}}$ (65 °C in dew point) (Kostyrko, 1979). This later design incorporated, in place of the u-tubes and desiccant, a cold trap in a bath of ethanol and dry ice, at approximately -70 °C.

In its 1977 configuration, this hygrometer had a measurement range of 3 g kg^{-1} to 16.5 g kg^{-1} (-3 °C to +21 °C in dew point), with an uncertainty ranging between ±0.054% and ±0.022% of result at the lower and upper extremes of the range respectively.

With the improvements in 1979, the range of measurement was extended to cover mixing ratios between 1 g kg^{-1} and 200 g kg^{-1} (-15 °C to +65 °C in dew point), with uncertainties varying from ±0.3% of result at the lower extreme to ±0.018% of result at the upper end of the measurement range.

Like the original facility of the United States, work on this gravimetric hygrometer has tailed off, and the instrument is no longer in use (Flakiewicz, 1994).

2.5.5. Other national measurement institutes

The gravimetric hygrometer at the National Research Laboratory of Metrology, Japan, (NRLM), follows the NBS design, with small practical improvements (Takahashi and Inamatsu, 1985). These include increased automation, improved valve arrangements, and the use of a critical flow nozzle between the water and gas collection stages, to guard against pressure and flow variations on switching between gas collection vessels. According to the published literature, it is intended mainly for verifying values of relative humidity. The reported uncertainty is ±0.1% of value. While it is not completely clear for what range this is valid, it does at least cover relative humidities from 10% to 100% at 20 °C, which is equivalent to a mixing ratio range of 1.5 g kg^{-1} to 15 g kg^{-1} (-10 °C to +20 °C in dew point).

CETIAT, the laboratory holding the French national humidity standard, operates a gravimetric hygrometer (Crétinon, 1984). In this case it is not a particularly precise instrument, but takes advantage of the accuracy and ease of use of this method in a limited range of mixing ratios between 50 g.kg^{-1} and 150 g kg^{-1} (dew points between 40 °C and 60 °C). A simple moisture-trapping assembly is used, analogous to the predryer in the NPL gravimetric hygrometer. The mass of water collected is then found by weighing. Residual moisture in the exit gas is measured using a condensation dew-point hygrometer, and a correction is applied. Mass of gas is deduced from measurement of flow rate, temperature and pressure. The reported uncertainty of measurement is 0.08 percent of result, or 0.15 °C in dew point.

One more national laboratory - the Korean Research Institute for Science and Standards is embarking on the construction of a gravimetric hygrometer. At the time of writing only a projected uncertainty figure is available, of ±0.5% of value (Nham, 1994). This is not an overly ambitious target uncertainty for moderate humidities, but will be a significant achievement if it extends down to a mixing ratio below, say, 0.1 g kg^{-1} (a dew point of around -40 °C). The construction of this instrument is an indication of the continuing importance and growth of this field.

2.5.6. The position of the NPL gravimetric hygrometer in this field

It is interesting to note how the NPL gravimetric hygrometer stands in relation to the others in existence. Figure 15 summarises the ranges and uncertainties of these facilities. In some cases the hygrometers have fallen out of use; presumably due to the cost of the relatively time-consuming measurements. In other cases they are designed with ambient humidities only in mind. Only the hygrometers of the US and Polish Standards offer uncertainties which approach the potential of the NPL instrument, though neither of these achieves a comparable measurement range.

For a primary realisation of mixing ratio it is relevant to consider whether the determination has any fundamental basis. The NBS hygrometer and most of the others described above are in a sense only partially gravimetric, with the mass of gas being found indirectly from density and volume or flow. Taking a rigorous approach, a gravimetric standard should genuinely employ weighing as the basis of the measurement. Pragmatically, on the other hand, it could be argued that the best realisation must be the most accurate one, irrespective of the basis of the measurement. In fact, the NPL instrument is able to fulfil both these criteria of accuracy and fundamental basis.

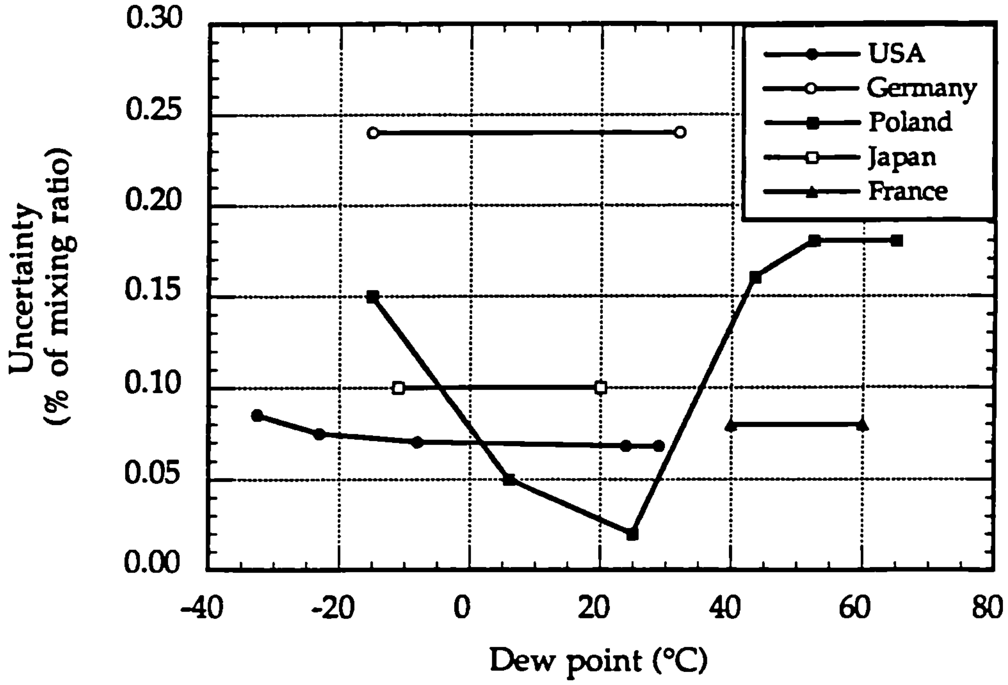

Figure 15 Graph showing the ranges and measurement uncertainties of gravimetric hygrometers at national measurement institutes worldwide, outside the UK

Broadly speaking, weighing is a more accurate technology than volumetric measurement. With care, a mass of 1 kg can be measured in a laboratory to better than 5 parts in 10^6, whereas volumetric measurement carries an uncertainty of at least one part in 10^4 for capacities of a few litres. From this starting point alone, the determination of mass of gas by the NPL method has better potential for accuracy than the NBS approach.

In terms of design, the NPL hygrometer owes a great deal to the Polish standard, as several features developed in the latter were adopted in the NPL instrument in improved form. These include the use of a cold trap, and the actual weighing of the collected gas. The papers by Kostyrko and Kacprzak (1977) and Kostyrko (1979) recorded some useful studies, which showed the way forward for the NPL instrument in several respects of design and measurement procedure. For example, their observation that desiccant is less efficient in flowing air than in still air showed the inadequacy of using a drying train of u-tubes alone. Having elected to use a cold trap, their assessment of its performance highlighted aspects of design which were later incorporated in the NPL instrument, such as the tailoring of the temperature profile to ensure even deposition of ice.

Notwithstanding the similarities to other instruments, the NPL gravimetric hygrometer has a number of unique features. These are: the high efficiency of the water collection process; the subsequent transfer of collected water to a receptacle (desiccant) of low dead mass; weighing in vacuum; and liquefaction of collected dry gas. Each of these offers advantages over previous designs, enhancing the potential performance of the NPL gravimetric hygrometer beyond that of others in existence. In particular, these features allow the unprecedented possibility of gravimetrically determining mixing ratios as low as 0.01 g kg^{-1} with an uncertainty of the order of 1% of value (at the 95 percent confidence level). This accuracy is adequate to provide a reference for hygrometer calibrations in that part of the humidity range where it is more usual to resort to other, less fundamental, methods.

2.6. Starting point for this work

When the instrument was developed and built at Sira, key components were validated as far as was necessary to give reasonable confidence that the system was capable of meeting the specification. (Full demonstration of this, of course, was the work of the validation exercise reported here.) Two pairs of trial measurements at dew points of -30 °C and +10 °C demonstrated a preliminary consistency of performance of respectively 1.6% and 0.4% of result. Following these acceptance tests, the instrument was installed at NPL, and commissioned jointly by Sira and NPL.

Sira supplied a manual containing a full description of the apparatus, and recommended procedures for operation. Also reported in this were results of some detailed acceptance tests of individual components, and forecasts of performance for the cold trap, desiccant, predryer and microbalance. A separate paper was published on the development of the microbalance (Forton and Day, 1986).

Sira produced a closing report suggesting the way forward for the validation of the instrument (Forton et al, 1987). This report contained some new suggestions and calculations, together with a written record of some points established in earlier discussions between Sira and NPL.

The report ventured further predictions of the uncertainties which might be associated with various components, including the balances, the stability in mass of the various collection vessels, gas volumes trapped in the assembly before and after measurements, surface adsorption and desorption of water, leaks, and efficiency of trapping of water vapour.

The report also contained suggestions on how to approach the evaluation of gas trapped in dead-spaces, repeatability of weighings, and reproducibility of values of mass of empty collection vessels. Also covered were proposals for testing leaks, measuring the gain of the microbalance, tests of the effect of handling and thermal cycling of collection vessels, and repeatability of vapour transfer from the cold trap to the desiccant. Guidance was included on how to put in place certain routine procedures such as substitution weighings for gas vessels and corrections for air buoyancy. Certain other actions were proposed which were later found to be unnecessary and were not adopted, e.g. full substitution method for weighings of predryers. Some comments were also made on sampling uncertainties (discussed later in Chapter 5).

Within the closing report and earlier documentation, some aspects were investigated and presented in sufficient detail by Sira that no further work was needed at NPL. These were: efficiency of the cold trap (Section 3.6.1.); theory of the desiccant efficiency (Section 3.6.2.); the quantity of water vapour extracted in the process of evacuating residual carrier gas from the cold trap (Section 3.10.); and some other contributions established to be insignificant.

The report also raised (without answering) a number of questions about transients on start-up and conclusion of measurements, sampling uncertainties, effects of dissolved gases, and about issues to do with the supply of gas from the NPL humidity generator.

The task in hand therefore was to answer these questions, to carry out the measurements for which a need was indicated, and to conceive and execute further measurements to the extent necessary to validate the gravimetric hygrometer's performance against the target specification. A number of other unforseen issues came to light, and were addressed in this process. Although the concepts of many of the experiments were suggested by Sira, the realisations were devised by the author (except in cases where the method was obvious or conventional practice, such as balance evaluation).

Conclusions and numerical results produced by Sira (where they are not superseded by the present work) are cited in the relevant sections in Chapter 3.

2.7. Chapter summary

Chapter 2 has described in some detail the NPL gravimetric hygrometer itself; the key components of the instrument and how they contribute to its overall function.

The field of other gravimetric hygrometers has been reviewed. This shows the NPL instrument to lead the field in respect of its unique design, which allows measurements through a wider range of humidities than any other gravimetric standard.

The background to its conception, design and realisation has been recorded, following through the stage of functional testing, and leading up to a definition of the starting point for the present work.

With this understanding of the task in hand, it is now possible to look in greater detail at the critical aspects of the gravimetric hygrometer's operation. This account proceeds to address the design and execution of experiments and analytical processes to characterise these individual aspects.

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CHAPTER 3

Experimental investigation of components of the gravimetric hygrometer

When water turns ice does it
remember one time it was water?
When ice turns back into water
does it remember it was ice?

Carl Sandburg 1878-1967
Metamorphosis in *Honey and Salt* 1963 (New York: Harcourt, Brace and World)

CHAPTER 3. EXPERIMENTAL INVESTIGATION OF COMPONENTS OF THE GRAVIMETRIC HYGROMETER

3.0. Abstract

This Chapter describes the investigation - both experimental and analytical - carried out to validate the operation of the NPL gravimetric hygrometer.

The philosophy of the investigation is first of all proposed, and this rationale justified in the light of accepted practice, and of the aims and objectives of this project. Reference is made to the ISO *Guide to the expression of uncertainty in measurement*, and criteria are set for the magnitude at which individual uncertainty contributions are considered significant.

The experimental investigation is then described. Each aspect is treated in a self-contained section, with statement of results of measurements or calculations for each variable. Each result is summarised in the form of an estimated standard deviation for the variable. Where relevant, results of previous work on the gravimetric hygrometer are re-evaluated and included. The main aspects covered comprise the weighing processes, the integrity and mass stability of the collection vessels for water and gas, the efficiency of the collection processes, the effects of trapped volumes of gas in the apparatus, leaks and stray water in the vacuum environment, and gas composition.

Finally the experimental results are summarised and considered, and thus where the need has been established for systematic corrections to aspects of the measurement results, these are specified.

3.1. Philosophy of the investigation

A primary standard for any measured quantity cannot, by definition (BS 5233 : 1975), be calibrated against a more authoritative reference for that quantity, although it can and must have traceability to one or more of the SI base units (NPL, 1993). Thus an estimate of the correctness of the standard must be made by some other means than calibration. To achieve the lowest possible level of uncertainty, any sources of systematic error must be recognised, their effects quantified, and compensating corrections applied to the results of measurements.

In any general case, the aim of calibrating an instrument, where this can be done, is to reveal any systematic error that may affect it. However, it must be understood that consistent agreement of results during a calibration does not guarantee that no systematic error is present, or that the uncertainty in subsequent use of the instrument is small. This is because the uncertainties in making and comparing measurements can be much greater than any disagreement that is found between them. Therefore, even if the gravimetric hygrometer could be calibrated, this action could not by itself indicate the uncertainty in using the hygrometer subsequently. In fact uncertainty of measurement can never itself be directly measured; it can only be estimated, using procedures such as those reported in this account.

To ensure recognition and acceptability in the widest circles, the uncertainty analysis must be treated using an approach which reflects agreed good practice. For the present work, agreed practice is perhaps best represented by the terms of the International Organization for Standardization's *Guide to the Expression of Uncertainty in Measurement* (ISO, 1993), also widely (but incorrectly) referred to by the title of its working group, "ISO TAG 4". This document is a recognised authority on the subject of measurement uncertainty at the national standard level across all fields of measurement. The approach of the ISO *Guide* is detailed further on in this Chapter. In addition, acceptability of an uncertainty analysis is enhanced by making the results and the process of analysis transparent to the reader, who can then make a judgement of it. This also makes it possible to re-analyse the data in the future, in the light of further information or changes in agreed practice. In view of all these points, the estimation of the overall uncertainty of the gravimetric hygrometer clearly must be approached by identifying all the individual sources of uncertainty and combining them to find an overall value.

The observed performance of the standard instrument as a whole is also an important indicator. Measurement comparisons of the standard against any suitable stable reference should give results that are consistent with the predictions made about the two instruments separately.

Each of the objectives of this work (as given in Chapter 1, Section 1) is addressed in the investigation as follows:

1. Verification of correct function of the individual aspects of the gravimetric hygrometer's operation, and evaluation of the contribution of each element to the overall uncertainty of measurement

The working of the gravimetric hygrometer can be broken down into small steps and operations which are individually straightforward and can be characterised. This has been undertaken in such a way as to check for systematic errors in each step, and to characterise the uncertainty for each step. The characterisations have been approached either by means of repetitive measurements, which allow an estimate of uncertainty to be made statistically; or by other methods, including single measurements, calculations and simulations, which allow conclusions to be drawn about the maximum bounds of uncertainty for each contribution. While it is commonly held to be most desirable to evaluate uncertainties by statistical means, the ISO *Guide* (ISO, 1993) fully endorses the use of other approaches where common sense dictates this. For example, adequate estimates of uncertainty can often be made from calculations and from experience, in cases where it is impractical to measure certain properties repeatedly.

2. Combination of the individual components of uncertainty to give an estimate of overall uncertainty of measurement for the gravimetric hygrometer, aiming to meet the performance specification required to fulfil the calibration needs of the UK humidity industry

The individual components of uncertainty are combined (in Chapter 4) by methods in line with the ISO *Guide* (ISO, 1993) to provide an overall estimate of uncertainty for the operation of the gravimetric hygrometer. The uncertainty depends on the exact conditions of use, and so the tailoring of measurements (in respect of duration and degree of care) to achieve better or worse values of overall uncertainty is also explored in Chapter 4. This deals with the objective of meeting the specification for the measurements, while not investing unnecessary resources in routinely exceeding the requirements.

3. Consideration of the implications of the relationships between different units of humidity measurement, the documented reference data for water vapour, and the nature of the interface between this primary standard and any system which would be calibrated against it

The calibrations for which the gravimetric hygrometer can most straightforwardly be used are those in terms of mixing ratio. In such cases, the uncertainty of the gravimetric standard together with the conditions of measurement (and the instrument under calibration) would dictate the uncertainty of the calibration. However it is an objective of this work to be able to calibrate (or intercompare values with) the NPL dew point generator, and (in principle) other instruments not directly indicating in units of mixing ratio. In this case, the uncertainty of a calibration depends also on the uncertainty in the conversion between mixing ratio and other humidity units. Therefore the data for the vapour pressure curve of water (and ice) are considered, together with water vapour enhancement factors, in Chapter 5. Most existing data and formulations for the enhancement factor are for measurements in air only. Since, for reasons discussed in Section 3.9, nitrogen gas was mainly used in this work, the formulae for air have been adapted for use with nitrogen. Sampling and possible sampling errors for the gravimetric measurements are also considered in Chapter 5.

4. Demonstration of satisfactory overall performance of the gravimetric hygrometer by carrying out gravimetric measurements of a repeatability consistent with the estimate of uncertainty

The intercomparisons of the NPL humidity generator with the gravimetric hygrometer provide an indication of their performance relative to each other. The exact nature of the information gained depends upon where most reliance is placed - on the gravimetric results, on the generated dew point, or on the reference data which link them. In any case such measurements should agree to within the combined uncertainties of these elements.

3.2. Statistical terms and definitions

The statistical approach adopted for this work is that of the ISO *Guide* (ISO, 1993). The procedures recommended in the ISO document are in keeping with the usual conventions for statistical treatment of data, while also providing useful guidance on how to treat non-statistically gathered data.

The following definitions, taken from the ISO *Guide*, are assumed in the account below. (See earlier Section 1.5 for definitions of uncertainty and accuracy.)

> *standard uncertainty* - uncertainty of the result of a measurement expressed as a standard deviation
>
> *Type A evaluation (of uncertainty)* - method of evaluation of uncertainty by the statistical analysis of series of observations
>
> *Type B evaluation (of uncertainty)* - method of evaluation of uncertainty by means other than the statistical analysis of series of observations
>
> *combined standard uncertainty* - standard uncertainty of the result of a measurement when that result is obtained from the values of a number of other quantities, equal to the positive square root of a sum of terms, the terms being the variances or covariances of these other quantities weighted according to how the measurement result varies with changes in these quantities
>
> *expanded uncertainty* - quantity defining the interval about the result of a measurement that may be expected to encompass a large fraction of the distribution of the values that could reasonably be attributed to the measurand. The fraction may be viewed as the coverage probability or level of confidence of the interval.

coverage factor - numerical factor used as the multiplier of the combined standard uncertainty in order to obtain an expanded uncertainty. A coverage factor, *k*, is typically in the range 2 to 3.

Other important terms, such as "repeatability", "reproducibility", "variance", "standard deviation", "error", "random error", "systematic error", "correction" and "correction factor" follow accepted usage, as defined in the ISO publication *International vocabulary of basic and general terms in metrology* (1993) (normally cited in this account and elsewhere as "VIM").

The evaluations in the remainder of this chapter result in estimates of uncertainty for each component. These results are variously expressed either in terms of standard uncertainty, or in terms of maximum bounds within which all values of the quantity are estimated to lie (ISO, 1993: Section F.2.3.3). All are given in terms of equivalent mass of collected water or gas. Subsequent treatment of these individual component uncertainties is addressed in Chapter 4.

For the individual evaluations, in some cases the resulting standard uncertainty will be characterised by the doubt in *estimating* the quantity (using the standard error of the mean). In others it will be characterised by the *variability* of the quantity (using the estimated standard deviation of the quantity). Where a result (e.g. an estimate of a systematic correction) is the average of a small set of *n* measurements with sample standard deviation $s(x)$, then the standard uncertainty in the evaluation is given by, $s(\bar{x})$, the standard error or standard deviation of the mean, i.e.

$$s(\bar{x}) = \frac{s(x)}{\sqrt{n}} , \tag{12}$$

and this takes the sample size into account. On the other hand, where an uncertainty is due to the random variability of a quantity, then the standard uncertainty is given by an estimate of the population standard deviation, $\sigma(x)$, from the sample standard deviation, using

$$\sigma(x) = \sqrt{\frac{n-1}{n}} \, s(x) . \tag{13}$$

Where any individual result is derived from a small set of measurements, the level of confidence in the estimate depends on the number of measurements. This is more fully discussed in Chapter 6, where degrees of freedom and confidence levels are addressed.

3.3 Practical approach to the investigation

The sections below describe the experimental and analytical work of the validation. Each subsection deals with a single aspect of the investigation in a self-contained account, with a statement of results for that aspect. Where relevant, the results of work carried out by Sira at the acceptance stage of the project are also stated. Analysis of the results is addressed in Chapter 4. Other investigative work is covered in Chapter 5.

It was borne in mind throughout this work that the overall uncertainty expected was (in parts of the range) as low as 0.05% of result, i.e. 5 parts in 10^4 (at a level of confidence of 95%). In aiming for a specified target uncertainty, it was necessary to find criteria for deciding at what level a contributing source of uncertainty would be significant. Below a certain magnitude, contributions would be small enough to be neglected, while there would be an upper level at which a contributing uncertainty would be so significant that methods for reducing it should be sought. Clearly the upper desirable limit for any individual uncertainty source would be somewhat less than the overall limit of 5 parts in 10^{-4}. However at the low end of the measurement range, larger contributions could be tolerated.

When a number of uncertainties are combined in quadrature the largest components dominate the result. (Combination of uncertainties is more fully discussed in Chapter 4.) For example, when two components of the same magnitude are combined, the outcome is

$$\sqrt{(1)^2 + (1)^2} \approx 1.414 \ . \tag{14}$$

A ten percent reduction in one of the components reduces the total by about 5%, i.e.

$$\sqrt{(1)^2 + (0.9)^2} \approx 1.345 \ . \tag{15}$$

This is an illustration of the extent to which it is worthwhile reducing major sources of uncertainty in the measurement.

On the other hand, when an uncertainty is combined with another one-twentieth its size, the overall uncertainty is increased by barely more than 0.1%, i.e.

$$\sqrt{(1)^2 + (0.05)^2} \approx 1.00125 \ . \tag{16}$$

A precision of about 0.1% in the evaluation of overall uncertainty was considered more than adequate for this exercise. Therefore uncertainties contributing less than one-twentieth as much as the largest component were treated as negligible. Since the largest components of uncertainty for the gas mass were expected to have standard deviations of order 20 mg to 50 mg of gas, then contributions with standard deviation smaller than 1 mg could reasonably be ignored. Correspondingly, for water mass, it was expected that the standard deviation for the dominant uncertainty in using the microbalance would be as small as 10 µg for parts of the measuring range. This would render significant all those contributions with standard deviations greater than 0.5 µg. In the case of measurements using the predryer, the lower limit for significance was considered to be a standard deviation of 0.1 mg. Similarly, any known systematic errors requiring corrections to be applied would also be significant at those levels of magnitude.

In many cases it was sought to simplify practical operations where possible. Where generalised estimates could be made, instead of measurements on every occasion of use, this was favoured as long as there were no unacceptable penalties, e.g. in increased uncertainty.

Throughout the following sections, the discussion is confined to those sources of uncertainty intrinsic to the gravimetric hygrometer. Other sources of uncertainty in using the hygrometer which might be termed "sampling uncertainties" are considered in Chapter 5.

3.4. Evaluation of performance of balances

Before any other work was carried out, the balances were assessed, so that they could subsequently be used to carry out tests for other aspects of the validation.

Balance assessment is a routine aspect of using balances. The methods used are well established and documented (NPL, 1954; Prowse, 1985). In the present work, some aspects of balance performance, such as calibration of graticule sensitivity, have been re-assessed regularly on occasions of use. Other aspects were assessed only once, or from time to time in keeping with normal good practice.

The process of evaluation of balances differs according to their principles of operation. The balance for weighing the gas vessels is a two-pan three-knife-edge balance. The predryers are weighed on a single-pan electromagnetic-force-compensation balance. The microbalance is a two-pan type balance with electromagnetic force compensation. The process of evaluation also differs according to conditions of use (for example in air or not).

Care was taken at all times to distinguish between those effects which relate to the performance of the balance itself, and other effects that are features of the artefacts being weighed. The weighing properties of artefacts are considered later below.

The laboratory environment is controlled at a temperature of 20 °C ±2 °C, and laboratory humidity is within the range 35 %rh to 60 %rh.

3.4.1. Complementary weighing

Like any other measurement, a "good" weighing is one which is reproducible and does not suffer from any systematic errors. In this respect, the key factor limiting the performance achieved in any weighing measurement is normally air buoyancy, which has a systematic effect which is of order 0.01% to 0.1% for a weighing of any single object. Therefore for weighing accuracy of better than 1 part in 10^{-4}, the effects of air buoyancy must be taken into account.

In this work the use of complementary weighing, with duplicate vessels as counterpoise weights, eliminates the effects of air buoyancy, to a first approximation. As mentioned in Section 2.4.2, a complementary weighing is one in which the empty vessel and the reference (counterpoise) vessel are first balanced using calibrated weights equivalent to (or exceeding) the mass of gas to be collected. After collection, fewer weights are applied; the difference corresponding to the mass of collected gas. This is analogous to the more widely used procedure of substitution weighing (NPL, 1954). In general, substitution weighing is designed to eliminate errors which can occur if weighings are carried out under varying load (for example errors due to unequal length of arms), and errors which vary with the rest point of the balance arm. In the special case where the counterbalancing item has the same density as the one being weighed, then air buoyancy, as well as the other potential errors, is compensated.

Alternatively a correction may be applied for air buoyancy, by calculating the air density. However in this work, for simplicity, it was sought to make a general allowance for air buoyancy in the estimate of uncertainty, rather than having to evaluate the density of air on every occasion.

For the microbalance, the complication of air buoyancy is avoided altogether by weighing in vacuum.

3.4.2. Equal-arm balance

3.4.2.1. General use of equal-arm balance

The balance used for weighing collected gas is a three-knife-edge, nominally two-pan balance (nominally because in fact there are no pans, only hooks). (Figure 9 shows a photograph of the balance.) The validation therefore followed the conventional practice for two-pan balances. The balance has a capacity of 15 kg, with a resolution of the order of 2 mg.

Normal measurements are made by visual observation of swings of the balance, finding the balance rest point from the turning points of five swings (Prowse, 1985). In the descriptions below, a single weighing is termed to be a single release, determination of rest point, and arrestment of the balance.

In routine use, all the weighings are performed by a complementary method, as described in the previous section.

3.4.2.2. Weights used with the equal-arm balance

Throughout the work described here a set of solid stainless steel weights was used of Class E2 (International Organisation for Legal Metrology Recommendation 20) with denominations 1 kg to 100 mg. These weights were calibrated and their masses were found to lie within 3 parts in 10^6 of the nominal value, for denominations between 1 kg and 10 g, and within 0.03 mg of nominal value for denominations between 5 g and 0.1 g; with an uncertainty of less than those deviations. (Positive and negative deviations from nominal values were almost evenly distributed about zero, with a majority close to zero.) It was therefore possible, for simplicity, to treat the nominal values as true values for these weights. The uncertainty in the mass of collected gas due to this approximation is ±3 mg at worst, for any combination of weights in the range of use.

For the counterbalancing weights an uncalibrated set of Class E2 weights is used.

Because of the symmetry between the pairs of vessels weighed together, changes in air buoyancy would be expected to have no significant effect on weighing results. This was tested experimentally, and is dealt with more fully below, under Section 3.5. However, account must be taken of the air displaced by those weights which are applied for "empty" weighings but not for "full" weighings, when the corresponding mass is in the content of the collection vessel. These stainless steel weights displace 0.125 litre of air per kilogram of gas collected (i.e. about 150 mg per kilogram in normal laboratory conditions, taking air density to be 1.2 g m^{-3} (Giacomo, 1982)). The uncertainty in correcting for this displaced air is that due to the uncertainty in the density of laboratory air. If an average value only of air density is used for this correction, this leads to an uncertainty whose standard deviation corresponds to the standard deviation of the density of air. This mainly depends on barometric pressure, the standard deviation of which varies seasonally between about 13 mbar in winter and 6 mbar in summer (Knott, 1994). Therefore the standard deviation in laboratory air density ranges between approximately 1.3% and 0.6% of value (under laboratory temperature control within 2 °C of 20 °C). Thus the standard uncertainty due to this is 1.3% of value of correction, i.e. 2.1 mg per kilogram of gas, at worst. To improve this uncertainty, the density of the laboratory air could routinely be evaluated from pressure, temperature and humidity measurements. However the benefit is not considered to justify this. The uncertainty in assuming the density of the steel weights to be 8000 kg m^{-3} is included in the calibration uncertainty and does not contribute any further in this context.

3.4.2.3. Balance tests

A variety of tests were conducted with the balance either unloaded or under the loads normally used (i.e. approximately 8 kg or 14.5 kg on both sides).

General inspection and specific tests were employed to confirm satisfactory condition and parallelism of knife edges, and correct functioning of the arrest mechanism.

When viewing the balance scale, it is estimated that fractions of a graduation of the scale can be correctly read to one tenth of a division about 95% of the time. (This is equivalent to 2 mg at maximum sensitivity (maximum load).) However any errors of this type would tend to average out in a series of readings of extrema of swings. For an average of more than one weighing this uncertainty becomes negligibly small (a small fraction of a milligram). Error due to parallax in reading the graticule is confined to within plus or minus one tenth of a division by the use of fiducial marks on the case of the balance. This, too, becomes an insignificantly small uncertainty for a series of readings.

For the purpose of the subsequent validation tests, the rest point of the unloaded balance was found. The balance was tested by repeatedly releasing and arresting the mechanism to find the rest point of the pointer on the graticule, and the stability in the value of this. A typical standard deviation for 10 measurements of the rest point for the unloaded balance was less than 0.5 division (5.2 mg). The stability of rest point under maximum load was also evaluated, and this had a typical standard deviation of 0.3 division (5.4 mg) for an equivalent set of measurements. (See below for a discussion of graticule sensitivity.)

The equality of effective arm length was tested under full load by applying a 100 mg weight first to one side of the balance and then to the other, and observing the symmetry between the two deflections. The arms were found to be equal in length to within 2 parts in 10^6. However, the practice of complementary weighing avoids the need to routinely account for arm length inequality.

The overall repeatability of weighing was found by multiple weighings of a pair of vessels. In between sets of weighings the entire load on one side of the balance was occasionally removed and replaced. This was conducted in a range of ambient pressures and humidities, and at controlled temperatures between 20 °C and 23.5 °C. In this way a set of 10 removals and replacements of the load was found to have a typical standard deviation of 6 mg, (including the effects of normal laboratory environmental variations). From equation (13), this leads to an estimate of standard uncertainty which is also approximately 6 mg.

Before each gravimetric determination, the graticule (graduated scale) of the balance is calibrated for the load in question, to determine the sensitivity reciprocal (the mass required for a deflection of one graticule division). Sensitivity is determined from the deflection produced by applying a 100 mg weight to one side of the balance (repeatedly, if necessary). Typical values for this balance range from approximately 11.5 mg per division (un-loaded) to approximately 18 mg per division (under a load of 14.5 kg on each side). The uncertainty in this aspect is found from a series of measurements having the same uncertainties in resolution, etc. as established for routine weighings, i.e. with a typical standard uncertainty of 6 mg. If the estimate is an average of 4 weighings, the resulting estimate of sensitivity has a standard uncertainty (from equation (12)) of 3 mg per 100 mg. Since the balance rest points being compared (before and after collection) can easily be adjusted to lie within 0.05 g of each other, the graticule reading accounts for at most 50 mg of the overall mass result. Hence the effective standard uncertainty is up to 1.5 mg. The graticule non-linearity was measured to be 0.3 mg division^{-2}, and under the above conditions contributes an uncertainty of ±2 mg at worst.

Errors due to off-centre loading of weights have been estimated to be negligible (since these constitute only a minor fraction of the overall weight suspended on each side of the balance).

In transport across the laboratory, the weight of the gas vessels is normally borne by tensators (constant force springs) suspended from an overhead rail. While the vessels are on the balance, however, they are decoupled from the tensators, and these are hooked onto the balance case (see Figure 7 and Figure 9). The effect of this was tested to verify that the upward force exerted on the balance case did not affect weighings. This was checked by adjusting the tensators to apply a range of forces to the balance case, and performing a weighing for each adjustment. No variation above the normal repeatability could be discerned. Therefore this was judged not to have any significant effect on the weighing results.

The effect of heating due to illumination of the graticule with a lamp was assessed. Within the normal time scale of weighings this was not found to have any significant effect.

All other sources of error were judged to be represented in the overall repeatability of weighing.

3.4.3. Analytical balance

The top-loading analytical balance uses the principle of electromagnetic force compensation. A coil attached under the pan allows vertical movement within the field of a permanent magnet when current is passed. When a load is added to the scale pan, current is applied to restore the pan to the unloaded position as measured by a displacement sensor. This compensating current changes in proportion to the mass on the pan. The balance used in this work has a range of 300 g and a digital display resolution in this range of 1 mg. It also has a "fine" range of 80 g for which the resolution is 0.1 mg. An internal 300 g weight within the balance provides a reference for the electronic range.

This balance is used strictly as a comparator to weigh the predryer used for collection of water against the unused one. As in the case of the equal-arm balance above, this practice eliminates the need to account for some types of error; principally that due to air buoyancy.

The empty mass of each predryer is approximately 126 g, and the mass of water collected within is between about 1 g and 60 g. Therefore only the 80 g floating electronic range with 0.1 mg resolution is normally used. The balance resolution of 0.1 mg in this range leads to an uncertainty of up to 0.05 mg in any single reading.

However this uncertainty is reduced by taking an average of a series of varying readings, and the overall effect is negligibly small.

The repeatability of the weighing process was evaluated and the standard deviation for sets of 10 comparative weighings of the empty predryers was found to be better than 0.1 mg, including balance repeatability and environmental variations. This repeatability was judged to be sufficiently good that routine measurements need only involve of a pair of weighings; subject to the criterion that any variation between the two results of greater than 0.2 mg should be suspected to indicate insufficient thermal stability, or some other anomaly in need of investigation. However, pairs of weighings as described would be repeated at least three times over a short time interval, to confirm the stability in mass of the items being weighed (see Section 3.4.4. below).

Following adjustment of the electronic range, using the integral weight, the balance indication was calibrated in both the full and floating ranges by placing calibrated weights on the scale pan. Errors in indication were found to be less than one digit in the last place of resolution, i.e. less than 0.1 mg in the floating (80 g) range, and less than 1 mg in the coarse (300 g) range. No hysteresis was observed. As long as this performance is sustained, this suggests that the balance performs linearly to better than the threshold for significance of uncertainty contributions. Since the hysteresis and non-linearity are negligibly small, no significant error is caused by using the balance under somewhat differing loads for initial and final sets of weighings.

The integral 300 g weight is made of stainless steel, but the manufacturer (Sartorius) has advised that a buoyancy correction for the weight is incorporated as if for brass. However it was calculated by Sira, and confirmed in this study, that the resulting error is less than the resolution of the balance (0.1 mg) in the range of interest here and can therefore be considered insignificant.

The effect of off-centre placing of the load on the scale pan was considered, but, since the loads in question can easily be placed near-centrally, the effect was judged to be negligible.

There was no evidence of any drift due to self-heating of electronics provided sufficient warm up time had been allowed. (One hour was the time recommended by Sartorius.)

3.4.4. Microbalance

The microbalance is a Sartorius model 4410 symmetrical double beam electronic balance with electromagnetic force compensation. It has a capacity of 25 g and a resolution of 1 μg within a floating electronic range of ±12 mg. In use, the desiccant is approximately counterbalanced by a steel weight (tare). Changes in the mass of the desiccant package are evaluated by offsetting the change approximately, using weights to bring the balance within ±12 mg of the equilibrium rest point. The residual mass difference is then counterbalanced electromagnetically, and the equivalent mass difference indicated on the display electronics. Differences of greater than 12 mg can also be counterbalanced electromagnetically, but the residual values are then displayed with poorer resolution; 10 μg for differences above 12 mg, and 100 μg for differences above 120 mg and up to 1.2 g.

3.4.4.1. Microbalance weights

A set of platinum wire weights is used which, together with a counterpoise weight and the calibrated electronic range of the balance, enables changes of mass of the desiccant to be measured through a range of 1600 mg, with a resolution of 1 μg. The weights (denominations 10 mg to 800 mg) have been calibrated at NPL with an uncertainty of 5 parts in 10^5 or better. This calibration uncertainty contributes negligibly to the overall uncertainty in the mass of water. The values found by calibration differed from the nominal values by up to 95 μg, so the actual values are used in all calculations.

These weights are maintained always under vacuum and are manipulated remotely. Therefore it is unlikely that their masses could change due to contamination or wear, but this possibility needs to be acknowledged. It is impractical to remove the weights on a regular basis for checking, so self-consistent checks of groups of the weights *in situ* have been devised. This involves using the electronic range of the balance to compare (for example) the mass of the 50 mg weight with the mass of the 10 mg and 25 mg weights (totalling 35 mg). Such checks would indicate if any one weight had changed in relation to the others. A matrix of intercomparison measurements can be analysed by least squares fitting to give estimates of variance for the individual weights, as described, for example, by Morris (1992). A specimen printout is shown in Appendix 1, indicating the process of calculation of variances and covariances for the set of weights. Given the resolution of the balance, checks of the form shown in Table V are capable of confirming the stability of the masses of individual weights with a standard uncertainty of no more than 55 μg for the 10 mg weight, no more than 63 mg for the 25 mg weight and between 29 μg and 45 μg at most for the higher denominations. These figures vary because of the need to switch to a more coarse electronic range for the larger denomination weights, and because there is less redundant information for the largest and smallest value weights. This gives a standard uncertainty of at most 5.5 parts in 10^3 in measuring a desiccant weight change of the order of 10 mg, with the relative uncertainty improving where larger denominations or combinations of weights are involved.

Aside from the 10 mg weight, the worst case generally is represented by a change in desiccant mass equivalent to a combination of small denominations (e.g. 185 mg

Table V Matrix for intercomparison of microbalance weights

Weighing No.	Denomination (mg)							Result
	10	25	50	100	200	400	800	
1	0	0	0	0	0	0	1	w_1
2	0	0	0	0	0	1	1	w_2
3	0	0	0	0	1	1	1	w_3
4	0	0	0	1	1	1	1	w_4
5	0	0	1	1	1	1	1	w_5
6	0	1	1	1	1	1	1	w_6
7	1	1	1	1	1	1	1	w_7
8	-1	1	1	1	1	1	1	w_8
9	0	-1	1	1	1	1	1	w_9
10	0	0	-1	1	1	1	1	w_{10}
11	0	0	0	-1	1	1	1	w_{11}
12	0	0	0	0	-1	1	1	w_{12}

made up of 10 + 25 + 50 + 100). The best case is one where the change in desiccant mass is close to the value of a single denomination (e.g. 200 mg). In individual cases, the uncertainty for a particular gravimetric measurement can be found according to the combination of weights used. It is sometimes possible to choose the amount of water collected to avoid "worst-case" combinations. A generalised figure for this uncertainty is much harder to represent, but the graph in Figure 16 shows the envelope of best and worst cases through the measurement range of the microbalance. For any combination of weights, the standard uncertainty is always less than 140 μg.

The self-consistency criterion constitutes a conservative approach to this source of uncertainty, but this procedure is adopted in preference to regular removal of the weights, which would require opening the vacuum system to ambient air and possible contamination.

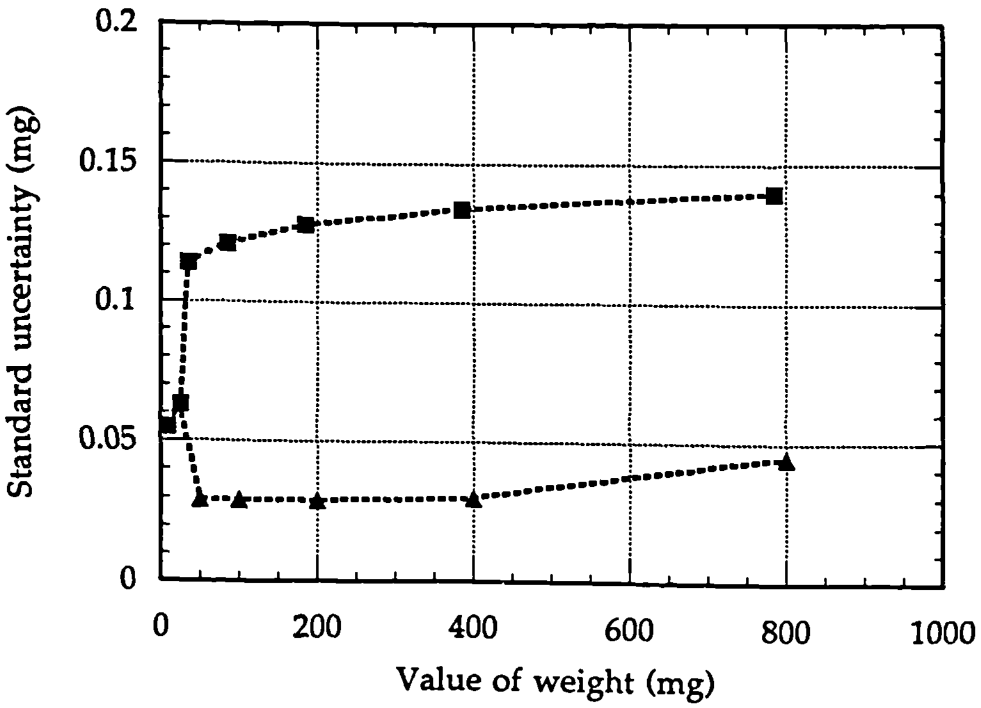


Figure 16 Envelope of standard uncertainties for best (▲) and worst (■) combinations of microbalance weights

3.4.4.2. Microbalance tests

The microbalance is used in vacuum of 0.01 mbar or better. Therefore air buoyancy has no significant effect. (Tests using a dummy load at a range of vacuum pressures between 0.007 mbar and 0.30 mbar have confirmed this.) The effects on the balance of variations in ambient temperature are minimised by its situation inside a temperature controlled enclosure. The display electronics are external to the enclosure but are within a laboratory environment which is controlled at 20 ±2 °C. Consequent temperature effects on the balance were found to be within a limit of ±2 μg, by observing how the microbalance readings changed in phase with periodic variations in room temperature.

The weighing procedure employed is a complementary method, so load-dependent factors and arm inequality do not affect the accuracy of weighings. The exception to this is the sensitivity of the electronic range of the balance, which may depend on load to some degree. The sensitivity (gain of the electronics) is determined in the course of each weighing. The value of gain, defined as the ratio of the actual mass to the value displayed, is normally found to be in the approximate range 1.0011 to 1.0018. Any weighing where the value of gain is found to be outside this range is examined for arithmetical errors, or other anomalies. A worked example of evaluation of the gain, and correction of results accordingly, is shown in Appendix 2.

The overall repeatability of the performance of the balance was evaluated from a series of weighings of a stable dummy load, consisting of a solid aluminium cylinder of mass approximately 25 g. On each occasion, the connecting gate valve was opened, the load was manipulated from its chamber on to the balance and later off again, and returned to the original position with the valve finally being closed. This simulates the routine weighing process. For a set of 7 weighings, the results of this process were found to have a standard deviation of 7 μg. Attempts were made to improve the repeatability by varying the handling procedure, but with no success. However even at the lower limit of operation, at a mixing ratio of 0.01 g kg^{-1}, this standard deviation is equivalent to only 0.1% of the total mass of water collected, which is acceptable at this extreme of the measurement range.

3.5. Evaluation of performance of collection vessels

The pair of predryer vessels and both pairs of gas collection vessels were subjected to tests to evaluate the uncertainties that might arise in their use. The aim was to ensure that any observed change in vessel mass could be attributed to collected gas or water, with no erroneous mass changes from other causes. However, anomalous changes were in fact found to occur in the masses of both types of vessel. Methods were devised to eliminate or account for these anomalous mass changes, as described in the sections below.

3.5.1. Gas collection vessels - general tests

Each of the following tests was performed on both large and small vessels.

3.5.1.1. Volume difference between gas collection vessels

The vessels were assessed to determine any difference in volume between the pairs while empty, or with one vessel partly full. Any such volume difference between a pair of vessels would require air buoyancy effects to be considered whenever the ambient air density changed between the occasions of full and empty weighings. Where relevant during the tests, the mass of air displaced by the weights applied was taken into account. Laboratory air was taken to have an average density of 1.200 $kg.m^{-3}$ (Giacomo, 1982).

The vessels were weighed in pairs, with valves closed, under a range of laboratory ambient conditions to ascertain any volume difference which might be revealed by changes in ambient air density. However, no correlation was found between the variations in graticule reading and changes in ambient air density (nor any correlation with temperature, pressure or humidity individually.) This was concluded both for measurements of empty pairs, and for measurements with one vessel partly full. This implied that the effects of volume difference were negligible and would be included in general figures for repeatability of weighing for the vessels.

However, as an additional check, dimensional measurements of the vessels while full and empty were made, using a micrometer and a vernier calliper. The vessels appeared to expand slightly while under pressure. For example, the increase in diameter of a high-humidity vessel after collection of 254 g of gas was found from sets of 8 measurements to be 0.06 mm in 68 mm (0.09%) for the lower part, and 0.16 mm in 102 mm (0.16%) for the upper part. The sets of measurements had standard deviations of approximately 0.04 mm and 0.2 mm for the respective parts of the vessel. This increase in diameter was associated with an internal pressure, *p*, of about 85 bar, which was calculated approximately from

$$p = \frac{nkT}{V} \tag{17}$$

using knowledge of the internal volume, *V*, temperature, *T*, and number of moles, *n*, of nitrogen (deduced from its mass). The simplifying approximation was made that the expansion could be treated as uniform, averaging 0.13% in each dimension per 254 g of collected gas. From this it could be deduced for the small vessels that an extra 98 mg of laboratory air at a density of 1.2 kg m^{-3} would be displaced by the full cylinder for every kilogram of gas collected (to a maximum of 0.4 kg for these vessels). Therefore a corresponding correction should be subtracted for the measured value of gas mass. The large (low-humidity) vessels develop only about 81 bar of internal pressure per kilogram of collected gas. For these vessels, the equivalent correction was found to be less, at 68 mg per kilogram of gas collected.

The degree of strain observed under these pressures is well within the elastic regime for this material, and is quite safe. In any case, to fulfil safety requirements, the vessels were also tested to a pressure of 210 bar.

The correction above accounts for the total upthrust due to the buoyancy of displaced air at an average density of 1.2 kg.m^{-3}. Variations in air density would lead to changes in apparent mass with a standard deviation of up to 1.3% of the value of the correction. For instance, after collection of 1 kg of gas in the large vessel, the variation in air density would correspond to a variation in mass with standard deviation of only 0.9 mg. Therefore it is not surprising that this effect was not detected experimentally. It can be concluded that it is sufficient in this case simply to correct for an average air density, and that the uncertainty due to variations in air density can be neglected. The uncertainty in this correction, then, is mainly that due to the dimensional measurements. The standard deviation of the measurements leads to a standard error of the mean for the dimensional change of about 0.44 of value, i.e. a standard uncertainty of 44 mg per kilogram of gas for the small vessel and 34 mg per kilogram for the large one.

In contrast to the expansion of the vessels under pressure, linear thermal expansion of Duralumin is of the order of 1 part in 10^5 per °C, and has no significant effect in this context.

3.5.1.2. Long-term stability of masses of gas collection vessels

The vessels were also weighed with valves open, against calibrated custom-made weights, to find their masses exclusive of contents. The aim of this was to enable monitoring of the long-term stability of these values. Any change might indicate corrosion, accumulation of dirt, or some other problem. It was found that these weighings were distinctly sensitive to variations in air density, since the stainless steel weights were only about one third of the volume of the aluminium vessels they counterbalanced. In the end, careful weighing against the reference vessels was considered a more reliable method of routine monitoring, while the special weights could be retained as a last resort for resolving ambiguities. To date this method has not indicated any significant long-term drift in the masses of the vessels.

3.5.1.3. Stability of gas vessel masses under handling and thermal cycling

The effects of handling were tested by subjecting the vessels to simulated conditions of use. The full procedure for measurement was executed, but without the collection of any gas. The aim of this was to confirm that the handling and the thermal cycling normally experienced by the vessels did not in themselves lead to any mass changes. Such changes could in principle arise from contamination or surface adsorption on the exterior of the vessels, or from wear at the screw thread at the connection to the flow path.

These tests involved initial weighing, sealing in the cryostat, connecting the vessel valve (closed throughout) to the main pipework, cooling the vessel to 68 K, and then reversal of all these steps. At the end of this process, the vessel was re-weighed. Small increases in mass (or occasionally decreases) were observed. The average change in mass of the small vessels due to this procedure, in the absence of any collection of gas, was an increase of 0.7 mg, with a standard deviation of 6 mg for four measurements. For the large vessels, the average increase was 15 mg, with a standard deviation of 9 mg, for four measurements. There was no evidence to suggest that these increases were cumulative, i.e. the total gain in mass after four cycles was not 4 × 15 mg. A possible explanation of this effect would be the temporary adsorption of water onto the external surface, or slight accumulation of liquid water or other surface contamination in crevices. However, care was always taken to allow the vessels to dry before weighing, and to keep the vessels clean and dust-free, handling them only with clean gloves.

To account for this effect corrections of 0.7 mg and 15 mg are subtracted from the respective final masses of the small and large vessels.

3.5.2. Gas collection vessels - anomalous changes in mass

Ideally, a rigorous weighing comparison of the reference vessel against the collection vessel would involve three weighings. The collection vessel would be initially empty with excess weights applied, then full with weights removed corresponding to the gas collected, and finally empty for a repeat weighing. The repetition of the empty weighing would allow correction of any drift in the measurements with time. This was the procedure adopted at the beginning of this work, as recommended by Sira. However this practice was eventually ruled out because of short-term anomalous gains in mass of both the large and small vessels, as described below.

In the course of early measurements it was observed that, in normal use, the two empty weighings - before and after - did not agree. For each collection cycle, the empty mass of a vessel appeared up to 0.5 g greater after a measurement run than before it. The extra mass was always found to disappear later. Variations in external ambient pressure and temperature were easily discounted as a possible cause. Other causes external to the vessels were also considered unlikely, since the effects had not appeared in the cycling tests described in 3.4.2.3. above. It was clearly essential to resolve this problem, as the disparity was in some cases equal to, or greater than, the target overall uncertainty.

Routinely, the initial empty readings were taken with the vessel closed; the interior having been equilibrated with a known value of atmospheric pressure, by opening and closing the valve at room temperature. Following the full weighings, the vessel was exhausted to atmosphere over a period of 20 to 80 minutes, to dispose of the collected gas. (The slow venting was recommended at the commissioning stage so as to avoid thermal shock to the vessels, since cooling occurs on expansion of the escaping gas.) Immediately after venting, the valves were closed so as to conserve the composition of the gas within, which was exclusively dry nitrogen. (Knowledge of this was intended to enable correction of results to account for the trapped gas, if necessary. If different amounts of gas - equilibrated at different ambient pressures - were enclosed during initial and final "empty" weighings, then a correction would be applied.) The vessel would then be allowed to equilibrate in temperature before weighing. At this stage, the mass would regularly be found to be a significant fraction of a gram greater than on initial weighing. Only on venting the vessel prior to the next measurement run (perhaps weeks later) would the mass return to near the original value.

It was realised that the mass change might be due to the cooling of the vessel by the expanding gas: at the conclusion of venting, the vessel would be relatively cold and therefore the gas inside would also be colder - and therefore denser - than gas at ambient pressure and temperature. This possible explanation was investigated experimentally for a small vessel, as follows.

The full vessel was vented normally, with thermocouples in contact with the surface. These indicated the temperatures reached during and after venting. The changes in the vessel temperature during this process are shown in Figure 17. After venting for 25 minutes, the vessel reached ambient pressure, and was closed. At this stage the surface temperature was about 5 °C below room temperature. Weighing was considered unreliable while the vessel was cold, but the expected mass of excess gas was calculated to be approximately 50 mg - not enough to explain the disparity.

The vessel was then equilibrated for over 2 hours to within 0.4 °C of room temperature, and was then opened and closed, with a small but audible release of gas (the 50 mg). It was then weighed and still found to be 0.8 g heavier than the empty weight before filling.

The phenomenon was eventually explained through a second experiment. A full vessel was vented as in the initial experiment, and the temperature monitored. This time, it was subsequently vented 12 times over a period of 17 days, and was weighed on each occasion. A graph of the change in mass with elapsed time is shown in Figure 18. From the exponential decay in the mass, it was clear that a steady value would not be reached within any reasonable time-span. It was concluded that the use of "final zero" weighing values would have to be abandoned.

The cause of this phenomenon was concluded to be some kind of physical adsorption or absorption of gas onto or into the inner surface while the vessels were under internal pressures of up to 85 atmospheres. Surface-adsorbed quasi-liquids many monolayers thick can form in equilibrium with gases at high pressures (Gregg and Sing, 1982). The internal surface of the vessel so covered could in principle account for the mass change observed in this case. However a more likely mechanism would be porous adsorption into imperfections in the internal surface,

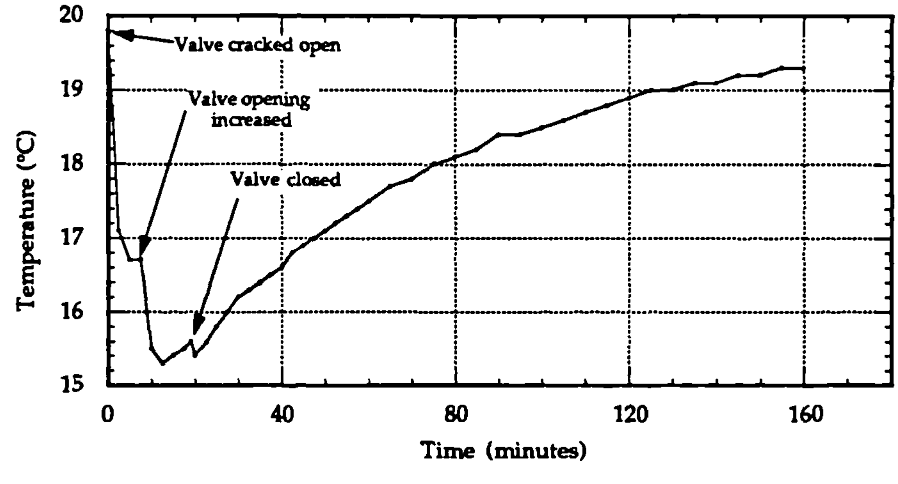


Figure 17 Graph of surface temperature of gas collection vessel during and after venting of enclosed gas to atmosphere

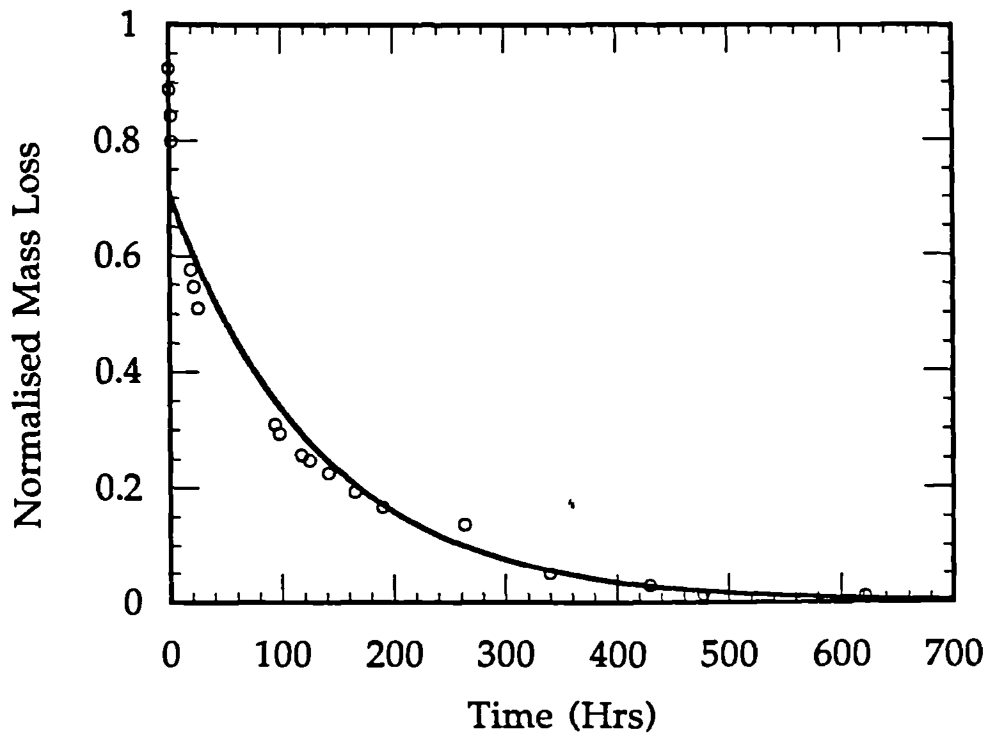


Figure 18 Change in mass of nominally empty gas collection vessel with time

which was not manufactured with any special quality of finish. Gas under pressure could permeate deep into such crevices. This might not immediately be released on venting the bulk of the gas to ambient pressure. However over a longer timescale (days or weeks) the adsorbed gas would be able to diffuse out of these sites inside the sealed vessel, at near-atmospheric pressure. Opening the valve on a later occasion would then allow the escape of this residual gas, to whatever extent it had desorbed.

From this understanding it was clear that only the initial empty mass value should be used in calculations. Both initial and final measurements of empty mass had originally been seen as necessary in the operating procedure devised by Sira. However the penalty in uncertainty in omitting the final empty measurement is relatively small: it simply requires the inclusion of the uncertainties already established in the thermal cycling tests. In fact, the revised approach also dispenses with the need to know what mass or species of gas was in the vessel at the start of a gravimetric measurement. The mass of gas collected would simply correspond to the increase in mass of the vessel, irrespective of what else it contained initially.

The possibility of undesirable losses in mass, in the form of leaks, was also carefully investigated. Leak testing was effectively conducted by observing the mass of full vessels over periods of weeks or months to confirm that they did not become lighter. This was performed on a number of occasions. The worst leak found was detected as a loss of 1.5 mg per day. Over the usual timescale between collection and weighing, this is estimated to lead to a loss in mass with a 90% probability of being between 0 and 10 mg, with no likelihood of gas leaking *into* the full vessel. This figure might be expected to slowly deteriorate with wear of the valves. Therefore testing is repeated from time to time.

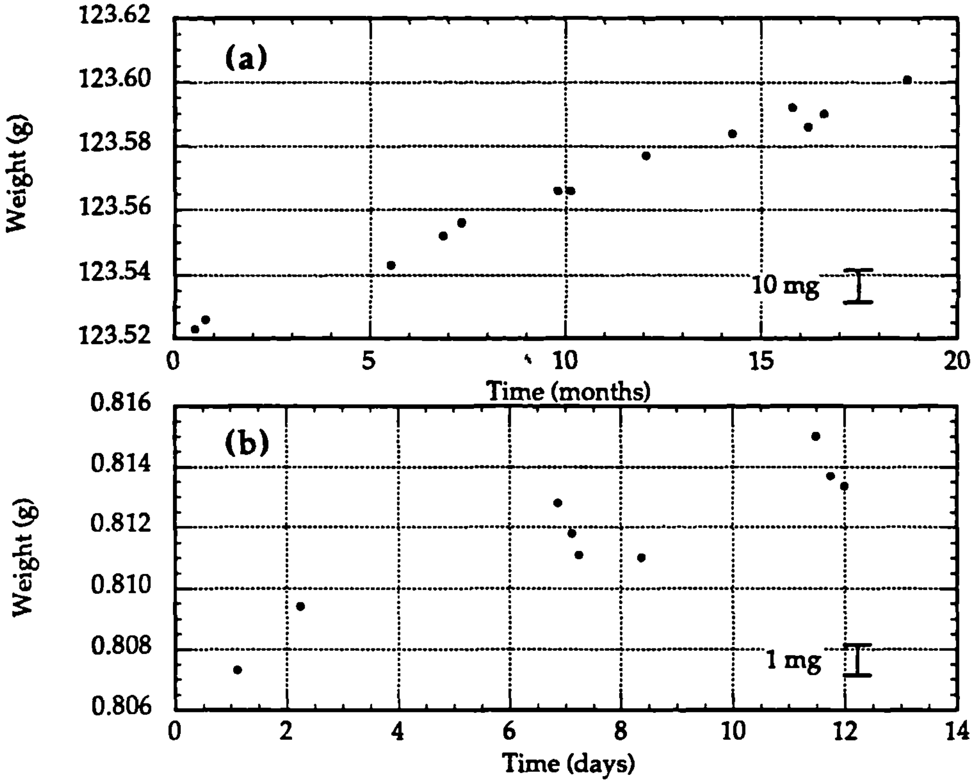
3.5.3. Predryer vessels - overview of tests

The predryers were subjected to tests analogous to those carried out on the gas collection vessels. Considered below are: the volume difference between the pair of vessels; freedom from leaks (and leak-tight connection to the main apparatus); internal volume and gas trapped in operation; efficiency in trapping water vapour; and the extent of changes in mass due to handling and thermal cycling. These are discussed in Section 3.5.5. However, during early measurements, all subtle effects were masked by significant mass instability, the nature and solution of which are described in the following section.

3.5.4. Predryer vessels - anomalous changes in mass

The masses of both predryers were initially found to be unstable; varying up and down through a range of milligrams on a daily or weekly timescale. Superimposed on this variation was a slow continuous gain in mass of about 1 mg per week for the main predryer, and slightly less for the reference one. The long term drift is shown in Figure 19 (a) for the reference predryer. (Although the drift was more pronounced in the main predryer, the general trend was harder to illustrate, since the overall mass was changed after each gravimetric measurement, i.e. every few weeks or months.) Figure 19 (b) shows a graph of typical short-term variations during a 12-day period. These variations could not be directly accounted for by changes in air buoyancy, and were difficult to explain, as they seemed to be connected with changes in ambient temperature and pressure, but in a complex way. The resulting mass instability was sufficient to lead to doubt of up to 10 mg, between initial and final weighings. In the worst case, for measurements where

Before modification



After modification

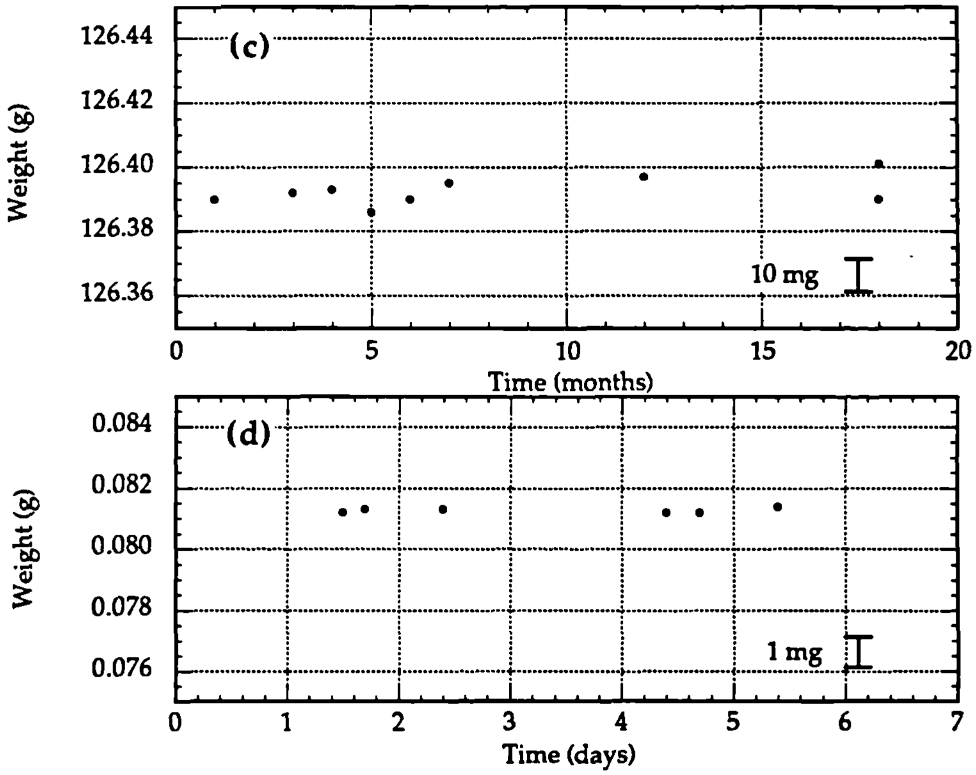


Figure 19 Mass of pre-dryers: (a) initial typical day-to-day variations (b) initial long term drift (c) day-to-day stability after modification (d) long term stability after modification

only about 1 g of water was collected, results would be unsure by up to 1% of value. This would clearly be unacceptable in view of the target specification.
As an interim solution, the rate of drift was estimated, and a correction applied to the results of measurements. This correction itself was estimated to have a lesser standard uncertainty of about 2 mg. However, as long as the effect remained unexplained, measurement results could not be viewed with the confidence that this uncertainty might imply. Further tests were undertaken to explore and resolve the problem.

The investigation involved a large number of comparative weighings of the two vessels, over a long time-span which was interspersed with several gravimetric runs. Leak testing was also conducted, and leaks at the valve seals of up to 1×10^{-3} mbar l s^{-1} were found. However, since the predryer would be at - or slightly above - ambient pressure, it did not seem that simple movement of gas across such leaks could explain an *increase* in mass. Numerous tests were also conducted on the molecular sieve to explore how its sorptive action might contribute to the effects observed.

Eventually it was concluded that the vessels were "breathing" with changes in ambient pressure. When ambient pressure rose, gas would leak into the vessels: when ambient pressure fell, gas would leak out. The slight over-pressure after any gravimetric collection would also gradually equalise with ambient pressure through this leak. This explained the short-term fluctuations in mass. Additionally, the interchange of gas between the interior and the surroundings had allowed the molecular sieve to gradually absorb atmospheric water vapour: the air would have been moist when breathed in, and dry when breathed out. This accounted for the slow background gain in mass.

Modifications were made to the sprung ball valves, by substituting the balls with ones of better surface finish, and by using firmer springs. These measures improved the leak-tightness of the valves, and reduced any mass variations to an imperceptible level. The improved long-term stability is shown in Figure 19 (c) and the day-to-day stability in Figure 19 (d). The performance reported below was evaluated after these improvements.

3.5.5. Predryer vessels - general tests

A number of tests analogous to those in Section 3.4.2. above were performed on the predryers, as described below.

3.5.5.1. Volume difference between predryers

The external volume difference between the pair of vessels was estimated by dimensional measurement, and by weighings in varying ambient conditions to check for any signs of variable upthrust due to air buoyancy on the vessels. No significant variation was found.

The predryer vessels experience no large internal pressures and therefore no corresponding expansion when full. From the argument developed for the gas vessels in Section 3.3.6.1. it can be seen that, in general, where vessels change in volume between empty and full conditions, a correction to the results should be made. However, for a constant volume difference between vessels, while a correction might ideally be applied, the error is not significant provided it is small enough not to be revealed by weighing in a range of air densities. This was the case for the predryers. Therefore, any uncertainty due to volume difference is effectively included in the overall stability of the predryer masses relative to each other. Therefore no separate allowance is made for difference in the effect of air buoyancy according to volume difference.

3.5.5.2. Stability of predryer masses under handling and thermal cycling

The effects of handling and thermal cycling in the course of normal use were tested. Analogously to the tests carried out on the gas vessels, this required simulation of the gravimetric measurement process, but without any collection of water. This involved weighing the main predryer relative to the reference one, immersing it in the temperature-controlled bath at 1 °C for some hours, removal, rinsing, drying and equilibration, and finally re-weighing. The resulting changes in mass were too small to be discerned within the general repeatability of weighings. Therefore the standard uncertainty due to this is estimated to be less than 0.1 mg.

3.5.5.3. Other tests

The predryers were tested for leaks. It was not appropriate to test the valves using a conventional type of vacuum leak tester, as the sprung mechanism could not be exposed to vacuum without increasing or reducing the closing force, hence providing an artificially good or bad seal. Instead, the vessels were flushed with helium gas, the valves were allowed to close, and leaks were observed using a "sniffer"-type thermal conductivity based sensor. The limit of detection of these measurements was approximately 1×10^{-4} mbar l s^{-1}. At this resolution, the bodies of the vessels were found to be free of leaks and the valves to have leaks of less than 1×10^{-4} mbar l s^{-1}. Bearing in mind the high diffusivity of helium molecules relative to those of oxygen, nitrogen or water, the figures above would be expected to be over-estimates of the leak rates for the gases normally involved.

The seal on connection of the predryer to the pipework of the main gravimetric system was also tested from time to time and never found to leak by more than 2×10^{-4} mbar l s^{-1}.

The efficiency of the water trapping function of the gravimetric system is clearly an important parameter to characterise. However the efficiency of the predryer part of the process is not critical, as any residual water vapour not absorbed at the predryer stage is recovered by the cold trap. Therefore predryer efficiency has no bearing on the overall uncertainty of measurement. However the efficiency can be deduced during any gravimetric measurement by noting what fraction of the total water is collected in the cold trap. This enables monitoring of correct function of the predryer. Typically the predryer leaves a residual moisture content in the gas of about 50 mg of water per kilogram of gas.

In common with the gas vessels, only the initial empty predryer mass and the mass when full were used in calculations. The final empty mass was not reproducible after regeneration of the molecular sieve (and this was never presumed in the planned method of use for the predryers). However, unlike the gas vessels, the entire contents of the predryer used must be taken into account in the calculation of the collected water. This requires knowledge about the gas occupying that space not filled by collected (liquid) water or by molecular sieve. The effective volume of this space was originally estimated by Sira during manufacture. After the valves were modified, and the molecular sieve renewed with a fresh charge, the effective internal volumes of both predryers were re-estimated at NPL. These volumes, for the collection and reference predryers respectively, were found to be 0.198 litre and 0.199 litre. The maximum bounds of uncertainty for each of these figures is estimated to be ±0.015 litre. The evaluation of the systematic correction for gas trapped in the predryer is discussed fully in Section 3.7. below, where trapped volumes of gas are considered generally.

In addition to the need to account for gas trapped in the predryers, it is important to be sure that what is adsorbed in the molecular sieve within the predryer is only water, and not also a proportion of carrier gas. This would lead to an over-estimate of mixing ratio. The properties of the grade of molecular sieve used (1/16 inch pellets of Grade 3A) were investigated. As advised by the manufacturer (B.D.H. Limited, 1986; Clayson, 1989), adsorption of species other than water is not significant for this grade of molecular sieve, except for helium and hydrogen. In this case these are only present in trace amounts. (Composition of gas is discussed in Section 3.8 below, and in Chapter 5.) The sorptive properties of the molecular sieve were experimentally tested in situ within the main predryer, by connecting it to a dial pressure gauge (containing ambient air), using a clamp similar to that used in the main hygrometer. The pressure was observed over a period of six weeks and there was no evidence of suction to suggest that the molecular sieve was absorbing either nitrogen or oxygen. On subsequent weighing, the predryer was in fact found to have *lost* 1 mg in mass; which might easily be explained by the action of opening and closing the valves (even in an enclosed air space). Accordingly, adsorption of these gas species is not thought to contribute to the uncertainty in the mass of water collected. However the grade of nitrogen used (Air Products *Zero Grade*) was reported by the manufacturer to contain up to 5.0 parts per million by volume (ppm_V) of helium, and up to 0.5 ppm_V of hydrogen. Since these molecules would be small enough to be adsorbed by the molecular sieve, their masses would add to the predryer mass. However they jointly would contribute at most 0.9 mg to the value of predryer mass, per kilogramme of gas passing through. The absence of this from the measured mass of gas can be neglected, but it should be accounted for in the mass of water, as a correction of 0.45 mg to be subtracted from the measured mass with an uncertainty of ±0.45 mg at most.

3.6. Water trapping efficiency

The efficiencies of water-trapping components are considered below. The predryer efficiency is not considered here, as this is not critical; the predryer always being backed up by use of the cold trap.

3.6.1. Cold trap

The efficiency of the cold trap was evaluated in detail by Sira during acceptance tests of the apparatus. Using a specially constructed condensation dew-point hygrometer, they measured the residual moisture levels in gas which had passed through the cold trap. After painstaking experimentation, this exhaust gas was found to have a dew point below -90 °C, for a flow rate of 0.8 litres per minute, and some 10 °C lower for a flow rate of 0.4 litres per minute. Subsequent analysis of the effect was carried out by NPL.

At the low mixing ratios concerned, values of mixing ratio are proportional to saturation vapour pressure, from equation (10) in Chapter 1. Therefore mixing ratio, like saturation vapour pressure, varies logarithmically with temperature in this range. Considering this, and the fact that temperature of the gas passing through the cold trap would be proportional to flow rate, the results of the observations are appropriately shown in terms of mixing ratio on a logarithmic scale in the graph in Figure 20. For the worst case measured, i.e. the faster flow rate of 0.8 litres per minute, the mixing ratio of the exhaust gas is approximately 6×10^{-5} g kg^{-1}. This means that in a gravimetric measurement where 1 kg of gas was collected at this flow rate, 60 μg of water would be in the gas vessel, instead of in the cold trap. As an error in the gas mass, this is insignificant and can safely be ignored. However in terms of the mass of water, at the lower limit of operation of the gravimetric hygrometer, near 0.01 g kg^{-1}, this constitutes over 0.5% of result. Therefore a flow-dependent correction is applied whose value is estimated from a logarithmic interpolation between the experimental values on a curve whose formula is

$$r' = \ln(1.35 \times 10^{-4} f + 0.999952) \tag{18}$$

where r' is the exhaust gas mixing ratio, and f is the flow rate.

This correction to results of gravimetric measurements is most simply made by adding the relevant value of exhaust mixing ratio from equation (18) to the overall value of mixing ratio. There is an uncertainty in this correction due to a number of factors, including the difficulty of the original dew-point measurements, the availability of only two data points, and the assumptions made in the interpolation. The bounds of uncertainty are therefore estimated to lie at plus or minus the value of the correction applied. Dependence of this uncertainty on the humidity of the gas entering the cold trap is estimated to be minimal.

3.6.2. Desiccant

The desiccant is the eventual receptacle for the water collected in the cold trap, and the accuracy of determining the mass of water relies on the desiccant's performance. Therefore it is important to confirm that changes in mass of the desiccant relate to the collection of water, and not to other effects.

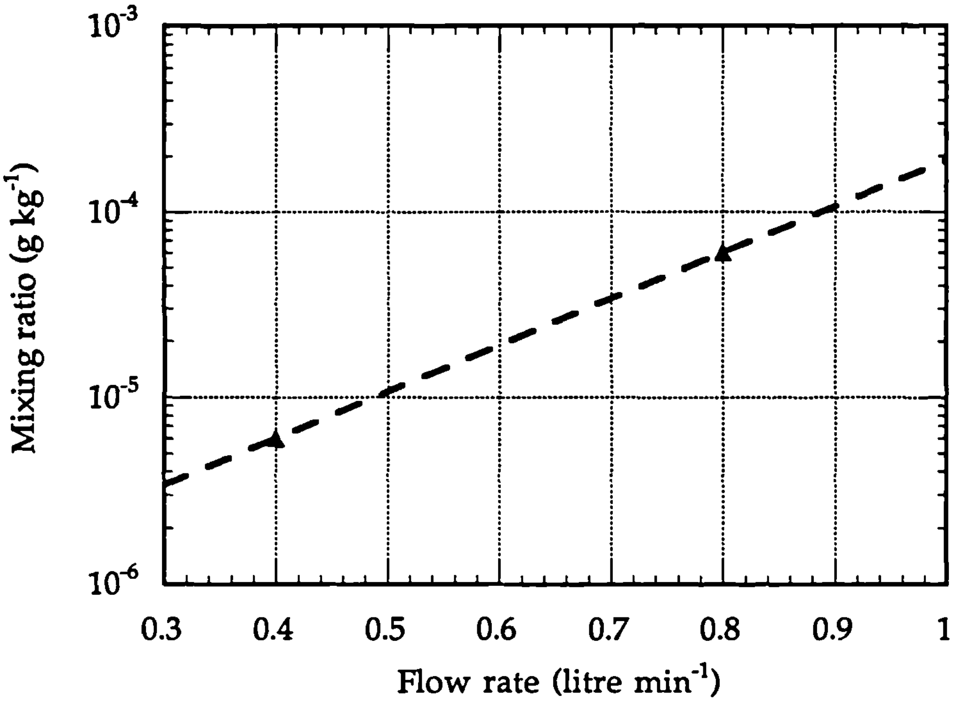


Figure 20 Graph showing estimated moisture content of exhaust gas from cold trap as a function of flow rate.

The desiccant-microbalance system as a whole was tested for weighing repeatability, since the mass of the desiccant, by its reactive nature, might be unstable. However the repeatability of weighings was not found to be significantly different from the repeatability measured using an inert (aluminium) dummy load. On isolated occasions, the lack of repeatability appeared to take the form of drift in the mass of desiccant. The possibility of systematic influences was considered but none was identified. In routine measurements, if drift is suspected, extra weighings are carried out, and a larger uncertainty assigned if necessary.

The desiccant is re-used successively until the total mass collected exceeds the range of the balance, or until the efficiency of the desiccant deteriorates - whichever is sooner. The desiccant efficiency of magnesium perchlorate has been documented (Besley and Bottomley, 1969), and this literature researched by Sira. In equilibrium, at 30 °C, a mixture of anhydrous material with the first hydrate ($Mg(ClO_4)_2.2(H_2O)$) maintains a water vapour pressure of 1.2×10^{-4} mbar. A mixture of the first and second hydrates ($Mg(ClO_4)_2.2(H_2O)$ and $Mg(ClO_4)_2.4(H_2O)$) maintains 4.2×10^{-2} mbar. Therefore, as long as the material is not exposed to partial pressures of water vapour above 4.2×10^{-2} mbar, then only the first hydrate is formed and maximum hygroscopicity is maintained. Suitable conditions are ensured by driving off the water slowly from the cold trap, and monitoring the pressure during the process. Provided the residual pressures in the initial and final conditions of the measurement are both within the regime of the first hydrate, no correction need be made for variations in the small amount of water vapour in the environment surrounding the desiccant. The total water enclosed within this volume of 7 litres at 1×10^{-4} mbar totals approximately 1 μg at worst, and the variability in this leads to an uncertainty of less than that amount.

3.6.3. Transfer of water from cold trap to desiccant

As well as considering the efficiencies of the cold trap and the desiccant, it is relevant to consider the effectiveness of the transfer of water vapour from one to the other.

In the course of normal gravimetric measurements, the cold trap is prepared by baking at approximately 110 °C under vacuum. The assembly is then cooled for the collection of water. After conclusion of the collection, and evacuation of the trapped carrier gas, the cold trap is slowly heated, eventually reaching the original bake-out temperature of 110 °C. The initial and final conditions of the whole assembly are therefore the same. Consequently, while there may be moisture adsorbed on surfaces throughout the vacuum system, the amount present at the beginning of a measurement is expected to be the same as that at the end. Therefore there should be no net contribution to the uncertainty in the mass of water on the desiccant from this source.

To test this, the reproducibility between the initial and final conditions of the cold trap and desiccant system was assessed experimentally. In tests analogous to those carried out on the gas vessels and predryers, measurement cycles were simulated for the cold trap system without the collection of any gas or water. This involved the full process of baking in vacuum, cooling with liquid nitrogen, dwelling at this temperature, and heating gradually to drive any water vapour present onto the desiccant. The mass of the desiccant was measured before and after this simulation. Repetition of this test five times gave an average gain in mass of 25 μg, with a standard deviation in this value of 34 μg. By any statistical test of significance (e.g. a *t*-test) this result is not significantly different from zero, and further measurements would be more than likely to show the true value to be smaller. However 25 μg remains the best estimate without further work, and therefore a correction of 25 μg should be subtracted from the mass of water collected. A genuine systematic error of this size could conceivably be the result of some inconsistency between the initial and final condition of the vacuum environment.

3.7. Gas trapped in dead spaces

At the end of each measurement, a quantity of the gas being measured is unavoidably trapped in various parts of the pipework. In general, since the water from this gas has been collected, so the mass of the gas itself must correspondingly be accounted for in the overall gas mass figure. The evaluation of the mass of gas trapped in various parts of the apparatus is described below.

Each of these corrections due to trapped gas depends in principle on the pressure of the gas being supplied. For this work, the pressure, is determined by the pressure controller in the humidity generator. This pressure is always controlled to within 0.1% of a nominal value of 105.0 kPa and measured with an uncertainty of 0.02% This contributes an uncertainty of just over 0.1% to the values of mass of trapped gas, and has been included in the values below. Were other operating conditions to be employed for any reason, then the values of these corrections should be reconsidered.

3.7.1. Cold trap

The gas trapped in the cold trap is responsible for one of the largest systematic corrections required in the operation of the gravimetric hygrometer. Trapping of a significant quantity of gas arises here because the cold trap is under vacuum at the start of the collection, and is full of gas at the pressure supplied by the humidity generator at the end of the collection. This gas is then pumped away before the transfer of the water to the desiccant. (This conserves the vacuum environment around the desiccant and microbalance, and also removes any traces of oxygen which could in principle react with the cold trap surface while hot.) The water corresponding to the evacuated gas is retained in the cold trap. Therefore the gas removed must be taken into account in the overall calculation.

An estimate of the mass of this gas based on temperature, pressure and volume is not straightforward, because of the temperature gradient of some 160 °C from top to bottom of the cold trap. The cold trap volume also cannot conveniently be measured directly. Preliminary calculations by Sira gave a first approximation for the correction required, of 2.3 g ±0.5 g (at the 95% confidence level). Therefore experiments were carried out to estimate this correction more precisely, and with a smaller uncertainty.

Figure 21 shows the experimental arrangement used to evaluate the quantity of gas trapped. A representative quantity of gas was trapped in the cold trap by simulating the normal final stages of a gravimetric collection. This was accomplished by flushing the (cooled) cold trap briefly with air of low moisture content (with a dew point of -40 °C) and then closing the relevant valves to terminate the flow. The trapped gas was brought to a uniform temperature (thereby reaching a pressure of approximately 1.6 bar) and then expanded into a previously evacuated vessel of known volume of approximately 2.1 litres. The pressure of the gas was measured beforehand and afterwards. The known volume was then isolated by means of a valve, and evacuated again. The expansion and measurement of the remaining gas was then repeated. A series of five such expansions was conducted. This enabled calculation of the volume of the cold trap, from an average of five readings of pressure ratio. The density of the trapped gas at each stage of expansion was found from the pressure and temperature, using the equations for the density of air given by Giacomo (1982). The mass of gas originally trapped was calculated from knowledge of the total volume. The mass of nitrogen that would be trapped under the same conditions was then calculated from the density of nitrogen relative to air (Jacobsen and Stewart, 1973), treating the gases as ideal gases for this purpose. The expansion chamber ("known") volume was calculated from careful dimensional measurements of the chamber itself and the intervening pipes and valves. In particular, the internal dimensions of the chamber were measured using a coordinate measuring machine, with an uncertainty of better than 0.05 percent.

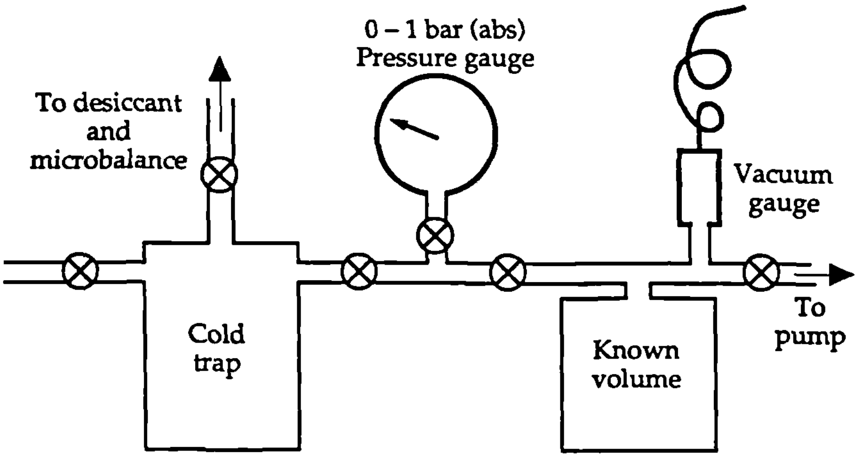


Figure 21 Block diagram of experimental configuration used to evaluate the mass of gas trapped in the cold trap

The repetition of this exercise a total of four times gave close agreement in resulting estimates of the mass of the trapped gas. The volume of the cold trap was estimated to be 1.375 litres with a standard error on the mean value of 0.009 litres. The mean quantity of nitrogen that would be trapped was estimated to be 2.531 g with a sample standard deviation of 0.022 g, and hence an estimated standard uncertainty of 0.019 g. To arrive at this estimate of the correction to be applied, and its uncertainty, various factors were taken into account after referring to previously published work on series expansion techniques at NPL (Elliott and Clapham, 1978). Allowances were made for non-uniformity and drift in temperature measured during the expansion measurements, leaks (also measured), non-ideal behaviour of gases, desorption, uncertainty in the dimensional measurements, and for the small quantity of water also trapped in the experiment.

3.7.2. Predryer

In normal use, at the conclusion of a collection, the predryer contains water (at least some of which is immobilised in the molecular sieve), and some carrier gas trapped as the collection was terminated. In general, because of pressure and temperature of use, the gas finally present has a different mass from that initially present. A correction is made to account for this, as detailed fully in Appendix 3.

Briefly, the correction depends on the internal volume of the predryer used, on the pressure, temperature and composition of gas contained before and after the collection, on any change in effective internal volume when some of the gas is displaced by collected liquid and gaseous water, and on the solubility and ideality of the gases.

In Section 3.5.5.1 the volumes were evaluated, for the collection and reference predryers respectively, to be 0.198 litre and 0.199 litre. (This leads to contents of order 240 mg of gas in each predryer.) The maximum bounds of uncertainty for each of these estimates of volume are estimated to be ±0.015 litre. The temperature and pressure of the trapped gas contribute negligible uncertainties in comparison. The correction found on any occasion due to gas trapped in the predryer is in the approximate range -40 mg to +40 mg, at most, and is normally less than half of this magnitude. However the worst-case uncertainty of 1.5 mg is an upper limit, whatever the value found for the correction.

The degree of departure from ideal gas behaviour in the range of interest here has an additional effect equivalent to up to 0.1% of density, as concluded by Sira. This corresponds to an uncertainty of up to about 0.25 mg for each density determination, and to about 0.35 mg, at most, for the difference between initial and final gas masses (by combination of the two uncertainties in quadrature). The contribution of this to the uncertainty in the mass of gas is negligible, but it is included in the uncertainty for the mass of water.

The solubility of nitrogen at 1 °C is approximately 0.03 mg per gram of water (Kaye and Laby, 1986). This in requires a correction of up to 0.003% of water mass to be subtracted from the measured value. The uncertainty in this is taken to be equal to the magnitude of the correction applied, at worst. As a contribution to the uncertainty in the mass of gas, this is just significant if tens of grams of water are collected. It is significant for the mass of water even for collection of only a few grams.

The reference predryer is left intact and un-vented throughout a given gravimetric measurement. The contents, and therefore the mass of the reference predryer, are therefore taken to be constant throughout the initial and final weighings.

3.7.3. Other dead spaces

The part of the flow path between the cold trap and the gas collection vessel holds gas at the end of the collection which must be taken into account. The conditions vary for different parts of this flow path. (See Figure 3 and Figure 8 for labelled diagrams.)

The manifold beyond the cold trap, is empty at the start of a measurement, and full of dry gas at the supply pressure at its finish. However, in contrast to the cold trap, this portion of the pipework is near ambient temperature and the quantity of gas trapped can reasonably be estimated from temperature, pressure, volume and gas laws. Hence the gas trapped under normal operating conditions has been estimated at 0.447 g, with a standard uncertainty of 0.008 g, taking into account the uncertainties in estimation of volume, and the typical range of gas temperatures and pressures.

The pipework beyond the manifold, reaching to the gas collection system, also traps gas which must be considered in this analysis. In this case, adequate measurements of the relevant temperatures and pressures can easily be made (on each occasion or just a few times). In fact the correction relevant to this portion of the flow path need only account for the difference between ambient air contained initially and dry nitrogen at 1.05 bar at the conclusion of the measurements. For the temperature profile concerned these initial and final conditions virtually cancel out, to an estimated difference of only 0.2 mg, with an uncertainty estimated at ±5 mg, at most.

In cases where the predryer is used, there is a portion of pipe between the predryer and the cold trap which holds gas from which water has been (largely) removed without the gas being collected. This small stretch of pipe has a volume of approximately 8 cm^3. Given the typical efficiency of the predryer, the 8 cm^3 of gas would hold less than 1 μg of water, which is negligible. The nitrogen gas itself would weigh approximately 9.8 mg, and this mass is therefore added to the measured mass of gas. The uncertainty in this correction is estimated to be ±1 mg at most.

3.8. Leaks

3.8.1. Leaks into the vacuum system

When the gravimetric instrument is not in use, continuous vacuum pressure of less than 10^{-2} mbar is maintained. In addition to the benefits of weighing in vacuum, evacuation prevents the accumulation of contaminants, of which water vapour is the most undesirable. The extent of leaks can be deduced from the rate of pressure rise in the sealed system, and from any gain in mass of the desiccant in its sealed chamber. These signs are also indicators of any outgassing from internal surfaces. In general, leaks and outgassing into the vacuum system were found to be so small that the quantity of water vapour leaking inwards during the course of a normal gravimetric measurement would be expected to affect the desiccant mass by well under 1 μg. This is therefore negligible in comparison with the other uncertainties involved.

3.8.2. Leaks at the connection to the predryer

The leak at the point of connection of the predryer to the gas flow path (see Figure 8) has been measured to be between zero and 2×10^{-4} mbar l s^{-1} at each of the two ports, for helium at the normal operating condition of 5% above ambient pressure. The corresponding leak rate for nitrogen or air is estimated to be 2/5 of this, due to the lower diffusivity of the heavier gases. In the case of the inlet port any leak can be neglected, as loss of gas prior to the collection stages has no effect. For the outlet port, a nitrogen leak of $0.4 \times 2\times10^{-4}$ mbar l s^{-1} at worst corresponds to a loss of 0.16 mg of gas per hour. The effect on the mass of water collected is negligible. The effect on the measured mass of gas is equal to 0.16 mg per hour of running time, (i.e. 0.96 mg over 6 hours) with an uncertainty in this correction estimated at plus or minus the value of the correction, at worst. For a six-hour collection, therefore, this is also below the threshold for significance for the mass of gas, and can be neglected.

3.8.3. Leaks at the connection to the gas collection vessel

Apart from the insertion of the predryer, the only connection frequently assembled and disassembled is that of the gas collection vessel to the rest of the gravimetric system. This is attached via a Swagelok connector, and the join is made and unmade with care not to wear the thread on the gas collection vessel. Therefore the seal in general is not ultimately tight, but has a small leak on most occasions. During collection of gas this region is below ambient pressure, so air can leak into the vessel from outside. A correction must be made for this. The leak rate is routinely evaluated prior to each gravimetric measurement by briefly opening the valve of the gas vessel to generate suction. After closing the valve again, the pressure rise in the connecting pipe is monitored for a short time. The rise in pressure enables the calculation of the rate of admission of air. The correction to be subtracted from the measured mass of gas is generally found to be between 1 mg and 5 mg per hour of collection, with an uncertainty estimated to be no more than 10% of value. The worst case uncertainty is therefore 0.5 mg per hour of running time, e.g. 10 mg for a long collection lasting 20 hours.

3.9. Gas composition

Air, pure nitrogen, or other inert species of gas can in principle be used as the carrier in the humid gas stream to be measured. Air is the gas of most general interest, and this is the gas routinely used in the NPL humidity generator. However nitrogen was considered the better choice for use in gravimetric determinations, for the following reasons.

In principle, the mixing ratio of a humid gas can quite properly be evaluated without knowing even the species of the carrier gas. Therefore, the composition of the gas has no bearing on the uncertainty of the gravimetric determination. However, to make meaningful use of the mixing ratio results by relating them to other units of humidity measurement, it is most important to know the average molar mass of the measured gas, taking into account any important minor constituents such as argon. In the present work it is preferable to know the molar mass to within a few parts in 10^5. Nitrogen is easily obtained in high purity, and for many purposes, including dew-point generation, it is negligibly different from air. It was also selected as a CO_2-free gas, in case traces of this component might be adsorbed by the molecular sieve in the predryer, though fears of this proved to be unfounded. The adsorption of other trace gases in the predryer is discussed in 3.5.5.3.

The other argument against using atmospheric air (with 1% argon) to feed the supply of humid gas for gravimetric measurements is a practical one. It is important that all the carrier gas is condensed in the gas vessel, and none of it in the cold trap. Argon at atmospheric pressure condenses at about 87 K. At the approximate temperature of the gas collection cryostat (68 K) argon will condense only at a partial pressure of around 5 kPa, or 5% of atmospheric pressure. Since, in atmospheric air, argon would be present at a partial pressure of around 1 kPa, it would not at first condense in the collection vessel, but would instead accumulate, still in gaseous form, until the concentration increased such that it reached its saturation vapour pressure. Although this would be 5 kPa at the coldest point as described, the partial pressure could be higher in less cold regions of the flow path as a backlog built up. The consequences of this might be errors in the calculated values of trapped gas within the flow path, or - perhaps worse - an impairment of the cryopumping action.

A similar problem would not be expected to occur with the oxygen component of atmospheric or synthetic air (composed only of 79% nitrogen and 21% oxygen). This is because oxygen at 21 kPa condenses at about 79 K, well above the active temperature of the cryopumping system in the gravimetric hygrometer, and would therefore be collected effectively. Some trial measurements were in fact performed using CO_2-free synthetic air to establish that the gravimetric system would function in this case, although the uncertainties for operation with air were not addressed in full detail.

In the cold trap, no gas species other than water are trapped, since the other gases present are far from their saturation pressures at the temperatures concerned (down to about 100 K).

The intercomparison of the gravimetric hygrometer with the NPL humidity generator is documented in Chapter 5. Measurements involving both pure nitrogen and air are reported, and details of the reference function used for the water vapour enhancement factor in nitrogen are given.

3.10. Other sources of error

A few other sources of error exist which do not fall into the categories above, and are discussed below.

The error due to evacuation of a small fraction of the collected water from the cold trap was estimated by Sira. This arises because at the end of a collection, the cold trap is pumped to restore it to vacuum before the transfer and weighing of the water. On pumping this gas away, some water vapour is unavoidably carried out with it. In this case, as during collection, the dew point of the exit gas (even at low vacuum pressure) is estimated to be in the region of -90 °C. An analysis, based on the total fall in pressure and the number of times the cold trap is flushed through by escaping gas, resulted in an estimate for the lost water of 3 μg. The uncertainty associated with this correction is estimated to be plus or minus the value of the correction, at most.

A number of factors contribute to the uncertainty in the comparison of the gravimetric hygrometer with other instruments, while contributing nothing to the uncertainty in mixing ratio itself. Since the values of such uncertainties depend upon instrument in question, no general analysis can be made. However for the NPL humidity generator, the uncertainties of intercomparison are dealt with in Chapter 5.

3.11. Potential sources of uncertainty considered negligible

Several other possible influences on results were considered (some by Sira) and their contributions to the overall uncertainty judged to be insignificant. As well as those already mentioned, these included the efficiency of the desiccant, the composition of the collected water, magnetic and static electrical effects on the balances and ambient humidity.

3.12. Summary of results

Table VI shows a summary of the contributions to the overall uncertainty in the mass of gas from all significant sources identified in this work, together with systematic corrections, where required. Table VII shows a corresponding summary of systematic corrections and uncertainties for the mass of water. Where a particular uncertainty has been estimated using a Type A (statistical) evaluation, then the figure given is the estimated population standard deviation. Where the estimate is derived by a Type B (non-statistical) approach (e.g. by calculation, estimation or single measurement) then either the estimated population standard deviation or the estimated maximum bounds of uncertainty are given. As appropriate, the estimates are expressed as functions of mass of water or gas, as functions of time or flow rate, or as constants.

Some points may be noted concerning the summary. Terms relating to the predryer are obviously not relevant to the range of measurement where the predryer is not used. In cases where the predryer is used, the uncertainties relating to the cold trap and microbalance constitute a much less significant fraction of the whole uncertainty. Certain effects contribute in opposite senses to both the water and gas masses and so corrections appear in both tables, but with opposite signs.

3.13. Chapter conclusion

A detailed discussion and numerical summary of the origins and the magnitudes of individual uncertainties has been produced for the gravimetric hygrometer. Where there are systematic errors whose values are known or can be estimated, the values of corrections to be applied to results have been identified. This meets the first of the four objectives of the work overall, listed at the beginning of this Chapter. The treatment of these data to arrive at an overall estimate of uncertainty, and the calculation of mixing ratio results, are addressed in Chapter 4.

Table VI Summary of estimates of individual sources of uncertainty and corrections required for mass of gas. HH and LH indicate the high humidity (small) and low humidity (large) vessels respectively.

Source of uncertainty in mass of gas	Section reference	Systematic correction	Maximum bounds of uncertainty	Estimated standard deviation
Use of nominal values of weights for weighing gas	3.4.2.2.	-	3 mg	
Buoyancy correction of weights for average (not true) air density	3.4.2.2.	150 mg per kg gas		2 mg per kg gas
Calibration of balance graticule sensitivity	3.4.2.3.	Factor evaluated each time		3 mg
Graticule non-linearity	3.4.2.3.	-	2 mg	
Overall repeatability of weighings of gas	3.4.2.3.	-		6 mg
Buoyancy correction due to volume change of gas vessel under pressure HH: LH:	3.5.1.1.	+98 mg per kg gas +68 mg per kg gas		44 mg per kg gas 34 mg per kg gas
Handling and thermal cycling of gas vessels HH: LH:	3.5.1.3.	-1 mg -15 mg		6 mg 9 mg
Leaks from full gas vessel	3.5.2.	+5 mg	5 mg	
Gas trapped in cold trap	3.7.1.	+2.531 g		19 mg
Gas trapped in predryer	3.7.2.	Evaluated each time	1.5 mg	
Solubility of nitrogen within predryer	3.7.2.	-	0.03 mg per g water	
Gas trapped in manifold	3.7.3.	+0.447 g	(8 mg)	8 mg
Gas in pipes to gas vessel	3.7.3.	-	5 mg	
Gas in pipe from predryer to cold trap	3.7.3.	+10 mg	1 mg	
Leak at connection to gas vessel HH: LH:	3.8.3.	Evaluated each time	3 mg 10 mg	

Table VII Summary of estimates of individual sources of uncertainty and corrections required for mass of water

Source of uncertainty in mass of water	Section reference	Systematic correction	Maximum bounds of uncertainty	Estimated standard deviation
Predryer				
Repeatability of weighings of predryers on analytical balance	3.4.3.	-		0.15 mg
Handling and thermal cycling of predryer	3.5.5.2.	-		0.1 mg
Molecular sieve adsorption of other gas species	3.5.5.3.	-0.45 mg	0.45 mg	
Gas trapped in predryer	3.7.2.	Reduction evaluated each time	1.5 mg	
Deviations from ideal gas behaviour for gas in predryer	3.7.2.	-	0.35 mg	
Solubility of nitrogen within predryer	3.7.2.	-	3×10^{-5} x mass of water	
Cold trap and microbalance				
Calibration uncertainty/stability for microbalance weights	3.4.4.1.	-		0.006% to 0.55% of value, evaluated each time
Effect of ambient temperature variations on microbalance	3.4.4.2.	-	2 µg	
Repeatability of microbalance weighings	3.4.4.2.	-		7 µg
Cold trap efficiency	3.6.1.	$+6\times10^{-6}$ to 1×10^{-4} g.kg^{-1}, calculated each time	6×10^{-6} to 1×10^{-4} g.kg^{-1}, calculated each time	
Repeatability of water vapour transfer from cold trap to desiccant	3.6.3.	-25 µg		34 µg
Water lost from cold trap during evacuation	3.10.	+3 µg	3 µg	

3.14. References

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CHAPTER 4

Treatment of uncertainties

If your experiment needs statistics,
you ought to have done a better experiment.

(Lord) Ernest Rutherford 1871-1937
In N T J Bailey *The Mathematical Approach to Biology and Medicine* 1967 (New York: Wiley)

CHAPTER 4. TREATMENT OF UNCERTAINTIES

4.0. Abstract

This Chapter deals with the derivation of an estimate of overall uncertainty of measurement for the gravimetric hygrometer, based on a knowledge of the performance of individual aspects of its operation.

The treatment of the experimental results is conducted in accordance with the recommendations in the ISO *Guide to the expression of uncertainty in measurement*. The estimates of individual uncertainty are reviewed, assessing the probability distribution and therefore the standard uncertainty for each. The outcomes of these considerations are then used to compose an expression for combined standard uncertainty for the gravimetric hygrometer.

In the light of this analysis, the optimisation of gravimetric measurement is considered, weighing the benefits of improved uncertainties against the penalties of longer measuring times and other actions capable of improving the performance. The expression for combined standard uncertainty is then evaluated for a range of values of humidity.

The uncertainty statement for a level of confidence of approximately 95% (a coverage factor of k=2) is finally achieved and summarised. The overall uncertainty at this level of confidence has a minimum of 0.015% of value at a mixing ratio of 155 g kg^{-1} (a dew point of 60 °C), and rises towards low humidities reaching 1.27% of value at a mixing ratio of 0.007 g kg^{-1} (-60 °C). The uncertainty also peaks in the middle of the measurement range to a value of 0.1% of result at a mixing ratio of about 4 g kg^{-1} (near a dew point of 0 °C), where there is a crossover between two modes of operation. In the original target range of 0.14 g kg^{-1} to 40 g kg^{-1} (-35 °C to +35 °C) the uncertainty is found to meet the specification, except below about 0.05 g kg^{-1} (-20 °C), where the uncertainty increases rapidly.

4.1. Approach to the treatment of results

The individual contributions to uncertainty must be combined to give a figure for the overall uncertainty, and this can be itemised for each part of the measurement range. The ISO *Guide to the expression of uncertainty in measurement* (ISO, 1993) forms the basis for the analysis of these uncertainties.

The treatment in this chapter addresses only the uncertainties directly associated with the gravimetric hygrometer itself. However in any measurement situation there will be sampling errors associated with the interface between the gravimetric system and any instrument being compared with it. These uncertainties depend upon the case in question, and are considered for comparisons against the NPL humidity generator in Chapter 5.

The steps for evaluating and expressing uncertainty, as detailed in the ISO *Guide* (ISO, 1993), can be summarised as follows:

1. Express mathematically the relationship between the measurand Y and the input quantities X_i on which Y depends: $Y = f(X_1, X_2, \ldots X_N)$, including all corrections and correction factors required.

2. Determine x_i, the estimated value of input quantity X_i, either on the basis of statistical analysis of series of observations, or by other means.

3. Evaluate the *standard uncertainty* $u(x_i)$ of each estimate x_i.

4. Estimate the covariances associated with any input estimates that are correlated.

5. Calculate the result of the measurement, that is, the estimate y of the measurand Y, from the functional relationship f using for the input quantities X_i the estimates x_i obtained in step 2.

6. Determine the *combined standard uncertainty* $u_c(y)$ of the measurement result y from the standard uncertainties and covariances associated with the input estimates.

7. To give an *expanded uncertainty*, U, multiply the combined standard uncertainty

$u_c(y)$ by a *coverage factor, k,* (selected on the basis of the level of confidence required of the interval) to obtain $U = ku_c(y)$.

8. Report the result of the measurement y together with its combined standard uncertainty $u_c(y)$ or expanded uncertainty U, describing how y, and $u_c(y)$ or U were obtained.

This series of operations is executed in the following sections, with additional definitions and explanations where necessary.

4.2. Analysis of uncertainties

4.2.1. Expression for mixing ratio

The simple formula for mixing ratio r

$$r = \frac{\text{mass of water}}{\text{mass of dry gas}} \tag{19}$$

becomes a more complex function when corrections to the measured values listed in Table VI and Table VII are incorporated. The expression then takes the form

$$r = \frac{m_w + \Sigma a_i(m_w) + \Sigma b_i(t) + \Sigma c_i}{m_g + \Sigma d_i(m_g) + \Sigma e_i(t) + \Sigma f_i} + g_i(f) \tag{20}$$

where m_w is the measured mass of water, m_g the measured mass of gas, and other terms are corrections which are functions of m_w, m_g, time t (duration of a measurement), flow f, or are constants. Values of some of these terms are evaluated on each occasion: others are common to all gravimetric measurements. All the entries in Table VI and Table VII can be identified as one of the parameters a_i, b_i, . . . etc. (Where the mass of water and mass of gas appear as input variables in the expressions $a_i(m_w)$ etc, the uncertainties in the measured masses do not lead to significant uncertainties in these expressions.)

4.2.2. Estimated values of input quantities

Chapter 3 examined the methods of measurement of the masses of water and gas, and documented the corrections required to be applied to each mass to account for known systematic errors. In terms of this analysis, each correction constitutes an estimated value of an input quantity to equation (20). Where an uncertainty is associated with an effect for which no systematic correction is applied, then this may be understood as an input quantity whose estimated value is zero.

4.2.3. Standard uncertainty of each input estimate

The individual uncertainties can be categorised as Type A (statistically evaluated) and Type B (evaluated by other means). This affects how the results of the evaluations are subsequently interpreted as standard uncertainties.

The individual uncertainties, as discussed so far, are each expressed with an estimate of dispersion or spread. An estimate must be made of what the distribution of probability is within this spread. This process is discussed below for each aspect, arriving at a value of standard uncertainty for each.

4.2.3.1. Type A evaluations

Only a few parameters in the gravimetric determination are statistically evaluated from a series of measurements on each occasion. These are: the measured (i.e. uncorrected) mass of the gas vessel mass (full and empty), the measured mass of the predryer (full and empty) and the measured mass of the desiccant before and after collection. Though the values of certain systematic corrections were also evaluated statistically, these fall in the "Type B" category, as the values of standard deviation were estimated once, rather than on every occasion of measurement.

A Type A standard uncertainty $u(x_i)$ is defined by

$$u(x_i) = s(\overline{X}_i) \tag{21}$$

where $s(\overline{X})$ is the experimental standard deviation of the mean found from

$$s^2(\overline{X}_i) = \frac{s^2(X_{i,k})}{n} \tag{22}$$

where $s^2(X_{i,k})$ is the variance of k independent repeated observations of the quantity X_i. Values of $s(X_i)$ are produced as the outcome of those Type A uncertainty evaluations that are performed on each occasion of measurement, and representative values are included in Table VI and Table VII in the column headed "estimated standard deviation". These values are divided by √n to give estimates of the Type A standard uncertainties.

In each case, the grounds for assuming the observed variations to be random and normally distributed are considered. Details for each component are as follows.

Overall repeatability of weighings of gas vessels - The population standard deviation for these weighings was estimated to be 6 mg, for maximum load. This is the result of a combination of minor influences such as temperature effects on the balance and vessels, variability in the point of action of the knife edges, etc. which, although unmeasured, could reasonably be expected to be approximately normally distributed and randomly varying. From equation (22), a single weighing leads to a standard uncertainty of 6 mg, the average of two weighings will have standard uncertainty of 4.2 mg, three weighings 3.4 mg, and so on. Since at least three weighings would normally be conducted both before and after collection of gas, this results in a standard uncertainty from this source of typically less than 3.4 mg for both the initial and final masses of gas. Relative to this, the contribution of variations in air density is insignificant, as discussed in Section 4.3.3.2.

Repeatability of predryer weighings on analytical balance - The population standard deviation for these weighings was estimated to be just less than 0.1 mg, and therefore negligible.

Repeatability of weighings of desiccant on microbalance - The population standard deviation for these weighings was estimated to be 7 μg. In routine gravimetric measurements, the result used is the average of three weighings. Therefore from equation (22) the typical standard uncertainty is approximately 4 μg. This uncertainty contributes for both initial and final values of desiccant mass. In cases where the predryer is used, the microbalance result contributes only a small correction (and negligible uncertainty) to the overall value of mass of water. In such cases, only one initial and one final microbalance weighing may be carried out.

These standard uncertainties are tabulated along with other contributing standard uncertainties in Table VIII.

4.2.3.2. Type B evaluations

A Type B evaluation results from non-statistical estimates based on "imported data", on calculations based on experience and general knowledge, and on previous measurements (even if these were themselves given statistical treatments). Estimation of standard uncertainty for a Type B evaluation depends upon what information is known about the probability distribution of the variable, and upon the coverage factor or level of confidence of the estimate. In general, the standard uncertainty for a Type B evaluation is taken to be equal to the population standard deviation.

In interpreting data to give estimates of standard deviation, some common conventions are followed. Where the information available is in the form of maximum bounds within which the input quantity will lie, and where nothing can be assumed about the distribution, then it is taken to obey a uniform or rectangular distribution, with equal probability of the value lying anywhere in the in the stated interval. In that case, for bounds of $\pm a$, the expectation or expected value of the quantity is the mid-point of the interval, and the standard uncertainty is

$$u(x_i) = \frac{a}{\sqrt{3}} . \tag{23}$$

(Sometimes, however, a uniform distribution is not a logical physical interpretation. In cases where it can reasonably be supposed that the values are likely to fall nearer to the centre than to the bounds, then it is legitimate to assume a trapezoidal or triangular distribution.)

In other cases, the available information may be in the form of an interval and an estimated probability, i.e. an estimate that there is an n percent chance that the variable lies in the interval a_+ to a_-. If the distribution can be assumed to be normal, then the standard uncertainty can be recovered by dividing the quoted uncertainty by the appropriate factor for the normal distribution. For example, the factors corresponding to intervals of 50, 90, 95 and 99 percent levels of confidence are respectively 1.48, 1.64, 1.96 and 2.58.

Where external sources of data such as manufacturers' specifications or calibration certificates are used, reports in terms of standard deviation or confidence level are taken to indicate that a normal distribution was the basis for calculation of that uncertainty.

The derivation of a value of standard uncertainty is discussed below for each significant component of uncertainty identified in this work. The cases at the head of this list are dealt with in some detail: cases lower down follow these examples. The largest uncertainties are approached the most carefully. Where the magnitude of dispersion is small, it is less critical what the distribution is found to be. However, where an uncertainty contributes more than once to the overall measurement this is mentioned below.

Use of nominal values of weights for weighing gas - Positive and negative deviations from nominal values are almost evenly distributed about zero, with a majority close to zero. Considering the weights are used in combination, the Central Limit Theorem[6] would suggest that the resulting uncertainty would be close to a normal distribution . In that case, taking the maximum limits of ±3 mg to most closely approximate to a 99%, the estimate of the population standard deviation is equal to the half-width (3 mg) divided by 2.58; i.e. 1.2 mg. This uncertainty contributes once to the initial mass and once to the final mass.

Use of average (not actual) air density for buoyancy correction of weights - Over time spans of the order of a month or less, air density is normally distributed (Brooks and Carruthers, 1953), and the standard deviation is at worst 1.3% of value of correction, leading to a standard uncertainty of 2.1 mg per kilogramme of gas.

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[6] According to the Central Limit Theorem, a combined standard uncertainty resulting from several input variables is approximately normally distributed, no matter what distributions characterise the input variances, provided the value of combined standard uncertainty is much larger than any individual non-normally distributed variance (ISO, 1993: Appendix G2).

This uncertainty contributes once to the difference between initial and final weighings. (However, although air density is normally distributed in the medium term, it is not likely to vary randomly on a short timescale: for instance, barometric pressure on any given day is most often close to the pressure on the previous day. If anything, this makes the above figure an over-estimate, while also raising the question of whether the uncertainties in weighings are correlated. Correlations between components of uncertainty are considered in Section 4.2.4.)

Calibration of balance graticule sensitivity - Though the sensitivity is usually measured for each gravimetric measurement, the estimated uncertainty in this aspect is a generalised value with a standard deviation of up to 1.7 mg. This uncertainty is judged to normally distributed in the same way as the overall repeatability of weighings. The uncertainty in sensitivity contributes once to the initial value of mass and once to the final mass.

Graticule non-linearity - The distribution of this uncertainty cannot be concisely characterised and it is most simply treated as a uniform distribution in the interval between the estimated limits of -2 mg and +2 mg. Therefore the standard uncertainty is found from the half-width divided by $\sqrt{3}$, giving a value of 1.2 mg. This will contribute once to the initial value of mass and once to the final mass.

Buoyancy correction due to volume change of gas vessels under pressure - The systematic uncertainty in this correction arises mainly from the dimensional measurements. Each value was the average of repeated measurements which would be expected to be normally distributed. The measurements had a standard error of the mean (and hence a standard uncertainty) equivalent to 44 mg per kilogram of gas for the small vessel and 34 mg per kilogram of gas for the large one, for air of average density 1.2 $kg.m^{-3}$. This contributes once to the uncertainty in change in mass of the vessel. As described above, the standard deviation for variations in the density of air would affect this correction by 1.3%, or less, therefore contributing negligibly to this component of uncertainty.

Handling and thermal cycling of gas vessels - These series of tests resulted in corrections with associated estimates of standard deviation. Hence these estimates provide values of standard uncertainty of 6 mg for the small vessel and 9 mg for the large vessel. This uncertainty contributes once to each gravimetric measurement.

Leaks from full gas vessel - The effect of leakage is estimated to be a loss of between 0 and 10 mg, with a 90% probability. Little can be said about this distribution, although it is clear that there is no likelihood of gas leaking *into* the full vessel. The best approach would seem to be to attribute an exponential distribution (Chatfield, 1983). Based on a probability curve for which 90% of the area falls between 0 and 10 mg, this gives an estimated mean of 4.3 mg and standard deviation 4.3 mg. This uncertainty contributes once to the gravimetric result. (For an asymmetric uncertainty distribution, it may seem counter-intuitive to interpret the standard uncertainty identically to that for a symmetrical distribution. However such an uncertainty can be combined arithmetically in the normal way without producing anomalous results, provided it is not a large proportion of the overall combined standard uncertainty (ISO, 1993).)

Gas trapped in cold trap - The uncertainty in the mass of gas trapped arises from variations in pressure and temperature at which the gas is trapped, combined with the uncertainty in dimensional, pressure and temperature measurements for the expansion experiments. No large component among these is believed to be rectangularly distributed. Therefore, from the Central Limit Theorem, a normal distribution would be expected. The population standard deviation was estimated from four determinations to be 19 mg. This standard uncertainty contributes once to the gravimetric result.

Gas trapped in predryer - The estimate of ±1.5 mg is a maximum limit for this uncertainty. Assuming a uniform distribution, the standard uncertainty, from equation (23), is 0.87 mg. This uncertainty contributes once to the overall uncertainty in mass of water, and is below the limit for significance for contribution to the uncertainty in mass of gas.

Deviations from ideal gas behaviour for gas trapped in predryer - This contributes at most ±0.35 mg to the uncertainty in the mass of water, giving a standard uncertainty of 0.20 mg.

Solubility of nitrogen for gas in predryer - Treated similarly to the above, the standard uncertainty is 1.73×10^{-5} of the mass of water (1.4 mg at worst, for 80 g of water), and contributes only once to the result.

Gas trapped in manifold - Like that for the cold trap gas, this uncertainty arises from variations in temperature and pressure of operation, plus the uncertainty in volume, and is expected to be normally distributed. The correction has been estimated to be 90% certain to lie within ±10 mg of the mean value. Dividing this by the appropriate factor (1.64) gives an estimated standard deviation of 6.1 mg. This contributes once to the uncertainty in gas mass.

Gas trapped in pipes to gas vessel - The uncertainty of ±5 mg at most is treated as being uniformly distributed, leading to a standard uncertainty of 2.9 mg. This contributes once to the uncertainty in gas mass.

Leak at connection to gas vessel - This uncertainty in gas mass is estimated on every occasion according to the measured leak rate. The generalised worst case is an uncertainty of 0.5 mg per hour of running time. Taking this uncertainty to be rectangularly distributed, the standard uncertainty, from equation (23), is 0.29 mg per hour, or 1.7 mg for a 6-hour run, and 5.8 mg for a 20-hour run. This contributes once to the overall uncertainty in gas mass.

Molecular sieve adsorption of other gas species - This uncertainty is estimated to be 0.45 mg at worst per kilogram of gas passing through the predryer. Assuming a rectangular distribution, equation (23) gives a standard uncertainty of 0.26 mg per kilogram of gas. This contributes once to the overall uncertainty in mass of water.

Calibration uncertainty/stability of microbalance weights - Although the actual combinations of weights are considered when evaluating uncertainties on each occasion, conservative generalised estimates of standard uncertainty can be given. These are; 0.55% of value for the 10 mg weight, 0.25% of value for the 25 mg weight, 29 μg to 45 μg for the other individual weights, and up to 140 μg for combinations of weights. It is assumed that the uncertainties for the single weights are rectangularly distributed, and that those for the combinations of weights approach a normal distribution. Although these figures represent a worst case, in the sense of being conservative, the values are estimates of standard uncertainty, and not maximum bounds of uncertainty. However the pessimistic assumptions leading to these estimates might be revised if some justification were found. Treated as an uncertainty in the difference between initial and final masses, this contributes once to the overall uncertainty in the mass of water.

Effect of ambient variations on microbalance - the bounds of ±2 μg or less for this uncertainty lead to a standard uncertainty of 1.2 μg in the mass of water, contributing for both the initial and final masses of water.

Cold trap efficiency - The bounds of uncertainty are estimated to be plus and minus the value of the correction r' (in g kg^{-1}), where

$$r' = \ln(1.35 \times 10^{-4} f + 0.999952) \tag{24}$$

where f is the flow rate of the gas in litres per minute. Assuming a uniformly distributed uncertainty (as little can be said about the form of the distribution) leads to standard uncertainties of $1/\sqrt{3}$ of the results of equation (24), i.e.

$$u(r') = \frac{1}{\sqrt{3}} \ln(1.35 \times 10^{-4} f + 0.999952) \ . \tag{25}$$

For example at a flow rate of 0.4 litre per minute the standard uncertainty would be 3.5×10^{-6} g kg^{-1}, and at 1.0 litre per minute it would be 5.0×10^{-5} g kg^{-1}. This contribution to uncertainty becomes insignificant at mixing ratios of about 1 g kg^{-1} and above, i.e. in the range where the predryer is used. This uncertainty contributes once to the overall result.

Repeatability of water vapour transfer from cold trap to desiccant - the standard deviation of this component is estimated at 34 μg, and is expected to be normally distributed. This directly leads to a standard uncertainty of 34 μg contributing once to the uncertainty in the mass of water.

Water lost from cold trap during evacuation - This uncertainty is estimated at plus or minus 3 μg at most. A uniform uncertainty distribution is assumed, leading to a standard uncertainty of 1.8 μg. This contributes once to the uncertainty in the mass of water.

A summary of the values of standard uncertainty is given in Table VIII. In this summary, components whose magnitudes vary with length of running time are approximated, assuming durations of either 6 hours (high humidity) or 20 hours (low humidity). Components which are evaluated on every occasion of use (i.e.

Table VIII Summary of component standard uncertainties

Source of uncertainty		Standard uncertainty
Gas		
Use of nominal values of weights for weighing gas		1.2 mg
Use of average (not actual) air density for buoyancy correction of weights		2.1 mg per kg gas
Calibration of balance graticule sensitivity		1.7 mg
Graticule non-linearity		1.2 mg
Overall repeatability of weighings of gas		3.4 mg
Volume change of gas vessel under pressure	HH: LH:	44 mg per kg gas 34 mg per kg gas
Handling and thermal cycling of gas vessels	HH: LH:	6 mg 9 mg
Leaks from full gas vessel		4.3 mg
Gas trapped in cold trap		19 mg
Gas trapped in manifold		6.1 mg
Gas trapped in pipes to gas vessel		2.9 mg
Leak at connection to gas vessel - generalised uncertainty of 0.29 mg per hour. (Normally individually evaluated)	HH: LH:	1.7 mg 5.8 mg
Water in predryer		
Gas trapped in predryer		0.87 mg
Deviations from ideal gas behaviour for gas trapped in predryer		0.20 mg
Solubility of nitrogen within predryer		1.73×10^{-2} mg per gram of water
Molecular sieve adsorption of other gas species within the predryer uncertainty of 0.26 mg per kg of gas, i.e. 0.10 mg for 6 hour run		0.10 mg
Water on microbalance		
Repeatability of desiccant weighings		4 μg
Stability of platinum weights - generalised uncertainty (Normally individually evaluated)		0.006% to 0.55%
Effect of ambient variations on microbalance		1.2 μg
Cold trap efficiency $(1/\sqrt{3}\ \ln(1.35 \times 10^{-4} f + 0.999952))$		between 3.5×10^{-6} g kg^{-1} and 5.0×10^{-6} g kg^{-1}
Water lost from cold trap during evacuation		1.8 μg
Water vapour transfer from cold trap to desiccant		34 μg

uncertainty in microbalance weights, and leak at connection to gas vessel) are shown for a generalised worst case approximation in the table. Components which are proportional to mass of gas or water collected are not generalised to a particular value.

At this point it can be seen which sources of uncertainty stand out as more significant than the rest. For the microbalance and cold trap combination the most significant uncertainty in most of the range is the uncertainty in confirming the stability of the weights. (However, for changes in desiccant mass corresponding to a single large weight (e.g. 200 mg) this reduces to a similar significance to that of the repeatability of vapour transfer.) For the predryer, the largest uncertainty is that due to the trapped gas, except when over 50 g water is collected, in which case the uncertainty due to dissolved nitrogen is greater. In measurements where the predryer is used, the uncertainty contributions from the microbalance and cold trap are negligibly small fractions of the overall uncertainty in mass of water. Hence either the predryer contributions or the microbalance and cold trap contributions need to be included for a given measurement, but never both.

For the gas aspect of the measurement, the most significant uncertainties are that due to the volume change of the full cylinder under pressure and that due to gas trapped in the cold trap. Other components contribute less than half this magnitude. However the uncertainties in mass of gas are considerably less significant overall than those connected with the water aspect of the measurement. Relative significance of uncertainty components is considered in more depth in Section 4.3.

4.2.4. Covariances of input estimates

When the input quantities are correlated their covariance contributes to the combined standard uncertainty in the same way that individual variances do. This reflects the fact that highly correlated errors are unlikely ever to cancel each other out, as uncorrelated errors might. The degree of correlation between x_i and x_j is characterised by the correlation coefficient

$$r(x_i, x_j) = \frac{u(x_i, x_j)}{u(x_i)u(x_j)} \tag{26}$$

where $-1 \leq r(x_i,x_j) \leq +1$. This definition embodies an approach to evaluating the correlation coefficient from a statistically evaluated covariance. In general, values of correlation coefficient, like estimates of quantities themselves, may also be arrived at by non-statistical means. The estimates of correlation coefficient discussed below are all found non-statistically.

The use of an average (not actual) value of air density for all buoyancy corrections means that the deviations from this approximation are likely to be somewhat correlated for weighings of the predryers and gas vessels. However the standard uncertainty due to variation in air density is, in the case of the predryers, small enough to be neglected, and that for the gas vessels is only just significant. The covariance, being some fraction (<1) of the product of the two standard uncertainties, can also be considered negligibly small.

Corrections due to trapped volumes of gas within the flow path might also be considered to be correlated since they all depend on the pressure at which the measured gas is supplied. For a controlled supply pressure consistent to better than 0.1% for all measurements, values of covariance are less than 1 mg, even between the largest contributing sources of uncertainty for trapped gas. This source of covariance can therefore be considered negligible as long as pressure conditions remain repeatable to within 0.1%.

The uncertainties in the stability of the microbalance weights are somewhat correlated since, in the matrix of weighings, the weights are all used to confirm the values of one another. In fact, the least squares analysis provides not only estimates of variances, but also of covariances. Hence for any given combination of weights, the uncertainty can be calculated from the square root of the sum of the relevant variances and covariances. The generalised values of uncertainty for combinations of weights shown in Figure 16 and quoted elsewhere, were, in fact, calculated in this way. Therefore no further allowance needs to be made for these correlations.

It might be questioned whether corrections which are proportional to mass of gas or water should be treated as correlated. In fact, by separating off the collected mass as a multiplying factor, the remaining coefficients are not themselves correlated (unless for some other reason).

Overall, according to the general criteria in use for significance of components of uncertainty, no covariances between variables are found which are significant, other than those already included in the figures for the microbalance weights.

4.2.5. Calculation of measurement results

Equation (20) indicated the general form of the expression for calculating the mixing ratio for gravimetric measurements in this work. Routine calculation of actual results has been conducted using a software spreadsheet into which are entered the input variables. A specimen printout of a calculation is shown in Appendix 4. This spreadsheet facilitates the calculation of some uncertainties on an individual basis for each occasion of measurement, (for instance by allowing for a particular combination of microbalance weights). However the combined standard uncertainty evaluated in the following section applies for the most general case.

4.2.6. Combined standard uncertainty

If input quantities are independent (uncorrelated), the combined standard uncertainty $u_c(y)$ is the positive square root of the combined variance $u_c^2(y)$, which is given by

$$u_c^2(y) = \sum_{i=1}^{N} \left(\frac{\partial f}{\partial x_i} \right)^2 u^2(x_i) \qquad (27)$$

where f is in this case the general expression for mixing ratio given in equation (19). This is the procedure commonly referred to as the combination of uncertainties in quadrature.

Individual (relative) standard uncertainties $\frac{\partial f}{\partial x_i} u(x_i)$ are those listed in Sections 4.3.2.1. and 4.3.2.2., and in Table VIII. They are partially combined in quadrature in Table IX into terms which are functions of mass of gas (in kilograms), mass of water (in grams), mixing ratio (in grams per kilogram), etc. Where any particular standard uncertainty contributes twice (once for initial weighings and again for final weighings) the relevant term from Table VIII is incorporated twice in the combination evaluated in Table IX. (If some of the uncertainties are correlated the evaluation of the combined standard uncertainty should include covariances in the summation. Since it has been demonstrated in the present case that covariances are insignificantly small (or already included, in the case of the microbalance weights), then they need not be considered further here.)

It is useful here to evaluate the relative (fractional) combined standard uncertainty in mixing ratio $\frac{u}{r}$, which can be expressed

$$\frac{u^2(r)}{r^2} = \frac{u^2(m_w)}{m_w^2} + \frac{u^2(m_g)}{m_g^2} + \frac{u^2(f)}{r^2} ,$$

with

$$u^2(m_w) = a^2 + b^2 m_w^2 , \qquad (28)$$

$$u^2(m_g) = c^2 + d^2 m_g^2$$

and

$$u(f) = \frac{1}{\sqrt{3}} \ln(1.35\times10^{-4} f + 0.999952) ,$$

where r is nominal mixing ratio, m_g and m_w are nominal measured masses of gas and water, f is flow rate and a, b, c, and d are the partially-combined standard uncertainties summarising the individual contributions that are multiples of mass of water, mass of gas, etc. (See Table IX.)

Hence

$$\frac{u^2(r)}{r^2} = \frac{a^2 + b^2 m_w^2}{m_w^2} + \frac{c^2 + d^2 m_g^2}{m_g^2} + \frac{1}{3\,r^2} \left[\ln(1.35\times10^{-4} f + 0.999952)\right]^2 \qquad (29)$$

i.e.

$$\frac{u^2(r)}{r^2} = \left(\frac{a}{m_w}\right)^2 + b^2 + \left(\frac{c}{m_g}\right)^2 + d^2 + \frac{1}{3\,r^2} \left[\ln(1.35\times10^{-4} f + 0.999952)\right]^2 \qquad (30)$$

and

$$\frac{u(r)}{r} = \left[\left(\frac{a}{m_w} \right)^2 + b^2 + \left(\frac{c}{m_g} \right)^2 + d^2 + \left(\frac{1}{\sqrt{3}\, r} \ln(1.35 \times 10^{-4} f + 0.999952) \right)^2 \right]^{\frac{1}{2}} . \tag{31}$$

Equation (31) is evaluated using values of a, b, c, and d selected from Table IX according to whether the large or small gas vessels are used, and according to whether the predryer is used or not.

Table IX Partial combination of uncertainties into terms which are functions of mass of water, mass of gas, etc.

	Combined standard uncertainty by addition in quadrature (summation of variances)	Corresponding coefficient in equation (31)
Water	Predryer	
	0.90 mg	a
	1.73×10^{-5}	b
	Microbalance *	
	144 µg	a
	0	b
Gas	HH vessels	
	22.3 mg	c
	4.41×10^{-5}	d
	LH vessels	
	24.0 mg	c
	3.41×10^{-5}	d
Additive contribution	$(1/\sqrt{3})\, r \ln(1.35 \times 10^{-4} f + 0.999952)$	$u(f)$

* Excluding changes of 25 mg or less, for which values of a and b are calculated individually

4.3. Optimisation of operation

To arrive at actual values of estimated uncertainty for the gravimetric measurements, it is necessary to enter values of the variables m_w, m_g, flow rate, etc. in equation (31). The duration and flow rate of the collection can be selected to optimise the uncertainty (while bearing operational constraints in mind).

Below, uncertainties versus length of measurement time, mass of water, mass of gas, and flow rate are considered. Certain trends are obvious - for instance the more gas and water that are collected, the greater the relative precision of weighing these. Certain constraints are also obvious - for example, when water mass and gas mass appear as input variables in the uncertainty, the ratio of these is fixed for measurements of a given value of humidity. For collection of a given mass, there may be a trade-off between duration and flow-rate. The cases are considered below for the extremes of the measurement range, and for other key points in the range; namely the crossover from use of desiccant alone to use of desiccant plus predryer, and the crossover from use of large to small gas collection vessels. A summary of the optimal conditions for measurement is given in Table X.

At the lower limit of measurement, the fractional precision in measuring the mass of water becomes poor. Generally, for measurements in the low part of the range, the uncertainty depends as much on the combination of weights used as on the total mass measured. Where it is not possible to minimise the uncertainty by tailoring the quantity collected to an advantageous combination of weights in the set, then uncertainty is otherwise minimised by collecting as much water (and therefore gas) as possible.

Just above this range, in the region of 0.6 g kg^{-1} (around -20 °C dew point), the uncertainty in measuring both gas and water masses is relatively low. Although improvements could be achieved by longer measurements using the large vessels, sufficient accuracy is achieved using the small ones.

Throughout the range below 0 °C, the contribution to the overall uncertainty from the cold trap efficiency is significant, but is always outweighed by the contribution from the microbalance. Therefore, while the former contribution can be reduced by minimising the flow rate for the collection, it is more advantageous simply to

Table X Suggested conditions for achieving the minimum uncertainties in gravimetric measurements

Mixing ratio g.kg^{-1}	Dew point at atmospheric pressure °C	Optimal conditions to minimise measurement uncertainty			
		Mass of gas g	Mass of water g	Sampling flow rate l.min^{-1}	Duration hours
155	60	400	62	1.0	6
50	40	400	20	1.0	6
15	20	400	6	1.0	6
3.8	0	400	1.5	1.0	6
0.64	-20	400	0.26	1.0	6
0.080	-40	1000	0.08	0.7	20
0.007	-60	1000	0.007	0.7	20

maximise the collected water, at whatever flow rate.

The crossover point from the use of the cold trap alone to use of the cold trap plus predryer is in principle at a mixing ratio of about 2.5 g kg^{-1} (or -5 °C in dew point), assuming the collection of 400 g gas. This would result in collection of about 1 g of water, which is close to the full capacity of the desiccant. In practice the highest humidity measured without the predryer is 1.6 g kg^{-1} (-10 °C in dew point), resulting in the collection of some 0.66 g water. (This reduces the frequency of change of desiccant, which is a time-consuming procedure.) The uncertainties just above and just below the crossover point are considered as follows.

Just below the crossover point, the most significant uncertainties are in the mass of gas; due to the uncertainty in the gas held by the cold trap, and due to expansion of the gas vessel under pressure. The maximum mass of water collected (and hence the mass of gas) is constrained by the limit imposed on consumption of the desiccant, hence precluding further optimisation. (However, the overall uncertainty is at an acceptable minimum at this point anyway.)

Just above the crossover point, the conditions for use of the predryer are at their least advantageous. If the lowest measurements using the predryer are at a mixing ratio of 4 g kg^{-1} (a dew point of just above 0 °C, avoiding the difficult range between -10 °C and 0 °C), then about 1.6 g of water is collected for 400 g of gas.

In this situation, the largest contribution to the uncertainty is the gas trapped in the predryer, whose several uncertainty components contribute a standard uncertainty of almost 1 mg, or 0.06% of water mass. The impact of this can be reduced if more gas and water are collected, by using the large gas vessel, and collecting for longer (overnight). If so, then the contribution of the standard uncertainty of this component is reduced to 0.015% of water mass, for collection of 1 kg of gas and 4 g of water.

At the upper limit of measurement, the relative uncertainty in the mass of gas predominates over that associated with the mass of water. However both uncertainties are acceptably small, provided a full 400 g of gas and the corresponding water are collected.

For collection of 400 g of gas, the overall uncertainty in finding the mass of gas is no greater for the large vessel than the small one. Only when about 300 g or less is collected does the smaller size give an appreciably lower uncertainty. Therefore, for most measurements of about 400 g of gas, either size of vessel may be used, as convenient.

4.4. Evaluation of overall uncertainty statement for the gravimetric hygrometer throughout the range of operation

Below, values of combined standard uncertainty and expanded uncertainty are given.

4.4.1. Values of combined standard uncertainty throughout the range of operation

Values of mass of gas, mass of water and flow rate chosen in the light of the optimisation criteria discussed above are used in equation (31) to produce the values of combined standard uncertainty shown in Table XI below. Figure 22 shows a graph of the combined standard uncertainty expressed (a) as a percentage of mixing ratio, and (b) in terms of dew point.

Table XI Values of combined standard uncertainty for the gravimetric measurements

Mixing ratio g kg^{-1}	Dew point at atmospheric pressure °C	Combined standard uncertainty for gravimetric hygrometer	
		Percentage of mixing ratio result %	Dew point equivalent °C
155	60	0.0075	0.0013
50	40	0.0086	0.0015
15	20	0.0164	0.0026
3.8	0	0.057	0.0073
0.64	-20	0.056	0.0057
0.080	-40	0.179	0.0150
0.007	-60	0.630	0.0418

4.4.2. Expanded uncertainty

Following the ISO guideline (ISO, 1993) the standard uncertainty can be re-presented in terms of expanded uncertainty, expressing a level of confidence that the measurand lies within a stated interval. In this work, the chosen level of confidence is 95 percent. The overall standard uncertainty is therefore multiplied by a coverage factor of $k = 2$ which gives a level of confidence of just over 95 percent. This assumes that the number of degrees of freedom for the uncertainty analysis can be considered close to infinite (based on a large number of contributing data). The validity of this assumption is discussed later in Chapter 6.

Hence the expanded uncertainty at a level of confidence of at least 95% is shown in Table XII.

Special conditions apply where the uncertainties combined are unlikely to obey the Central Limit Theorem. This needs to be considered when a single rectangularly distributed component estimated from a Type B evaluation is the main contribution to the uncertainty, i.e. when the estimated limits $\pm a_d$ of one such component fall outside the expanded uncertainty $\pm U$ that would be found by the usual method. In this work, although there are cases where a relatively large rectangularly distributed component is present (e.g. gas trapped in the predryer is fairly significant near 4 g kg^{-1} (0 °C)), the criterion given above is not exceeded, and no

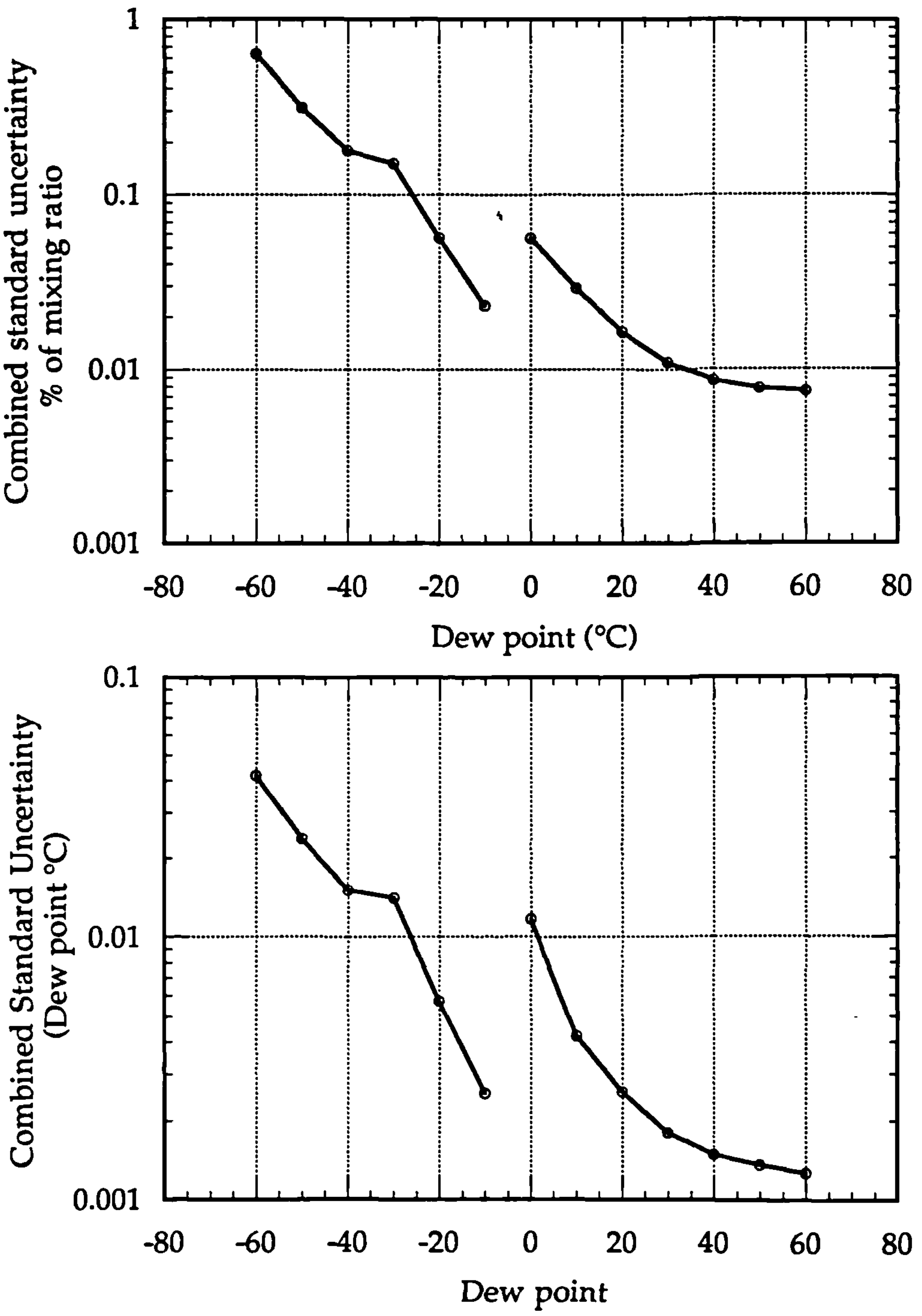

Figure 22 Combined standard uncertainty for gravimetric hygrometer (a) as a percentage of result (b) in dew-point equivalent

Table XII Uncertainty of measurement of the gravimetric hygrometer at a level of confidence of approximately 95% (a coverage factor of *k*=2)

Mixing ratio g.kg^{-1}	Dew point at atmospheric pressure °C	Uncertainty of measurement for the gravimetric hygrometer at a level of confidence of at least 95%	
		Percentage of mixing ratio result %	Dew point equivalent °C
155	60	0.015	0.0026
50	40	0.017	0.0030
15	20	0.033	0.0054
3.8	0	0.113	0.015
0.64	-20	0.113	0.012
0.080	-40	0.36	0.030
0.007	-60	1.27	0.84

special treatment is required.

4.5. Chapter conclusion

Figures have been established for the uncertainty of measurement of the gravimetric hygrometer throughout its range of operation. This achieves, in part, the second objective of the project. To complete this objective it remains to be considered whether the target specification for this instrument is met. Figure 23 shows a graph comparing the final estimated uncertainty for the gravimetric hygrometer against the target uncertainty, and against the expected performance. It can be seen that the actual result is well within the specified target, except below 20 °C, where the uncertainty rises rapidly. It can also be seen that the estimated performance is qualitatively in keeping with the prediction made at the design stage, though better in some parts of the range and worse in others.

Achievement of Objectives 1 and 2 of the project has been demonstrated. The two remaining objectives are addressed in Chapter 5, where results are reported for intercomparison measurements between the gravimetric hygrometer and the NPL humidity generator.

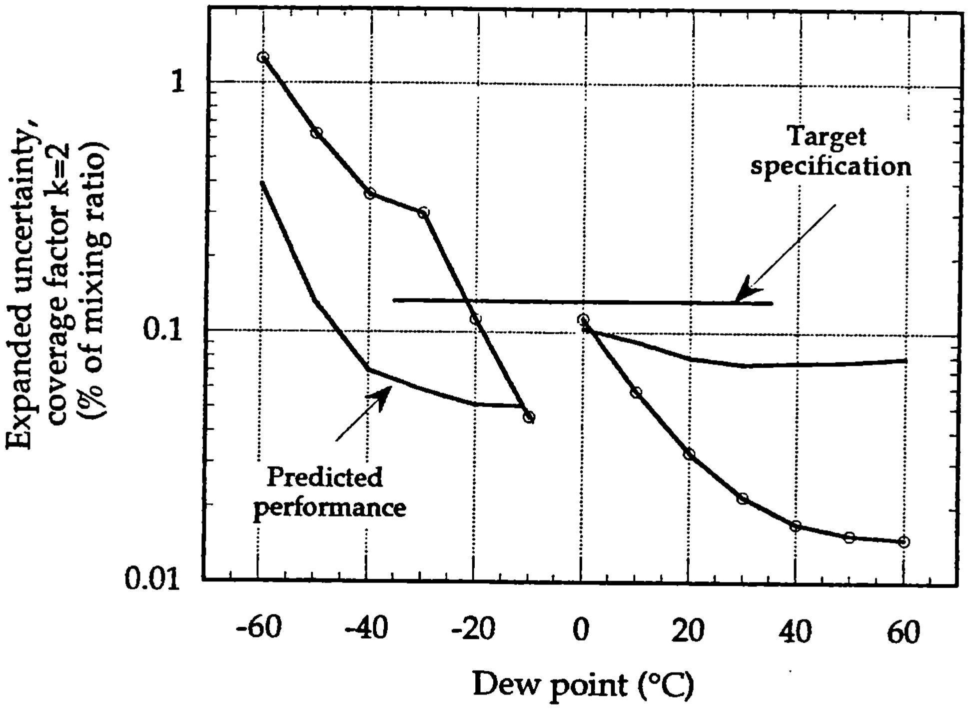

Figure 23 Comparison of the uncertainty of the gravimetric hygrometer (⦶) with the target specification for the humidity facility, and with the predicted performance of the hygrometer

4.6. References

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CHAPTER 5

Gravimetric measurements: intercomparison with the NPL humidity generator

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Daniel 5:25

CHAPTER 5. GRAVIMETRIC MEASUREMENTS: INTERCOMPARISON WITH THE NPL HUMIDITY GENERATOR

5.0. Abstract

The gravimetric hygrometer has been used in measurements to intercompare values of mixing ratio with values of dew point realised using the NPL humidity generator. These measurements are an important part of the overall project, since they provide unique evidence that the performance of both these instruments is consistent with the predictions made about each separately.

The use of reference data for converting between units of mixing ratio and dew point is discussed. The uncertainty in the reference function for the vapour pressure of water is considered. The selection and use of an expression for the water vapour enhancement factor is also discussed. This is particularly considered in the light of the use of nitrogen, rather than air, as the carrier gas for the measurements and a new calculation of the water vapour enhancement factor for nitrogen is presented.

Results are reported for 14 intercomparisons of the gravimetric hygrometer with the NPL humidity generator. The difference between the two was found to have a mean value of 0.36% of result, with a sample standard deviation of 1.38% and hence a standard error of the mean of 0.37%. This is not considered to indicate a significant systematic difference between the two humidity realisations. The results are mostly consistent with the estimated uncertainties of the two instruments, bearing in mind the uncertainties in the reference functions for vapour pressure and water vapour enhancement factor used to convert between values of dew point and mixing ratio.

5.1. Aim and basis of intercomparison measurements

The actual execution of gravimetric measurements is an important part of the validation project. One natural aim of these measurements has been to make real use of the information gained in the earlier stages of the validation. Without this application, the work described in the preceding chapters would have value only as an informative but theoretical exercise. In addition, the execution of complete gravimetric measurements was found to be a particularly effective way of highlighting and understanding the sources of error in the gravimetric process. Therefore, throughout the overall evaluation of the instrument, the full gravimetric measurements have been quite as important as the individual experiments conducted on particular components of the instrument.

As initially conceived, the aim of comparing the NPL humidity generator with the gravimetric hygrometer had been to underpin the realisation of dew point with a more fundamental and more accurate measurement. However, as both the projects developed, that approach was modified somewhat. This was because, concurrently with the validation of the gravimetric hygrometer, a similar self-contained validation of the humidity generator also took place. The results of this were better than expected, allowing the values of generated dew point to be confirmed with uncertainties smaller than the figures in the target specification, for most of the range of measurement. However, this did not negate the value of comparing the two standards. It simply became more appropriate to regard the comparison of one against the other as an intercomparison of two instruments of near-equal standing, rather than as a calibration of one against the other.

5.2. General consideration of reference data

It was noted in Section 1.3.3. that any comparison between the gravimetric hygrometer and another instrument indicating in units of measurement other than mixing ratio would rely on a conversion via values of vapour pressure of water, using a relation based upon the Clausius-Clapeyron equation (1). As discussed earlier, the conversion between pure vapour pressure e and mixing ratio r at an overall pressure P is through the relation

$$r = C\frac{ef}{P - ef} \tag{32}$$

where f is the water vapour enhancement factor and C is the ratio between the molar masses of water and the carrier gas in question. The water vapour enhancement factor, accounts for the real - rather than ideal - behaviour of the gases involved.

The value of C for this work was calculated as the ratio of the molar masses of water and nitrogen based on the figures given by Giacomo (1982). This results in a general value of C = 0.643092 for nitrogen, with an uncertainty of the order of 1 part in 10^6, which is negligible relative to the uncertainties relating to the actual gas composition, discussed earlier. For the measurements where air was used as the carrier gas, alternative values were individually calculated on the basis of certificates of analysis for the supply gas.

In this work, values of e are taken from the formulations by Wexler for water and ice (1976; 1977), updated to ITS-90 by Sonntag (1990), as widely adopted in standards applications in the field of humidity measurement.

The selection of a reference function for the water vapour enhancement factor f is less straightforward. Values of f for air have been documented, albeit on the basis of few experimental realisations (Hyland, 1973; Greenspan, 1976). However these relate only to air, and not to nitrogen which was used as the carrier gas for the majority of the gravimetric measurements reported here. There is no widely accepted formulation for the enhancement factor in pure nitrogen, and few experimental data. Therefore new values of enhancement factor have been calculated for nitrogen in the course of this work.

It is necessary to consider the uncertainties in the quantities e and f in order to report their influence on the results of intercomparisons between the gravimetric hygrometer and the NPL humidity generator. In the following sections, the uncertainty in using the vapour pressure formulations is discussed, as well as the uncertainty in the water vapour enhancement factor for air and for the adaptation for nitrogen.

5.3. Vapour pressure data for pure water

The versions of the formulations for pure phase vapour pressure by Wexler (1976; 1977) have been adopted by consensus in the field of humidity standards. These have been updated to ITS-90 by Sonntag (1990) as follows for water (in hPa)

$$\begin{aligned} \ln e_w(T) = {} & -6096.9385\, T^{-1} + 16.635794 - 2.711193 \times 10^{-2}\, T \\ & + 1.673952 \times 10{-5}\, T^2 + 2.433502 \ln T \end{aligned} \tag{33}$$

and for ice

$$\begin{aligned} \ln e_i(T) = {} & -6024.5282\, T^{-1} + 24.7219 - 1.0613868 \times 10^{-2}\, T \\ & - 1.3198825 \times 10^{-5}\, T^2 - 0.49382577 \ln T\, . \end{aligned} \tag{34}$$

The Wexler formulations are structured around integrations of the Clausius-Clapeyron equation (1) taking into account the departure of pure water vapour from the ideal gas model.

The values given by Wexler and adapted by Sonntag agree closely with the earlier authority, Goff and Gratch (1946) later updated by Goff (1965) (and widely referred to as "Goff-Gratch"). The Goff-Gratch formula, in modified form, has been adopted by the World Meteorological Organization. The close agreement cited between the Wexler and Goff-Gratch values (e.g. by Wexler, 1976)) has tended to promote confidence in both of these sets of values, and for most normal purposes this agreement is close enough.

However, the level of disagreement is actually greater than the best measurement capability of the gravimetric hygrometer over much of its range. (See Table XIII.) As observed by Gibbins (1990) in his review of the subject, the two sets of values differ by between 0.04% and 0.15% of value in the range of interest here. The disagreement between the two formulations also happens to be greater than Wexler's estimated uncertainties, though of similar magnitude to the uncertainties estimated by Goff and Gratch for their expression. Gibbins' survey goes on to show that formulae by other workers give results which vary from one to another by similar or greater amounts. It is perhaps for this reason that Sonntag assigns much larger values of uncertainty than Wexler did for his versions of the reference functions.

Further to all of this, the few recent experimental data that have been reported do not provide wholly unqualified support of these formulations (Jancso *et al.*, 1970; Marti and Mauersburger, 1992). In parts of the measurement range there is clear disagreement between the values calculated by Wexler and those measured by Jancso *et al.*, and by Marti and Mauersburger. For example, at -60 °C, the values differ by up to 10 percent. However the latter divergences should perhaps simply be taken as an illustration of the difficulty of direct measurements of the vapour pressure of water.

In the light of these factors, the uncertainties for values of vapour pressure adopted for the present work are those given in Table XIII. These estimates of uncertainty were arrived at for a selection of humidities, based on Sonntag's and Wexler's uncertainty estimates and on the actual differences between the Wexler and Goff-Gratch values. The most pessimistic of Sonntag's figures below 0 °C are not universally applied, as these were generalised to embrace the worst case he

Table XIII Comparison of uncertainties in Wexler's vapour pressure formulation with those assigned by Sonntag, differences between Wexler and Goff-Gratch values, and uncertainties assigned for this work

Dew point at atmospheric pressure °C	Percentage difference in vapour pressure between results of Wexler and Goff-Gratch	Percentage uncertainty at a level of confidence of 95%			
		Estimates of uncertainty in saturation vapour pressure			Uncertainty for the gravimetric hygrometer shown for comparison
		Wexler (1976; 1977)	Sonntag, (1990)	Estimates adopted in this work	Percentage of mixing ratio result
60	0.05	0.002	<0.01	0.05	0.015
40	0.06	0.004	<0.01	0.06	0.017
20	0.06	0.009	<0.01	0.06	0.033
0	0.08	0.001	<0.01	0.08	0.113
-20	0.10	0.068	<1.0	0.10	0.113
-40	0.12	0.094	<1.0	0.12	0.36
-60	0.15	0.171	<1.0	0.50	1.27

considered (-70 °C).

The applicability of the reference values must also be considered, since the gas environment in this work, while clean, may fall short of the highly pure conditions of most pure-phase vapour pressure measurements. For example, although the water is purified in a process of reverse osmosis, atmospheric gases remain in solution, or are dissolved later. Another question of applicability arises because the data refer to "plane" surfaces of water: curved surfaces in general support lower equilibrium vapour pressures. The vapour pressures reached inside most humidity generation equipment would reflect somewhat the curvature at the water meniscus and in water-filled surface imperfections which are no doubt present. Penman (1955) quantitatively discusses these effects. Both these issues must however be considered as uncertainties for humidity generation, not for the reference data or the gravimetric determination.

5.4. Water vapour enhancement factor

Expressions for the water vapour enhancement factor, f, in air have been formulated by Hyland (1975), Greenspan (1976) and others. The value of f for air near atmospheric pressure is about 1.005 (compared with a factor of 1 in the absence of air or other gas), and varies only slightly with temperature.

In this work nitrogen gas was normally used as the carrier gas for gravimetric measurements. The practical argument against using atmospheric air as the carrier gas for gravimetric measurements is detailed in Section 3.8. and concerns the possible accumulation and delayed condensation of the argon component. Synthetic air (free of argon) would not be expected to present the same problem, and might be practically straightforward to use, in this context. However the use of nitrogen (with a calculable correction to the value of enhancement factor) appears as appropriate as the use of synthetic air, and more convenient in this case. For measurement and generation of humidity in many other contexts nitrogen is often freely substituted for air. However there is no widely adopted expression for the enhancement factor in nitrogen, and few published experimental values. The few data that are available relate mainly to elevated pressures.

A good first approximation to an enhancement factor for nitrogen would simply be to use the value for air. A prediction of the goodness of this approximation, and its significance, can be attempted by looking at how different *f* for nitrogen might be from *f* for air. One would expect that thermodynamic properties of two such similar substances as N_2 and O_2 might at least differ in proportion to their molecular weights; ie by about 12.5%. Hence the properties of nitrogen might differ from those of air (21% oxygen) by some 2.6% (i.e. 12.5% of 21%). The overall effect of *f* in air at atmospheric pressure is about 0.5%, and so the additional difference for *f* in nitrogen might be at least 2.6% of 0.5%, leading to a value of, say, 1.0051 (or perhaps 1.0049) compared with the equivalent for air of 1.0050. This predicted systematic difference of at least 0.01% of value is almost half the total uncertainty of the gravimetric hygrometer in some parts of the operating range. A systematic correction of this magnitude should therefore not be neglected. It should also be viewed in the light of the uncertainty (at the 95% level of confidence) in *f* for air which ranges between about 7×10^{-6} and 4×10^{-4} for the humidity range of interest in this work.

An estimate of the enhancement factor for nitrogen has been made for this work. Hyland's (1975) formulation for air (elaborated upon by Hyland and Wexler (1983)) provided a convenient and authoritative starting point for this undertaking, although it is more complex than other, more empirical, formulations. Hyland's expression for enhancement factor in air is given in Appendix 5. It is a thirteen-term polynomial function of the second and third virial and cross-virial coefficients for air and water, the Henry's Law constant for air, and other variables relating to pure phase water or ice. Since this equation is expressed solely in terms of values of physical quantities such as virial coefficients, mole fractions, compressibilities, etc., it can therefore logically be adapted to produce an expression for use with nitrogen. To do this, values of virial coefficients and Henry's constant for nitrogen were entered in place of those for air. The adaptation is detailed in Appendix 5. The outcome of the adaptation is shown in the graph in Figure 24, where values of *f* at 105 kPa and a range of dew points are plotted.

It should be emphasised that empirical formulae for the enhancement factor are much simpler than Hyland's expression and much easier to use for most purposes.

All the above calculations of water vapour enhancement factor refer to temperature

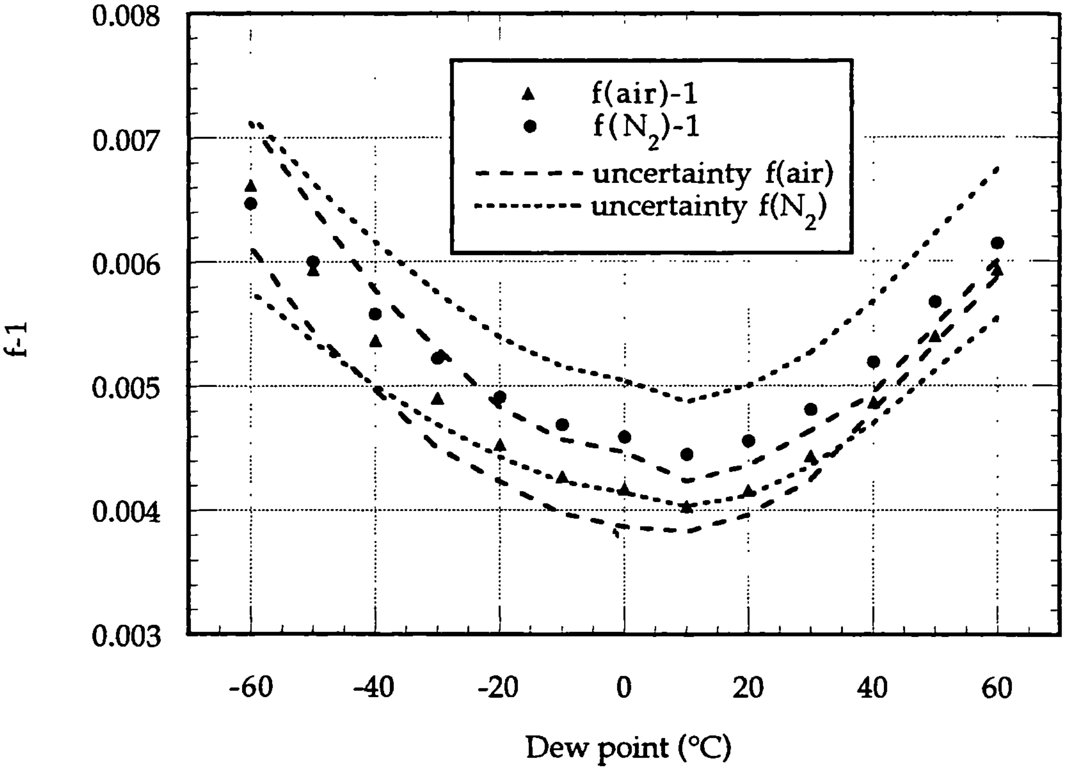

Figure 24 Calculated values of the water vapour enhancement factor, *f*, at 105 kPa and at a range of temperatures. Values are shown for air (Hyland, 1975) and for nitrogen (this work).

in the International Practical Temperature Scale of 1968 (IPTS-68). Since the enhancement factor varies only slowly with temperature, the error introduced by applying these values to results given in terms of ITS-90 is less than 1 part in 10^{-6}.

An estimate of the uncertainty in values of enhancement factor for nitrogen was arrived at by considering Hyland's estimates of uncertainty (based on his uncertainties for the virial coefficients) and incorporating the uncertainties in the replacement coefficients and approximations for nitrogen.

The estimated uncertainties in this version of enhancement factor for nitrogen are shown for various values of humidity in Table XIV along with the uncertainties in the Hyland formulation for air, with the uncertainties of the gravimetric hygrometer shown for comparison. All the values tabulated refer to a pressure of 105 kPa, which is the nominal pressure of operation of the NPL humidity generator.

5.5. Other sources of error that can affect intercomparison results

There is a category of measurement uncertainties which may neither be intrinsic to the gravimetric hygrometer nor to the instrument being compared against it, but relates to the interface between the two. Broadly speaking, these can be termed "sampling uncertainties".

Any measurement with the gravimetric hygrometer always involves sampling over an extended period of time, resulting in an average or integrated value of humidity. It is therefore desirable to ensure that the humidity source being measured (or being used as a transfer medium between the gravimetric hygrometer and other instrument) is stable during the course of the measurement. If an average estimate of input humidity (in whatever units) is to be compared with the gravimetric "integrated" value, then any variability of the input gas must be symmetrically distributed about the mean. This condition is normally easily satisfied, with no significant uncertainty in the mean. Where there is any doubt about even distribution, or about steady flow rate, the values of sampling flow rate and input humidity can be monitored throughout the sampling period. If necessary, an allowance for variations can be made by the inlet humidity according to flow rate before calculating an average.

In any sampling process there is always a risk of systematic errors due to the

Table XIV Uncertainties in water vapour enhancement factor for nitrogen calculated for this work, with uncertainties for air (Hyland, 1975) and those for the gravimetric hygrometer shown for comparison.

Dew point at atmospheric pressure °C	Estimated worst-case uncertainty in water vapour enhancement factor, (percent)		Uncertainty of measurement for the gravimetric hygrometer at a level of confidence of 95% (shown for comparison)
	Hyland (1975) for air	This work, for nitrogen	Percentage of mixing ratio result
60	0.01	0.05	0.015
40	0.01	0.07	0.017
20	0.02	0.08	0.033
0	0.04	0.10	0.113
-20	0.05	0.12	0.113
-40	0.06	0.13	0.36
-60	0.08	0.14	1.27

method of sampling. In the case of gravimetric measurements, it is important to consider possible sources or sinks of water vapour which may act on the flow path between the instrument under test and the gravimetric system. The possible effects of leaks and desorption of water vapour from the inner surface of the connecting pipe to the gravimetric hygrometer must therefore always be considered. In practice the possibility of error due to desorption is minimised by purging the inlet pipe prior to the collection, using gas of the humidity to be measured, until the inner surface has equilibrated with the gas. At high humidities, this is quickly achieved. At low humidities care is taken to purge the pipe for some time. For this purpose, a bypass valve was installed. This allows flushing with gas during the preparation for a collection, with minimum disturbance to the other initial conditions of the measurement.

The pressure of the sample gas is obviously significant in the interpretation of gravimetric results, if they are to be expressed in units other than mixing ratio (which is itself independent of pressure). Pressure is also significant in a secondary sense. The values of all corrections for trapped volumes of gas depend upon supply pressure of the sample gas. For sample gas supplied at 105 kPa, the corrections given in Section 3.11 are valid.

5.5.1 Sampling uncertainties in this intercomparison

For the particular measurements reported here sampling uncertainties were estimated as follows:

Leaks and desorption

For sample gas supplied to the gravimetric hygrometer at a few percent above atmospheric pressure, leaks on the path between the two instruments can be assumed to be mainly outwards, with no effect on measurements. Desorption, on the other hand, can be expected to act on the gas in the pipe between the humidity generator and the gravimetric hygrometer. According to Kochsiek (1982), clean stainless steel at room temperature is host to some 0.25 μg to 0.7 μg of adsorbed water per cm^2 of surface. The maximum error due to desorbed gas occurs if all this water is released into the gas stream. For the connecting pipe used, this would result in an increase of 70 μg to 200 μg in the mass of collected water (most significant at low humidities). Realistically, prior conditioning by flushing with sample gas is estimated to reduce the effect to less than one-tenth of this, leading to a worst case uncertainty of 20 μg and hence a standard uncertainty of 12 μg of water. This leads to a standard uncertainty of 12 μg kg^{-1} divided by the mass of gas in kilograms, e.g. 30 μg kg^{-1} when 400 g of gas is collected. The effects for a range of mixing ratios are shown in Table XV. The converse effect - adsorption of water by the connecting pipe at above-ambient humidities - is considered to have negligible influence on the results.

Gas composition

Any uncertainty in the molar mass of the carrier gas leads directly to an equivalent uncertainty in the intercomparison results. The main uncertain component in the supply gas was reported by the manufacturers to be argon, said to be present at a rate of between 0 and 50 parts per million by volume (ppm(v)). In the worst case, an uncertainty between presence of nitrogen and argon at 50 ppm(v) leads to an uncertainty of 50×10^{-6} times the difference in molar mass between argon and nitrogen molecules. This results in an uncertainty of 0.002% of the mass of gas collected. Hydrogen at a rate of 0.5 ppm(v) contributes 0.001% of gas mass, and Helium at 5 ppm(v) 0.005% of gas mass. Similarly taking into account small impurities of oxygen, CO, CO_2 and hydrocarbons, the standard uncertainty from this source is 0.005% of the average molar mass. This is small enough, relative to the other sampling uncertainties, that it can be neglected.

Gas pressure

The calibration of the pressure sensor used was reported with a worst-case uncertainty of ±0.02 percent of result for the values of pressure considered in this work. Assuming a rectangular distribution, this results in an estimated standard deviation of 0.012% of pressure value, leading directly to an uncertainty of this amount in the intercomparison results.

Other contributions to be taken into account in considering the uncertainty of these intercomparison measurements are the uncertainties in vapour pressure (values are listed in Table XIII) and in water vapour enhancement factor (values in Table XIV).

The sampling uncertainties for use of the gravimetric hygrometer to measure gas supplied by the NPL humidity generator are summarised in Table XV. The overall effect is found by addition in quadrature to give the combined standard uncertainties due to sampling, shown in the final column.

5.6. Gravimetric measurements of the output from the NPL humidity generator

A total of 25 gravimetric measurements of gas supplied from the NPL humidity generator were carried out in the course of this work. Results of 14 of these are detailed below.

The results of the gravimetric measurements were calculated using SMARTII Spreadsheet software. The spreadsheet analysis incorporated all the corrections detailed in Chapters 3 and 4. An example of a printout of the spreadsheet formulae and results is shown in Appendix 4. For the 14 measurements detailed below, flow-weighted averages of generated dew-point values were calculated prior to entering the data in the spreadsheet.

Table XV Sampling uncertainties for use of the gravimetric hygrometer to measure gas supplied by the NPL humidity generator.

Dew point °C	Standard uncertainty in mixing ratio from individual sources %				Combined standard uncertainty %
	Estimated desorption	Measured pressure	Vapour pressure data	Enhancement factor data	
60	0	0.012	0.05	0.03	0.06
40	0	0.012	0.06	0.04	0.07
20	0	0.012	0.06	0.05	0.08
0	0.001	0.012	0.08	0.06	0.10
-20	0.005	0.012	0.10	0.07	0.12
-40	0.014	0.012	0.12	0.07	0.14
-60	0.12	0.012	0.17	0.08	0.22

5.6.1. Early trial measurements

The early results were not intended to be judged as an intercomparison between the gravimetric hygrometer and the humidity generator. Many of these early measurements did not benefit from a full understanding of the measurement processes, and were exploratory only. For example, during early work no great care was taken concerning the composition of the nitrogen gas supply: this was only considered important later. In fact, for measurements up to and including Number 11 the nitrogen gas passed through a dryer normally used for air. By this process, oxygen in unknown quantity would have been inadvertently incorporated into the nitrogen gas stream. In addition to this, the first few measurements were compromised by the instability in the masses of the collection vessels. Therefore most of these measurements carried much larger uncertainties than have since been established. Developments in the techniques of humidity generation during that time are also a reason for disregarding these results.

Preliminary runs 1 to 11 can be briefly summarised as follows. Measurements were carried out at dew points of -60 °C, -30 °C (twice), -10 °C (three times), 1 °C, 10 °C (three times) and 30 °C. In general, the values of humidity determined gravimetrically were lower (more dry) than the values of dew point indicated by the humidity generator for the same gas. The average difference was 1.34 percent of result, or 0.17 °C in dew point.

5.6.2 Results of intercomparison measurements

The results of the 14 most recent measurements are given in Table XVI, grouped according to value of humidity measured. The results are shown graphically in Figure 25.

Some points which should be noted for certain measurements are as follows:

Run 13 (at -60 °C) carries an enlarged uncertainty due to an exceptionally large leak at the connection between the gas vessel and the main assembly. A repair solved this problem for later measurements.

Runs 19 and 20 at -30 °C were carried out using air as the carrier gas, to demonstrate the feasibility of this. The synthetic air used was Air Products "Alpha-Grade" made with electrolytic oxygen, supplied with a certificate of analysis of the composition. The corrections applied for trapped gas were all adapted by multiplying values by the ratio of the densities of air and nitrogen. These measurements are assigned uncertainties as if for nitrogen, although it is conceivable that other uncertainties may be associated with the use of air.

The humidity generator underwent some improvements during the period when the measurements took place. Accordingly, the uncertainties in the generated values of dew point were improved by approximately one half between the measurements numbered 16 and 17. This is the reason for the variation in the uncertainties reported for the values of generated dew point for particular humidities.

The measurements were carried out before the comprehensive analysis of uncertainties was completed (but results were reviewed in the light of this). Therefore no special care was taken, for example, to avoid unfavourable combinations of microbalance weights, which did in fact occur for Run 13, and less so for others.

5.6.3. Initial comments on the intercomparison results

Preliminary inspection of the results of the intercomparison leads to the following conclusions. The gravimetric hygrometer and humidity generator largely agree to within the combined uncertainties, especially if the sampling uncertainties are taken into account. Where slight disagreements are found, there does not appear to be any significant systematic trend in the deviations. The extent of any systematic trend can be judged from the difference between the average values given by the gravimetric hygrometer and the average values for the humidity generator. This gives an overall agreement of 0.36 percent of result (equivalent on average to 0.04 °C in terms of dew point) with the gravimetric determination showing the gas to be on average more dry than was indicated by the value of generated dew point. This should be viewed in the light of the average uncertainty in the gravimetric results (1.1 percent of value at the 95% confidence level), the average uncertainty for the humidity generator (equivalent to 0.99 percent of value) and the typical

Table XVI Summary of measurements of the NPL humidity generator using the gravimetric hygrometer. Measurements marked with an asterisk (*) employed air as the carrier gas.

Results			Percentage uncertainties (at 95% confidence)		
Dew point °C	Run number	Difference (measured value minus generated value) %	Gravimetric uncertainty	Uncertainty in generated dew point (converted into percent of mixing ratio)	Other (sampling) uncertainties
60	12	-1.67	0.05	0.86	0.12
10	22	+1.11	0.11	0.34	0.18
	23	-0.56	0.04	0.34	
	24	+0.55	0.04	0.34	
1	21	-0.41	0.18	0.36	0.20
-10	17	+0.37	0.07	0.45	0.22
	18	-0.11	0.07	0.45	
-30	15	+0.12	0.26	1.56	0.26
	16	+0.63	0.21	1.56	
	*19	+0.06	0.17	0.52	
	*20	+0.11	0.13	0.52	
-60	13	-4.56	9.5	2.7	0.44
	14	-0.59	2.2	2.7	
	25	-0.15	2.2	1.2	

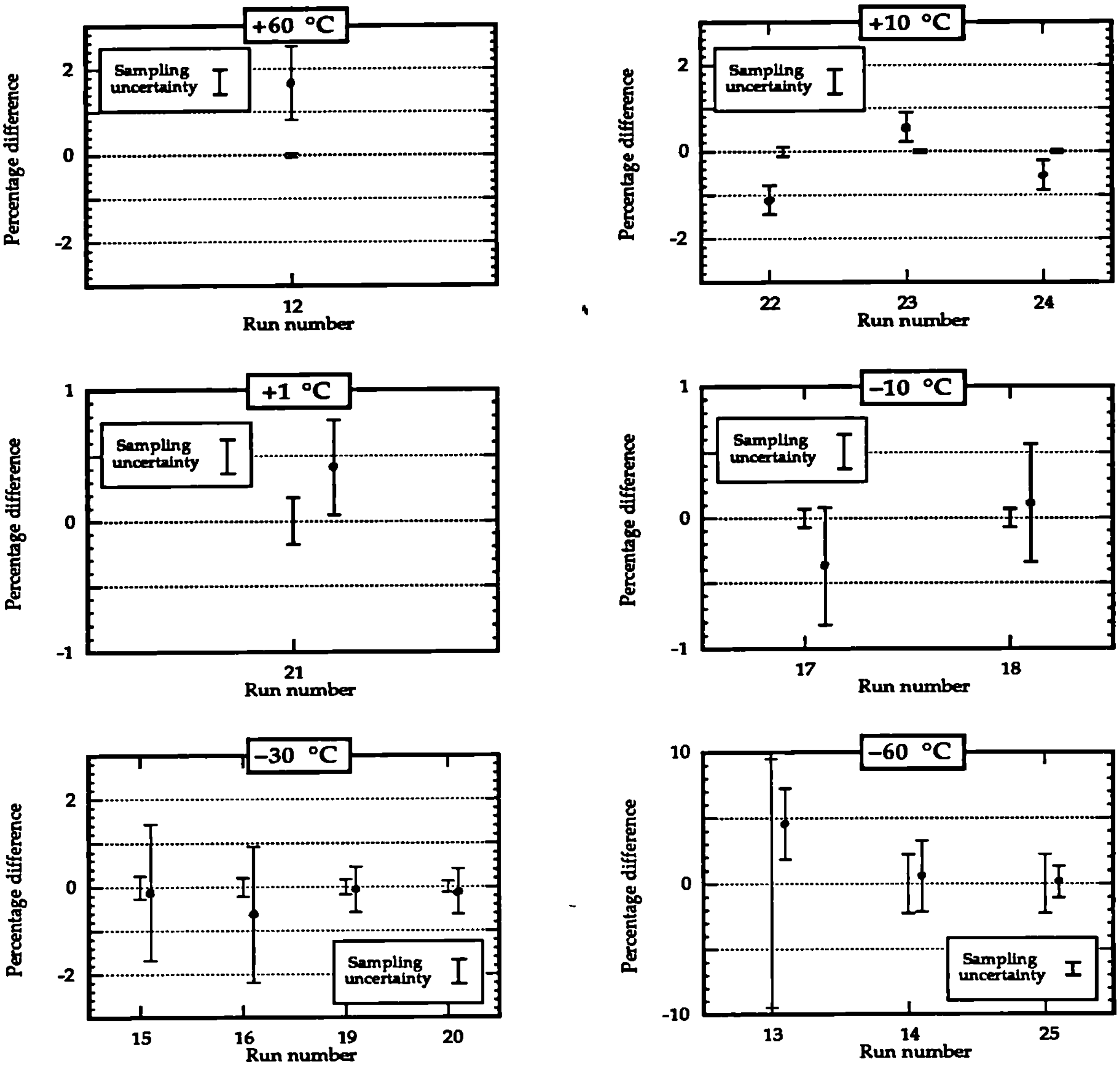

Figure 25 Graphs showing the results of measurements intercomparing the gravimetric hygrometer and NPL humidity generator.

The data points (•) show the values for the humidity generator, relative to the gravimetric values (taken to lie on the x-axis). Error bars shown symmetric about the data points (⫯) are the uncertainties for the humidity generator. Error bars shown symmetric about the x-axis are uncertainties for the gravimetric hygrometer. Error bars shown inset indicate sampling uncertainties. All are shown at a level of confidence of approximately 95%.

sampling uncertainty (0.26 percent of value). The standard deviation of the individual differences between the generated and measured values of humidity is 1.38 percent of value, giving a standard error of the mean for the results of 0.37 percent of value.

5.7. Significance of results of this Chapter

In this Chapter, the work has been reported in support of the third and fourth objectives of this project (given in Section 1.1).

To meet the third objective, the interface between the gravimetric hygrometer and other humidity instruments has been considered. This assessment has covered both the theoretical and the practical aspects of the interface. On the theoretical side, the data for converting between mixing ratio and other units of humidity have been considered. A novel adaptation of the water vapour enhancement factor has been calculated for use with nitrogen. On the practical side, the sampling errors associated with the gravimetric measurements have been considered, particularly for intercomparisons with the NPL humidity generator.

Results of the gravimetric measurements have been reported for a comparison of this instrument against the NPL humidity generator. The results show the two realisations to agree within the combined uncertainties for most of the measurements, thus meeting the fourth and final objective of the work.

These findings are discussed in more depth in the following Chapter, where the whole of this work is viewed in perspective.

5.8. References

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CHAPTER 6

Discussion of the performance of the gravimetric hygrometer

Sherlock Holmes: "From a drop of water a logician
could predict an Atlantic or a Niagara."

Sir Arthur Conan Doyle *A Study in Scarlet* 1929 (London: Murray) p 29

CHAPTER 6. DISCUSSION OF THE PERFORMANCE OF THE GRAVIMETRIC HYGROMETER

6.0. Abstract

The results of the validation of the NPL gravimetric hygrometer have been discussed at a detailed level throughout the earlier chapters, but the work as a whole can now be viewed in perspective.

The established performance of the hygrometer is reviewed. The practical factors influencing the overall uncertainty are considered in overview, including criteria for the continuing validity of this estimate. The quality of the uncertainty analysis is assessed, with comment on the degree of reliance that can be placed on the estimate of uncertainty. From the effective number of degrees of freedom, the "uncertainty in the uncertainty" is statistically estimated to be approximately 3%, and other measures of confidence are discussed.

The implications of this for the intercomparison with the NPL humidity generator are considered, with a discussion of the relative significance of random and systematic components of uncertainty. In the light of this, the degree of variability in the agreement between the gravimetric hygrometer and the humidity generator is found to be reasonable. The average difference of 0.36 percent of value found between the gravimetric hygrometer and the humidity generator is not found to be statistically significant in comparison with the spread of results.

The influence and quality of the reference data are reviewed, especially the water vapour enhancement factor adaptation for nitrogen used in this work.

The position of this work in the field is reviewed, comparing the present work with that on other gravimetric hygrometers. The advantages of the NPL instrument lead to a wider operating range, and uncertainty equal to or better than others reported, and the practical reasons for this are highlighted.

Other possible interpretations of the gravimetric hygrometer results in relation to the reference data and the generated dew point results are also considered.

6.1. Estimated performance of the gravimetric hygrometer

The operation of the NPL gravimetric hygrometer has been validated in the range 0.01 g kg^{-1} to 155 g kg^{-1} (-60 °C to +60 °C in dew point), and corrections for significant sources of error have been evaluated. For humidities in this range, the uncertainty in the mixing ratio is found to range between 0.015 percent and 1.27 percent of result at a level of confidence of at least 95% (a coverage factor of k=2). This offers the possibility of calibrating other hygrometers or humidity generators to these levels of uncertainty (plus any uncertainty in converting between units of mixing ratio and dew point, and any other sampling uncertainties, which would depend partly on the instrument in question).

The estimated overall uncertainty differs in places from the early prediction - quantitatively, if not qualitatively. It is better than expected at high humidities, but somewhat less good at lower humidities. There may be no distinct reason for these differences, other than the approximate nature of the prediction. However the estimate is discussed below, highlighting the reasons for the results, and considering where they might differ from earlier assumptions.

6.1.1. Practical factors affecting the uncertainty of measurement

The factors leading to a small or large overall uncertainty have been partially discussed in Chapter 4 in order to consider optimisation with respect to these factors. Figure 26 shows the overall uncertainty in the gravimetric measurements, with the contributions from water and gas aspects also shown for comparison. This clearly shows how the overall uncertainty is dominated by the uncertainty in the mass of water for low and medium humidities, and by the uncertainty in the mass of carrier gas for high humidities. Only above a dew point of 40 °C does the uncertainty in evaluating the collected gas become more significant than that associated with the water component.

The overall uncertainty is greatest where least advantageous conditions hold; either at low humidities where only small quantities of water can be collected, with large relative error in using the microbalance; or at the crossover point around a dew point of 0 °C where the predryer comes into use for collection of only a gram or

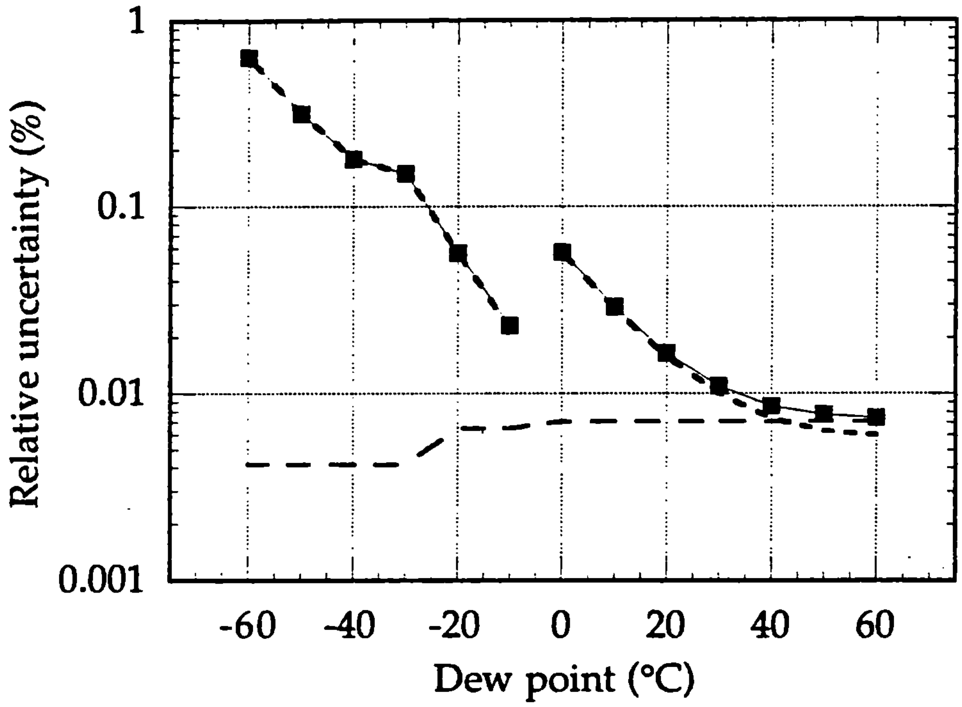

Figure 26 Comparison of the overall uncertainty for the gravimetric measurements (—■—) with those for the water (- -) and gas (— —) aspects of the measurement

two of water.

In most respects, these variations in accuracy are common to just about any approach to humidity measurement. Qualitatively, accuracy is always difficult to achieve at low humidities, and easier at medium to high humidities. However, the local peak in uncertainty in this case near ambient humidity is substantially unique to this gravimetric method as applied here.

Although the design of this hygrometer leads to a maximum in uncertainty at the crossover between the two modes of operation there is nothing about the general gravimetric principle, nor intrinsically about the humidity region itself [7], that

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[7] However the region just below 0 °C is often considered "intrinsically" difficult because of the possible presence of supercooled water.

What does create an impression of some regions having intrinsically better or worse uncertainties is the relationship between dew point and mixing ratio. At dew points near 50 °C, a step of 1% is equivalent to nearly 0.18 °C. The equivalence becomes more advantageous above and below (continued...)

necessarily places that crossover just above a dew point of 0 °C. It is simply the design and the usage of this particular instrument which place the crossover point where it is. Were the capacity of the microbalance or gas collection system to be different or differently used, then the transition to using the predryer could be engineered to lie at a different point in the humidity range. Alternatively, if it were considered practically acceptable to consume the full charge of the desiccant in a single use, the crossover point could be relocated a few degrees above 0 °C in dew point. However, due to the logarithmic form of the mixing ratio curve, it would require quite a radical change in one of the above capacities (of perhaps an order of magnitude) to shift the crossover point significantly.

6.1.1.1. Peak in uncertainty mid-range due to predryers

Where the uncertainty peaks near a mixing ratio of 4 g kg^{-1} (a dew point of 0 °C), this is due to the large uncertainty contribution associated with the predryers in this region. Practical work on these did not (after the "breathing" anomaly was resolved) throw up any particularly surprising sources of uncertainty. However, the need to estimate an allowance for retention of other gases in the molecular sieve was not originally foreseen. This and the uncertainty in quantifying the gas trapped in the dead space in the predryer seem to be the only factors here which are potentially open to any improvement. The allowance for other species trapped in the molecular sieve might be lessened if even purer supply gases could be used. Alternatively, the method of quantifying the gas trapped in the dead space could be re-considered. The latter, being the largest component of uncertainty, offers the most benefit if it can be reduced.

6.1.1.2. Uncertainty at low mixing ratios due to limited collection of water

At the lowest values of humidity, where relatively little water can be collected, the most significant limiting factor is the performance of the combination of cold-trap,

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[7](...continued)
this value, with 1% ≈ 0.16 °C at a dew point of 70 °C, while for 10 °C 1% ≈ 0.15 °C and for -60 °C 1% ≈ 0.07 °C. Hence the value, in terms of dew point, of a given percentage uncertainty depends on the particular humidity concerned.

desiccant and microbalance. This has several important contributions; the efficiency of the cold trap, the repeatability of transfer of water vapour from the cold trap to the desiccant, and the uncertainty in the microbalance weighings.

Any improvement on the uncertainty in the cold trap efficiency would be difficult to achieve. The original tests of efficiency were time consuming and involved technically demanding measurements at the extreme low end of the measurable humidity range. Though techniques have advanced a little since that work was done, re-evaluation would still be difficult and costly, without any guarantee of a better result. In any case, this uncertainty is less significant than the others below.

The repeatability of transfer of water vapour from cold trap to desiccant was tested by repeated transfers from the cold trap in a nominally empty condition, and by other step-wise transfers, weighing at intervals to ascertain when transfer was complete. These tests, though not especially difficult, were time consuming and this restricted the number of repetitions that could be performed to five. Clearly a larger sample would be desirable. However, although the standard error of the mean and the accuracy of the estimate of standard deviation could be improved by repetition, the variability of the condition itself (i.e. the standard deviation) could not. Perhaps the main justification for more work on this aspect would be the hope of finding some systematic effect behind this variability, which might then be eliminated or reduced. Additionally, the characterisation of the transfer repeatability would be better if the repeatability of the microbalance measurements could be improved.

The use of the microbalance accounts for the most significant component of uncertainty at very low humidities. The cautious approach to allowing for drift in the platinum weights, using only the evidence of consistency checks *in situ* in order to avoid opening the vacuum chamber, is clearly a disadvantage. The initial prediction of the expected performance of the gravimetric hygrometer would certainly have been based on less cautious assumptions. Taking the uncertainty in the masses of the weights to be that given on the calibration certificate leads to an uncertainty from this source of no more than 2 μg, rather than the 25 μg to 140 μg uncertainty allowed for in this case. Using the smaller (2 μg) figure to calculate the overall uncertainty, by the method described earlier, results in values of uncertainty for the lower half of the operating range which are easily within the forecast values, down to -40 °C, as illustrated in Figure 27. At some time in the future, the weights

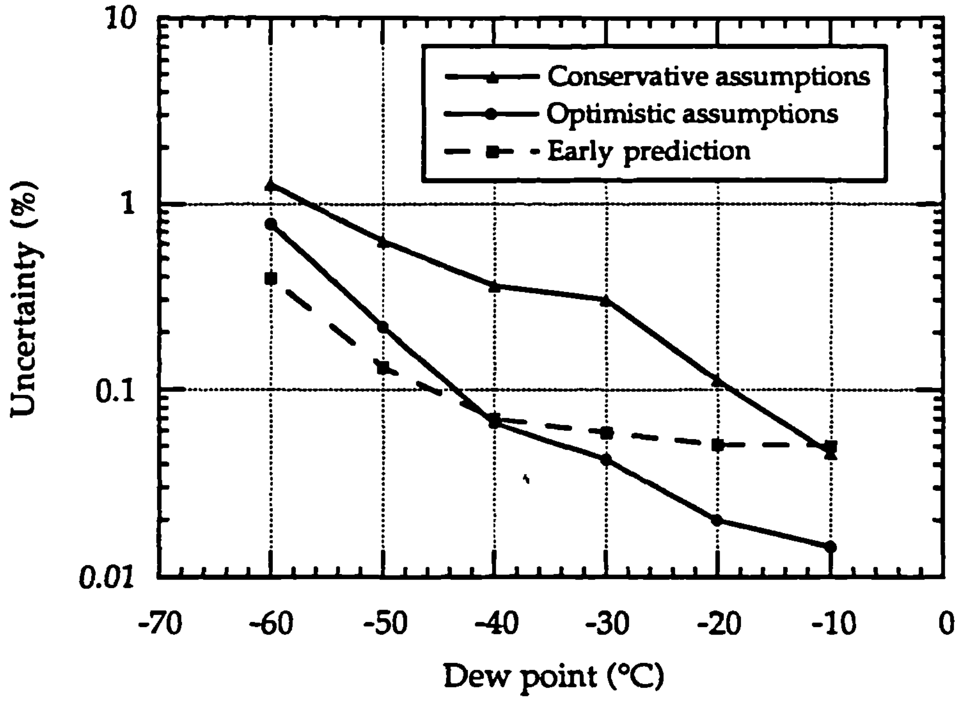

Figure 27 Comparison of best (cautious) estimate of uncertainty with optimistic estimate and original forecast, for the lower half of the operating range of the gravimetric hygrometer

will have to be removed and recalibrated. Recalibration would almost certainly show the weights to be more stable than allowed for in the uncertainty budget, and would provide a basis for a prediction of their ongoing stability. Overall it is likely that this would reduce that aspect of uncertainty, allowing the overall estimate to be revised to lie somewhere between the upper and lower curves in Figure 27. However, until this can be undertaken, the cautious estimate, based on the limited possibility for checking, must continue to apply.

The repeatability of the microbalance itself, while not a major contribution to uncertainty, was somewhat disappointing, with a typical estimated standard deviation of 7 μg. This may simply reflect the intrinsic level of "noise", the effects of vibration or mechanical disturbance, or perhaps the temperature sensitivity of the electronics. However it is possible that the variability is symptomatic of some other effect, perhaps even with a systematic component. Among the potential problems warned of by Sira at the design and commissioning stages were; static charges on the microbalance assembly, thermal "radiometer-type" effects, and the effects of convection processes at low pressure. Each of these is capable of exerting an anomalous force on one side of the balance. Forton and Day (1986) in their paper on the development of the microbalance concluded from the design, and from their tests, that there should be no significant effects of these kinds. However the isolation of the balance under vacuum makes it virtually impossible to investigate these possibilities fully.

6.1.1.3. Contribution to the overall uncertainty from gas aspects

In the measurement of the collected gas, there appeared to be few serious difficulties after the weight-gain anomaly was resolved. As was expected, the largest fixed uncertainty was in the estimate of the mass of gas retained in the cold trap. This estimate could be improved slightly by further measurements in addition to the four conducted so far. However it is estimated that the main contribution to this uncertainty is the variability of conditions such as pressure, temperature and the precise timing of the operation of the valves. This variability could not be reduced through repeated measurements, though automation of the valve system might improve the repeatability of the process slightly.

Comparable with the above in magnitude is the uncertainty due to the change in buoyancy in air associated with the expansion of the gas vessels. In evaluating this, the outcome was dominated by the uncertainty in the dimensional measurements. This was practically dictated by the need to make measurements *in situ* using a vernier calliper. Were it possible to transport the vessels safely, while pressurised, to a precision measurement facility (e.g. a coordinate measuring machine), then a better estimate could be made. However, in the parts of the operating range where this would make a significant improvement ,the overall uncertainty is already relatively small.

Surprisingly, there appears to be only slight benefit, in terms of uncertainty, to using the small vessels where the quantity of gas permits, instead of the large ones. The advantages in handling and weighing an item of smaller overall mass are almost balanced by the disadvantage of uncertainty in the volume change, which (uncertainty) is greater for the smaller vessels. This difference in uncertainty is because both sizes of vessel accommodate about the same pressure when full, but for a given mass of gas, the small one is more full (and so reaches a higher pressure) than the large one.

In the analysis of the uncertainties, it has been assumed that no more than 1000 g of gas is collected in the large size of vessel, even though they have a nominal capacity of 1100 g. This was for operational reasons since, during the collection of sample gas, neither the control nor the monitoring of the flow rate could be relied upon precisely. Therefore, to allow a margin of safety, especially in view of the unsupervised overnight operation, the upper target of 1000 g was set. Were this target quantity to be increased by 10% to 1100 g, then the uncertainty would be reduced. However, the improvement would not be as much as 10%, since those components of uncertainty proportional to collected water or gas would not thereby be reduced.

6.1.2. Quality of the uncertainty estimate

What can be said about the reliability of the uncertainty analysis? Below, a number of factors are considered, such as the effective number of degrees of freedom, the effect of deviation from normal distribution, the uncertainty in the uncertainty, and the applicability of the estimate.

The number of degrees of freedom associated with a statistical estimate is an indication of how reliable the estimate is, according to how it was derived. For a Type A evaluation of uncertainty based on simple repeated measurements of a single quantity, the number of degrees of freedom is usually n-1 where n is the number of measurements carried out. The situation is different for Type B evaluations, which are a more significant contribution in this case. For any single Type B estimate, the effective number of degrees of freedom may sometimes be taken to be infinite, reflecting the fact that, where bounds of uncertainty are estimated, this is usually done conservatively. Where there is any doubt in such an estimate, $u(x_i)$, the effective number of degrees of freedom, υ_i, can be estimated approximately from

$$\nu_i = \frac{1}{2}\left(\frac{\Delta u x_i}{u(x_i)}\right)^{-2} \tag{36}$$

where the quantity in large brackets is the estimated relative uncertainty in $u(x_i)$, based on scientific judgement (ISO, 1993). Hence, for any given Type B estimate for which the "uncertainty in the uncertainty" is believed to be, say, one third, the effective number of degrees of freedom is about 5. (In fact this would probably be a worst case for the Type B estimates of uncertainty in this work.) For simple repeated measurements of a single quantity, a confidence level for the result would usually be found using the Student's *t*-distribution to allow for the effect of sample size, or number of degrees of freedom. However for evaluations of the present type the ISO *Guide* suggests that the overall effective number of degrees of freedom υ_{eff} can be estimated from component uncertainties $u_i(y)$ and combined standard uncertainty $u_c(y)$ using the Welch-Satterthwaite formula (Welch, 1936; Fairfield-Smith, 1941; Satterthwaite, 1941):

$$\nu_{\mathrm{eff}} = \frac{u_c^4(y)}{\sum_1^N \frac{u_i^4(y)}{\nu_i}} . \tag{37}$$

For this work, a worst-case value of υ_{eff} has been estimated. This worst case is taken to occur at 0 °C, where equation (36) has a relatively large denominator (from a large single component of uncertainty) and a relatively small numerator (from the overall fractional uncertainty which is small in comparison). At this level of humidity, there are 16 significant sources of uncertainty listed in Table VIII. Approximating crudely and pessimistically; the largest has a relative standard uncertainty of 0.054%, and the others are all of order 0.01% or less (most are in fact much smaller). Pessimistically taking all these estimates to have $\upsilon_i = 5$, then for $u_c = 5.7\times10^{-4}$, equation (36) gives $\upsilon_{\mathrm{eff}} > 700$. More careful calculation would give a larger number, as would evaluation for more advantageous regions of the measurement range. The effective number of degrees of freedom can thus be considered to be "close to infinite". (At $\upsilon = 120$, the Student's *t*-distribution is within 1% of the normal distribution given by an infinite number of measurements.)

The ISO *Guide* (ISO, 1993) offers an approach to ascertaining the "uncertainty in the uncertainty" (ISO, 1993; 4.3.2., Note). For a normally distributed variable q, with mean $\bar{q}$, then the standard deviation of the standard error of the mean, $s(\bar{q})$, relative to that of the population, $\sigma(\bar{q})$, is approximately $[2(\upsilon)]^{-1/2}$, where υ is the number of degrees of freedom. Thus, for $n = 10$ observations, the relative uncertainty in $s(\bar{q})$ is 24 percent. Similarly, for 700 effective degrees of freedom, as estimated above, the uncertainty in the uncertainty is less than 3%. This might appear to require the addition of this figure to the standard uncertainty estimated so far. However there is no convention for doing so.

The above process is one way of estimating the uncertainty in the uncertainty. However, this depends heavily upon the assumptions made about the individual estimates, and would fail to give a sensible result whenever particularly conservative judgements were made in evaluating the individual components. If so, then by judgement alone, one could assert that the estimate was likely to be "safe", with less than the calculated likelihood of being an underestimate. In this work, it is tempting to believe that the estimate of the stability of the microbalance weights is conservative, and that a higher level of confidence might therefore be associated with the result. However the latter is simply an estimate which is limited by the resolution of the measurements that can be made (for the time being).

In some parts of the measurement range of the gravimetric hygrometer, there is one predominant component of uncertainty. This is the case, for example, at the lowest humidity where the predryer is used. Where one rectangularly distributed contribution to the uncertainty dominates, the overall uncertainty may not in fact closely follow a normal distribution (upon which assumption the assignment of confidence interval depends). Qualitatively, convolution of a normal distribution with a rectangular distribution would tend to result in a probability distribution with wider "shoulders" and more shallow "tails" than the normal curve. However it is noted in the ISO *Guide* (ISO, 1993; Appendix G2.2, Note 1) that for levels of confidence greater than about 92%, the coverage factor for a normal distribution is greater than that for a distribution dominated by a rectangular component. As a consequence, the uncertainty estimate in this work is, if anything, a slight overestimate (i.e. the coverage factor of k=2 gives well over 95% confidence).

Some individual aspects were conservatively estimated (despite the recommendation of the ISO *Guide* that estimates should be realistic, not cautious). It may even be true that some uncertainties have effectively been counted twice because of the complexity of the process. On the other hand, there is some danger of sources of uncertainty being overlooked, and of correlations between components not being taken into account. In all the analysis so far, there is no allowance for the very special kind of errors called mistakes. Errors of this kind are inevitable in real situations. They fall into two categories: operator errors, where a mistake is made once or repeatedly in the execution of measurements; and errors of principle, where some aspect of theory or design has been misunderstood or overlooked in the first place. It is hoped that errors of the second kind have been reduced to a minimum through the combination of many years' attention by the author, the designers, and those who have explored the subject in the past. But in any case the recommendation of the ISO *Guide* is (perhaps surprisingly) that a realistic uncertainty budget can have no allowances for the unforseen. In that sense, the approach in this work is realistic, rather than conservative.

It is important to note the conditions under which this estimate of uncertainty is valid. First of all, it applies to the ideal measurement conditions characterised by the flow rates, durations and masses of water and gas set out in Table X. Without being in any way over optimistic, these conditions lead to the best possible accuracy for the gravimetric hygrometer measurements. Any less optimal usage, such as the collection of a smaller sample of humid gas, leads to larger uncertainties. The circumstances of many of the intercomparison measurements reported here were not optimal, and this is shown in the individually calculated values of uncertainty; most of which do not reflect the best measurement capability.

Secondly, these estimates of uncertainty only apply if the measurement procedure remains unchanged from that reported here. Certain aspects are particularly important. For example, the supply pressure of the test gas being measured is assumed to be within 0.1 percent of 105 kPa. If another value of pressure were used then the values of corrections due to gas trapped in dead spaces would have to be re-evaluated. Any change in the usage of the cold trap (for example at a different temperature) would also require this. A different cold-trap temperature would also lead to a change in the efficiency of retaining water. On the other hand, a change of operator would not, in principle, be expected to invalidate the current estimate of uncertainty, since the operator-dependent processes such as visual balance readings are not a significant contribution to the overall uncertainty. The only cause for concern would be that in practice an inexperienced operator might make mistakes, or might not understand the importance of certain actions in operating the hygrometer. It is hoped that the present written account will help to safeguard against these risks in the future.

6.2. Comments on the intercomparison between the gravimetric hygrometer and the NPL humidity generator

The intercomparison results reported in Chapter 5 show broad agreement between the gravimetric hygrometer and the NPL humidity generator, within the combined uncertainties, except just above a dew point of 0 °C, where the results appear marginally more variable than would be expected from the estimated uncertainties. This variation might seem to cast doubt on the estimate of uncertainty for this range, and perhaps even for the rest. However, some explanatory points are raised below.

It should be noted first of all that, for these particular measurements, the individually calculated uncertainties are larger than the generalised values given in Chapter 4. The particular values are larger because the measurements were all carried out in less than optimal conditions: for example, less than the maximum quantities of gas and water were collected in all these cases. This entirely accounts for the differences in uncertainty between generalised ideal measurements and the particular results reported here.

6.2.1. Spread of results

Detailed discussion of the systematic and random nature of components of uncertainty has been avoided so far. That distinction has not been an explicit consideration in the uncertainty analysis as conducted here, and this is in line with the ISO recommendation. However some discussion of this at this stage will help in considering the intercomparison results.

After correction of known systematic errors, the remaining uncertainties fall into categories which are associated with effects such as:

- unknown systematic errors that are expected to be constant in all cases;
- unknown systematic errors that are constant on any single occasion of measurement, but are expected to vary randomly from occasion to occasion; and

- random effects for which the uncertainty can be reduced on any occasion if the number of observations is increased.

In terms of the analysis in Chapter 4, only the third of these categories is referred to as Type A. However both the second and third categories can be considered random in this discussion. This illustrates how the distinction between Type A and Type B uncertainties is not the same as between random and systematic.

Re-examining the component standard uncertainties, which are summarised in Table VIII, the approximate balance between random and systematic contributions can be noted qualitatively. For the gas aspect of the measurement, the large component uncertainty due to gas trapped in the cold trap has a minor systematic contribution (volume of the cold trap) and a major random contribution (temperature and pressure at which gas is trapped), shown in the variability among the four experimental determinations. The other large uncertainty due to expansion of the gas vessels is liable to be systematic, since the coefficient of expansion would have a single value in practice. Significant but lesser contributions to the uncertainty in mass of gas are in the handling of gas vessels (random) and other smaller effects, of which about half are judged to be random, while the rest are estimated to arise from some mixture of random and systematic effects. Therefore, giving most weight to the major contributions, the estimated uncertainty in the mass of gas is seen to be balanced between a random and a systematic character.

A similar analysis can be conducted for uncertainties relating to the predryer. The dominant uncertainty, due in the gas trapped in the dead space in the predryer, is taken to be essentially systematic, arising from the uncertain knowledge of the (fixed) internal volume of the vessel. The other aspects of uncertainty for the predryer are judged to be evenly divided between random and systematic types.

Concerning the key aspects of the microbalance-cold trap uncertainty, the variations in the water vapour transfer are taken to be random. The uncertainty in cold trap efficiency might be dominated by random or systematic effects with equal likelihood. The uncertainty allowance for drift in the microbalance weights is characterised as systematic, since the most likely types of drift would be a universal increase in actual masses due to contamination, or a universal decrease due to wear. The outcome for this aspect, therefore, would be mainly random where relatively small quantities of water are collected in the cold trap, but mainly systematic for larger amounts.

The sampling uncertainties include contributions some of which are estimated to be systematic (vapour pressure and enhancement factor; these both having unknown but constant errors for any given value of humidity), some randomly varying (desorption), and some mixed (pressure). The systematic contributions dominate the sampling uncertainty throughout the humidity range concerned here.

In all these cases it should be recalled that, from equation (14), two evenly matched uncertainties are each equivalent (if alone) to $1/(\sqrt{2})$ of the total, i.e. about 0.7 of the full amount. Therefore, if random contributions equal systematic contributions, then random variations in the overall result should typically equal 0.7 of the full estimated uncertainty. If random contributions outweigh systematics, then it should be no surprise to find that the total variability is almost as great as the total uncertainty.

Overall, then, at the lower limit of operation, the uncertainty for the gravimetric hygrometer should be mainly random. At humidities just below where the predryer comes into use, the uncertainty should be mainly systematic. In the predryer range, systematic components slightly outweigh random contributions; increasingly so for larger quantities of collected water. Therefore the gravimetric results in general should be expected to vary through a large part of the overall span described by the limits of confidence, especially at low humidities. (Incidentally, this is no less true for measurements in sub-optimal conditions, e.g. for smaller samples of gas.) On the other hand, such a wide variation would not be expected if the dominant contributing factors were mainly unknown constant systematic errors - as is perhaps more usual in other first-principles primary standards of measurement.

The situation for variability of the NPL humidity generator is similar to that for the gravimetric hygrometer. Analysis and experiment have shown that the spread of results for any generated dew point is nearly as great as the magnitude of the overall estimated uncertainty in the dew point (Stevens and Bell, 1993).

6.2.2. Overall agreement of results

How does the above discussion help in the interpretation of the results of the intercomparisons between the gravimetric hygrometer and the humidity generator? It allows for a degree of variability in the agreement of the results. However it does not entirely account for the relatively large variations that are found - at moderate to high humidities where the predryer is used. In these cases, however, the level of disagreement only just exceeds the combined uncertainties. For each of the measurements at 10 °C, there was some difficulty with the automated data logging of the generated dew point, adding an additional uncertainty to the estimate of the value of dew point. Bearing in mind all these things, and noting that three measurements at 10 °C is a rather small sample in statistical terms, the results may not conclusively indicate a problem. However, further measurements would certainly be desirable, to clarify the situation.

On the other hand many of the results agree as well or better than expected, notably at the lower humidities. It is particularly encouraging that the two measurements using air appear just as successful as those using nitrogen as the carrier gas.

The results obtained using air should be interpreted with caution, since no special care has been taken to consider uncertainties which might be specific to air in this context. What the results do suggest, however, is that there is no marked difference between using the system for nitrogen and other "inert" gas. These results are not enough to verify the accuracy of the estimate of water vapour enhancement factor for nitrogen evaluated for this work. The difference between values of f for air and for nitrogen is smaller than the variability in the results. A much larger set of measurements would be needed to draw any conclusion on this subject.

A measure of the overall agreement between the gravimetric hygrometer and the humidity generator can be found from a statistical test of the significance of the difference between the two. A *null hypothesis* test (e.g. Chatfield, 1983) quantifies the likelihood that the difference is significant by comparing the statistic

$$t_0 = \frac{\bar{x} - \mu}{\sigma/\sqrt{n}} \qquad (38)$$

with the normal (or Student's) distribution. In this case $\bar{x}$-μ is the average difference between the gravimetric and the generated values of humidity. For the set of 14 results as a whole, this test indicates that the difference is "not significant at the 20% level", i.e. if the true difference between the gravimetric and generated values was zero, there would still be well over a 20% probability of seeing experimental disagreements as great as those observed. This is the case irrespective of whether the estimated uncertainties or the actual spread of results is used as the basis of σ for the test. It is also instructive to apply this test to the region where the differences appear to be the most striking; in the range above 0 °C. For the five measurements in this range, a test based on the actual spread of results again shows that the difference is not significant at the 20% level. However, if the estimates of the gravimetric, generated, and sampling uncertainties, combined in quadrature, are used for σ in this test, then the test result is significant at the 20% level. That suggests that, based on those figures, there is less than a 20% chance of finding such extreme differences if the gravimetric and generated values were truly equal on average. What this implies is that there is moderate (though not strong) evidence that the uncertainties are in some respect underestimated, whether for the gravimetric hygrometer, the humidity generator, or the sampling errors.

Given that the difference found between the humidity generator and the gravimetric hygrometer might reflect a genuine systematic difference between the two realisations, it is important to consider what might cause this. Ruling out errors in the reference functions for water vapour of this magnitude, it must be considered whether the humidity generator might be "over-reading", or the gravimetric hygrometer "under-reading". Various explanations could be envisaged for either of these cases. For example, is quite possible in principle for the humidity generator to be less efficient in saturating gas than was originally thought. On the other hand, for the gravimetric hygrometer to under-read, some water would have to be inadvertently lost (or its mass underestimated), or some dry gas gained spuriously (or its mass overestimated). All these things are possible, so a genuine disagreement between the two instruments - while not conclusively demonstrated by the results - cannot be ruled out.

Overall it is obvious that a larger set of measurements would be advisable so that a more reliable statistical analysis could be carried out on the results. Further measurements in the humidity range above a dew point of 0 °C would be particularly desirable. However, it took some 9-12 months of direct effort to complete 25 gravimetric measurements, of which only 14 (the most recent) could be considered valid. This is to say nothing of the abortive attempts not detailed here, which were a small additional fraction. This indicates the scale of the resources needed for such a study.

6.3. Comments on the reference data

The formulation for the saturation vapour pressures over water and ice used in this work is Sonntag's (1990) adaptation of the formulae by Wexler for water and ice (1976; 1977). The authority of Wexler's data is long established, and the present work is not capable of affecting the confidence already associated with them. However, in much of the humidity range, particularly above a dew point of 0 °C the gravimetric hygrometer is capable of measuring with a smaller uncertainty than that claimed by Sonntag for his published values. (See Table XIII.) The uncertainties given by Sonntag are in every case larger than Wexler's original estimates for the same values of vapour pressure. (Wexler's values are smaller in all cases than the gravimetric uncertainty.)

Sonntag has interpreted the uncertainties in Wexler's original papers rather cautiously, perhaps assuming that his (Sonntag's) conversion into ITS-90 contributes significant additional uncertainty. Alternatively, Sonntag's uncertainties may be intended to reflect the point made earlier, in Chapter 5, that the available formulations for saturation vapour pressure, including Wexler's, vary within a band of values which is fairly reflected by Sonntag's figures. What is more, the profusion of formulations (Gibbins (1990) cites over 60 for water and 30 for ice) is founded on relatively scant experimental evidence. This is particularly true in the case of ice, where the basis of these 30 curves is a small handful of measurements some of which date back to the early 1900s. While some historic measurements may have been more painstaking than is usually possible nowadays, this is not reliably true. In any case, for many of those experimental data it is clear that estimates of uncertainty were not as careful as they might be today. A common fault seems to be the derivation of uncertainty estimates simply from standard deviations of measurements or from residuals of curve-fitting, without consideration of any systematic error in the estimated values.

The difference shown in Figure 24 between the values of water vapour enhancement factor for air and the adapted values for nitrogen ranges between about 1×10^{-4} and 5×10^{-4}. They therefore typically differ by more than the forecast figure of 1×10^{-4}. For the range below 0 °C the difference is less than the uncertainty for air at the 95% confidence level. Above 0 °C the difference is greater than this uncertainty. From this it appears that it would not, in fact, have been appropriate to use the factor for air as an approximation for that for nitrogen. The envelope of the uncertainties assigned to the function for nitrogen (which are two to three times those for air) easily embraces both sets of data points. From this it might be concluded that simply broadening the uncertainties would be sufficient instead of using a subtly differing equation. However the adaptation remains the best estimate available for nitrogen.

It would be interesting to explain the character of the difference between the enhancement factors for air and nitrogen. It may be that the approximations that were made in deriving the version for nitrogen are more significant in some parts of the humidity range than others. This might explain, for instance, why the two curves appear to converge more closely at some humidities than others. For example, where the third cross virial coefficient for air C_{aww} was used, (C_{nww} for nitrogen not being available), the significance of this would be greatest where interactions involving two water molecules with one carrier gas molecule were most common, i.e. at high humidities. However a more detailed study would be required before this could be discussed fully.

This adaptation is an original step in formulating a water vapour enhancement factor for nitrogen. Further to this, some experimental verification of this function at atmospheric pressure would be desirable. Indeed it could be considered whether further gravimetric measurements of the kind reported here could be used to confirm (or modify) the formulation for nitrogen. There is already a precedent for this approach, as Hyland (1975) used the results of gravimetric measurements, together with calculations, to assign a value to the second cross-virial coefficient for air and water, B_{aw}. However caution must be exercised in a process of this kind which, while being self-consistent, might risk failing to be consistent with anything outside this self-contained frame of reference.

6.4. Significance of this work in the field of gravimetric hygrometry

Now that the measurement capability of the NPL gravimetric hygrometer has been established, its performance in comparison to other gravimetric hygrometers can be critically reviewed.

Figure 28 shows a graph of the uncertainty of measurement achieved by the NPL gravimetric hygrometer compared to the uncertainties for other gravimetric hygrometers. This illustrates that the NPL instrument lives up to the expectation of providing the widest range of measurement of all the gravimetric facilities worldwide, with a measurement uncertainty among the best reported to date. It can be seen that the uncertainty estimated for the NPL gravimetric hygrometer is by far the best at high humidities, and is comparable with others in the middle of the humidity range. At lower humidities, in the dew-point range from -20 °C to -40 °C the NPL uncertainty exceeds that of NIST, USA. However, the NPL instrument alone offers a measurement capability below this range. The graph also illustrates that the local peak in uncertainty in mid-range for the NPL instrument is not shared with other designs of gravimetric hygrometer. However the aspects of the NPL design that lead to this disadvantage are also those which lead to superlative performance elsewhere in the measurement range.

In overview, the factors which put the NPL hygrometer ahead of the others are: the dual mode of operation (with and without the pre-dryer); the efficient cold trap and subsequent transfer of water to a light receptacle (the desiccant) for weighing; and the collection of the dry gas by condensation. The water collection process in the NPL cold trap is two steps removed from being an "on-line" measurement, since it involves trapping, then transfer and eventual weighing. This is in contrast to only one "extra" step for the other gravimetric hygrometers; namely trapping followed by weighing. It is this extra step in the NPL process - the transfer of water to the relatively light desiccant - which allows reasonably sensitive measurements right down to low humidities. On the other hand, the use of the predryer is what makes the NPL instrument so effective where large amounts of water are involved, at high humidities. Other designs of gravimetric hygrometer have exploited a cold trap (Kostyrko and Kacprzak, 1979) or a high capacity condensation trap (Crétinon, 1984), but never both.

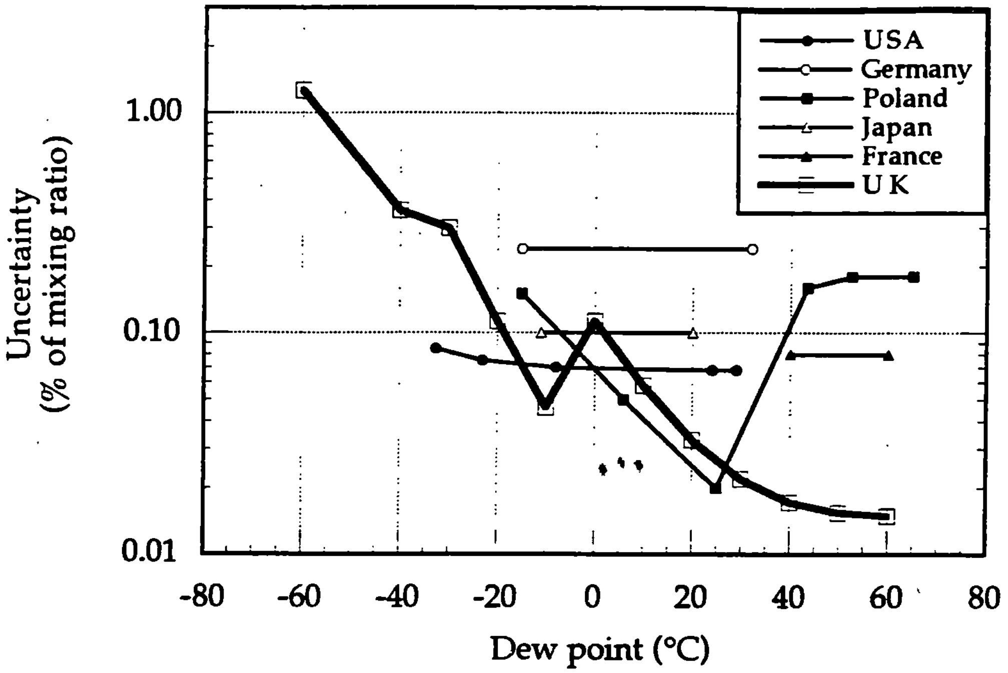

Figure 28 Graph showing the uncertainty of measurement for the NPL gravimetric hygrometer together with the uncertainties for other gravimetric hygrometers worldwide

In the measurement of the mass of dry gas, it is the combination of a large but compact collecting capacity with a high precision measurement (weighing) that gives the NPL instrument its particular advantage. The NIST/NBS design (Wexler and Hyland, 1964) should, in principle, have a benefit at low humidities of being able to sample indefinitely large quantities of gas (given enough time). However the calculation of the gas mass from the volume and density has relatively large uncertainties which cannot substantially be improved simply by collecting more gas. The gas measurement in the Polish design, on the other hand, while capitalising on weighing as a precise technique, loses by having large vessels of low density to weigh, with significant air buoyancy effects. These thin-walled gas vessels are also relatively much more prone to volume change from changes in internal (and external) pressure and temperature than those in the NPL instrument.

6.5. Other points of interest

This work originally set out to use gravimetric measurements in conjunction with "known" reference data for water to validate a realisation of dew point. In fact, on the contrary, the gravimetric hygrometer might be better used in conjunction with "known" values of dew point to validate the reference data. It would be difficult to improve knowledge of the saturation vapour pressure of water by this approach without first assuming values for the water vapour enhancement factor. Conversely, though, values of the water vapour enhancement factor could usefully be evaluated from gravimetric measurements, for other (non-reactive) gases as well as for air. However, such measurements are only as good as the knowledge available about the composition of the gas sample in question.

At low humidities, below a dew point of -50 °C, the gravimetric results, although apparently repeatable, have larger uncertainties than the dew-point uncertainty for the NPL humidity generator. Therefore in this range there is no advantage in using the gravimetric hygrometer to calibrate or validate the humidity generator. However, at low levels of humidity the intercomparison measurements could in fact be viewed as a validation of the gravimetric instrument using the humidity generator - the converse of the original idea. It might be possible to feed back information of this type into an iterative process of mutual validation of both instruments, using each instrument to investigate the weaker range of the other.

The operating range of the gravimetric hygrometer has been restricted somewhat arbitrarily in the discussions so far to a top figure of 155 g kg^{-1} (a dew point of 60 °C). In fact there is no reason, in principle, to impose a limit at that particular point, and the gravimetric hygrometer would easily function up to a dew point of, say, 80 °C (570 g kg^{-1}). The only important practical precaution would be to ensure that the sample gas was kept hot enough on its path to the gravimetric hygrometer to prevent condensation. However the uncertainty of measurement begins to increase dramatically above this point because there is simply less and less carrier gas present in proportion to water. At a dew point of +90 °C the mixing ratio would be about 1.5 kg per kg, and therefore for the 100 g of water that could be collected, the corresponding dry gas would be only 60 g. The overall uncertainty would approach 1 percent of result, and while this magnitude of uncertainty represents the state of the art at very low humidities, at high humidities it would be unacceptable.

Gravimetric hygrometry is a complex analytical process. It is always time consuming, and never a real-time measurement. It gives a single-valued average result for the period over which humid gas is sampled. As a consequence of all these facts, a single mistake in operating the NPL gravimetric hygrometer can be enough to invalidate the result, with the loss of a week or two of work. This is in contrast to continuous types of measurement which can generally track changes, and which may recover in real time from transient error conditions.

Even among gravimetric hygrometers, the NPL instrument is difficult to use. It entails some particularly cumbersome procedures; the baking of certain components in vacuum, and cooling of other components to the temperature of liquid nitrogen. While these are not in themselves difficult precision processes, they add to the complexity and to the duration of routine measurements. The isolation in vacuum of weighings and other processes also makes the operation unwieldy. If the NPL gravimetric instrument has any serious shortcoming, it is this combination of complexity with labour-intensiveness, leading to both a high likelihood and a high cost, in effort, for unsuccessful measurement attempts. The success rate of completing measurements correctly may well be operator dependent - perhaps more so than any technical aspect of the gravimetric measurement process.

In compensation for the difficulty and cost of measurements, the gravimetric method has other benefits. It commands a high degree of international recognition because of its accuracy and fundamental basis. As well as the benefit of the actual measurements that can be undertaken, this gravimetric hygrometer plays a valuable role in signalling the competence and high international standing of the UK and of the NPL in the field of humidity standards. This value as a status symbol, while often unspoken, should not be overlooked.

Finally, this account deals only with the most important work done to evaluate and minimise the uncertainty of measurement. Much other information relevant to the operation is recorded elsewhere. In particular, considerable effort was directed not at quantifying uncertainties, but rather at developing techniques which made measurements run more smoothly and reliably, without directly affecting the uncertainty of measurements. Examples are the development of computerised data logging for at some parts of the measurement process, refinements in the operation of the humidity generator to provide trouble-free measurements, automatic handling of liquid nitrogen coolant, refinement of the technique for replacing the desiccant from time to time ...and many other details.

6.6. Chapter summary

A critical review of the work reported here shows that the quality of the conclusions drawn and the results for the instrument itself are satisfactory. With the inevitable proviso that more work would be desirable, the project can be said to have reached a successful conclusion.

The four objectives of the work set out at the beginning of this thesis were all achieved, namely:- an assessment of individual aspects of the operation of the gravimetric hygrometer; a resulting estimate of overall uncertainty which met the initial specification through most of the target range; a treatment of the interface, both practically and theoretically, between the gravimetric hygrometer and other humidity instruments; and a satisfactory intercomparison with the NPL standard humidity generator.

In the final section ahead, the results and conclusions from this work will be summarised. On the basis of points raised in the foregoing discussion of the work, suggestions for further work will be made.

6.7. References

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CHAPTER 7

Summary and conclusion

May these findings carry weight
and these arguments hold water.

CHAPTER 7. SUMMARY AND CONCLUSION

7.1. Summary of findings

The operation of the NPL gravimetric hygrometer has been validated for the measurement of mixing ratios ranging from 0.01 g kg^{-1} to 155 g kg^{-1} and above. The correct working of the individual aspects of the gravimetric hygrometer's operation has been verified. The uncertainty associated with each aspect of the measurement has been evaluated, with the identification of over 20 significant sources of uncertainty. Where the effects of systematic errors can be quantified, corrections to the measured values have been estimated, resulting in some 15 different variable or constant corrections to be applied in the calculation of mixing ratio results.

The individual components of uncertainty have been combined to give an estimate of overall uncertainty of measurement for the gravimetric hygrometer. The outcome is an uncertainty of measurement for a coverage factor $k=2$ (i.e. a level of confidence of at least 95%) which ranges from 0.015 percent of result at a mixing ratio of 155 g kg^{-1} to 1.27 percent of result at a mixing ratio of 0.01 g kg^{-1}, with a local peak in value of 0.113 percent of result near 4 g kg^{-1}. Over most of the specified range, this outcome meets the performance targets established for the gravimetric hygrometer in order to underpin the humidity measurement requirements of industries in the UK and elsewhere.

The implications of the relationships between different units of humidity measurement have been considered. The documented reference data for water vapour have been reviewed for this application, and the general nature of the interface between this primary standard and other humidity instruments has been considered. The uncertainty in the reference data for water vapour contributes a moderately significant uncertainty to the comparison of any instrument against the gravimetric hygrometer: in some cases the uncertainties in these data exceed that for the hygrometer itself. For the intercomparison measurements in this work, which featured nitrogen as the carrier gas, a new adaptation of the enhancement factor for nitrogen has been created by substituting thermodynamic variables for nitrogen into Hyland's (1975) formula for the water vapour enhancement factor for air.

Satisfactory overall performance of the gravimetric hygrometer has been demonstrated by carrying out gravimetric measurements in comparison with the NPL humidity generator, of a repeatability broadly consistent with the estimate of uncertainty. The average agreement of 0.36 percent of value, equivalent to 0.04 °C in dew point, between the gravimetric hygrometer and the humidity generator was satisfactory compared with the spread of results. The agreement was especially good, relative to the uncertainties, for measurements at the low end of the gravimetric range, only casting slight doubt on the uncertainty estimates for higher humidities. Measurements where air was employed as the carrier gas appeared just as successful as those where nitrogen was used.

7.2. Significance of this work

The results of the validation of the NPL gravimetric hygrometer show this to be one of the foremost realisations of its type reported so far. It largely achieves the minimum performance target specified to underpin the NPL calibration service. With some further work, this performance could be improved to fully achieve the performance initially forecast at the design stage. However the capability for high accuracy and the fundamental nature of the measurements have already established a high international standing for this facility.

7.3. Possible future work

Some suggestions are made here for possible future work - both on improving the gravimetric hygrometer itself, and other projects which could in future be undertaken using this instrument.

The first suggestion for further work is that the gravimetric hygrometer should remain in active use. A programme of occasional intercomparisons with the NPL humidity generator should be established to provide continuing confidence in both these primary measurements. This will also ensure that the gravimetric instrument does not become neglected, or the operating skills become lost - which could be all too easy with such a complex instrument.

It would also be desirable to carry out some further measurements using the full collection capacity of the hygrometer, now that the benefit of this has been quantified. These more demanding measurements would, it is hoped, give stronger evidence of agreement with the NPL humidity generator. This would be particularly desirable at medium to high humidities, where such measurements would help in resolving any remaining doubts about the validity of the uncertainty estimates for this range.

Naturally, the instrument should be maintained. This extends beyond the simple mechanical maintenance of components of the instrument, and the calibration of critical components such as the balances and the sets of weights. A schedule of upkeep should be established which includes the re-testing of properties which might be expected to deteriorate with time. This, in effect, is a precaution against what would be observed as "drift" in the instrument performance as a whole, were it possible to measure this. For example, with repeated use the cold trap might be expected to become progressively contaminated with oil vapour or other substances inadvertently carried in with the sample gas. It is also conceivable that significant traces of desiccant could somehow spill within the vacuum assembly, or be deposited on the walls by evaporation. If either of these occurred, the measurement results would be affected and it would be necessary to clean the instrument - an extremely delicate undertaking which should be avoided if at all possible. Monitoring of the quality of the vacuum that can be maintained, and of the pressure-temperature-time characteristic of the water vapour transfer process, have been suggested as precautions to indicate whether significant contamination could be present.

Any radical changes to the established instrument are ruled out; if not on the grounds of cost, then on the basis that such changes might invalidate the characterisation done so far, or might even risk impairing the existing performance. Above all, where the instrument already achieves most of what is required, any further development work requires careful justification. However there are a number of new projects that could be undertaken without any major change to the existing hardware or the method of use.

7.3.1. Further work to improve the performance of the gravimetric hygrometer

Ideally, some measures would be taken to improve the accuracy of measurement at low humidities. The highest priority would be to improve the uncertainty associated with the microbalance weights. Potentially, knowledge of the stability of the weights could be improved by overcoming the limit of resolution of the microbalance. This might be possible if the electrical signal could be accessed directly, instead of through the digital panel meter display. Alternatively, it might be possible to design more complex but effective comparisons to confirm the relative values of the weights. Ultimately, the microbalance weights should be removed and recalibrated. (This would probably require a temporary cleanroom environment to be set up around the gravimetric pipework while the weights were removed and re-installed.) The need for (and uncertainties in) the coarse self-consistency checks could then be reconsidered if the weights were found to be close to the original values.

Uncertainties for individual measurements could be further optimised *ad hoc* by collecting just the right quantity of water to use advantageous combinations of microbalance weights, avoiding combinations with large uncertainties. The duration of a given collection could be timed to result in a chosen increment which would make the best of this. A more general improvement in this respect would be to carry out a proper mathematical analysis to optimise the measurement conditions. The analytical expressions representing the uncertainty calculation could be solved to find minima, given any particular constraints on the input variables of flow rate, duration, and total masses of water and gas. However, such a rigorous optimisation would only have significant benefit after a reduction in the dominant uncertainty due to the microbalance weights.

The uncertainty relating to the predryer could possibly be improved by reviewing how the contents of the pre-dryer are evaluated. This would have a significant benefit, since this is a major factor in the uncertainty in the middle of the operating range.

Many other interesting but minor improvements to the uncertainty could in principle be made fairly easily. However, most of these would have negligible benefit in comparison to the more significant points above. It is therefore not important to note these in any detail.

Other kinds of improvement could be made to the instrument to improve the reliability of operation. Greater automation would help in this respect. For example, a higher degree of automated data logging for the microbalance would remove the risk of mistakes in noting weights applied. (If such a mistake occurs, it can probably be detected as a gross error, but this might not always be so.) Another constructive measure would be to operate the vacuum system valves automatically using electrical or pneumatic actuators. This would make the execution of the initial and final valve sequences simple and highly repeatable. It would lessen the variability in the amount of gas trapped in the cold trap at the end of each collection. Hence the measurement uncertainty could be slightly improved as well as the reliability.

The range of use could be increased almost without any further work. The highest measurements carried out so far have been at a mixing ratio of 155 g kg^{-1} (a dew point of 60 °C). The application of the conclusions drawn so far need not be restricted to this upper limit, and the useful range can be considered to extend up to 80 °C (570 g kg^{-1}).

The only way of significantly improving the speed and ease of use of the gravimetric hygrometer would be to operate it in a much simplified way. For example, the use of the cold trap could be abandoned at very high humidities in favour of a more approximate real-time measurement of the dryness of gas emerging from the predryer. The gas aspect of the measurement could be undertaken as a real-time flow measurement rather than by weighing. These methods might be acceptable in parts of the measurement range but in general there would be high penalties in the associated uncertainty.

7.3.2. Further work using the gravimetric hygrometer

In the first instance, the gravimetric hygrometer should be utilised for the kind of measurements for which it was specifically developed: to continue the verification of the NPL humidity generator, and to provide calibrations for any other suitable humidity instruments. In particular, other national standards laboratories which do not employ gravimetric hygrometry may seek to add this to the measures of confidence that underpin a particular humidity standard. International intercomparisons or calibrations can provide such an input either directly, for a standard that can be transported, or indirectly, through a transfer standard. Of course, it would also be interesting to conduct such intercomparisons between laboratories which do hold gravimetric facilities. However, at the moment no transfer standards exist which have sufficient stability and precision to allow meaningful intercomparisons between gravimetric hygrometers, while doing justice to the small uncertainties reported for these.

More interesting possibilities for further work lie in measuring values of the water vapour enhancement factor, for which there is a lack of reported experimental data. Measurements could be undertaken for nitrogen and synthetic air (free of argon and CO_2). Since there does not appear to be any marked difference between using the instrument for nitrogen and other "inert" carrier gas, measurements of other gases could also be attempted. A suitable gas, in addition to being chemically passive, would need to condense at a temperature below that of the cold trap and above that of the cryostat. Since the enhancement factor is mainly a function of pressure (depending less on temperature) the generation of humid gas at elevated pressures using a two-pressure generator would give most opportunity for experimentation. The gas would however be reduced to atmospheric pressure before entering the gravimetric hygrometer. Although such measurements would be of interest for a wide range of humidities, it would be particularly interesting to concentrate on the range where the best performance is likely to be achieved from the gravimetric hygrometer; some way above and below a dew point of 0 °C. Additionally, a more thorough theoretical estimate of enhancement factor for nitrogen would be valuable.

The gravimetric hygrometer cannot, of course, be directly used to measure the pure vapour pressure of water, since in the absence of any carrier gas the value of mixing ratio is always infinite. However there remains a need for more work on the saturation vapour pressure of water by other methods.

Appendix 1: Specimen printout of analysis of uncertainties for microbalance weights

EQUATION MATRIX

M =7

N =8

$$X := \begin{bmatrix} 0 & 0 & 0 & 0 & 0 & 0 & 1 \\ 0 & 0 & 0 & 0 & 0 & 1 & 1 \\ 0 & 0 & 0 & 0 & 1 & 1 & 1 \\ 0 & 0 & 0 & 1 & 1 & 1 & 1 \\ 0 & 0 & 1 & 1 & 1 & 1 & 1 \\ 0 & 1 & 1 & 1 & 1 & 1 & 1 \\ 1 & 1 & 1 & 1 & 1 & 1 & 1 \\ -1 & 1 & 1 & 1 & 1 & 1 & 1 \\ 0 & -1 & 1 & 1 & 1 & 1 & 1 \\ 0 & 0 & -1 & 1 & 1 & 1 & 1 \\ 0 & 0 & 0 & -1 & 1 & 1 & 1 \\ 0 & 0 & 0 & 0 & -1 & 1 & 1 \end{bmatrix}$$

WEIGHT MATRIX

$$B = \begin{bmatrix} 800 \\ 400 \\ 200 \\ 100 \\ 50 \\ 25 \\ 10 \end{bmatrix}$$

RESULTS MATRIX

$$y = \begin{bmatrix} 10.001 \\ 35.01 \\ 85.01 \\ 185.1 \\ 385.1 \\ 785.1 \\ 1585.1 \\ -15.1 \\ -15.1 \\ -15.1 \\ -15.1 \\ -15.1 \end{bmatrix}$$

ESTIMATION OF WEIGHT VALUES (Bh)CALCULATED FROM X AND y MATRICES

$$Bh = \left(X^T \cdot X\right)^{-1} \cdot X^T \cdot y$$

$$Bh = \begin{bmatrix} 800.1 \\ 400.041 \\ 200.023 \\ 100.029 \\ 50.018 \\ 24.947 \\ 10.001 \end{bmatrix}$$

CALCUALATION OF RESIDUALS (r)

$$r = X \cdot Bh - y$$

$$r = \begin{array}{c|c} & 0 \\ \hline 0 & 0 \\ 1 & -0.062 \\ 2 & -0.044 \\ 3 & -0.105 \\ 4 & -0.082 \\ 5 & -0.041 \\ 6 & 0.059 \\ 7 & 0.059 \\ 8 & 0.077 \\ 9 & 0.071 \\ 10 & 0.037 \\ 11 & 0.031 \end{array}$$

$$var := \frac{r^T \cdot r}{N - M}$$

$$var = 0.046$$

$$var := 0.003$$

WEIGHTING FOR RESIDUALS

$$varco = var \cdot \left(X^T \cdot X\right)^{-1}$$

$$varco = \begin{bmatrix} 0.002 & 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 9.271 \cdot 10^{-4} & -2.188 \cdot 10^{-4} & -8.333 \cdot 10^{-5} & -3.125 \cdot 10^{-5} & -2.083 \cdot 10^{-5} & 0 \\ 0 & -2.187 \cdot 10^{-4} & 8.437 \cdot 10^{-4} & -2.5 \cdot 10^{-4} & -9.375 \cdot 10^{-5} & -6.25 \cdot 10^{-5} & 0 \\ 0 & -8.333 \cdot 10^{-5} & -2.5 \cdot 10^{-4} & 8.333 \cdot 10^{-4} & -2.5 \cdot 10^{-4} & -1.667 \cdot 10^{-4} & 0 \\ 0 & -3.125 \cdot 10^{-5} & -9.375 \cdot 10^{-5} & -2.5 \cdot 10^{-4} & 8.437 \cdot 10^{-4} & -4.375 \cdot 10^{-4} & 0 \\ 0 & -2.083 \cdot 10^{-5} & -6.25 \cdot 10^{-5} & -1.667 \cdot 10^{-4} & -4.375 \cdot 10^{-4} & 0.004 & -0.003 \\ 0 & 0 & 0 & 0 & 0 & -0.003 & 0.003 \end{bmatrix}$$

$$i = 0..6$$

$$varm_{0,i} = varco_{i,i}$$

$$varm = \begin{pmatrix} 0.002 & 9.271 \cdot 10^{-4} & 8.437 \cdot 10^{-4} & 8.333 \cdot 10^{-4} & 8.437 \cdot 10^{-4} & 0.004 & 0.003 \end{pmatrix}$$

Appendix 2: Worked example of gain-correction of microbalance results

Weighings using the microbalance are compensated for any non-linearity in the electronics as follows.

Zero reading of microbalance, initially = R_0
Reading for 10 mg weight = R_{0+10}
Reading for mass of desiccant package (desiccant package plus counterweight plus calibrated weights, W, applied) = R
Reading for mass of water with additional 10 mg added or removed = $R_{\pm 10}$

Gain (i.e. sensitivity), unloaded $$= \frac{R_{0+10} - R_0}{\text{true mass of 10 mg weight}} = G_0$$

Gain, loaded $$= \frac{(R_{\pm 10} - R)}{\text{true mass of 10 mg weight}} = G$$

Corrected value for mass of desiccant package $$= \frac{R}{G} - W - \frac{R_0}{G_0}$$

If the final zero reading, R_f, reading differs from the initial value, R_0, due to any slight drift during the weighing, the corrected mass is calculated from the average zero, i.e. from $$\frac{R}{G} - W - \frac{R_f + R_0}{2G_0}.$$

N.B. Although the true value for the 10 mg weight should be used, the uncertainty in knowing this true value does not give rise to any significant uncertainty in the process above.

Appendix 3: Worked example of calculation of predryer contents

The method of calculating the correction for gas trapped in the predryer is as follows.

The reference predryer is left intact and un-vented throughout a given gravimetric measurement. The contents, and therefore the mass of the reference predryer, are therefore taken to be constant throughout the initial and final weighings comparing the two predryers.

Prior to initial weighing, the main (collection) predryer is vented momentarily to ambient pressure. From the values of ambient pressure, p, and temperature, T, the density of the contained gas is calculated, assuming its composition to be 100% nitrogen, and using the density of dry nitrogen, as tabulated by Jacobsen and Stewart, (1973). From the density, ρ_{N2}, and internal volume, $V_{predryer}$, the initial mass $m_{initial}$, of contained gas is calculated from

$$m_{initial} = \rho_{N_2}(p,T) \times V_{predryer} \ . \tag{39}$$

For the "full" measurements, the internal volume is modified by the presence of water collected. During the course of measurements it was found that collected water up to a maximum of about 3.5 g would be entirely absorbed by the molecular sieve, effectively occupying no volume. Any water collected in addition to this amount is retained as liquid at the bottom of the predryer. This displaces a volume, V_{water}, of 1 cm^3 of gas per gram of liquid water.

When the collection is terminated, the predryer is at an internal pressure of 105 kPa and a temperature of 1 °C. If liquid water is present, a proportion of the internal pressure is made up of water vapour at a dew point of 1 °C, corresponding to a partial pressure of approximately 660 Pa. This water vapour has a mass of the order of 1 mg. This is properly included in the water mass, and excluded from the gas mass. In that case the pressure used to calculate the density of the trapped carrier gas is the final value less 660 Pa. If no liquid water is present, the vapour pressure of water inside the predryer is taken to be negligibly small.

The mass, m_{final}, of gas present in the "full" condition is then calculated analogously to the "empty" condition, i.e.

$$m_{final} = \rho_{N_2}((p-660\ \mathrm{Pa}),T) \times [\,V_{predryer} - V_{water}\,]\ . \qquad (40)$$

The difference between the masses of trapped gas before and after the collection is added to the total measured mass of gas, and (more significantly) subtracted from the measured mass of water.

The uncertainty in determining the mass of trapped gas is mainly governed by the uncertainty in volume, and is equal to the product of this uncertainty and the difference in gas density between full and empty conditions, i.e.

(uncertainty in gas volume) × (maximum difference in gas density)

$= \quad \pm 15\ \mathrm{cm}^3 \times 0.1\ \mathrm{mg\ cm}^{-3}$

$= \quad \pm 1.5\ \mathrm{mg}$

The correction found on any occasion due to gas trapped in the predryer is in the approximate range -40 mg to +40 mg, at most, and is normally less than half of this magnitude. However the worst-case uncertainty of 1.5 mg is an upper limit, whatever the value found for the correction.

The calculation assumes the entire initial contents to be nitrogen, flushed through during regeneration of the molecular sieve. However, on initial venting, air may be admitted (rather than nitrogen being expelled) changing the composition, and therefore the mass, of contained gas. The change in mass on initial venting is normally a few milligrams, and the consequent uncertainty corresponds to the pressure change multiplied by the difference in density between air and nitrogen. This figure is normally negligible. If necessary, though, the pressure before venting, and hence the subsequent gas composition can be deduced by additionally weighing the predryer before venting it, as well as afterwards. Similarly, extra information confirming the final internal pressure can be deduced, if required, from the change in mass when it is vented one more time at room temperature after completion of the "full" weighings.

Reference

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Appendix 4: Specimen printout of spreadsheet formulae and results for a calculation of mixing ratio from gravimetric data

```
FORMULAS FOR WORKSHEET specimen

 ROW    COL     FORMULA

   2      7     today
   5     14     if r5c13 = "lh1" then 1 else if r5c13 = "LH1" then 1 else if r5c
                     c13 = "lh2" then 1 else if r5c13 = "lh2" then 1 else if r5c
                     c13 = "LH2" then 1 else 0
         15     let #lh= r5c14
   6     14     if r6c13 = "a" then 1 else if r6c13 = "b" then 1 else 0
         15     let #pd= r6c14
  16     19     if r16c16 <> r16c18 then r16c23 else 0
         20     (r16c18-r16c16)*r16c23
  17     19     if r17c16 <> r17c18 then r17c23 else 0
         20     (r17c18-r17c16)*r17c23
  18      5     r17c2*r18c2
         19     if r18c16 <> r18c18 then r18c23 else 0
         20     (r18c18-r18c16)*r18c23
  19      5     r17c2*r19c2
         19     if r19c16 <> r19c18 then r19c23 else 0
         20     (r19c18-r19c16)*r19c23
  20     19     if r20c16 <> r20c18 then r20c23 else 0
         20     (r20c18-r20c16)*r20c23
  21     19     if r21c16 <> r21c18 then r21c23 else 0
         20     (r21c18-r21c16)*r21c23
  22     19     if r22c16 <> r22c18 then r22c23 else 0
         20     (r22c18-r22c16)*r22c23
  23      2     (r20c2*r18c5)/(r12c2*100000-r18c5)
          5     r23c2*1000
  24      2     (r20c2*r19c5)/(r12c2*100000-r19c5)
          5     r24c2*1000
         20     sum(r16:22c20)
  27     10     r21c9
         13     r16c12
  30     10     average(r16:21c9)
         11     average(r16:21c12)
  31     10     stdev(r16:21c9)
         11     stdev(r16:21c12)
  33     14     r27c13-r27c10
  35     14     r24c20+r33c14+r36c14+r37c14
  41      9     r6c13
  50     12     r46c12-r46c9
  55      9     if #pd = 1 then -0.00045 else 0
         10     #pd
  57      9     r35c14/1000
  60      9     sum(r55:58c9)+r50c12
  66     10     r5c13
  73     11     r71c10-r71c14
  78     11     r76c14-r76c10
  83     12     -0.001*r81c10*r78c11+r73c11
  89      9     r73c11*(-0.00015)
  91     15     if r1c4 = r14c26 then r14c27 else 0
  92      9     -1*r56c9
         15     if r1c4 = r15c26 then r15c27 else 0
  93      9     if #lh = 1 then 0*r83c12 else 0
  94      9     if #lh = 1 then -0.015 else -0.0007
  96      9     if #pd = 1 then .01 else 0
  97     15     if r1c4 = r16c26 then r16c27 else 0
```

```
FORMULAS FOR WORKSHEET specimen

 ROW   COL    FORMULA

  98     9    sum(r88:96c9)
        15    if r1c4 = r17c26 then r17c27 else 0
  99    15    if r1c4 = r18c26 then r18c27 else 0
 100    15    if r1c4 = r19c26 then r19c27 else 0
 101    15    if r1c4 = r20c26 then r20c27 else 0
 102    11    r83c12+r98c9
        15    if r1c4 = r21c26 then r21c27 else 0
 103    15    if r1c4 = r22c26 then r22c27 else 0
 104    10    0.001*ln(1.35*10^-4*r8c5+0.999952)
        15    if r1c4 = r23c26 then r23c27 else 0
 105    10    r104c10+r60c9/r102c11
        15    if r1c4 = r24c26 then r24c27 else 0
 106    15    if r1c4 = r25c26 then r25c27 else 0
 107    15    if r1c4 = r26c26 then r26c27 else 0
 108    15    if r1c4 = r27c26 then r27c27 else 0
 109     9    r105c10
        11    1000*r109c9
 110     9    r24c2
        11    1000*r110c9
 111    10    (r109c9-r110c9)*100/r109c9
 112    10    r111c10*sum(r91:108c15)
 159    10    r159c9
 160    10    r160c9*r60c9
 161     9    #pd
 163    10    sqrt(r161c9*(r159c10)^2+(r160c10)^2)
        12    r60c9
 167    10    r167c9
 168    10    0
 170    10    sqrt((r167c10)^2+(r168c10)^2)
        12    r35c14
 172    10    sqrt((r163c10)^2+(r170c10*0.001)^2)
        12    r60c9
        14    r172c10*100/r172c12
 176     9    if #lh = 1 then 0.024 else 0.0223
        10    r176c9
        11    r65c10
 177     9    if #lh = 1 then 0.0000341 else 0.0000441
        10    r177c9*r102c11
 180    10    r180c9*#pd
 182    10    sqrt(r176c10^2+r177c10^2+r178c10^2+r179c10^2+r180c10^2)
        12    r102c11
        14    r182c10*100/r182c12
 184    10    (1/sqrt(3))*ln (1.35*10^-4*r8c5+0.999952)
        12    r109c11
        14    100*r184c10/r184c12
 188    10    r109c11*r188c12/100
        12    r172c14+r182c14+r184c14
 189    12    r188c12*sum(r91:108c15)
 191    10    r188c10*2
        12    r188c12*2
 192    12    r189c12*2
```

```
         1          2          3          4          5          6          7
1   Test No. =     23     Dew-point 10           Date =    Aug 92   entered on
2                                                                   30/05/1995
3   SHG Parameters        (SHG data logging absent for most of run
4                         but preformance seemed stable)
5   Average dp9.98                  gas        N2
6   Means used =   ?                T - purged6
7   spread     =   ?                draw off  1
8   start SD   =   ?                pgh flowpg0.55
9   max SD     =   ?                recirc     N/K
10  max diff.  =   ?                 DP meter MBW
11                                  correction-0.02
12      Druck 1.0499                 duration 19.5
13  after corr of -0.1 mb
14    uncert.  0.1 mb
15
16
17    svp SHG 1226.35
18    enhance 1.00404                vp air = 1231.3044
19    N2hance 1.00445                 vp N2 = 1231.8072
20  C Ratio = 0.643092  (N2)
21
22
23  r SHG air 0.0076315             ORx1000 = 7.6315728
24   r SHG N2 0.0076347             ORx1000 = 7.6347262
25
```

```
         8          9          10         11         12         13         14
1
2
3   PGH Parameters
4
5   T purged =          6                     cyl no. =     1h1    1
6   N2 conn.d =         2                     p-d no. =      b     1
7
8
9   Microbalance results
10
11  Before Run                      After Run
12
13  Weigh No. Result    Gain        Weigh No. Result    Gain
14
15
16       ?          ?          ?        x12       12.759     1.0007
17       ?          ?          ?        y12       12.763     1.0011
18       ?          ?          ?         ?          ?          ?
19       ?          ?          ?         ?          ?          ?
20      v12      11.578     1.0011     (z12)      12.759     1.0007
21      w12      11.582     1.0012       ?          ?          ?
22
23
24
25
26
27  Result chosen   =   11.582      Result chosen   =    12.759
28
29
30  Average result =        11.58 12.760333
31  Standard dev   =    0.0028284 0.0023094
32
33                                            Weight Difference =     1.177
34
35                                  Total Desiccant Weight Gain =      1.18
36                      after       Desorption Correction      =  -2.5E-2
37                      and         CT lost water        =          0.003
38
```

```
39  Predryer Parameters
40
41  p-d no. = b
42
43  Before Run                      After Run
44
45  Last weight                     First weight
46  chosen =  -0.1865               chosen =  6.2242
47  Standard                        Standard
48  Deviation  =   ?                Deviation  =   ?
49
50                        Weight Difference =    6.4107
51
52
53  Corrections (in g)
54
55  other gase -0.00045     1
56  p-d gas     -0.025


       8         9        10         11         12         13         14
57  mic-bal =   0.00118
58
59
60  total wate  6.38643
61
62
63  Gas Parameters
64
65  cylinder used =
66  collect    =       lh1        right
67  ref.       =       lh2        left
68  subs wt    =       1000
69
70  Before run                               After run
71  weights added =    1224.7                weights ad          386.5
72
73                     difference    838.2
74
75
76  Scale reading =    22.5                  Scale reading =     18
77
78                     difference     -4.5
79
80
81  Sensitivity mg/div =   19.6                                  0.1960784
82
83            Total weight difference =      838.2882
84
85
86  Corrections
87
88  CT gas =    2.531
89  Wt buoy =  -0.12573 Air density = 1.2
90  Pipe gas =  0.447
91  W&T leak =  -0.039
92  p-d gas =   0.025
93  GC d vol =0.0821522
94  Handling =  -0.015
95  GC leaks =  0.005
96  PD pipe =    0.01
97
98  Total =   2.9204222
99
100
101
102           Corrected Gas Mass =841.20862
103
104 CT efficiency =       2.62E-08
105 Mixing ratio =        7.59E-03
106
107
108
109 r PGH =   0.0075919 g/g       7.5919955 g/kg      (N2)
110 r SHG =   0.0076347 g/g       7.6347262 g/kg      (N2)
111 PGH-SHG %diff =     -0.562838 (N2)
112 deg C          =    -0.083862 (N2)
```

```
          8          9          10          11          12          13          14
155 UNCERTAINTY*****************************  IN QUADRATURE
156
157 Predryer water (in g)             1-SIGMA
158
159 fixed        0.0009  0.0009
160 x mwater   0.0000173 0.0001104
161 1 if p-d        1
162
163 sum                  0.0009067 out of     6.38643     g
164
165 Microbalance water (in mg)        1-SIGMA
166
167 fixed           0       0
168 x mwater        0            0
```

```
          8          9          10          11          12          13          14
169
170 sum                        0      out of     1.18        mg
171
172 Total water (g) =    0.0009067 out of      6.38643    i.e. %     0.0141981
173
174 gas (in g)
175
176 fixed         0.024     0.024
177 x mgas     0.0000341 0.0286852
178 x mwater
179
180 if p-d       0.0009     0.0009
181
182 sum gas              0.0374119 out of     841.20862 g   i.e. %0.0044474
183                              \
184  + CT eff            0.0000151 out of     7.5919955 g/kg i.e.%0.0001996
185
186 Others?
187
188 total uncertainty    0.0014307 g/kg    =  0.0188451 % of result
189 at 1-sigma                              =  0.0028079 deg C
190
191 total uncertainty    0.0028614 g/kg       0.0376903 % of result
192 x coverage of 2                           0.0056158 deg C
193
194
195                                           THE END
```

```
          15        16        17        18        19        20        21
10
11                Before Run          After Run
12
13                 Weights   Nominal   Weights  True      Mass
14                  Removed   Mass      Removed  Mass(mg)  Gain
15
16   Enter 1 if      ?       800         ?             0         0
17   so, 0 if        ?       400         ?             0         0
18   not so!         ?       200         ?             0         0
19                   ?       100         ?             0         0
20                   ?        50         ?             0         0
21                   ?        25         ?             0         0
22                   ?        10         ?             0         0
23
24                                                sum =          0
25

88   If Dew-point = x then Error = y else 0
89
90
91             0
92             0
93
94
95
96
97             0
98             0
99             0
100            0
101        0.149
102            0
103            0
104            0
105            0
106            0
107            0
108            0
109
110
111
112
```

```
          22        23        24        25        26        27        28
1
2
3
4
5
6
7
8
9
10
11                                              Dew-point   degC=1%
12
13   Nominal   True      Uncertainty
14   Weight    Weight                                 70       0.16
15                                                    60      0.173
16      800     799.941                               50      0.177
17      400     399.938                               40      0.174
18      200     200.095                               30      0.167
19      100      99.905                               20      0.158
20       50     50.0897                               10      0.149
21       25     24.9709                                1      0.138
22       10     10.0025                              -10      0.112
23                                                   -20      0.104
24                                                   -30     0.0961
25                                                   -40     0.0884
26                                                   -50     0.0808
27                                                   -60     0.0742
```

Appendix 5: Adaptation of water vapour enhancement factor for use with nitrogen

Section 5.4 discusses the significance of the water vapour enhancement factor in accounting for the non-ideal behaviour of mixtures of water vapour with other gases. Below, the water vapour enhancement factor in air is detailed, followed by an adaptation for nitrogen.

Hyland's (1975) formulation for the enhancement factor, *f*, in air is given by

$$\begin{aligned}
\ln f = {} & \left(\frac{(i + \kappa p)(P - p) - \frac{1}{2}\kappa(P^2 - p^2)}{RT}\right)\bar{v}_c + \ln(1 - k x_{as} P) \\
& + \left(\frac{x^2_{as} P}{RT}\right) B_{aa} - \left(\frac{2x^2_{as} P}{RT}\right) B_{aw} - \left(\frac{P - p - x^2_{as} P}{RT}\right) B_{ww} \\
& + \left(\frac{x^3_{as} P^2}{(RT)^2}\right) C_{aaa} + \left(\frac{3x^2_{as}(1 - 2x_{as}) P^2}{2(RT)^2}\right) C_{aaw} \\
& - \left(\frac{3x^2_{as}(1 - x_{as}) P^2}{(RT)^2}\right) C_{aww} - \left(\frac{(1 + 2x_{as})(1 - x_{as})^2 P^2 - p^2}{2(RT)^2}\right) C_{www} \\
& - \left(\frac{x^2_{as}(1 - 3x_{as})(1 - x_{as}) P^2}{(RT)^2}\right) B_{aa} B_{ww} - \left(\frac{3x^4_{as} P^2}{2(RT)^2}\right) B^2_{aa} \\
& - \left(\frac{2x^2_{as}(1 - x_{as})(1 - 3x_{as}) P^2}{(RT)^2}\right) B^2_{aw} - \left(\frac{p^2 - (1 + 3x_{as})(1 - x_{as})^3 P^2}{2(RT)^2}\right) B^2_{ww}
\end{aligned} \tag{41}$$

where

B_{ii} = second interaction (cross) virial coefficients relating to interactions between pairs of molecules. (See Chapter 1 equation (8) and accompanying text for an introduction of virial coefficients in the equation of state of a gas.) Subscripts *i* refer to water (*w*) or to "average molecules" of air (*a*), in a theoretically homogeneous mixture of nitrogen and oxygen. The validity of this "homogeneous" treatment is justified by Wylie and Fisher (1974).

C_{iii} = third cross-virial coefficients relating to interactions between any three molecules

P = Total pressure

p = pressure of saturated vapour over pure saturated condensed phase

κ = isothermal compressibility of ice or water

k = Henry's Law "constant"

x_{as} = mole fraction of air in the saturated mixture and

$\bar{v}_c$ = molar volume of the condensed phase (either water or ice)

R = universal gas constant, 8.31441 J mol^{-1} K^{-1}

T = absolute thermodynamic temperature, Kelvin

The elements making up this expression are given by Hyland (1975) and Hyland and Wexler (1983) as follows:

κ is given for water at temperatures $0 \le t \le 100$ °C by

$$\kappa = \left(\frac{\sum\limits_{i=1}^{5} J_i t^i}{1 + J_6 t} \right) \times 10^{-11} \quad \mathrm{Pa}^{-1} \tag{42}$$

where

J_0 = 0.5088496×10^{2}

J_1 = 0.6163813

J_2 = 0.1459187×10^{-2}

J_3 = 0.2008438×10^{-4}

J_4 = $-0.5847727 \times 10^{-7}$

J_5 = 0.4104110×10^{-9}

J_6 = 0.1967348×10^{-1}

and for ice by

$$\kappa = (8.875 + 0.165T) \times 10^{-11} \quad \mathrm{Pa}^{-1}\ . \tag{43}$$

The Henry's law "constant" k is given by

$$k = \alpha(\log_{10} k)^2 + (\gamma\tau + \delta)(\log_{10} k) + (\beta\tau^2 + \epsilon\tau - 1) = 0 \tag{44}$$

where

$$\tau = \frac{1}{1000\,T} \tag{45}$$

with

$$\frac{1}{k_A} = \frac{x_O}{k_O} + \frac{x_N}{k_N} \tag{46}$$

where

	Oxygen	Nitrogen
α =	-0.005493	-0.1021
β =	-0.1470	-0.1482
γ =	-0.5120	-0.01900
δ =	-0.1076	-0.03741
ε =	0.8447	0.8510

and k_A is converted into consistent units using

$$k = \left(\frac{10^{-4}}{k_A}\right)\left(\frac{1}{101325}\right) \quad \text{mol fract.Pa}^{-1} \ . \tag{47}$$

The value of k is taken to be zero for $t < 0$ °C.

The molar volume $\bar{v}_c$ of the condensed phase is given for ice by

$$\bar{v}_i = 19.27640 - 4.502667 \times 10^{-4}\,T + 6.694676 \times 10-6\,T^2 \tag{48}$$

and for water by

$$\bar{v}_w = \frac{18015.28\,(f_6 + f_7 T)}{(f_0 + f_1 T + f_2 T^2 + f_3 T^3 + f_4 T^4 + f_5 T^5)} \tag{49}$$

where

f_0 = $-0.2403360201 \times 10^{4}$

f_1 = $-0.140758895 \times 10^{1}$

f_2 = 0.1068287657

f_3 = $-0.2914492351 \times 10^{-3}$

f_4 = $0.373497936 \times 10^{-6}$

f_5 = $-0.21203787 \times 10^{-9}$

f_6 = -3.424442728

f_7 = 0.1619785×10^{-1}.

The virial coefficients B_{ii} and C_{iii} are all expressed as polynomials in T. The expression for B_{aa}, B_{aw}, C_{aaa} and C_{aaw} has the form

$$q_0 + q_1 T^{-1} + q_2 T^{-2} + q_3 T^{-3} + q_4 T^{-4} \quad (50)$$

where the coefficients q_i are as given in Table XVII. For the other virial coefficients the expressions are

$$B_{ww} = RT\,(0.70 \times 10^{-8} - 0.147184 \times 10^{-8} \exp(1734.29\, T^{-1})) \qquad (51)$$

$$C_{www} = (RT)^2 \left(0.104 \times 10^{-14} - 0.335297 \times 10^{-17} \exp\,(3645.09\, T^{-1}) + \left(\frac{B_{ww}}{RT}\right)^2\right) \qquad (52)$$

and

$$\begin{aligned} C_{aww} = {} & -1 \times 10^6 \times \exp(-\,0.10728876 \times 10^2 + 0.347802 \times 10^4 T^{-1} \\ & - 0.383383 \times 10^6 T^{-2} + 0.33406 \times 10^8 T^{-3}). \end{aligned} \qquad (53)$$

To evaluate f, the relevant values of P, p and T are entered in equation (40) and the equation is then solved iteratively for x_{as} and f.

Table XVII Temperature series coefficients for virial and cross-virial coefficients for air and water (Hyland and Wexler 1973)

Temperature series coefficients in equation (49) for air

Virial coefficient	$q_0 \times 10^{-2}$	$q_1 \times 10^{-4}$	$q_2 \times 10^{-6}$	$q_3 \times 10^{-8}$	$q_4 \times 10^{-10}$
B_{aa}	0.349568	-0.668772	-2.10141	0.924746	-
B_{aw}	0.32366097	-1.41138	-1.244535	-	0.2348789
C_{aaa}	12.5975	-19.0905	63.2467	-	-
C_{aaw}	4.82737	10.5678	-65.6394	294.442	-319.317

An adaptation of equation (40) has been made for the present work, using data for nitrogen where available. Where these are not available, or where the difference is insignificant, the corresponding terms for air are used, with an allowance for this approximation in the uncertainty assigned to the estimate.

Among the terms featuring virial coefficients in equation (40) for which values for nitrogen must be substituted, the most significant are the second virial coefficient for pure nitrogen (denoted B_{nn}) and the cross-virial coefficient for nitrogen and water (B_{nw}). Other virial coefficients involving only water (B_{ww} and C_{www}) are unchanged in the case of nitrogen as the carrier gas. The terms featuring third virial and cross-virial coefficients (C_{nnn}, C_{nnw} and C_{nww}) are relatively insignificant (since, at low densities, interactions (e.g. collisions) involving three molecules are uncommon compared with interactions between pairs). For this reason, and because of the difficulty in finding suitable data for nitrogen, the coefficients for air were used as approximations for these last three terms. However, at atmospheric pressure and in the temperature range of interest here, each of the terms involving C_{iii} contributes less than about 3 parts in 10^5, to the value of f.

The expressions used for terms specifically relating to nitrogen are as follows:

$$B_{nw} = -170.71135 + 0.665175T - 6.75849T^2 \tag{54}$$

and

$$B_{nn} = -247.291 + 1.76727T + 4.31378 \times 10^{-3}T^2 + 3.75471 \times 10^{-6}T\,. \tag{55}$$

The expression for B_{nw} was derived by fitting a curve to values calculated by Wormald (1985). That for B_{nn} was derived by fitting a curve to values given by Dymond and Smith (1969).

Expressions for κ, and $\bar{v}_c$ are as in Hyland and Wexler's version. A value of k is calculated for nitrogen alone, using the constants given for nitrogen in equation (46) above.

Strictly speaking the values of C_{iii} are approximate, since higher virial coefficients (D_{iiii}, etc) are ignored. The true coefficient taking this into account is termed C_{∞}. However the effect of ignoring this difference is extremely small.

Figure 24 in Section 5.4. shows the values calculated for the enhancement factor for nitrogen at 105 kPa and a range of temperatures. Values for air (Hyland, 1975: Hyland and Wexler, 1983) are shown for comparison, and the uncertainties are indicated for both. These uncertainties were estimated taking into account the estimated uncertainties in B_{aa} and B_{aw}, together with the difference between these and the estimated values of B_{nn} and B_{nw}. In addition the effects were considered of using C_{aaa}, C_{aaw} and C_{aww} as approximations for C_{nnn}, C_{nnw} and C_{nww}, but these have only a slight effect.

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Appendix 6: Further developments in the NPL humidity standards facility

Since the period when the validation work on the gravimetric hygrometer was carried out, and after much of the text was completed, there have been some new developments in the humidity facilities at NPL.

Firstly, a fire in 1994 destroyed the original humidity generator. This means of course that, on the face of things, the measurement history of the intercomparison between the old humidity generator and the gravimetric hygrometer is simply that . . . history. However, the generator has been replaced, replicating the original in its most recent form, but with small cosmetic and functional improvements. The commissioning and validation of the replacement generator shows its characteristics to be imperceptibly different from the original. So, although the results of past intercomparisons cannot strictly be applied to the replacement generator, much of what was learned in the first instance can give confidence about this instrument in its new incarnation.

Secondly, an additional humidity generator was brought into service at NPL during 1994, covering the range 0 °C to +82 °C (and a little above this in due course). This is mentioned to avoid any confusion. All the intercomparison measurements reported here involved only the original humidity generator built during 1981-84. None of these measurements involved the new "high-range" generator.