

Evaluation of trace moisture sensors – interim report

Stephanie Bell*, Tom Gardiner*, Mark Stevens*, Keith Waterfield⁺

*** National Physical Laboratory**

⁺ BOC Edwards

ABSTRACT

A review is presented of the current state of industrial trace moisture measurement below about 1 part per million, and of the current needs of users of trace moisture instruments. The review and consultation were undertaken as the first workpackage of a project in which the performance of a selection of trace moisture sensors will be evaluated, in order to provide general information and guidance to instrument users.

In this interim report, background information is given about the main measurement methods for this range, together with some discussion of the relative merits of the different approaches. Corresponding information is also given for trace moisture generating instruments. Consultation of users and suppliers of instruments is reported, with summary of their main measurement concerns.

Offers of loans a number of instruments have been received. A proposed shortlist is given, together with an evaluation plan incorporating input from the users surveyed and from the instrument suppliers. The proposed selection includes some precision laboratory instruments, but also several industrial-level probes, reflecting the widespread usage and importance of these.

Also included here is a synopsis of a laboratory study carried out by the US National Institute for Standards and Technology (NIST), evaluating permeation tube moisture generators – work that is complementary to the evaluation of sensors planned in this project.

© Crown copyright 2002
Reproduced by permission of the Controller of HMSO

ISSN 1469-4921

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

This document has been produced for the Department of Trade and Industry's National Measurement System Policy Unit under contract number GBBK/C/013/00011. Extracts from this report may be reproduced provided the source is acknowledged and the extract is not taken out of context.

Approved on behalf of Managing Director, NPL
by Dr D W Robinson, Head of Centre for Basic, Thermal and Length Metrology

CONTENTS

	Page
1 INTRODUCTION.....	1
1.1 OBJECTIVE.....	1
1.2 TERMINOLOGY	1
1.3 BACKGROUND - THE NEED FOR MEASURING TRACE MOISTURE	2
1.4 METHODOLOGY OF STUDY	3
2 REVIEW OF TRACE MOISTURE MEASUREMENT AND GENERATION	4
2.1 TRACE MOISTURE MEASUREMENT METHODS	4
2.2 DISCUSSION OF MEASUREMENT METHODS	5
2.3 TRACE MOISTURE GENERATION METHODS	7
2.4 DISCUSSION OF GENERATION METHODS	9
2.5 MATRIX GASES	11
3 NIST STUDY ON TRACE MOISTURE GENERATION.....	13
3.1 ACCESS TO INFORMATION ON TRACE MOISTURE GENERATORS	13
3.2 SUMMARY OF NIST STUDY	13
3.3 COMMENTS ON NIST STUDY	15
4 CONSULTATION	16
4.1 CONSULTATION OF INSTRUMENT USERS	16
4.2 SUMMARY OF MAIN USER CONCERNS	16
4.3 CONSULTATION OF INSTRUMENT SUPPLIERS.....	18
5 TEST AND VALIDATION PLAN	19
5.1 INSTRUMENTS PROPOSED FOR EVALUATION.....	19
5.2 DESIGN OF LABORATORY TESTS	20
5.2.1 Overview of laboratory tests	20
5.2.2 Test details	21
5.2.3 Detail of measurement facilities and protocols of NPL and BOC partners	21
5.2.4 Tables of workplan.....	21
APPENDIX A: APPROXIMATE CONVERSION BETWEEN UNITS	25
APPENDIX B: LIST OF PARTICIPANTS IN THE PROJECT	26
APPENDIX C: NIST STUDY OF PERMEATION TUBE MOISTURE GENERATORS.....	27
APPENDIX D: UK-NMS LOW FROST-POINT GENERATOR AT NPL	28
APPENDIX E: UK-NMS TRACE WATER FACILITY IN NPL ANALYTICAL SCIENCE GROUP	30
APPENDIX F: BOC MOBILE TRACE WATER FACILITY	32
APPENDIX G: GLOSSARY	34

LIST OF FIGURES

Figure NIST measurement configuration for testing permeation tube moisture generators

Figure 2: Time response of the Quartz Crystal Microbalance hygrometer successively exposed to streams from the NIST Low Frost Point Generator, test generator and Low Frost Point Generator.

Figure 3: Comparison of results for PTMG *A* and PTMG *B*

Figure 4: Illustration of the layout of the Low Frost-point Generator

Figure 5: Saturator of the Low Frost-Point Generator

Figure 6: Internal Layout of Trace Water Vapour Facility

Figure 7: Schematic diagram of BOC trace moisture facility

LIST OF TABLES

Table 1: Laboratory evaluation workplan

Table 2: Schedule of work

1 INTRODUCTION

1.1 OBJECTIVE

This report is a deliverable of a project commissioned by the National Measurement System Policy Unit (NMSPU) of the Department of Trade and Industry under contract GBBK/C/013/00011, for Project 2.2c of the NMS Programme for Thermal Metrology 2001 to 2004. The project involves a laboratory evaluation of the instruments and methods of measurement available to industries needing to handle and measure gases of very low moisture content, in the range below about 1 part per million.

The aims of this project are:

- To help UK industry benefit from a more fully informed choice of measuring instrumentation for trace moisture
- Dissemination of the information as widely as possible in the UK

The project comprises some initial background study, planning and consultation with instrument users, and a laboratory evaluation of a selection of trace moisture instruments representing the main types in industrial use. This report covers the initial planning and consultation phase of the project

1.2 TERMINOLOGY

In this document, terms will be used as defined below:

Moisture content, concentration - general terms referring to the amount of water vapour present, in whatever measured units

Trace moisture – minute amount of water, whose presence can be quantified in terms of both dew-point (frost-point) temperature, and volume (or mass or mole) fraction, or other units.

Trace moisture range - Broadly, the “trace moisture range” may be said to lie below about 1 part per million (a frost point of $-75\text{ }^{\circ}\text{C}$).

Dew point or frost point - The temperature at which dew or frost forms, on cooling a gas, expressed in degrees celsius ($^{\circ}\text{C}$). The general term "dew point" is used both above $0\text{ }^{\circ}\text{C}$ and below $0\text{ }^{\circ}\text{C}$, but where a clear distinction is needed below $0\text{ }^{\circ}\text{C}$, the form of condensate is specified. In the trace moisture range, the condensate is invariably frost.

Volume fraction, mass fraction, mole fraction (or corresponding ratios) – concentration expressed as a fraction (or ratio), in parts of water per million (10^6) parts of total gas, i.e. ppm; or in parts per billion (10^9), i.e. ppb. Where ppm or ppb are used without specifying,

they can be taken to refer to volume fraction. Mole fraction is also expressed in nanomoles per mole (nmol/mol), corresponding to parts per billion.

Appendix A shows a table giving the approximate conversion between a selection of values of frost point, vapour pressure and mole fraction.

1.3 BACKGROUND - THE NEED FOR MEASURING TRACE MOISTURE

Measurements of trace water vapour in other gases are becoming increasingly widespread and important. This is both because of the needs found in a number of industries, and because of advances in humidity technology.

Measurements of trace moisture are needed in a variety of different industrial sectors including, semiconductor manufacture, pure gas supply, atmospheric and climate research, aerospace, petrochemical processing, power generation, air filter and purifier manufacture, hygrometer manufacture and supply of reference standards for other trace gases. The number of different ways to measure trace moisture is equally diverse.

Some of the most stringent requirements come from the electronic wafer fabrication industry. Minimising the presence of moisture and other contaminants can maximise the quality of semiconductor devices, which is increasingly important for manufacturers of costly high-density integrated circuits. In recent years gas suppliers have guaranteed moisture in bulk gases at less than or equal to 100 ppb, and now specifications at 10 ppb or even as low as 1 ppb are not unknown.

Other drivers, both in support of end users, and in their own right, are the pure gas supply industry and the hygrometer industry. Britain is reportedly the biggest producer and exporter of humidity instrumentation worldwide, in a market for hygrometers, which has been estimated at £200 million per year. This makes it particularly important to underpin the UK's strength in humidity-related world markets by providing excellent support for product quality and improvement, and measurement traceability plays a key part in this.

Problems in measurements occur because, depending on type, trace moisture instruments are prone to failure, drift, slow response, "memory effects" (hysteresis), nonlinearity, and large deviations of the readings from "true values". At the root of most of these problems is the nature of water vapour as a difficult substance to measure at the ppm to ppb levels. Stabilisation times of weeks or even months can be required. Trace moisture measurement is an area of advancing technology, but some principles of measurement are being used in trace moisture ranges far beyond what would originally have been envisaged.

Throughout UK industry, there is a need for information on instrument capabilities and good measurement practice. This is in order to protect consumers and to ensure a "level playing field" in the supply of specialist goods and services for control and measurement of trace moisture.

In support of consumers and suppliers of these instruments, this project will look at the accuracy, response time, repeatability, linearity, hysteresis and long-term stability of trace moisture sensors.

1.4 METHODOLOGY OF STUDY

In this work, the study and planning phase has been led and mainly carried out by NPL, with input from partner BOC and participation of a number of organisations involved in trace moisture measurement. Contributors to the project so far are listed at Appendix B

Background information has been gathered from past studies, including NMS projects in which NPL has been involved, plus other literature. For information on industrial requirements, a number of users and suppliers of trace moisture instruments have been consulted, by phone, e-mail and face-to-face. Relevant contacts were found through channels such as the NPL-NMS Clubs, trade organisations such as SEMI (Semiconductor Equipment and Materials International), project partners' customer bases and other contacts. A plan for the laboratory evaluation is proposed - guided by these discussions with users, by existing measurement protocols of the project partners, by advice from the instrument suppliers, and by consideration of the practical issues and uncertainties involved.

Within this report, information is included about a study by NIST of permeation tube trace moisture generators. A published paper is reproduced at Appendix C, and key points of this are summarised in Section 3.

2 REVIEW OF TRACE MOISTURE MEASUREMENT AND GENERATION

Below, methods of trace moisture measurement and generation are reviewed. The main approaches are described, measurement issues are outlined, and some relative merits of the methods are discussed. Measurement issues for matrix gases other than air and nitrogen are discussed.

2 TRACE MOISTURE MEASUREMENT METHODS

Instruments commonly used for trace moisture measurement include the following types and principles:

Capacitive probe. Widely used hygrometers for process gases, these typically use aluminium oxide (AlO_x) or ceramic construction. The porous medium absorbs moisture and the complex impedance is scaled into frost point or concentration units. Gas species: most. Quantity realised: (indirectly) normally given in terms of frost point or volume concentration in ppm/ppb. Range may be from ambient humidity down to frost point of -120°C (nominal 0.1 ppb) but no single sensor covers the whole of this range.

Condensation hygrometer. The onset of condensation on a cooled mirror is detected optically and the temperature at which this occurs is the measured dew or frost point of the gas. Well-established approach for laboratory reference standard use. Gas: any not condensing above the water vapour dew/frost point. Quantity measured: dew-point temperature. Range depending on model, may be down to frost points as low as -100°C (nominal 14 ppb) and upwards to ambient humidities (and above, but not both extremes of range in the same instrument).

Electrolytic hygrometer (phosphorous pentoxide). Water vapour is absorbed by a film of P_2O_5 and a current is passed through it. Electrolysis takes place and the current that flows is proportional to amount of water vapour passing through per unit time. Workers do not fully agree whether these hygrometers can survive ultra-dry conditions, and at least one commercial instrument employs an internal moisture source which is "superimposed" on the gas to be measured. Gas species: various if non-reacting with P_2O_5 . Quantity realised: amount (in moles) of water vapour per unit mass or unit volume of flowing gas, reported in parts per million or billion. Range 1 ppb to 5000 ppm and above (frost points -90°C to $+10^\circ\text{C}$ and above), but no single instrument covers the full range.

Quartz oscillator hygrometer (quartz crystal microbalance) Moisture is absorbed onto a layer on the surface of an oscillating quartz crystal. A change in the adsorbed mass changes the resonant frequency of oscillation. The resonant frequency is used to infer the concentration. In the form presently commercially available, the hygrometer uses an internal moisture reference (permeation tube). Gas species: most. Quantity realised: (indirectly) normally given in terms of volume concentration in ppm. Range below 1 ppb to 1000 ppb (and above).

Mass spectrometer (particularly APIMS - atmospheric pressure ionisation mass spectrometer). The sample is ionised and proportions of substances species present are measured using the time of flight of ions in an electric field. In detail: ions of the trace

analyte are produced by corona discharge and subsequent collisions within the sample gas. A thin jet of the sample gas enters a vacuum chamber. Time of flight of the ions in an electric field is then measured, with gas species identified by their charge-to-mass ratio. Gases: Nitrogen and noble gases (and recently air – depending on the integral dryer used). Quantity measured: amount of substance. Range typically 100 ppb down to well below 1 ppb

Absorption spectrometer. (particularly TDLAS - Tuneable diode laser absorption spectrometer) and CRDS (Cavity ring-down spectrometer). The absorption of water vapour in the infrared is measured and used to deduce the concentration. The use of tuneable diode techniques and long multiply-reflected optical path lengths allows the measurement range to extend in principle down to a very few parts per billion for water. Gases: any, in principle, but avoiding those which have an absorption line overlapping the spectral lines used for water (carbon dioxide is a notable example). Quantity measured: adsorption proportional to spatial concentration. Output given in ppm or ppb units. Range TDLAS 1 ppb to 1000 ppm and above. CRDS 0.2 ppb to 5000 ppb.

Others. Other principles include Lyman-alpha emission, surface acoustic wave, residual gas analysers (in vacuum) and more. Although completely novel principles appear only rarely, instruments are always being refined to extend their range and performance.

2.2 DISCUSSION OF MEASUREMENT METHODS

Different users require different features in trace moisture measuring instruments. Below, an overview is given of some general classes of properties. Then for each of the main relevant instrument types, some features are highlighted.

Fundamental versus non-fundamental – in ranges where calibration and measurement traceability are limited in availability – the fundamental nature of an instrument takes on some significance. Some have a basis in a physical law which “fundamentally” realises the measured quantity (e.g. Electrolytic P_2O_5 , condensation hygrometers). In theory, moisture instruments on a fundamental principle may be capable of giving meaningful results without calibration traceable to a moisture standard. In practice they are still subject to error from numerous sources. Traceable calibration – where available – allows these errors to be accounted for. On the other hand, “non-fundamental” instruments (such as AlO_x) rely entirely on calibration to establish the relationship between the electrical response of the sensor and the trace moisture value.

Measurements required – the measurement performance may be specified in terms of

- Range (moisture range, and conditions of measurement such as temperature and pressure)
- “Accuracy” (uncertainty of measurement, and/or deviation from “true value”)
- Linearity
- Hysteresis
- Resolution, or sensitivity to small changes
- Response time (to rising or to falling values of moisture)
- Repeatability, reproducibility,
- Quantity/units displayed or output

Format and usage – issues include

- Configuration – (e.g. duct-mounted immersion probes, or sampling by extraction of flow either exhausted after measurement or returned to the process),
- Outputs (data logging, via electrical outputs, or remotely transmitted)
- Sampling configuration
- Dry-down time from ambient moisture to required moisture range
- Matrix/carrier gas – some sensors are said to respond more slowly in particular matrix gases (for example P_2O_5 in oxygen or hydrogen)
- Ease of use
- Error detection
- Data processing (averaging, trend analysis, predictive analysis, conversions between units)
- Use for control or monitoring – hysteresis and response time may be critical
- Intrinsic safety
- Ruggedness – e.g. against vibration, handling
- Reliability – relative to the criticality of the measurement
- Sensitivity to pressure and temperature

Cost and upkeep – Practical and commercial considerations may include

- Cost of purchase, and of ownership (maintenance, calibration, lifespan)
- Versatility
- Interchangeability (for replacement after failures, or during maintenance and calibration)

In terms of the issues listed above, some strengths (+) and weaknesses (-) of the main methods are as follows:

Capacitive probe

- + relatively low cost
- + can tolerate high working pressures
- relatively prone to drift – long-term drift can vary between 5 % and 50 % of reading, or even more at the low end of range
- can fail after long dry periods
- can be slow to dry down
- “non-fundamental”

... but variants of the principle can differ from these typical properties, for example in respect of response time.

Condensation hygrometer –

- + Fundamental principle
- + Can have good long term performance
- + Tolerant of some contamination (but affects results)
- Operation requires some skill
- Not suitable where other components condense above the water condensation point

Electrolytic hygrometer (phosphorous pentoxide)

- + Tolerates some aggressive gases
- + Can have good sensitivity
- + Fundamental principle
- Requires maintenance (re-coating of cells with loss of calibration)
- Flow rate of gas is critical
- May be damaged by ultra dry gas (some have built-in protection against this)
- May be damaged by normal ambient moisture levels (again, may have built-in protection against this)
- Contaminants such as hydrocarbons, ammonia, interfere with correct operation
- Adds traces of hydrogen and oxygen to the gas sample, which can recombine, leading to errors.

Quartz oscillator (quartz crystal microbalance)

- + Fairly fast response
- Not a fundamental principle
- Calibration "zero setting" dependent on dry gas supply
- May have some dependence on flow rate

Mass spectrometer - e.g. APIMS (atmospheric pressure ionisation mass spectrometer)

- + Can be set up for many matrix gases including aggressive ones
- + Can be used to measure concentrations of many multiple species at the same time – not just water
- + Fast response
- + High sensitivity
- + Expensive
- Time consuming and complex to set up and interpret

Absorption spectrometer – e.g. cavity ringdown ... and tunable diode laser ...

- + Can be set up for many matrix gases including aggressive ones
- + In some cases, can be set up to measure several species
- + Fast response
- + Fundamental principle (Beer's Law)
- Can be relatively expensive (CRDS)
- Some contaminants (e.g. carbon dioxide) may interfere with measurement, or may require operating wavelengths to be customised

2.3 TRACE MOISTURE GENERATION METHODS

Trace moisture generators, as laboratory instruments, are less directly applied in industrial use, but may in practice provide a basis for calibration and quality assurance of trace moisture measurements.

Instruments for generating gas of defined water content for the trace moisture range include the following (listed broadly in order of prevalence):

Flow-mixing or divided-flow generator in which gas of "known" moisture content is mixed or "diluted" with "dry" gas. The proportions of the mixture control the final moisture content. Actual value and reliability depend on the dryness of the supply gas, and on the accuracy of flow metering. Gas species: any, depending on the "defined moisture content" source gas. Quantity realised: amount (in moles) or mass of water vapour per unit mass or unit volume of flowing gas - depending on how the source moist gas is defined before dilution. Range – from ambient humidities down to 0.1 ppb.

Permeation tube generator. Water vapour permeates from a reservoir into a gas stream through a membrane. The rate of permeation is fixed by membrane material, temperature and dimensions. Moisture content is mass of water vapour per unit mass or unit volume of flowing gas,, and the final moisture content achieved in a gas depends on the dryness of the supply gas, and on the gas flow rate. Quantity realised: mass of water vapour per unit mass or unit volume of flowing gas. Range from tens of ppm down to very few ppb, depending on flow rate and dryness of supply gas, but any single device only covers one or two orders of magnitude.

Diffusion cell generator. Method similar to permeation cell, but source of water vapour diffuses through a hole or a tube. The rate of diffusion is fixed by temperature and dimensions of the path (in theory it is calculable from these). Moisture content is mass of water vapour per unit mass or unit volume of flowing gas, and the final humidity depends on the dryness of the dry gas, and on the gas flow rate. Gas species: any. Quantity realised: mass of water vapour per unit mass or unit volume of flowing gas. Range from 1000 ppm (or more) down to very few ppb, depending on flow rate and dryness of supply gas, but any single device only covers one or two orders of magnitude.

Dew-point (frost-point) generator (single-pressure). Gas is saturated at a known temperature, which defines its dew or frost point. Gas species: any non-condensing in the moisture dew-point range of interest. Quantity realised: dew-point temperature. Range from above ambient down to frost points of $-90\text{ }^{\circ}\text{C}$ or below (100 ppb or below).

Two-pressure generator. Gas is humidified at known temperature and elevated pressure and is expanded to a lower pressure. Expansion allows low trace moisture concentrations to be achieved. The final moisture content depends on the initial temperature of humidification and the pressure drop. Gas species: any non-condensing in the moisture dew-point range of interest. Quantity realised: dew-point or frost-point temperature (indirectly) - or others - since calculating the value "after expansion" involves a conversion into vapour pressure units. Range similar to single-pressure systems, down to frost points of $-90\text{ }^{\circ}\text{C}$ or below (100 ppb or below).

Coulometric generator. Hydrogen and oxygen produced by electrolysis are dried and then recombined over a hot catalyst. From current supplied and gas flow rate, moisture content is determined. When a zirconium dry electrolyte is used instead of aqueous electrolyte, the potential for the very low trace moisture range is improved. Gas species: Limited to inert and noble gases, or to hydrogen, depending on method. Quantity realised: amount (in moles) or mass of water vapour per unit mass or unit volume of flowing gas. Range potentially about 1000 ppm to 100 ppb.

2.4 DISCUSSION OF GENERATION METHODS

Of the methods listed, only perhaps the first three are used outside top-level national standard or research laboratories. These can be obtained commercially, whereas the other methods are rarely or never sold commercially, but would be individually designed and built to order for specialist laboratories.

All methods, except single-pressure and two-pressure dew-point generators, rely on the dryness of the supply gas. Any moisture in this “zero” gas causes an additive error, which has most significance at the low extremes of operation, but has less impact when generating higher values of moisture content. In practice, a “point of use” dryer using either a “getter” or a powerful molecular sieve, is used to provide “zero gas”.

“Fundamental” calibrations or traceability of generators are possible to varying degrees. As with measuring instruments, fundamental principle and linear extrapolation are desirable in the ranges where generators cannot be traceably calibrated in terms of moisture. Where the generated gas is simply the measurement medium, with the key measurement fulfilled by another instrument, then fundamental nature and some other aspects of performance are much less critical.

Speed of change to a selected moisture value is an issue – but irrespective of this, true response times depend on other aspects of the gas path downstream of the generator. The response time of measuring instruments tracking any change may also be relevant.

Other key issues are:

Required conditions to be generated – the generator performance may be specified in similar ways to measuring instruments:

- Range (moisture range, and conditions of measurement such as temperature and pressure, flow rate generated)
- “Accuracy” (uncertainty of measurement, and/or deviation from “true value”), linearity, response time (to step-change set point, and to full equilibration), repeatability, reproducibility,
- Quantity/units realised

Format and usage – issues include:

- Supply gas required (species, dryness, pressure, flow rate)
- Inclusion of “point-of-use” dryer
- Manifolds/connections/ gas bypass
- Dry-down time from ambient moisture to required moisture range – or maintenance of constant “standby” (dry) conditions
- Matrix/carrier gas
- Construction and materials specific for the ppb range

Cost and upkeep – Practical and commercial considerations may include:

- Cost of purchase, and of ownership (maintenance, calibration, lifespan)
- Versatility for other species than water

In terms of the issues listed above, some strengths and weaknesses (-) of the main methods are as follows:

Flow-mixing or divided-flow

- + Can supply high flow rates
- + Set points can be changed quickly
- Dependent on dryness of supply gas
- Dependent on flow measurement/control

Permeation tube generator.

- + Fundamental principle (gravimetric, by mass change of permeation tube)
- + Permeation tubes can be substituted to vary range or species
- + Step changes achieved easily by changing flow
- Dependent on dryness of supply gas
- Dependent on flow measurement/control
- Requires precise temperature control

Diffusion cell generator.

- + Fundamental principle (gravimetric, by mass change of diffusion cell)
- + Diffusion cells can be substituted to vary range or species
- + Step changes achieved easily by changing flow
- Dependent on dryness of supply gas
- Dependent on flow measurement/control

Dew-point generator (single pressure).

- + Fundamental principle
- + Does not rely critically on dryness of supply gas
- May be slow to change temperature between set points
- Needs temperature control at the dew point temperature (e.g. at -90°C)
- Not typically built for high flow rates (but can be)
- Not suitable for matrix gases that condense above the water dew/frost point
- Not normally commercially available

Two-pressure generator.

- + Fundamental principle
- + Does not rely critically on dryness of supply gas
- + Operation at pressure can supply high flow at lower test pressure
- + Rapid step changes possible by changing pressure
- Relies on data for vapour pressure and gas non-ideality (enhancement factor)
- Not normally commercially available

Coulometric generator.

- + Fundamental principle (amount of substance defined by Faraday's Law)
- + Dependent on efficiency of reaction of hydrogen and oxygen
- Dependent on dryness of supply gas
- Dependent on flow measurement/control
- Not normally commercially available

2.5 MATRIX GASES

The laboratory evaluation in this project will not feature matrix gases other than air and nitrogen. However some issues for measurements in other gases are:

Condensation - In general, condensation methods cannot be used where any component condenses at a higher temperature than the water present. Examples are natural gas (with many condensing components), and HCl used in the production of microelectronics, which liquefies at $-84.5\text{ }^{\circ}\text{C}$.

There are certain cases where this can be addressed. For example, ammonia has a boiling point of approx $-33\text{ }^{\circ}\text{C}$ and is reactive with water. To measure the moisture content below a frost point of -33 , the ammonia is “cracked” with N_2 or H_2 . This allows moisture levels down to 0.5 ppm to be measured, for the manufacture of wafers for the production of white and blue light emitting diodes. The lower the moisture content the greater the efficiency of the LED.

Chemical reaction - Moisture can be the most critical contaminant in some matrix gases where the gas becomes highly corrosive when moisture content becomes too high. In these circumstances, free water is unlikely to be detected – instead the corrosive product(s) will be present. Not only will this change the detection mechanism and accuracy, but also many sensor types are irreversibly damaged. Also reactions can occur between the gas and surfaces e.g. Chlorine and Aluminium.

Interference – In some cases the matrix gas can interfere with the water sensing process – for example in absorption spectrometry, where key spectral lines for water can overlap with lines for (particularly) CO_2 , and potentially other substances. A remedy is to select or tune the laser wavelength to avoid a particular interference.

Thermal properties - Some inert gases such as argon may have characteristics mainly similar to air and nitrogen. However some, such as hydrogen and helium, have significantly different thermal properties. This can affect heat transfer in thermal-based measurements, for example affecting the performance of condensation methods. Users also report other methods of measurement performing worse in certain matrix gases (e.g. P_2O_5 slower with H_2 and O_2 than with other gases).

Calculations and conversions - Conversions between concentration by mass and other units require knowledge of the composition of the matrix gas, or at least the average molar mass or density.

Gas non-ideality - When the pressure of measurement differs from a process pressure, results may need to be converted. To a first approximation, the proportion of water in a mixture remains the same when the mixture is expanded or compressed. However for large changes (which may be a factor of 100 or more) gases do not behave “ideally”, and volume changes are not exactly proportional to changes in pressure. Deviations from ideality vary for different substances, and can vary with composition of mixtures. Nitrogen and oxygen are

“near-ideal” gases. Water vapour and other polar or complex gases and vapours are not. This needs to be taken into account when measurements are expressed in proportion by volume. Unfortunately, the relevant information on non-ideality (enhancement factor) of many substances at the relevant pressures and mixing proportions is hard to obtain. Some gas/vapour mixtures are reported to deviate at high pressures by as much as 30% from the “ideal” model.

3 NIST STUDY ON TRACE MOISTURE GENERATION

3.1 ACCESS TO INFORMATION ON TRACE MOISTURE GENERATORS

While the main emphasis of this project must be on measuring instruments, which are of most industrial relevance, trace moisture generators are essential in calibration, and may themselves constitute the route of traceability for trace moisture measurements.

It would not be feasible for NPL and BOC to make measurements on generators within the given timescale and funding for this project. Instead NPL has identified a practical study already undertaken in this area. NIST (the US National Institute for Standards and Technology) has also been carrying out a trace moisture evaluation project. Unlike this UK NMS project, the NIST study addresses only trace moisture generators, not sensors. Below are summarised details so far of NIST's evaluation of commercially available trace moisture generators.

3.2 SUMMARY OF NIST STUDY

The US National Institute for Standards and Technology (NIST) has, like NPL, been developing trace moisture standards and calibration facilities. They recently undertook a study of permeation tube moisture generators (PTMGs). This was partly as a demonstration of their facility to calibrate these, and partly to provide information about performance to users and suppliers of these devices. Suppliers of PTMGs were invited to submit devices for evaluation, and results of two (unidentified) devices were reported.

The study looked at PTMGs operating in the range 10 nmol/mol to 100 nmol/mol (units of nanomoles of water per mole of gas are closely equivalent to ppb by volume). In principle PTMGs can be characterised in terms of weight loss over time, together with flow measurement to define the mass of water vapour per volume of flowing gas. However the study compares their values against a common trace moisture reference, directly in terms of mole fraction.

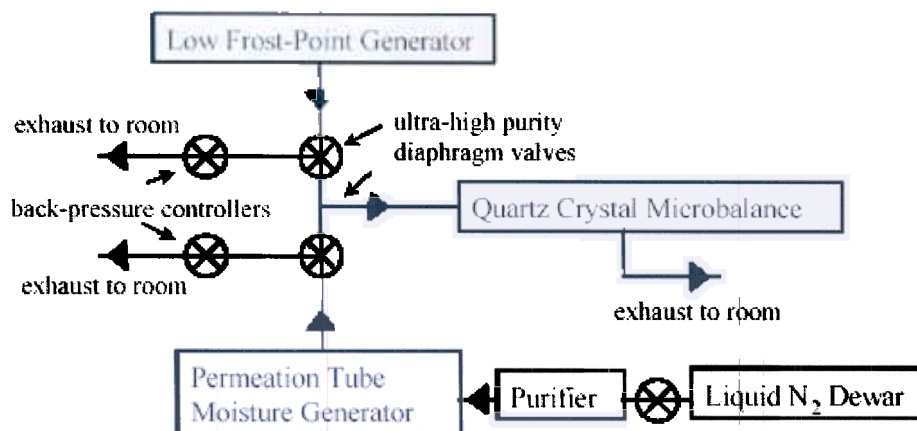


Figure 1. NIST measurement configuration for testing permeation tube moisture generators

The measurement configuration is illustrated in Figure 1. Briefly, gas streams from the NIST Low Frost Point Generator and from the generator under test were alternated through a hygrometer (Quartz Crystal Microbalance). The LFPG was set to two values bracketing the value of the PTMG generator under test, and interpolation was used to give a reference value for comparison with the PTMG value. The resolution of the measurement process was close to 0.1 nmol/mol. The additive background moisture supplied to the inlet of the PTMGs was said to be less than 1 nmol/mol. Figure 2 shows the resolution and timescale of measurements.

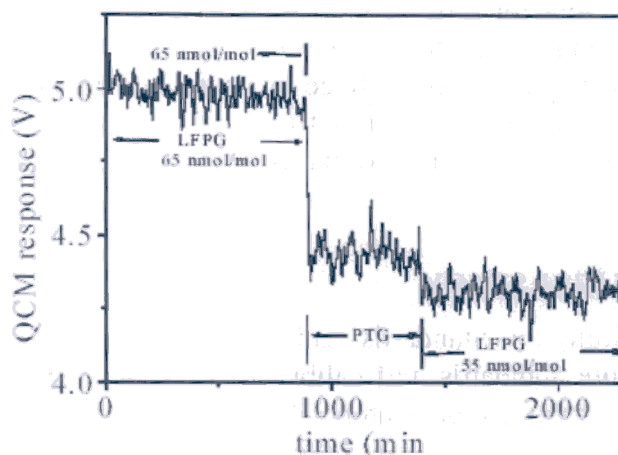


Figure 2: Time response of the QCM hygrometer successively exposed to streams from the LFPG, test generator and LFPG. The initial and final H₂O mole fractions were 65 nmol/mol and 55 mol/mol, respectively, and induced QCM responses bracketing that of the unknown stream. Fluctuations in the QCM output (standard deviation of ~0.04 V) had a period ranging from 20 min to 50 min.

The PTMGs tested were of permeation rates of 35 ng min⁻¹ (PTMG *A*) and 109 ng min⁻¹ (PTMG *B*), as determined by the suppliers. Each was used with several gas flow rates to achieve different values of moisture content. Measurements were time-consuming with each single determination lasting one week, and repetitions at various values spanning a total of 8 months.

Results are shown in Figure 3 as a graph of percentage difference (between PTMGs under test and NIST LFPG) against mole fraction. For both PTMGs, the data tended to show a small fractional difference from the LFPG, approximately constant across the range from 10 nmol/mol to 100 nmol/mol. The two PTMGs were valued above (wetter than) the LFPG by $(3.8 \pm 0.9) \%$ and $(2.9 \pm 0.7) \%$ respectively. At the lowest level, comparisons at 8 nmol/mol were reported as outliers and not included in the analysis on the suspicion that background water content was too significant at this level.

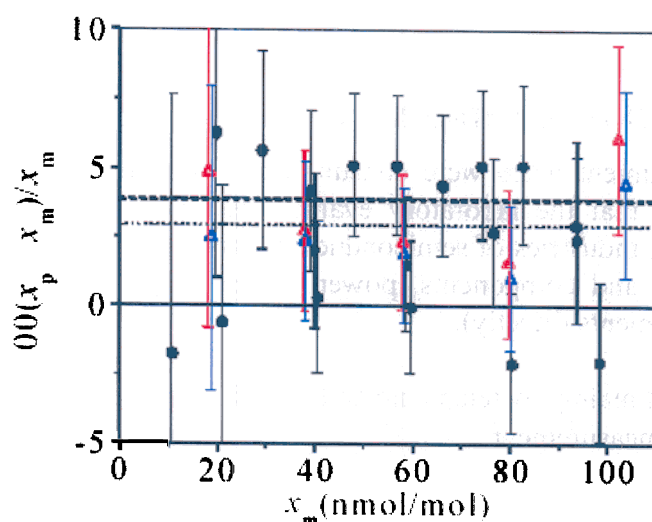


Figure 3: Comparison of results for PTMG A (circles) and PTMG B (triangles). The dashed curves represent the respective average values.

The standard uncertainties ($k=1$) in the individual results were reported to be about 1 nmol/mole, except below 20 nmol/mol, where they rose steeply. The main sources of uncertainty were acknowledged to be flow metering and background water vapour in the carrier gas. The latter is an uncertainty for the PTMGs, but not for the LFPG which, like NPL's Low Frost-point Generator, does not depend critically on the dryness of the supply gas.

NIST have made available a report of this work, which is reproduced at Appendix C of this report. This is available to download from the NIST website at <http://www.cstl.nist.gov/div836/836.05/thermometry/papers/humidity.htm>, and also published in the proceedings of TEMPMEKO 2001. The help of NIST, in permitting their work to be cited in detail within this report, is gratefully acknowledged.

3.3 COMMENTS ON NIST STUDY

It is interesting to note that the level of agreement found between the permeation tube moisture generators and the NIST standard was good, considering the difficulty of the measurements, and the completely independent basis of the generation methods. Based on a sample of two, it is hard to assign any significance to the fact that the suppliers may have underestimated the moisture generated by their devices.

It is also interesting that values realised using the NIST LFPG are everywhere reported in terms of mole fraction, even though their standard is in name a realisation of frost point, intrinsically defined and traceable in terms of temperature units. The output of the PTMGs is naturally expressed in mass of water per unit volume of gas.

The NIST work is still in progress and there is some prospect that they will make further reports of their work. If so, such details can be added to the final report of this NMS project.

4 CONSULTATION

4.1 CONSULTATION OF INSTRUMENT USERS

A selection of instrument users were consulted to establish their measurement needs and priorities, to ensure that the laboratory evaluations would be relevant to their concerns. Respondents were in industries of semiconductor manufacturing, high purity gas supply and distribution systems and components, power generation, and instrumentation (other than trace moisture instruments directly).

Users were contacted mainly by telephone and e-mail. The questions and discussion covered:

- Reasons for measurement
- Matrix gases
- Range of measurement (moisture, plus temperature, pressure)
- Quantity/unit of measurement measured and preferred
- Instrument type(s) in use
- Level of satisfaction with methods in use
- Key issues in trace moisture measurement
- Calibration method and frequency, and subsequent use of calibration results
- Desired improvements in measurement (and desired end result)
- Preferences for tests that should be carried out in this laboratory evaluation project
- Interest in a copy of project final report

4.2 SUMMARY OF MAIN USER CONCERNS

Interests of respondents spanned many applications, including prevention of corrosion of nuclear power station components, avoidance of corrosion or decomposition for bottled gases, testing of installed gas supply lines (with the implication that leaks, voids and surface imperfections can be diagnosed by moisture outgassing), process control of electronics manufacture (if 10 ppb exceeded – manufacturing stops), and others.

Among the comments made by users, some of the relevant and interesting points were:

- Matrix gases included CO₂, argon, nitrogen, oxygen, dry air, medical gases and other process gases
- Some interest in “cross-sensitivity”
Pressure from near-ambient up to (in one case) 150 bar, and also down to vacuum range.
- Some interest in temperatures outside laboratory ambient range (in one case up to 200 °C)
- Preferred units were ppm/ ppb by volume, occasionally ppm/ppb by weight
- Some applications only need a very limited range, e.g. working range of 1-10 ppb in some semiconductor plant
- There is wide variation about whether cost is a main deciding factor
- Speed of setting-up a key issue for commissioning pure gas supply lines (including dry-down times of sensors)

- Hysteresis not commonly a concern among respondents. However users might specify a response time with one direction in mind (either upwards or downwards). Upward surges in moisture level sometimes signify a key “alarm condition” to be detected. Downwards response time more often concerned with initial dry-down.
- Semiconductor manufacturer cited requirement to track steps upward or downward of 2 ppb, in range below 10 ppb
- Semiconductor industry expects to work at “parts per trillion” in reasonably near future
- Response times were perceived to be worse for certain matrix gases (e.g. in O₂ and H₂ for P₂O₅ sensors).
- Concern about loss of sensitivity after long periods at dry levels – for more than one type of sensor
- Concern about down-times for servicing and calibration of instruments. Process “up-time” is critical in many cases.
- Unreliable instruments responsible for “false alarms”.
- “Wish lists” included reliability, fast turnaround for calibration (servicing).
- Wide variation in usage of calibration data. In some cases, calibration data used in subsequent measurements or uncertainty estimates. In other cases, calibration used for “pass/fail” decisions about putting sensors back in service (versus adjusting or discarding them), or for review of past work that might have been affected by historic sensor drift.
- Willingness to calibrate frequently varied between “four times yearly” and “12 to 18-month intervals”
- Linearity a key issue, since calibrations often “extrapolated downwards”
- Concern that it can be hard to obtain “as-found” calibration data. Sometimes data given only “after adjustment”.

Where users commented on specific reasons for or against particular trace moisture sensor types, these included:

- Cost
Range – some applications span ranges not served by some of the sensors. For many purposes, the upper limit of APIMS (about 100 ppb) is too low. For one respondent, an upper limit of 10 ppm was considered too low.
- Capacitive probes preferred for usage in vacuum or at elevated pressures
- P₂O₅ sensors widely used in high-value or safety-critical measurements (due to being well-established?), but problematic because of the maintenance required.
- Capacitive (aluminium oxide) sensors said to be liable to drift.
- Alternative solid-state capacitive sensors used for rapid response
- Some respondents said they were working with less than ideal instruments because they were “the best available at the time”. This reflects a field where relatively high-cost technology is in relatively rapid state of advance.

Users’ perceived requirements may partially reflect the deficiencies of their existing equipment. In several cases, respondents who wished for maintenance-free equipment, or accurate, or responsive, or reliable equipment seemed to be using exactly the instruments that failed those needs. In some (but not all!) cases they perceived they had a problem, and wished to overcome it.

4.3 CONSULTATION OF INSTRUMENT SUPPLIERS

Discussions with instrument suppliers mainly centred on the loaning of instruments for evaluation, and on the test plan details. However, suppliers are also a valuable channel to information about user concerns. In this way, the following additional user interests were highlighted:

- It may not be fair to assume all “solid state” sensors can be classified together – several types of similar ones should be tested. Variants of the capacitance type may be particularly diverse in performance.
- Concerns about performance centre on: accuracy, repeatability long-term stability followed by reproducibility, linearity, hysteresis
- Suppliers seek measurement traceability below 1 ppm
- Currently many users rely heavily on linearity of instruments because calibrations at the lowest levels are based on extrapolations downwards

5 TEST AND VALIDATION PLAN

5 INSTRUMENTS PROPOSED FOR EVALUATION

Up to 14 trace moisture instruments have been offered on loan to the project by 10 suppliers. The list includes 8 capacitive-type instruments, 3 condensation instruments, and 3 different others.

The instruments offered are:

- Able/General Eastern capacitive DewPro MMY 245
- Alpha capacitive probe (model TBA)
- Alpha/Edgetech condensation hygrometer Dew Prime III S3 (partial availability - to be confirmed)
- APK/Ametek Quartz Oscillator 5910 (to be confirmed)
- IMA /Xentaur XDT AlO_x sensor (to -110 °C) possibly with integral dryer
- IMA/SpectraSense LH1 diode laser spectrometer
- MBW condensation hygrometer Model 373 LX (to be confirmed)
- MCM capacitive solid state sensor (to be confirmed)
- Michell capacitive Cermax (to -120 °C)
- Michell capacitive Cermet II (to -100 °C)
- Michell condensation hygrometer S4000 TRS (partial availability to be confirmed)
- Panametrics capacitive AlO_x sensor with sample cell (to be confirmed)
- Tiger Optics Cavity Ringdown Spectrometer MTO 1000-H₂O (partial availability)
- Shaw AlO_x modified molecular sieve capacitance sensor “silver spot” (to -100 °C) to be confirmed

Partial availability denotes an offer for part, but not all, of the duration of the project. Where this is the case, the suppliers have been encouraged to make instruments available for the initial calibration phase of the work, and then for whatever other time is possible on a basis of goodwill.

Some of the offers are yet to be confirmed. It is foreseeable that several offers may be withdrawn, leaving a total of no more than 11 (the target maximum number for the study). If more than 11 remain on offer, some may be de-selected, by keeping at least one of every distinct type offered, and then giving priority to capacitive probes. However since some are only offered for partial availability this may make it possible to accommodate the full set of instruments offered.

At this point there is still the possibility of including others. It has not yet been possible to agree loans of Electrolytic (P₂O₅) or APIMS instruments but these instrument types are part of the BOC facility, and can potentially be partly built in into the evaluation in this way.

DESIGN OF LABORATORY TESTS

Laboratory evaluation of instruments will constitute Workpackage 2 of this project as originally specified in the project proposal. Details of the workplan are given below, followed by a table and time chart of the workplan.

Among the points raised by users, some issues now to be considered for action in the test plan are:

- reporting of dry-down times, where possible
- observation of any loss of response after long dry periods
- hysteresis given less priority, but it easily is observed in the course of other tests.

Overview of laboratory tests

Measurements and tests will be made at nominal values of 1 ppm, 300 ppb, 100 ppb, 30 ppb and 1 ppb. The evaluation will cover:

- Initial calibration of sensors by NPL at (nominally) 1 ppm, 300 ppb, 100 ppb.
- Performance testing by NPL at suitable values between 1 ppm and 30 ppb, looking at dry-down time, repeatability, response time to step changes, and linearity.
- Calibration and performance testing by BOC overlapping the lower extreme of the NPL range and going down to about 1 ppb.
- Final recalibration of sensors

The initial calibration from 1 ppm downwards, and some of the performance tests will be directly against the UK National standard Low Frost-point Generator (LFG), validated down to 100 ppb (-90 °C) with an uncertainty of $\pm 2\%$ to $\pm 10\%$ of value in this range. Additionally, transfer standards extensively characterised against the LFG over the last year will be used.

General performance testing will employ the trace moisture facilities in NPL's Analytical Standards Group in the range of at least 30 ppb to 300 ppb.

The facilities of BOC mobile laboratory will be used to test down to 1 ppb and overlapping the NPL range up to 100 ppb, with the capability to test most or all instruments in parallel (simultaneously).

At all stages of testing, measurements will be monitored against a reference instrument. Precautions will be taken for sufficient overlap to assure consistency between measurements on the three different facilities.

Measurements will be made in air and nitrogen as the matrix gases, at temperatures near 20 °C, at nominally atmospheric pressure except where elevated supply pressure is essential to instrument operation.

A freely-available report will be produced on the evaluation and will concentrate on the general properties of the measurement methods avoiding "brand-specific" comments. In the report, participation of manufacturers and suppliers in the project will be acknowledged, unless they ask not to be identified. Where appropriate, more detailed feedback to suppliers of instruments will be given individually in confidence.

Test details

It is proposed to perform the following tests on each instrument:

- Initial calibration at several points across its measuring range establishing the level of agreement of readings with NPL standards. Calibration results will be reported at nominal values of 1 ppm, 300 ppb, and 100 ppb, including reporting of settling times.
- Short-term stability over a period of one hour after stabilisation at a set point of 1 ppm 300 ppb, 100 ppb and 30 ppb.
- Repeatability, after exposure to different moisture level. For example at 300 ppb the set point will be changed to be significantly wetter up to 1ppm and then back to the original set point, and repeated several times. The same will be done for a dryer set point.
- Response time, for step changes in the range 300 ppb to 30 ppb
- Linearity, based on calibration values between 1 ppm and 100 ppb (and possibly below)
- Hysteresis at values of 300 ppb and 100 ppb (and possibly below) by approaching from values above and below these.
- Functional test (possibly calibration) by BOC at 1ppb
- Long term performance by repeat calibration by NPL after 12 months, giving estimates of long-term drift. Tests during the course of the 12 months will also give some information on drift.
- Where the instruments are tested in batches, they will be grouped with others of similar range and response time.

Detail of measurement facilities and protocols of NPL and BOC partners

Some details of the facilities to be used and partial details of measurement protocols are listed in Appendices C, D and E.

5.2.4 Tables of workplan

Below are tables showing the remaining steps in the work plan, and the time schedule for completion. At the time of writing, there are no known limitations to the availability of the BOC mobile facility at the scheduled time. The development of the trace moisture facility in NPL Analytical Science Group is also on schedule, so the facility is expected to be available for the relevant work within this evaluation project.

Table 1 Laboratory evaluation workplan

	Action	Start	Finish	Who
Workpackage 2b				
6	Manufacture welded connecting pipes, manifolds, etc, if/as required	Jun 02	Jul 02	NPL
7	Obtain instruments on loan	Jun 02	Jul 02	NPL(H)
8	Initial calibrations of instruments in range of LFG from 1 ppm downwards	Aug 02	Nov 02	NPL (H)
9b	Ongoing tests of response time, repeatability etc.	Nov 02	Aug 03	NPL (H) NPL(A) if capability ready
10b	Calibrations and tests of response time, etc, in range down to 1 ppb	Early 03	Jun 03	BOC mobile facility while on NPL site
11b	Repeat calibrations and estimates of long term drift	Jul 03	Oct 03	NPL (H)
Workpackage 3				
12b	Issue of draft public and restricted reports to NMSPU	Early 03	Mid-Nov 03	NPL(H,A) and BOC
13b	Final Meeting	Late Nov 03	Late Nov 03	NPL(H,A), BOC and NMSPU
14b	Disseminate technical (public) version of report	End Nov 03	End Nov 03	NPL(H)
15b	Project management, reporting Quarterly and at NMS Thermal Programme annual reviews.	Continuing	Nov 03	NPL(H)

Table 2: Schedule of work

2002												2003											
		Jun	Jul	Aug	Sep	Oct	Nov	Dec	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov				
1-5	Workpackage 1 completed																						
Workpackage 2																							
6	Manufacture manifolds																						
7	Obtain instruments																						
8	Initial calibrations of instruments																						
9b	Ongoing tests on instruments																						
10b	Tests by BOC mobile laboratory																						
11b	Repeat calibrations and estimate of long term drift																						
Workpackage 3																							
12b	Preparation and issue of draft public and restricted reports																						
13b	Final meeting																						
14b	Disseminate information																						
15b	Project management																						

APPENDIX A: APPROXIMATE CONVERSION BETWEEN UNITS

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	Vapour pressure	Mole fraction	
		ppm	ppb
°C	Pa		
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	
-70	0.261854	3	2584
-80	0.054653	1	539
-90	0.009613	0.1	95
-100	0.001383		14
-110	0.000157		2
-120	1.34E-05		0.1

APPENDIX B: LIST OF PARTICIPANTS IN THE PROJECT

ABLE Instruments & Controls Ltd
Air Products plc
Alpha Moisture Systems
Berkeley Magnox – UK
BOC Gases
BOC Edwards
Cambridge Fluid Systems Limited
EdgeTech Moisture & Humidity Systems
International Moisture Analysers Ltd
Linde gases (UK) Ltd
MBW Elektronik AG
Michell Instruments Ltd
Microgas Systems Ltd.
Moisture Control & Measurement Limited
Motorola
National Institute for Standards and Technology, USA
National Physical Laboratory
Panametrics Ltd
Shaw Moisture Meters
Talbot Scientific Ltd
Telemark Cryogenics Ltd
Tiger Optics

APPENDIX C: NIST STUDY OF PERMEATION TUBE MOISTURE GENERATORS

The paper on the following pages is reproduced from the NIST website
<http://www.cstl.nist.gov/div836/836.05/thermometry/papers/humidity.htm>

APPENDIX D: UK-NMS LOW FROST-POINT GENERATOR AT NPL

The Low Frost-point Generator consists of a conditioning coil and a saturator coil immersed in a bath of fluid whose temperature is carefully controlled. Clean, dry gas (usually air, but other gases can be used) is introduced into the conditioning coil where its temperature is reduced to that of the frost-point temperature to be generated. The gas exits from the conditioning coil and enters the saturator coil where it passes over surfaces of de-ionised water so that the gas can be expected to be saturated with water vapour at the temperature of the gas/water interface and providing that this is the coldest temperature. The temperature of the gas is measured as it leaves the saturator and is supplied to hygrometers being calibrated.

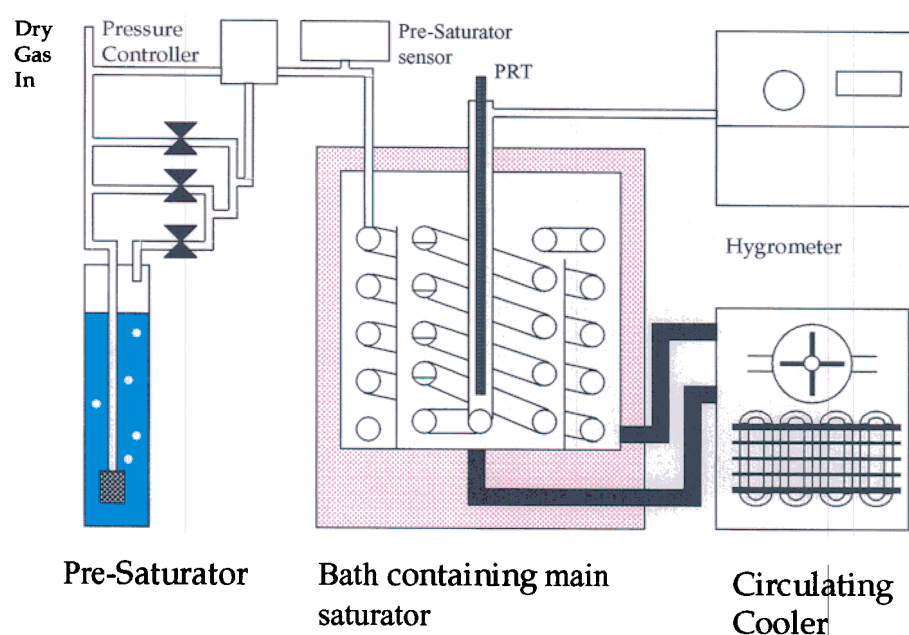


Figure 4: Illustration of the layout of the Low Frost-point Generator



Figure 5: Saturator of the Low Frost-Point Generator

APPENDIX E: UK-NMS TRACE WATER FACILITY IN NPL ANALYTICAL SCIENCE GROUP

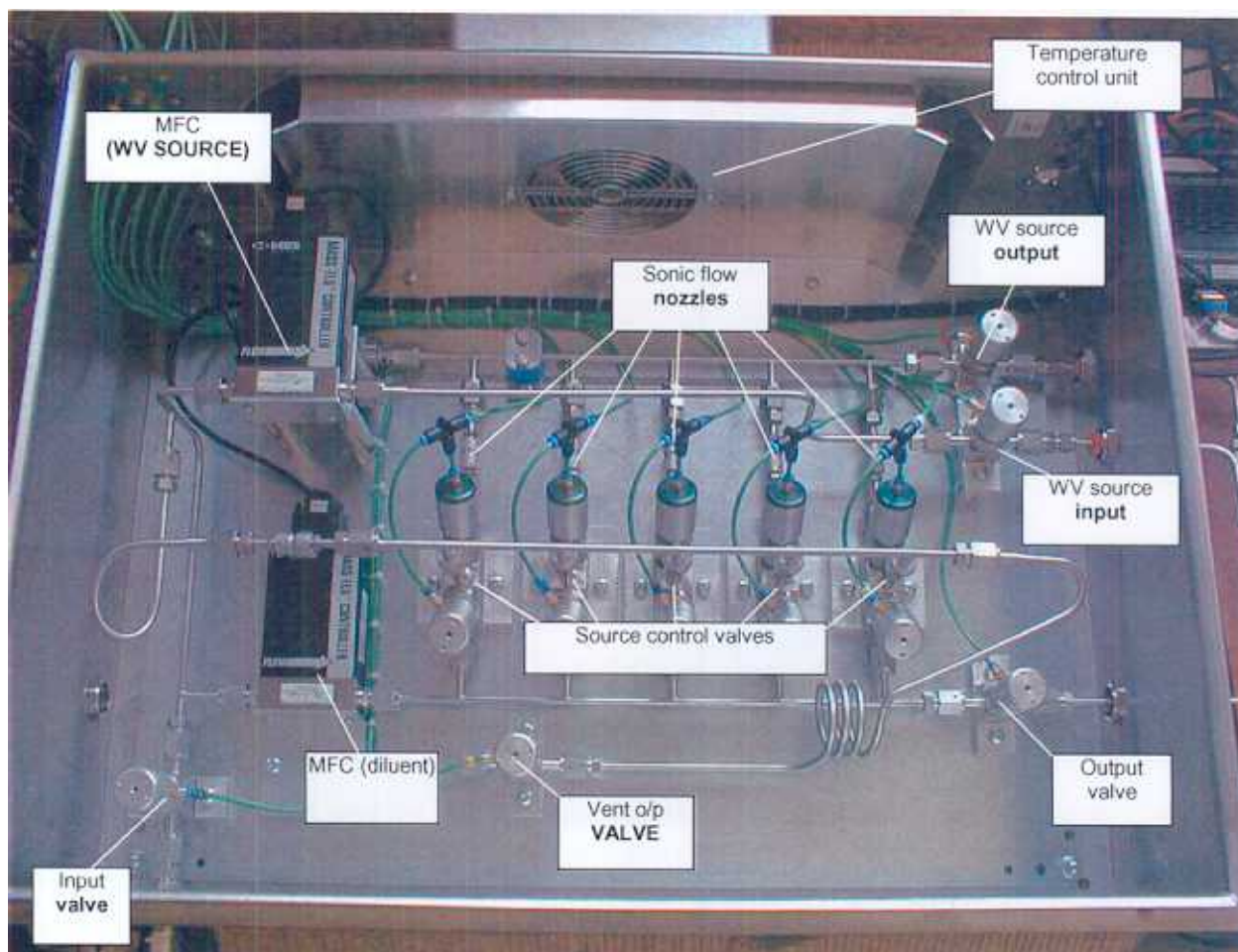


Figure 6. Internal Layout of Trace Water Vapour Facility

The trace water vapour facility (TWVF) being developed under the VAM programme combines gravimetric gas generation with dynamic flow mixing techniques to provide a source of trace water vapour in a nitrogen matrix. The internal layout of the trace water vapour facility is shown in Figure 1. This system is sealed in a metal cabinet which is continuously purged with dry nitrogen and maintained at fixed temperature. All pipework is made from electro-polished seamless stainless steel tube (316L VIM/VAR virgin melt, inner surface roughness 0.2 micron RA max) with clean-room welded VCR face-seal fittings. All active components (mass flow controllers and valves) have all-metal wetted surfaces and VCR fittings.

The procedure that will be used to generate the controlled levels of water vapour concentration is as follows :

- The matrix gas is taken from cylinders of ultra-high-purity nitrogen (specified at <20 ppb water vapour).
- The nitrogen then passes through a purifier system which further dries the gas to <1 ppb water vapour. The output from the purifier passes directly into the TWVF.
- Mass flow controllers are used to split the nitrogen flow into a diluent flow of 5 standard litres per minute and a source flow of 0.05 standard litres per minute. Both mass flow controllers are operated at fixed values near full scale giving a flow uncertainty of around 0.2%.
- The source flow passes over a water vapour permeation source with on-line weighing accurate to 1 microgramme. The permeation source is temperature stabilised to $\pm 0.05^{\circ}\text{C}$ to ensure a fixed permeation rate and negligible balance drift.
- Five sonic flow nozzles are then used to divide the source flow. Each nozzle is followed by a dual valve which can be set to either direct the output into the diluent gas (and then to the output manifold) or into a vent line.
- The output water vapour concentration can be varied rapidly between approximately 30 ppb and 1 ppm by selecting which of the nozzle flows are fed into the diluent line.
- The output manifold has five ports allowing a number of instruments to be tested simultaneously.

APPENDIX F: BOC MOBILE TRACE WATER FACILITY

This method statement covers the procedure of evaluating moisture analysers that are said to be capable of measuring moisture at levels below 100 ppb (v). The evaluation will look at dry down times to “Zero levels” and what levels are “Zero” as indicated by the instruments. Response to added moisture and the instruments indicated reading to that added moisture. In reverse, response to dry down from added moisture, recording the instruments indicated reading. Repeatability of the tests will be assessed. The evaluation will be carried out using the BOC Edwards UHP Mobile Laboratory.

Ultra High Purity Nitrogen (99.999999 %) will be introduced into a SAES Getter purifier at Point ‘A’ (see diagram). The SAES Getter will reduce the moisture content to 1 ppb (v).

2. One stream of the nitrogen will pass through the major mass flow controller of an Environics Blender at a 1000 cc / minute flow rate, into the test manifold therefore into the analysers on test, thus enabling to establish a “ Zero” for each individual analyser points ‘B through to ‘H’. This may take several days for the analysers to stabilise. Time to reach a stable reading for each analyser will be recorded.
3. The other stream of the nitrogen will be passed through a potassium nitrate moisture generator, this generator will add moisture to the nitrogen at a level of 18.0 ppm (v). A Meeco Aquamatic Plus analyser will monitor the moisture content.
4. The “wetted” stream will be passed through the minor mass flow controller and combined with the “dry” stream at the following flow rates;

1cc / minute	calculated moisture	18 ppb (v)
2 cc / minute	calculated moisture	36 ppb (v)
3 cc / minute	calculated moisture	54 ppb (v)
4 cc / minute	calculated moisture	72 ppb (v)
5 cc / minute	calculated moisture	90 ppb (v)

- 5 The tests for “added” moisture will start as above 1 cc / minute to 5 cc / minute, time to reach a stable at all moisture levels will be recorded.
- 6 Further tests will be in reverse order i.e. 5 cc / minute to 1 cc / minute, again time to reach a stable reading will be recorded.
7. The above tests will be carried out to establish repeatability.

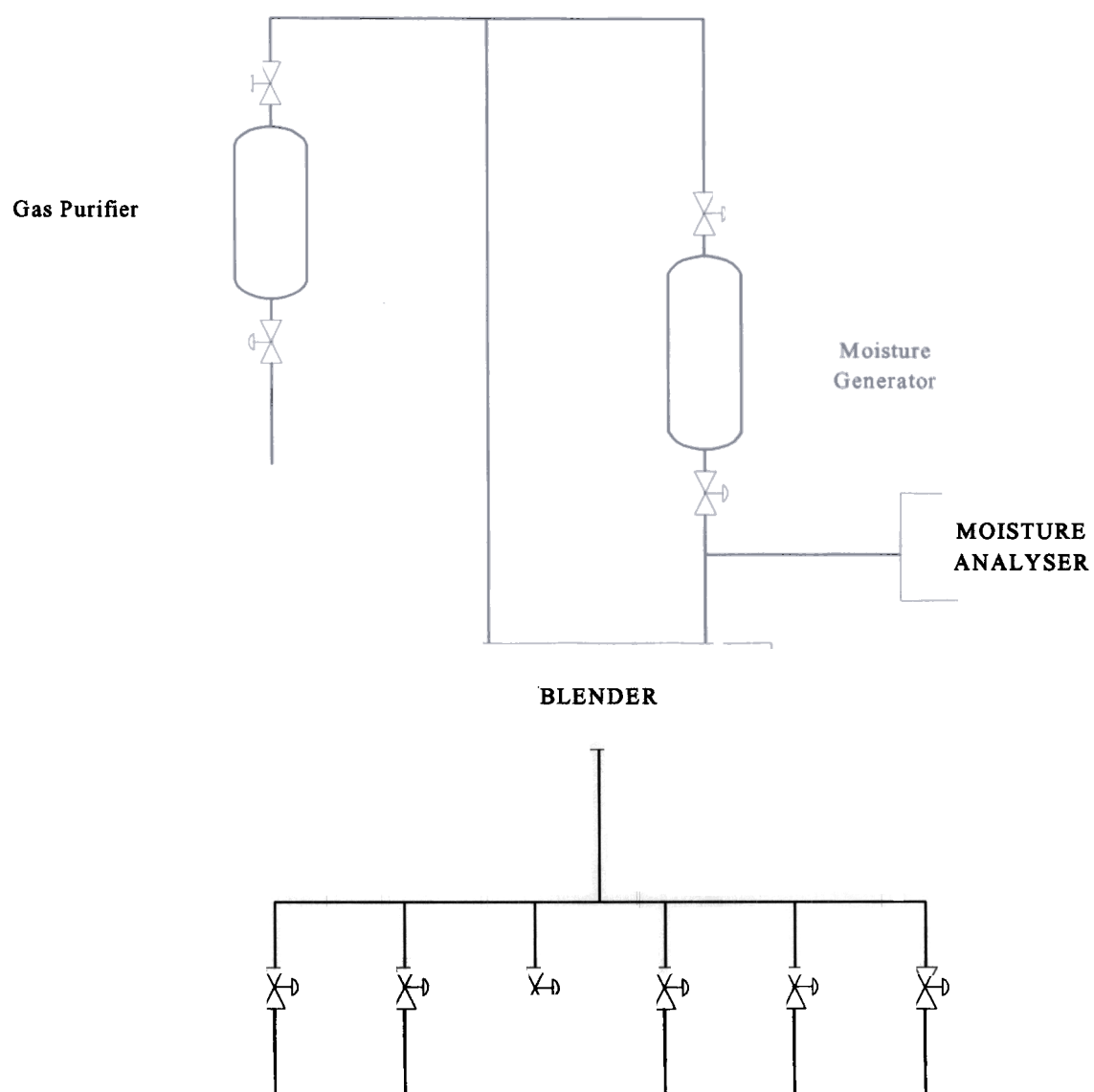


Figure 7: Schematic diagram of BOC trace moisture facility

APPENDIX G: GLOSSARY

APIMS	Atmospheric Pressure Ionisation Mass Spectrometer
CRDS	Cavity ringdown spectrometer
DTI	Department of Trade and Industry
ITT	Invitation To Tender
LFG	Low Frost-point Generator (UK-NMS)
LFPG	Low Frost Point Generator (NIST)
NIST	National Institute for Standards and Technology
NMS	National Measurement System
NMSPU	National Measurement System Policy Unit
NPL	National Physical Laboratory
NPL(A)	NPL Analytical Science Group
NPL(H)	NPL Humidity Group
ppb	parts per billion (10^9)
ppm	parts per million (10^6)
QCM	quartz crystal microbalance (quartz oscillator)
SEMI	Semiconductor Equipment and Materials International
TDLAS	Tunable diode laser absorption spectrometer
VAM	Valid Analytical Measurement
WP	Workpackage