

Study of conceptual design for flow-mixing stage of low-range humidity standard generator

Stephanie A Bell
Centre for Basic, Thermal and Length Metrology

ABSTRACT

A study has been made of flow mixing as a method of generating gas of defined moisture content. The study was undertaken with a view to adding a flow mixing assembly to the existing NPL Low Frost-point Generator to extend its range downwards to -85 °C or below.

Implementations of flow mixing generators at other national humidity standards have been reviewed. Modelling has been carried out to examine how the desired range could be achieved, and to see how the uncertainties in input flow rates and moisture contents might propagate. Critical influences such as the source “dry” gas and the gas handling lines are also discussed, and the practical requirements stated. Other key issues are discussed, such as measuring instruments for trace moisture, and data for conversions between measured quantities of mole fraction and frost point.

The likely performance of a flow-mixing system is considered together with the performance of the existing NPL Low Frost-point Generator. It appears that the required range can be reached using the LFG alone, and the uncertainty in frost-point generation is likely to be equal to or better than that achieved by flow mixing. In this case, the addition of a flow mixing stage to the NPL Humidity Standard has only limited value.

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National Physical Laboratory
Queens Road, Teddington, Middlesex, TW11 0LW

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Approved on behalf of Managing Director, NPL
by Dr Graham Torr, Head of Centre for Mechanical and Acoustical Metrology

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2 TECHNICAL SPECIFICATION

2.1 TECHNICAL PARAMETERS

The previously established technical specification for the stage to -85 °C is as follows.

Main requirements:

- **Range of traceable calibrations:** dew point down to -85 °C (0.2 ppm)
- **Gas species:** nitrogen or air
- **Pressure of operation:** atmospheric
- **Flow rates:** as needed for flushing of instruments and sampling lines, for which a range of 0 to 10 litres per minute would be adequate in most cases

Secondary requirements: (operational issues, plus requirements beyond the minimum)

- Partial overlap and compatibility with existing standards, for purposes of intercomparison.
- Capability to calibrate multiple sensors in parallel, for best service and turn-around time.
- Uncertainties to be achieved negotiable, with most users being more interested in traceability of any kind in this range, than in the uncertainties offered.
- Capability to calibrate a wide variety of industrial-grade sensors, not just transfer standard instruments
- Operation at elevated pressures, up to perhaps 7 atmospheres.
- Operation with oxygen, argon, helium.

Additionally, it is desirable for the operating range to extend below -85 °C as far as is reasonably possible.

2.2 GENERAL REQUIREMENTS

The requirements for a national (primary) standard are that it should be accurate (in the sense of being as correct as possible); stable in the long term; amenable to interface with instruments to be calibrated; and of a range and uncertainty which meet the calibration needs of users.

Any primary standard must be traceable ultimately to realisations of the base units of the SI. In this case the choice of traceability is governed by the practicalities of humidity realisation.

Mixing ratio is perhaps the best quantity to realise as a humidity standard, since it is invariant with changes in pressure and temperature. Mixing ratio is a dimensionless quantity but the realisation is traceable to the Kilogram. However, gravimetric hygrometers used to realise mixing ratio do not operate in the trace moisture range.

Second best is dew-point temperature, which is made traceable to the ITS-90, and is a practical basis for a standard although overall gas pressure must be taken into account.

In the trace moisture range, flow mixing is a very practical realisation, and gives a result which can be made traceable jointly to temperature (dew point) and mass (in terms of mass flow). This realisation is most commonly discussed in terms of concentration (e.g. mole fraction in ppm or ppb) although the actual value may be derived from measurements of dew point.

3 EXISTING FACILITY AT NPL

3.1 LOW FROST-POINT GENERATOR

The NPL Low Frost-point Generator (LFG) has recently been developed to complement and extend the NPL dew-point facility. Primarily, this was in order to phase out the use of the Standard Humidity Generator (SHG) in the lower half of its range, eliminating the need to use Trichloroethylene as the bath fluid. Secondly, design features have been incorporated in the LFG to allow the possibility of operation in an extended range down to $-85\text{ }^{\circ}\text{C}$ (0.2 ppm) or below.

The LFG saturates gas at a fixed pressure by passing the gas over a surface of water or ice and a controlled temperature in the range from $+20\text{ }^{\circ}\text{C}$ down to $-75\text{ }^{\circ}\text{C}$ and below. The inlet gas is pre-conditioned to the approximate dew point or frost point by the use of a pre-saturator. The final generated dew point or frost point is defined by the temperature at the exit of the saturator, where the gas is in thermal equilibrium and saturated with respect to the water or ice in the saturator.

The generator is designed with a closed fluid refrigeration system. This allows the safe use of ethanol as the heat exchange fluid, which remains liquid well below $-100\text{ }^{\circ}\text{C}$. The overall design also gives improved ease of use compared to the NPL Standard Humidity Generator previously operating in the range down to -75°C .

3.2 EXTENSION OF RANGE

It has been planned to extend the range of the LFG using flow mixing with dry gas, and this is discussed in the sections that follow. The use of flow mixing to define the trace moisture content of a gas is an approach favoured by the semiconductor and pure gas supply industries, and by some national standards laboratories working in this field of measurement.

However, the LFG, as it stands, already performs better than was expected. The range achievable is lower, and the operation easier and less time-consuming. The uncertainty of the LFG as it currently operates, down to $-75\text{ }^{\circ}\text{C}$, is yet to be evaluated. Below the present range,

the significance of stray moisture will increase, as will the difficulty of quantifying it. However, this is no more true for a frost point realisation than for any other method of working in this measurement range. Therefore, in the work reported here, the use flow mixing is considered alongside the possibility of achieving the same capability using the frost-point generator alone.

4 FLOW MIXING

Issues for flow mixing are considered below. Discussions of materials and construction follow later in Sections 5 and 6.

4.1 GENERAL PRINCIPLE

In a flow-mixing generator, "wet" gas is mixed or diluted with "dry" gas. The resulting moisture concentration is determined by the proportions of the mixture. The moisture contents of both the "wet" and the "dry" gas must be known accurately for a primary realisation. The actual values and uncertainties achieved depend on the moisture contents and uncertainties of the inlet gases, and on the accuracy of flow metering.

The choice of configuration of a flow-mixing generator depends on the range and uncertainties required. Two-stage dilution is a common strategy. This allows small fractions to be mixed while avoiding using flow meters at the low end of their operating ranges, where the uncertainty would be relatively high. Single-stage or multiple-stage dilution are also used.

It is worth noting that the overall output flow rate is generally not critical, but the mixing proportions of "wet" and "dry" gases must be known accurately. This means that calibration of the flow controllers relative to each other may be more important than their absolute calibration. Stability and linearity of flow instruments are also important.

The traceability of a flow-mixing realisation hinges on the moisture content of the input gases. Since the existing NPL Low Frost-point Generator is a fundamental realisation with a small uncertainty, it is advisable to use this to the maximum in the configuration of any flow-mixing design.

5 THE STATE OF THE ART

Existing flow-mixing facilities can be divided into two categories; industrial and laboratory. Industrial trace moisture generators are generally for supply of bulk gases at relatively high flow volumes. When generating gas in large quantity, fast flushing minimises the impact of leaks and desorption. In contrast, laboratory trace moisture generators usually handle less than 10 litres of gas per minute and so do not benefit from the same advantages of scale. In designing a generator for NPL it is most valuable to draw on the past experience of other standards laboratories, rather than that of bulk gas suppliers.

Below, some important flow-mixing standards at other national measurement institutes are described and discussed.

5.1 STANDARD AT AIR LIQUIDE, FRANCE

The French national standard in the trace moisture range is a flow-mixing generator at Air Liquide which is accredited by BNM for the range of dew-points from $-20\text{ }^{\circ}\text{C}$ to $-100\text{ }^{\circ}\text{C}$ (approximately 1000 ppm to 15 ppb) [1]. A diagram of the BNM standard is shown in Figure 1.

The generator features a set of up to four successive dilution stages. In most of the stages of dilution, flow meters of differing ranges are used. Broadly, flow of “wet” gas is between 0.05 and 1.0 litre per minute, and “dry” gas between 2.0 and 2.5 litres per minute. The “ 2σ ” uncertainty in flow they quote at 0.05 litre per minute is 2.1 % of reading, and at 1.0 litre per minute and above is 0.7 % of reading. In some cases, critical flow nozzles are used for flow control. This necessitates holding the upstream pressure at more than double the pressure at the point of use.

Several stages of drying with molecular sieve are used. The gas used is nitrogen, although the approach should be equally applicable to air.

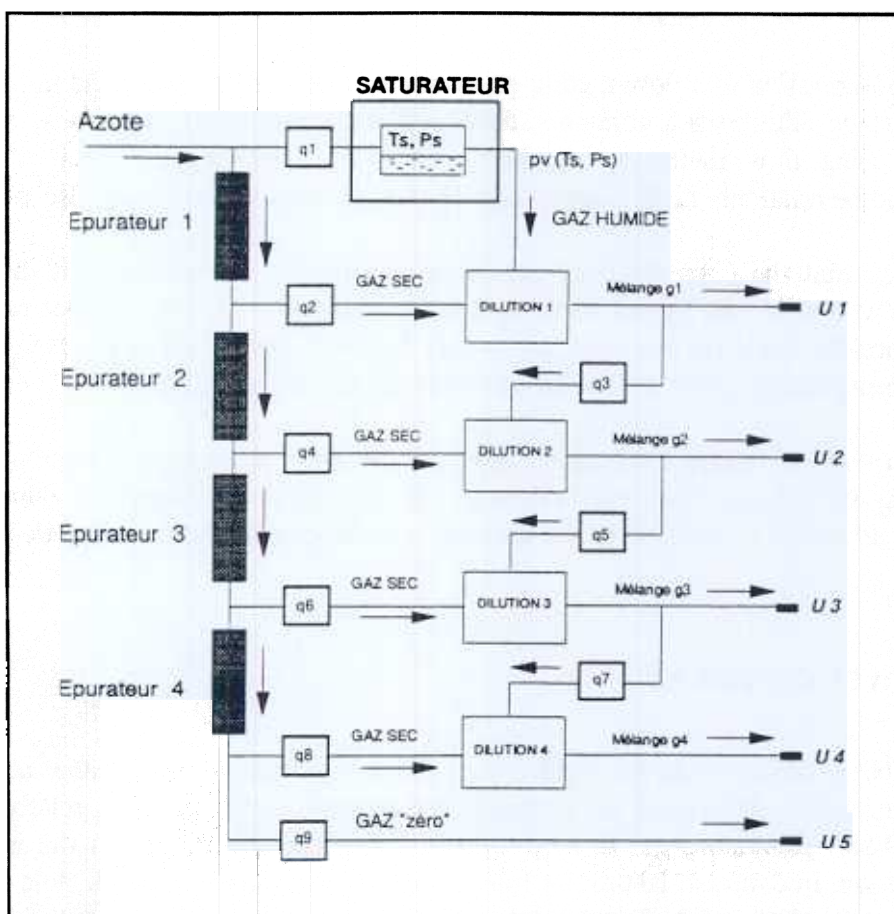


Figure 1 Schematic diagram of BNM flow-mixing generator at Air Liquide, France.

The published uncertainty in value of moisture content varies according to the use of the flow meters at the top or bottom of their full scales. The uncertainty at the 95% confidence level is just over $\pm 5\%$ near 15 ppb (i.e., about $\pm 2.3\text{ }^{\circ}\text{C}$ near $-100\text{ }^{\circ}\text{C}$). Near 1 ppm it is between about $\pm 2.5\%$ and $\pm 3.5\%$ of value (i.e., near $-75\text{ }^{\circ}\text{C}$ it is between about $\pm 0.15\text{ }^{\circ}\text{C}$ and $\pm 0.24\text{ }^{\circ}\text{C}$).

The uncertainty analysis treats pressure, flow and saturator temperature as the sources of uncertainty, while neglecting the uncertainties in moisture content of “dry” and “wet” inlet gases. The uncertainty analysis seems to assume a known upper limit of dryness of the “dry” gas of about 0.1 ppb, which is said to be confirmed using an APIMS (atmospheric pressure ionisation mass spectrometer) but no value of uncertainty is assigned. The uncertainty in moisture content of the “wet” inlet gas is dismissed as insignificant since it is said to be reduced in proportion to the dilution. This does not seem to be a valid conclusion.

Features we can usefully note are:

- The use of cooled molecular sieve dryers as a powerful last stage for drying input “dry” gas. These are suitable for either air or nitrogen.
The possibility of multi-stage dilution
- The use of flow meters away from their weakest ranges.

Features we cannot usefully adopt for NPL’s case are:

- The use of critical flow nozzles as pressure controllers (the pressure requirements for use would not be compatible with the LFG as a “single pressure generator”)
- Assumptions about (in)significance of uncertainty in moisture content of both “wet” and “dry” inlet gas streams
- Dependence on measurement using APIMS for confidence in gas drying.

5.2 STANDARD AT NRLM, JAPAN

The Japanese national standard for relative humidity consists of a flow-mixing generator [2]. Although this generator addresses a completely different moisture range, it is valuable to note their approach to the flow metering problems and analysis of uncertainty.

Figure 2 shows a schematic diagram of the NRLM generator. It consists of a simple one-stage dilution system, but an additional precision flow-meter is used to measure the total (combined) flow of gas. This allows in-situ checks between this flow meter and the two for “wet” and “dry” gas. They have published a protocol for measuring and analysing a matrix of values of flow among the set of flow meters. In the case of a generator for trace moisture, the benefit of in-situ checking would be especially great, since it adds confidence without the need to disassemble the parts and expose them to ambient moisture. Critical flow nozzles are not used within the generator, but are used as transfer devices for checking values of flow.

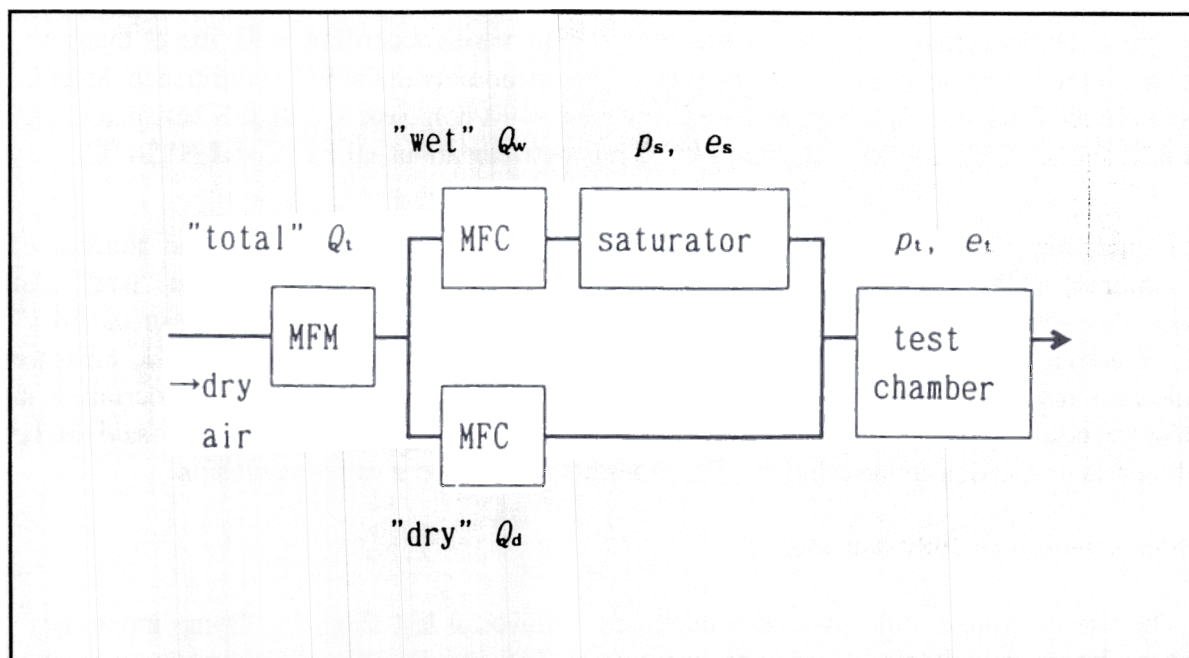


Figure 2. Schematic diagram of flow-mixing generator of NRLM, Japan.

Formulae are published by NRLM for the uncertainty in using the generator in the near-ambient (relative humidity) range, and also for use to generate low moisture contents, where the uncertainty in the moisture content of the “dry” inlet gas needs to be included. (This is discussed further below in Section 6.2.)

From this case we can usefully note:

- The use of a redundant flow meter to check flow metering performance
- The use of critical flow nozzles as transfer standards for checking flow
- Simplicity of construction
- Uncertainty formulations.

5.3 OTHER NATIONAL STANDARDS

The Dutch National Meetinstituut has been developing a flow mixing generator for the trace moisture range (exact range not yet specified). This demonstrates that interest continues in this method of primary realisation. However, some other national laboratories such as VNIIM (Russia) which have in the past said that flow mixing is an additional part of their standard do not seem to be favouring this approach now.

6 MODELLING PROCESSES IN THIS STUDY

In the following, scenarios for realisation using flow-mixing are compared to the equivalents using frost-point realisation.

To explore the best configuration for an NPL flow-mixing assembly, dilution systems were modelled using a spreadsheet written using Microsoft EXCEL. The spreadsheet used schematic visual representations of the dilution configuration. By entering values of “wet” and “dry” gas flow rates, values of inlet gas moisture content, and uncertainties in these, a variety of scenarios could be tried. A specimen printout of the spreadsheet is shown in Annex B.

The aim of modelling was firstly to select flow ranges suitable for achieving the desired range of moisture contents. Secondly the spreadsheet was used to propagate the uncertainties in the input variables (flow rate, moisture content) to give estimates of resulting uncertainty in the resulting moisture content (due to these influences only).

By looking at publications of other national standards based on flow-mixing generators, their analyses of uncertainties have been studied and applied to NPL’s case, particularly the NRLM analysis.

6. MODELLING THE MOISTURE RANGE ACHIEVED BY FLOW MIXING

Using the spreadsheet, simulated combinations of moisture contents of input “wet” and “dry” gas could be mixed in various proportions. This gives information about the best way to achieve the range of trace moisture required

In Table 1 below, some indicative values are shown of the flows (in l/min) needed to produce set values of moisture content from set input values of “wet” and “dry” moisture content (in ppm) in a single stage of dilution.

The immediate conclusion from the information in Table 1 is that the target range (from 1 ppm down to at least 0.2 ppm) can be achieved easily using moderate values of all the input variables. This range of values of moisture content, at a flow rate of 1.5 litres per minute, can be produced from inputs of “wet” gas at moisture content of 1 ppm, “dry” gas within the range 0.1 to 0.02 ppm, and flow meters operating in ranges 0.2 to 0.8 litre per minute and 0.9 to 1.5 litres per minute approximately. There is of course no unique combination - a given output can be reached using a range of suitable combinations of input conditions. More than one stage of dilution could also be considered, but in moderate ranges this gives no added advantage.

Therefore the trace moisture range required can easily be achieved by flow mixing with “wet” gas from the NPL Low Frost-point generator.

However, it should be noted that the LFG can also achieve the required frost-point range (down to -85 °C and some way below) without difficulty.

	ppm	l/min
Wet	1.0	0.65
Dry	0.1	0.80
Result	0.50	1.45

ppm
Wet
Dry
Result

ppm	l/min
1.0	0.75
0.05	0.85
0.50	1.6

ppm	l/min
1.0	0.25
0.05	1.35
0.20	1.6

ppm	l/min
1.0	0.09
0.05	1.5
0.10	1.59

ppm	l/min
0.02	0.82
0.50	1.6

ppm	l/min
1.0	0.30
0.02	1.3
0.20	1.6

ppm	l/min
1.0	0.13
0.02	1.5
0.10	1.63

Wet	1.0	0.05
Dry	0.02	1.6
Result	0.05	1.65

6.2 MODELLING THE UNCERTAINTY ACHIEVED BY FLOW MIXING

The uncertainty in using a flow mixing generator is considered in the light of other published studies, and with the use of the spreadsheet developed in this study.

For the French BNM standard, the published expression for the uncertainty [1, equation (11)] omits any terms due to the uncertainty in inlet “dry” and “wet” gas moisture contents. Instead, it is more helpful to look at the form of the explicit expression given by Takahashi [2, equation (4)] for the Japanese NRLM flow mixing generator. For a flow mixing generator, the vapour pressure, e , in the generator is given [2] by

$$e = p_2 \left(\frac{\gamma e_1}{p_1 - e_1} + \frac{(1 - \gamma)e_0}{p_0 - e_0} \right) / \left(1 + \frac{\gamma e_1}{p_1 - e_1} + \frac{(1 - \gamma)e_0}{p_0 - e_0} \right),$$

where

p_0 is the overall pressure of the inlet dry gas,

p_1 is the overall pressure at the saturator,

p_2 is the overall pressure at point of use (after mixing),

γ is the flow ratio $\gamma = q_w / (q_w + q_d)$,

e_0 is the vapour pressure of the dry inlet gas,

and

e_1 is the saturation vapour pressure of water at the temperature of the saturator t_1

For $p_0 \gg e_0$ and $p_1 \gg e_1$, the uncertainty, u , is given by

$$\begin{aligned} \left(\frac{u(e)}{e} \right)^2 = & \left(\left(\frac{1}{e_s} \frac{de_s}{dt} \right) \bigg|_{t_1} u(t_1) \right)^2 + \left(\frac{u(p_1)}{p_1} \right)^2 + \left(\frac{u(p_2)}{p_2} \right)^2 + (1-\gamma)^2 \left\{ \left(\frac{u(q_d)}{q_d} \right)^2 + \left(\frac{u(q_w)}{q_w} \right)^2 \right\} \\ & + \left(\frac{e_0}{p_0} \frac{p_1}{e_1} \frac{(1-\gamma)}{\gamma} \right)^2 \left\{ \left(\frac{u(e_0)}{e_0} \right)^2 + \left(\frac{u(p_0)}{p_0} \right)^2 \right\}, \end{aligned} \quad (2)$$

where

t is temperature in degrees celsius,

t_1 is the temperature of saturation,

t_2 is temperature at the point of use,

q_d is the flow rate of dry gas in the “dry” branch,

q_w is the flow rate of dry gas in the “wet” branch,

and

$e_s(t)$ is the saturation vapour pressure as a function of temperature t .

For small pressure drops across valves or flow controllers, and for small uncertainties in pressure measurement, this simplifies to:

$$\begin{aligned} \left(\frac{u(e)}{e} \right)^2 = & \left(\left(\frac{1}{e_s} \frac{de_s}{dt} \right) \bigg|_{t_1} u(t_1) \right)^2 + (1-\gamma)^2 \left\{ \left(\frac{u(q_d)}{q_d} \right)^2 + \left(\frac{u(q_w)}{q_w} \right)^2 \right\} \\ & + \left(\frac{e_0}{e_1} \frac{(1-\gamma)}{\gamma} \right)^2 \left(\frac{u(e_0)}{e_0} \right)^2 \end{aligned} \quad (3)$$

Study of the terms in equation (3) reveals the significance of the different contributions to uncertainty. In addition to this, the “flow mixing” spreadsheet was used to explore the effects of varying the uncertainties in the input values of moisture content and flow rate. Thirdly, uncertainties due to stray water vapour have been considered, although they do not feature in the equations above. These considerations lead to some general conclusions given in the following section.

7 CONSIDERATION OF UNCERTAINTIES OF DIFFERENT ORIGINS

7 UNCERTAINTIES RELATED TO LEAKS AND SURFACE EFFECTS

At very low values of moisture content, stray moisture from leaks and desorbing from surfaces (or rarely adsorbing) is typically the largest source of uncertainty in the value of frost point or mole fraction at the point of use of the gas. This influence normally adds water vapour to the process. The rate of addition of stray water vapour to a gas stream tends to reduce in time with lengthy equilibration, but the worst-case value is broadly independent of the value of trace moisture being generated. In this sense, stray water can be thought of as a “fixed” contribution to uncertainty. An uncertainty contribution of fixed magnitude becomes increasingly significant at lower overall concentrations of water vapour. This is true irrespective of whether the realisation is based on frost point or flow mixing. However, in a flow mixing system, the more complex arrangement of pipes, valves and vents carries more risk of leaks, crevices, etc.

It can be calculated [4] that a small leak of the order of 1×10^{-10} millibar litre per second (mbar l s^{-1}) could raise the moisture content of a gas flowing at 1 litre per minute by 1 ppb (0.5 % of value at 200 ppb). The actual size of leaks could be greater in practice. Operation at a slight positive pressure would reduce the impact of leaks.

Carefully designed tests and usage can allow the estimation of stray moisture added to a gas stream. At present at NPL, this approach allows stray moisture to be quantified with a standard uncertainty (at a coverage factor $k=1$) of the order of 0.03 to 0.05 °C at -75 °C, equivalent to up to 10 ppb of stray water vapour, i.e. up to about 0.8 % of value. This quantity of stray water at a frost point of -85 °C (0.2 ppm) would impact the measurement by about 0.25 °C (5 % of value). At -90 °C (0.1 ppm), the effect would be of the order of 0.5 °C (10 % of value).

7.2 UNCERTAINTIES RELATED TO TEMPERATURE EFFECTS IN GENERAL

Uncertainties which are a function of dew-point temperature of the inlet gas have increasing significance at ranges of lower concentration, since the slope of the vapour pressure-temperature curve becomes steeper at lower concentrations. (Near 0 °C (6000 ppm), 1°C corresponds to about 8% of vapour pressure. Near -90 °C (0.1 ppm), 1°C corresponds to about 18 % of vapour pressure.) The actual values of temperature-related errors are likely to be at their worst at lower temperatures, since thermal radiation increases as the difference from room temperature increases, and bath temperature becomes less uniform as the bath fluid becomes more viscous. However, the actual significance of temperature-related uncertainties can be evaluated from the first squared term on the right-hand side of equation (3). Calculation of this term may assume $u(t)$ to represent the purely temperature uncertainty of the kind described above. A more cautious approach would be to treat $u(t)$ as the total uncertainty in dew-point temperature realisation, including allowances for saturation efficiency and stray water vapour (which are not separately identified in equations (2) and (3)). If the first of these

two approaches is used, as the authors seem to recommend, this term assumes relatively small significance in the range of interest here.

UNCERTAINTIES IN MOISTURE CONTENT OF INLET "DRY" AND "WET" GASES

"Wet" inlet gas from the LFG at a frost point of (for example) $-75\text{ }^{\circ}\text{C}$ (1.2 ppm) can be supplied at a standard uncertainty ($k=1$) of about 10 ppb, about 0.8 % of value.

On the other hand, the fractional uncertainty in moisture content of "dry" inlet gas will be much larger than that of "wet" inlet gas. The "dry" gas could feasibly be specified at any given value between, say, 20 ppb and 100 ppb (or perhaps below 20 ppb). However, measurements of this gas, not being traceable, would carry large uncertainties, of easily 10 ppb to 20 ppb (at $k=1$).

On mixing, the overall uncertainty would depend on the mixing proportions, but in most cases, the uncertainty in the dry gas would dominate. For example, mixing flows of $1\text{ ppm} \pm 0.01\text{ ppm}$ and $0.02\text{ ppm} \pm 0.01\text{ ppm}$, in proportions approximately 13:3 would give an output of about $0.20\text{ ppm} \pm 0.01\text{ ppm}$ (disregarding other sources of uncertainty). In this case, inlet uncertainties of respectively 1 % and 50 % lead to output uncertainty of about 5%.

The uncertainty in the output value could be improved by measuring the "dry" gas significantly better, say with a standard uncertainty of 1 or 2 ppb. This is not likely to be achievable. Alternatively, a smaller uncertainty in output could be sought using a larger proportion of "wet" gas from the LFG at a (well characterised) lower frost point below $-75\text{ }^{\circ}\text{C}$. However, the logical extension of this argument points towards the use of the LFG directly to achieve the desired range, avoiding flow mixing altogether.

UNCERTAINTIES RELATED TO FLOW

A range of low moisture contents are achieved by mixing a small proportion of "wet" gas with a large proportion of "dry". The uncertainty in flow metering is normally greater for the smaller ("wet") flow. However the actual uncertainties, which could be of the order of 2 % (at $k=2$), are not as significant as some of those associated with the moisture content of the inlet "dry" gas.

CONCLUSIONS FROM THE BALANCE OF UNCERTAINTY CONTRIBUTIONS

Overall, in the range where there is a choice between flow mixing and saturation (dew-point) techniques, the benefit of flow mixing technique is not uncertainty, nor range, but speed of changing between set points by simply adjusting a gas flow rate. However, even the ability to rapidly to change set point does not lessen the time needed for equilibration at these very low moisture levels (days, or even up to a week, or more), so the benefit is limited.

From the arguments above, it appears that flow mixing can only improve upon frost point generation if uncertainties due to desorption can be characterised better for the "dry" gas than they can for the (well defined) "wet" gas. It is unlikely this could be achieved.

On balance therefore, there may be an advantage in using to the fullest the temperature-based aspects of trace moisture realisation. This points toward realisation using dew point rather than flow mixing.

These conclusions on uncertainty inform the decision of which method to adopt. However, the discussion of uncertainties here does not give a full picture - a detailed analysis could only follow after construction and measurement evaluation of the instrument in its extended range.

8 “DRY” GAS SUPPLY

8. METHODS OF GAS DRYING

The choice of drying method depends on which gas is to be used, nitrogen or air. For most purposes of humidity measurement these two carrier gases are interchangeable.

Liquid nitrogen boil-off can be a convenient source of dry gas. However without special precautions this may not supply gas any dryer than about 1 ppm. For ultimate drying, nitrogen can be purified using “getters” to achieve moisture content reportedly down to less than 1 ppb. (However this would be claimed at the point of purification, and would not apply to the value after piping to the point of use.)

Air can be readily dried using various methods, of which perhaps the most powerful is cooled molecular sieve. (Getter-type dryers cannot be used with air.) The degree of drying depends on the flow rate, the type and condition of the molecular sieve, and the temperature. Although not as powerful as getter techniques, it is still realistic to achieve a very few parts per billion in this way. This method is also suitable for drying nitrogen.

For powerful dryers (e.g. getters said to achieve <1 ppb) many users accept a value assigned (e.g. by an equipment manufacturer) to the “dry” gas moisture content. Users cannot substantiate this by traceable measurements (obviously not available), and other conclusive tests of dryness are difficult without major investment in equipment and time. (The method of choice in pure gas industries appears to be the APIMS (atmospheric pressure ionisation mass spectrometer) costing of the order of £0.25M.) This is naturally why most users rely on manufacturer’s claims. In a primary standard however, an assumption of this kind would not be acceptable. It remains preferable to work with gas of a somewhat higher moisture content that can be quantified. In this respect, minimising the moisture content would not be as important as minimising the uncertainty in its value.

Practical considerations include permanent running and constant availability of dry gas, quality of supply lines with the minimum of joints, and ideally a short path length between the dryer and the point of use.

There are three important uses of “dry” gas in a trace moisture generator. These are:

- as an input gas stream in a flow-mixing generator,
- as a flushing gas for drying down instruments and supply lines prior to measurements, and
- as a tool for generator validation.

These are discussed in the following sections.

8.2 “DRY” GAS SUPPLY FOR FLOW-MIXING GENERATOR

In a flow-mixing generator, the moisture content of the “dry” gas is critical. The value of moisture content dictates the range that can be achieved. The uncertainty in the moisture content dictates the uncertainty achievable. Any method of drying which supplies the necessary flow rate can be considered, subject to the more important constraints of range and uncertainty. In this case we have established that a value in the range of about 0.02 ppm to 0.1 ppm and uncertainty of less than 10 ppb would be needed.

8.3 “DRY” GAS SUPPLY FOR FLUSHING

Irrespective of the type of trace moisture generator, dry gas also has a vital role for flushing instruments and sample lines prior to measurement. The dryer the gas, the more powerful its drying effect, and the better the ultimate level of surface dryness achieved. However, the flow rate of flushing is not critical, and neither is the exact level of dryness, provided they are enough that the gas does not become significantly saturated by the water vapour it takes up, which would impair its drying efficiency. In this case, gas at least 1 order of magnitude dryer than the target measurement range would be adequate, e.g. for measurements at 0.2 ppm (-85 °C), flushing gas should probably be of the order of 0.02 ppm (-98 °C) or below.

8.4 “DRY” GAS SUPPLY FOR VALIDATION OF A GENERATOR

“Dry” gas is an important tool for the validation of a trace moisture generator. Tests of saturation efficiency, and estimates of stray moisture, rely on the use of “dry” gas.

Evaluation of saturator efficiency

For tests of saturation efficiency, the exact dryness of gas is not critical. However, it is valuable to have gas of frost point some degrees below the working range, to allow saturation by addition of water vapour (evaporation or sublimation), as an alternative to reaching equilibrium by removal (condensation) of water vapour.

Evaluation of stray moisture

Stray moisture is normally the largest source of uncertainty in trace moisture measurements, and the hardest to estimate reliably. At NPL, the established approach to this is to measure the impact of stray moisture on small flows of “moderately dry” gas in the range where measurements can reliably be made, and then to extend the conclusions to the faster flow rates

of real use, and to the real ranges of “dry” gas and “generated frost point”. This method does not require, or benefit from, the driest possible gas.

However, the newest condensation hygrometers currently operate to much lower frost points than in the past (down to around $-100\text{ }^{\circ}\text{C}$). It thus becomes viable to make (non traceable) measurements of small changes in that part of the range. This might offer an alternative way to study the additive effects of stray moisture actually in the driest ranges of interest. It is not certain that this would give better information than NPL’s existing method, but it is likely to be useful. In this case, there would be a benefit in having the driest gas reasonably possible.

8.5 “DRY” GAS SUPPLY FOR LFG USED IN AN EXTENDED RANGE

For extending the LFG without the use of flow mixing, most of the points above remain valid. However the value of dryness is not directly critical for the value of generated frost point. Since the LFG currently operates with air, pre-dried using (non-cooled) molecular sieve dryers, then the simplest extension to this would be to add a cooled molecular sieve dryer. The flow rates required (up to 3 litres per minute in the generator, and faster rates for flushing if needed) can easily be achieved by this.

8.6 CONCLUSIONS ABOUT THE REQUIREMENT FOR “DRY” GAS SUPPLY

There is limited benefit in having the driest possible gas, and claims for extreme levels of dryness are difficult to authenticate. If flow-mixing is to be used, the value and uncertainty for the “dry” gas must be as well known as possible, but this need not be extremely dry. For frost-point generation, the dryness of the gas does not critically affect the generation process, but is significant for use in characterising the performance of the generator. For either type of generator, preparatory flushing for measurements around $-85\text{ }^{\circ}\text{C}$ requires gas approaching a frost point of $-100\text{ }^{\circ}\text{C}$. This can be provided using a cooled molecular sieve dryer which would be suitable for either air or nitrogen.

9 GAS HANDLING TECHNIQUES

The considerations of gas handling apply to the use of both flow mixing and frost-point generation.

9.1 GENERAL PROVISIONS FOR HANDLING GAS AT ULTRA-LOW HUMIDITIES

To handle highly pure gases without contaminating them, precautions need to be taken to minimise the influences of desorption, leaks and anything else which could significantly affect the composition of the gas. Firstly, the measures are dictated by the range of moisture concentration required. Secondly, the care taken will directly affect the uncertainty in knowing the value of moisture concentration. In a laboratory environment the small scale of the operation means that more care may be needed than in an industrial setting where high flow rates can reduce the impact of any individual leak or poor component.

In the range of interest here stray water vapour would not impair the ability to reach the values of moisture content required. (This would be more of a problem in reaching much lower moisture ranges of the order of 1 ppb.) Therefore gas handling is not so much an issue for achieving the desired range here, but its relevance is mainly for the uncertainty of the realisation.

There are some well recognised gas handling practices which can maximise the measurement range or improve the uncertainty with which trace moisture measurements can be performed. These practices include: preparatory baking of pipework; evacuation or dry gas flushing; avoidance of materials prone to outgassing; minimisation of pipe lengths and dead ends; “bypass flows” or slight “bleeding” of gas system; fine finish of surfaces in contact with the gas sample ...and of course isolation of the gas system from ambient atmosphere.

Techniques can be devised to get the best information from measurements to evaluate the adequacy of gas handling. These include controlled addition of moisture to the sample gas, measurements at varying flow rates; pressure drop, prior purging with gas of known dryness, careful design of measurement and sampling system, and careful interpretation of measurement results.

While good materials and manufacture are important in the saturator of a generator, they are just as critical in the supply line from the saturator to the point of use (hygrometer under calibration). The aim is to ensure that the gas does not change in moisture content between leaving the saturator and reaching the point of use.

9.2 TO WORK AT A MOISTURE LEVEL OF ABOUT 1 PPB

There is no proposal here to offer calibrations at this low level, and little benefit from having even a “dry” gas supply at this level. The main precautions in handling this level of dryness would include painstaking selection and preparation of materials (stainless steel electropolished or with other treatments); special precautions to prevent contamination of the source gas (probably nitrogen) from origin to point of use; all welded joints (manufactured under ultra-dry gas blanketing), facility for baking under vacuum or inert gas, and continuous flushing with pure, dry gas throughout the manufacture and lifetime of the apparatus. In this case, the small benefit of having such ultra-dry gas does not justify such effort.

9.3 TO WORK AT ABOUT 10 PPB

A calibration standard operating in the region of 10 ppb (frost point below -100 °C) would require many but not all of the precautions listed in the paragraph above. Permanent flushing to exclude atmospheric air would be desirable, but need not be in place during manufacture and construction of the assembly. Construction would require electropolished stainless steel (or other treatments), avoidance of bending of tubes (which can crack the surface finish), all welded joints, facility for baking, etc.

If “dry” gas of 10 ppb were to be delivered to support the requirements of a generator in the range above this (say 100 ppb), it seems likely that it would be possible to use lesser

precautions for the source gas. Continuous gas flushing to permanently exclude atmospheric air, and clean, welded, all-metal (electropolished stainless steel) parts would still be recommended.

9.4 TO WORK AT ABOUT 100-200 PPB

A calibration environment in the region of 100-200 ppb (frost point around -85 °C to -90 °C) would require many but not all of the precautions listed in the paragraph above. Permanent flushing to exclude atmospheric air would be desirable. Construction would require electropolished stainless steel (or other treatments), all welded joints where possible, otherwise all-metal VCR-type connectors. Facility for baking the line between the generator and the point of use would be desirable but might not be necessary.

9.5 OTHER POINTS

In some applications, such as electronic wafer fabrication, it is critical to avoid impurities, especially particles. In a standard generator for trace moisture content, the general level of impurities may be less critical for the purposes of the calibration itself. However, sufficient precautions (e.g. filtration) would have to be taken to prevent contamination of instruments under calibration, and subsequent transfer of contaminants to the customer's process.

A flow mixing generator necessarily features a number of valves, flow controllers and vents, and each component should be of suitable quality for the moisture range of use. This may involve compromises where there are moving parts, seals etc., whose materials of construction cannot always be ideal for the ultra-dry gas environment. These problems are reduced in a frost-point generator, where there are fewer such components, so this is an advantage of a purely frost-point approach.

In minimising stray water, it is reported by some users that removal of surface adsorbed water by flushing is generally more effective than by evacuation. Therefore vacuum treatments are not necessarily recommended here for preparatory conditioning of pipework.

In baking, or in flushing with highly dry gas, it is possible to “over dry” pipework. Experience at NPL has shown that after intensive drying, it subsequently takes some time for pipework surfaces to re-adsorb even the small amount of water required to bring them back into equilibrium with generated gas at quite low moisture content of the order of 1 ppm or less. Therefore caution is needed after any kind of extreme drying.

9.6 CONCLUSIONS ABOUT GAS HANDLING

For calibrations down to 100-200 ppm (frost points of -85 to -95 °C) the level of care in construction and use of gas handling systems is slightly greater than the care currently taken for the existing NPL working range.

10. OTHER IMPORTANT ISSUES

SATURATION AT VERY LOW TEMPERATURES

In using the LFG to saturate gas at increasingly low temperatures, the approach to saturation using thermal and phase equilibrium remains valid. However the more extreme the temperature, the more necessary it is to question our assumptions about the actual processes taking place within the saturator. At lower temperatures, we can be less sure of our assumptions about (or are less able to measure);

- the efficiency of saturation with water vapour at the measured gas temperature
- the stability of the ice film in the saturator, (where ice may be in the form of brittle flakes which could be carried off into the gas stream)
- the crystalline structure of ice (of which more than one form exists at low temperatures)
- nucleation of airborne ice crystals if equilibrium is approached from above (supersaturation).

In extending the use of the LFG to lower temperatures, it may become increasingly important to consider these questions.

HYGROMETERS FOR USE IN SUPPORT OF THE LOW-RANGE GENERATOR

Hygrometers of suitable quality and measuring range are essential for assessment of performance of the NPL generator in its extended range of use. This is required for both the generated gas and the inlet “dry” gas supply, and must address both the initial validation and the day-to-day monitoring of performance.

Increasingly, optical dew-point hygrometers now serve the frost-point range down to about -100 °C, and represent a well established technology, and one familiar to NPL. They are effective for stable and reproducible measurement, and have been successfully used for validation and routine monitoring of NPL dew- and frost-point realisations.

Both the Low Frost-point Generator and optical dew-point hygrometers operate through equilibrium of the gas stream with ice. In this sense the two approaches form a consistent measurement system, and that has some benefits. However there would also be a benefit in using a hygrometer of a different type, which might give other information not apparent when comparing two instruments of related operating principle. It is worth considering what other hygrometers could be useful.

A technique of growing importance for trace moisture measurement is laser absorption spectrometry. Various instruments of this type are becoming commercially available, and they seem to promise significant advances over existing techniques. Absorption spectrometers typically work by measuring the absorption of a selected wavelength of infrared radiation by water vapour. The advantages include range (varying with instrument, but down to 100 ppb and below) and response time which may be much faster than any other hygrometer in this

range of measurement (although subject to the same need to dry down both the instrument and the sample lines). Instruments of this type offer great potential for tracking rapid changes in very dry gases in real time, in a way that condensation hygrometers cannot. This would be highly useful in exploring the performance of a frost-point generator in a range of operation where a number of new potential problems have to be considered.

For more routine measurement, there is a need for basic monitoring of the inlet “dry” gas. This is both to monitor the performance of the gas drying system, and to measure the dry gas flushing the generator and connected lines in order to routinely assess the level of stray moisture. Although the measurement in this range may not be traceable and may carry a large uncertainty, this monitoring is important to ensure the quoted uncertainties are achieved in practice. For this purpose it is appropriate to use capacitive aluminium oxide or ceramic sensors, mounted in the gas lines, with regular checks of their stability, since these sensors may be prone to drift.

10.3 CONVERSIONS BETWEEN UNITS OF MEASUREMENT

Users of measurements and calibrations in “trace” moisture ranges need to be able to convert between frost point temperature and units of concentration such as mole fraction or vapour pressure. Conversions are made using formulae representing the saturation vapour pressure curve of pure water, and the water vapour enhancement factor - the correction factor for non-ideality of the air-water mixture, especially at elevated pressures. The enhancement factor is of the order of 1.005 at atmospheric pressure and moderate temperatures, increasing slowly with pressure and at extremes of temperature (e.g to about 1.09 at 10 bar and -80 °C).

In the range of measurement considered here, the saturation vapour pressure formulae appear to be adequate. They are subject to some uncertainty, but this is small in comparison to the practical sources of uncertainty. The data and formulae for enhancement factor are not so satisfactory. Below -35 °C, there are no published experimental data for enhancement factor, and so formulae extending below this range are unsubstantiated and may well have significant errors [5]. To resolve this doubt, there is a need for measurements and further calculation of enhancement factors at and below -35 °C.

Although slightly beyond the scope of this study, it should be noted that there do not appear to be any recognised saturation vapour pressure formulae considered valid below -100 °C. However some users and suppliers of instruments do make conversions at this level, since sensors available on the market reach frost points as low as -120 °C (about 0.1 ppb). In practice, conversions in this range are made by using formulae outside their range of validity - apparently without serious problems - but the situation is not satisfactory.

As noted above, in NPL’s current facility, optical dew-point hygrometers are used alongside frost-point generation, forming a self-consistent system based on equilibrium with condensed water (ice). If there were a proposal to consider the relationship between the quantities of frost point and mole fraction or vapour pressure in this range of measurement, high quality instruments of other operating principles, such as absorption spectrometry, should be considered.

10.4 FLOW MIXING FOR VALIDATION

In any measurement system, validation using a complimentary method is always valuable. Although flow mixing may not represent the best way to realise the extension of the NPL humidity standard, there could be some argument for using a flow mixing generator as a tool for validation of the frost-point method in the extended range. On balance, however, a flow-mixing generator constructed on a trial basis for short-term use could not necessarily be well characterised. The effort and cost of building a flow-mixing “comparator” of sufficient quality for this purpose do not seem justified.

10.5 INTERFACE AND USAGE

Some operational issues can be considered at this stage. Computerised data logging is considered to be essential, especially in view of the need to monitor during long stabilisation periods over weeks of continuous use. On the other hand, general automation of the operation would have little benefit, since the main constraint is stabilisation time rather than time spent changing between set points.

Use of the LFG with the minimum of modification keeps a high degree of commonality with the existing facility. For example, this allows the use of nearly identical data-logging software, and operating procedures which are closely related to those already in use.

The LFG in its present form is relatively easy to use (for experienced operators). This advantage is best preserved by maintaining its operation similar to the present basis.

11 FORECAST PERFORMANCE

The likely performance of the generator is considered in the light of the technical specification outlined earlier in Section 2.

It is estimated that the required range down to at least -85 °C (0.2 ppm) can be achieved without difficulty by either frost-point or flow-mixing approach, as described in this report.

The methods proposed for the generator and for the cooled molecular sieve dry gas source are suitable for both nitrogen and air, and possibly other inert gases, e.g. argon.

Gas flow rates from the dry gas source would be according to agreement with the supplier, but the suggested upper limit of 10 litres per minute is easily achievable. Flow rate supplied by a flow mixing generator could achieve approximately the same upper limit. Frost point generation using the existing LFG would achieve a lower flow rate, probably limited to 3 litres per minute at most, but this is considered adequate, especially if “dry” flushing gas is not limited to this flow rate.

Maximum compatibility with existing standards would be achieved by extending the range of the LFG with minimum alteration.

Capability to calibrate multiple sensors can be achieved using a suitable manifold and gas flow rate. A flow rate of 3 litres per minute would be sufficient to supply several sensors. For instruments requiring fast flow (e.g. large-volume spectrometers), this flow rate would be adequate but might limit the accommodation of multiple sensors.

The uncertainties achievable will depend on validation of the built instrument and particularly on our capability to quantify the effect of stray water vapour. However, reasonable nominal target uncertainties (at a coverage factor $k=2$) at selected points would be:

± 0.1 °C (± 0.02 ppm)	at	-75 °C (1 ppm)
± 0.2 °C (± 0.02 ppm)	at	-80 °C (0.5 ppm)
± 0.5 °C (± 0.02 ppm)	at	-85 °C (0.2 ppm)

These target uncertainties should be achievable using either the LFG or a flow-mixing generator added to the LFG, although flow mixing would not be expected to improve the uncertainty achieved and would therefore offer little or no gain over the use of the LFG alone.

12 TECHNICAL RISK

In weighing up the arguments about using a flow mixing realisation at NPL, it is also important to consider the level of technical risk that a chosen method might prove unsuccessful.

This study has not found a sound technical basis to justify statements of range and uncertainty which are claimed by some users for flow-mixing and other trace moisture techniques in use. It would be possible to continue with the original plan of building a flow mixing assembly, hoping that in the process information might emerge to support this method after all. However that would be an undertaking of high technical risk.

On the other hand, dew-point (frost-point) generation is a familiar technique in use by NPL, and the technical risk in extending its use to lower temperatures is relatively small.

13 CONCLUSIONS

The addition of a flow mixing assembly to the NPL LFG does not overall appear to be the best way to extend its range downwards to achieve the target measurement range down to 0.2 ppm (a frost point of -85 °C).

Flow mixing is a useful approach in some circumstances:

- for higher humidity ranges than that considered here
- for speed of operating at trace moisture ranges (although it does not save on equilibration time, only on the time it takes to change set point)
- for range - if that is the only way to reach the range
- for a generator of “nominal” value dry gas, using some other definitive or calibrated instrument to assign a value

But where it is available, dew-point (frost-point) generation has much to recommend it

- if the temperature range can be achieved (using suitable coolant and refrigeration)
- if the exact moisture content of “dry” gas cannot be well characterised

For the provision of an extension to the UK national standard, the addition of a flow mixing stage to the existing NPL Low frost-point Generator could in principle extend the range downwards. However the LFG already operates some way below the expected range, and can reach -85 °C easily, and -90 °C without much difficulty.

Apart from range, the other consideration is uncertainty of realisation. From the arguments considered in detail here, there is nothing to suggest that the uncertainty achieved in any given range by flow mixing can improve on that achieved by frost-point generation at the corresponding moisture content. Therefore this, too, suggests that flow mixing should not be adopted as an addition to the existing facility.

On grounds of technical risk, frost-point generation is preferred over flow mixing, as the frost points method is established practice at NPL.

Whether or not flow mixing is used as part of the realisation, the “dry” gas is a critical element. In a flow-mixing system the moisture content and uncertainty hinge on those of the dry gas. For flow-mixing or frost point realisation, “dry” gas is a tool for validation, and is essential for prior conditioning of instruments and sample lines.

Although it may not be recommended as a primary realisation for a UK standards, flow mixing for trace moisture realisation remains a satisfactory approach in cases where no strong reliance is placed on the absolute value, for example in secondary or industrial laboratories, where a value is assigned to the gas moisture content, using measurements from a traceably calibrated hygrometer.

Otherwise, the only added benefit of flow mixing would be for reaching a small range below that achievable using the LFG, and this would be with a relatively large uncertainty. However this range may be more suited to realisation using a completely different approach.

14 SUGGESTIONS FOR FURTHER WORK

The finding of this study was unexpected. It was anticipated that construction of a “dry” gas supply and flow mixing assembly would be the recommended course of action, and that this would follow in the next NMS Programme for Mass Metrology. One year of this Programme (October 1999 to September 2000) has already been approved.

The potential range and ease of use of the LFG have also exceeded expectations. The use of alcohol as the coolant in a sealed refrigeration system located external to the temperature cooled bath has proved a dramatic improvement over previous arrangements. This allows the possibility of reaching saturator temperatures at and below -85 °C relatively easily, albeit with increasing uncertainties at lower temperatures.

Bearing in mind both these points, the downward extension of the range of the NPL standard should be pursued using the LFG solely. Therefore, in place of construction of a flow mixing assembly, it would be better to validate the LFG to a lower limit in its current mode of operation, with small modifications if needed to enhance its performance. The existing objective to construct and assess a “dry” gas supply remains necessary, but its significance is now slightly different. The “dry” gas would no longer be a critical input to the value of generated moisture content, but it is highly necessary for preparatory flushing of the LFG and instruments awaiting calibration. The highly dry gas would also be needed in the course of assessing the uncertainties due to desorption and leaks, as these would be the dominant source of uncertainty in the use of the LFG in the extended range.

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ANNEX A. APPROXIMATE CONVERSION BETWEEN FROST POINT AND MOLE FRACTION

Values of frost point in air and corresponding approximate pure vapour pressures, and mole fractions in air at total (atmospheric) pressure of 101325 Pa.

Frost point °C	Vapour pressure Pa	Mole fraction		
		ppm	ppb	ppt
0	611.153	6032		
-10	259.837	2564		
-20	103.2538	1019		
-30	38.03154	375		
-40	12.85799	127		
-50	3.944492	39		
-60	1.083071	11	10689	
-70	0.261854	3	2584	
-80	0.054653	1	539	
-90	0.009613	0.1	95	94875
-100	0.001383		14	13653
-110	0.000157		2	1549
-120	1.34E-05		0.1	132
-130	8.12E-07			8
-140	3.23E-08			0.3
-150	7.59E-10			0.01

ANNEX B. SPECIMEN PRINTOUT OF SPREADSHEET

