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REPORT

Study of alternative fluids for use in the humidity generator at NPL

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ABSTRACT

The Standard Humidity Generator operated by the National Physical Laboratory requires careful temperature control over a range of temperatures down to -75 °C. Until now this has been achieved using well stirred temperature controlled fluid baths. The fluid used for sub-zero operation is trichloroethylene which is toxic, environmentally unfriendly and whose production may be phased out in the near future. Alternative fluids have been considered and the best method of their use is examined. This report concludes that the most viable option is to design and construct a low-temperature humidity generator which will operate using a sealed temperature controlled bath containing alcohol. The progress to achieve this is briefly detailed. This project has been initiated as part of the DTI's National Measurement System Programme for Mass, 1996 to 1999, project 4, Humidity Standards.

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CONTENTS

1 INTRODUCTION

The National Physical Laboratory (NPL) operates a range of humidity generators as part of the provision of the UK's National Measurement System. These humidity generators provide traceable measurements of humidity dew point for UK industry, in particular for laboratories accredited by the United Kingdom Accreditation Service, and for national measurement institutions in other countries. The principle of operation of these dew-point generators is to saturate a gas (commonly air) with water vapour at a known temperature and pressure. Saturation of the gas is achieved by forcing the gas through a coiled pipe in which a moisture source is located. The temperature of the gas and the moisture source will determine the saturation temperature or dew point of the gas in the generator, therefore careful control of temperature is essential for high-accuracy dew point generation. To maintain a stable temperature throughout the saturator coil, it is immersed in a well-stirred temperature controlled fluid bath.

The properties of the fluid in the bath will determine the range of dew points available. At present NPL offers a calibration range of -75 °C to 82 °C. This range is covered by two bath fluids: for the range -20 °C to 82 °C a mixture of ethylene glycol and water is used and for the range -75 °C to 20 °C trichloroethylene is used.

The projected availability for trichloroethylene in the future is unsatisfactory. It is environmentally unfriendly and its use is discouraged which will make it increasingly expensive and difficult to obtain. In view of this, considerable thought has been given to reducing the amount of trichloroethylene used to operate the NPL dew point generators and to consider the alternative fluids available and their limitations in use.

This report details the existing system used and the problems experienced, then suggests several options and details the most appropriate solution.

2 EXISTING GENERATORS

NPL presently operates two dew-point generators which cover the calibration range -75 °C to 82 °C. The High-range Dew-point Generator operates from -3 °C to 82 °C and does not use trichloroethylene. The Standard Humidity Generator (SHG) covers the whole of the calibration range, and uses trichloroethylene in its temperature controlled baths when generating dew points in the region of 0 °C and below. The SHG has two temperature controlled baths, one housing the main saturator coil and the second a pre-saturator coil [1,2]. Each bath has a capacity of 40 litres. The baths are stainless steel open construction with 50 mm Rockwell insulation. A lid of nylon has been fitted on top to thermally-insulate and to semi-seal the bath. The shafts of the stirrers pass through the nylon lid as does access for the saturator coil. The cooler probes have a split nylon collar fitted around the neck of the cooling probe, this collar fits into a recess in the bath lid.

3 PROBLEMS ENCOUNTERED WITH EXISTING GENERATORS AT LOW TEMPERATURES

Difficulties are experienced in humidity generation at low dew points associated with effects due to the materials used, the cleaning process adopted and the quality of joints in the pipe work. However there are also problems associated with the low temperature itself.

3.1 ICE BUILD UP

When the SHG is generating a low dew-point, moisture from the surrounding air begins to condense on the cold surfaces. The moisture build-up will be greatest at the areas of minimum temperature which are the heat exchanger probes in the baths with temperatures approaching -100 °C. The tubes leading to these probes are also extremely cold especially near the probe itself. Ice builds up on areas of the probe that are not in the bath fluid and on the tube-probe join where there is no insulation. This join has been utilised to locate a split collar that semi-seals into the bath lid. After a length of time the ice builds up on the outside and inside of the bath lid around the heat exchanger probes. When the ice has built up to the point where it contacts the bath fluid, the fluid migrates by capillary action up the ice and is then present on the outside of the bath lid where it evaporates into the laboratory. This can cause the vapour level in the laboratory to rise to such an extent that the long term exposure limit for safe working is exceeded.

3.2 CONTAMINATION OF THE BATH FLUID

The complexity of the pipe work of the saturator coils, stirrers and coolers makes it difficult to effectively seal the bath, so the surface of the bath fluid is partially open to the atmosphere. When the baths are operated at sub-zero temperatures, moisture from the air in contact with the cold liquid condenses on the surface. The moisture is mixed with the bath fluid by the action of the stirrers in the bath (vigorous stirring is essential to maintain an even temperature distribution throughout the bath). As the water vapour condenses from the air, fresh air is drawn towards the surface of the liquid, bringing more water vapour with it.

The stirring action also brings the water into contact with the cooling elements, where it freezes and eventually forms a thick layer of ice. This ice insulates the cooling element and reduces its effectiveness in cooling the fluid. Cooling any liquid system to temperatures approaching -75°C requires a large input of energy, and the cooling systems used with the SHG are working close to their maximum capacity when maintaining pure trichloroethylene at these temperatures. The cooling systems are incapable of cooling a water/trichloroethylene mixture to temperatures of -75°C when the water content exceeds a certain level.

The length of time that the present NPL generator can maintain a temperature of -75 °C is approximately 4 to 5 days. After this time the contamination of the bath fluid reaches such a level that the temperature will rise slowly. At this stage to use the fluid for further low dew-points, the contamination must be removed.

3.3 DEALING WITH CONTAMINATION OF THE BATH FLUID

Because water is not soluble in trichloroethylene, it is possible to remove much of the water from the mixture by raising the temperature of the bath above 0 °C. After several hours with the stirrers off, the water will float to the surface where it can be removed. This removes the greater portion of the water but a proportion remains mixed with the trichloroethylene. It would appear that the amount of water remaining in the trichloroethylene increases with repeated use, because the minimum temperature achieved by the cooling system increases after each water removal cycle. Eventually the lowest required temperatures cannot be achieved at all and the contaminated trichloroethylene is disposed of and replaced with a fresh supply. This method would not be appropriate for other fluids which are soluble in water.

It may be possible to improve the efficiency of separation of the water and trichloroethylene. But at room temperature the trichloroethylene itself readily evaporates and quickly generates an unsafe working environment. The staff handling trichloroethylene at these temperatures are required to wear chemical filter face masks and undergo regular health screening. Any approach which requires extended handling of trichloroethylene at room temperatures is therefore considered unsatisfactory on health grounds.

Another option is to reduce the contamination of the trichloroethylene by preventing the water vapour having access to the trichloroethylene surface. This requires temperature controlled baths which can be fully sealed from atmospheric air. Baths made to this specification could also be made suitable for use with other fluids.

4 REDUCING THE QUANTITY OF FLUID USED

At present the quantity of trichloroethylene required to successfully operate the SHG is approximately 80 litres split into two baths. The quantity could be reduced in two ways:

a/ reduce the size of the baths

With the present design of saturator coil it would be impossible to reduce the size of the baths and still maintain the quoted uncertainty.

b/ reduce the number of baths containing trichloroethylene

One bath contains the main saturator and the other contains the pre-saturator. Careful control of the temperature of the main saturator is essential as this defines the generated dew point. The use of a saturator coil in a temperature controlled bath provides much better uncertainty of pre-saturation dew point than is thought necessary. An alternative approach would be to provide the pre-saturation using a flow-mixing technique, where dry and moist gases are mixed in different quantities to produce a supply of gas of variable humidity. The humidity of this gas mixture could be adequately measured using a calibrated hygrometer. The moist gas would be obtained from a saturator coil in a temperature-controlled bath, as now, but the control temperature need not be very low so the bath could be filled with ethylene glycol mixture. Implementation of this approach would reduce the use of trichloroethylene by 50 %.

5 AVAILABLE BATH FLUIDS

The range of fluids that are available that remain fluid at temperatures down to -75 °C fall into three main categories

- fluids that are flammable
  fluids that are viscous
  fluids that are toxic

The properties of some fluids are detailed in the following table

Fluid	type	Freezing point °C	flash point °C	auto-ignition point °C
Trichloroethylene	toxic	-87	32	420
Ethanol	flammable	-117	12	363
Methanol	flammable	-94	11	385
Acetone	flammable	-97	-19	538
perfluorinated polyethers	viscous	<-130	-	-
silicone oil	viscous	<-110	-	-

The evaporation rate of some of the above fluids is very much higher than trichloroethylene. These chemicals would require either:

(a) the continual topping up of the baths. This would involve disturbing the equilibrium and producing larger bath gradients, increasing the uncertainties that are presently quoted. The running cost of such a system could potentially be great.

(b) covering the bath. The lids that cover the baths would have to be sealed effectively because of the problems described in section 3.

5.1 FLAMMABLE FLUIDS

Flammable fluids in the quantity required by Humidity Section are already used in laboratories at NPL. Temperature Section have for many years used acetone over a range of temperatures between -100°C and +20°C. Alcohol is used by other National Measurement Institutes covering the range -80 °C to +50°C but the safety regulations in these countries may not be as stringent as in the UK.

To comply with the regulation regarding the use of flammable fluids in the quantities needed considerable modifications to the existing equipment and environment will be needed.

5.1.1 Making the humidity room safe

All electrical switches, motors for stirrers and controllers would need to be replaced with "spark free" equipment. Some specialised instrumentation needed for the work would not be able to be used in the room unless substantially modified. A serious obstacle to this approach is that customers' instruments to be calibrated would not themselves be spark proof and therefore would have to be encased and isolated from the room environment.

A possible solution would be to construct an inner enclosure around the generator, with all electronic switching and heat sources outside. To achieve this, modifications to the control of the temperature of the bath would be needed. At present cartridge heaters are in direct contact with the bath fluid. The stirrer motors would need to be relocated outside the enclosure and a good seal would need to be made around the exiting pipes, cables, stirrer shafts and chiller probes. The enclosure should be linked to an extraction unit to avoid a build up of vapour. Provision for emptying and filling the bath safely would need to be addressed.

If this approach were to be chosen a system of fire prevention, where the laboratory is flushed with inert gas, could be introduced. The gas presently used for this application is HALON or S6 (replacement for Halon). Both are potentially lethal to anyone caught in the room if the system were to operate.

Sealing the bath

The bath could be sealed to the atmosphere, enclosing the fluid and its vapour in a confined space. The bath itself could be made flame retarding and a pressure relief system could exhaust the excess vapour to a safe location. Extraction would only be required when filling or emptying the bath. This solution also solves the problems associated with the evaporation rate of the fluid.

5.2 VISCOUS FLUIDS

Attention has been given to a range of viscous fluids that remain fluid in the temperature range required. The viscosity of these fluids varies considerably with temperature. The least viscous of this range has a boiling point of 55 °C, its viscosity at -60 °C is approximately equal to that of water at 0 °C. This fluid is more than 10 times as expensive as trichloroethylene and has a much higher evaporation rate. The high viscosity causes problems with temperature gradients in the bath and has an adverse effects on the thermal transport properties.

5.2.1 Bath temperature gradients

As the viscosity increases the effectiveness of the bath stirring decreases, potentially causing large temperature gradients in the bath. As the temperature uniformity of the saturator coil contributes to the uncertainty of the generated dew point, a near uniform bath temperature is essential. If a viscous fluid is to be used the method of circulation in the bath will need to be examined.

5.2.2 Thermal transport properties

The thermal transport properties of these fluids are the subject of investigations by another National Measurement Institute and a commercial humidity generator manufacturer. Initial unofficial results show that the cooling power input and the time taken to achieve the required temperature is substantially greater than for the other fluids examined in this report.

5.3 TOXIC FLUIDS

As the bath fluid will occasionally need topping up and eventually changing it is essential that the fluid be handled safely. Careful consideration must be paid to the choice of these fluids with regard to the safety of the staff handling them.

Trichloroethylene is toxic and therefore potentially dangerous to the health of the Humidity Section staff. Humidity Section staff have been using trichloroethylene for many years and are aware of the associated hazards. Precautions are already in place to deal with spillage and personal safety protection equipment is readily available. A system of measuring the vapour content of the laboratory is in operation which includes alarms for long and short term exposure limits.

The use of trichloroethylene is discouraged because it is environmentally unfriendly and could be phased out in the future.

6 DISCUSSION

The fluid used at present in the SHG is trichloroethylene. This fluid is toxic and therefore poses hazards to the health of the Humidity Section staff. Its use is discouraged on health and environmental grounds and this will affect its availability and cost. It is therefore not recommended for future use.

The behaviour of the range of viscous fluids has not yet been proven sufficiently in the temperature ranges required in terms of the potential bath temperature gradients and the time and cooling power needed to achieve the desired temperature.

The preferred bath fluid will be one of the range of flammable fluids as the thermal and fluid properties have already been proven at NPL and other National Measurement Institutes. The problems associated with the use of flammable fluids will need to be addressed. The options available for safe operation are to make the room spark free or enclose the fluid. Making the room safe is impracticable for the reasons detailed in section 5.1.1. The favoured option is to contain the fluid within an enclosed volume, this has the advantage of confining the fluid and its vapour in a confined space and avoids the problems associated with evaporation.

6.1 SEALING THE EXISTING BATH

To seal the existing baths would include sealing the stirrers, chillers and pipework for the saturator coil. The orientation and complexity of the generator layout would make sealing difficult. The present bath is made of thin stainless steel, sealing against this could prove difficult in itself. To seal around the obstacles could possibly be accomplished by splitting the bath lid. The quality of seal achieved in this way is unknown but is not expected to be good enough to be acceptable.

There will also be a need to access the bath to change the fluid to enable high dew point calibrations to be undertaken. This would open the flammable fluid to the laboratory which could potentially be hazardous.

6.2 CONSTRUCTING A NEW SEALED BATH

An alternative to sealing the existing bath would be to construct a purpose built sealed bath. This would involve the design and build of a new saturator coil to fit into the bath The suggested type of bath design has been used successfully in NPL Temperature Section for many years at high temperatures and copied at other National Measurement Institutes and used at low temperatures with alcohol as the bath fluid. This type of bath has double concentric tubes, see figure 1.

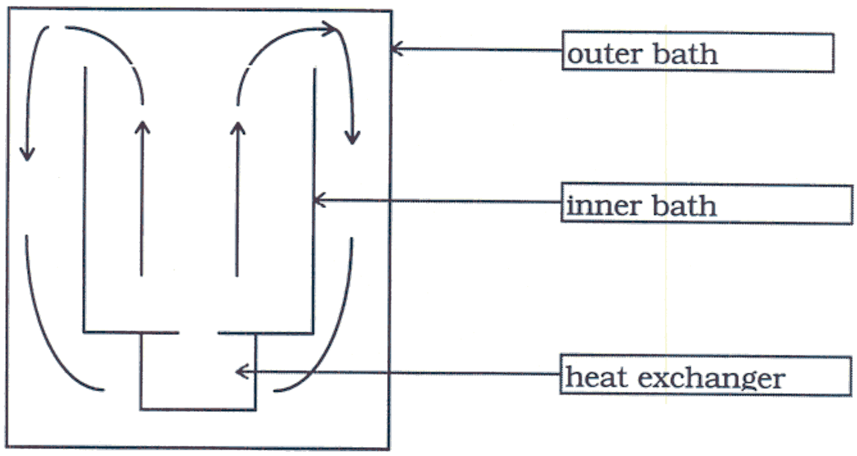

Figure 1: proposed bath configuration (schematic)

The fluid is pumped up the inside tube and spills over into the outside tube and is recirculated.

These baths have temperature gradients of approx. 0.005 °C at -100 °C (this is better than the gradients in the present humidity baths). The heating for the temperature control would be performed in the heat exchanger unit, separate from the inner bath. The bath that would be constructed for the humidity work would have a capacity of 35 litres.

The new saturator coil has already been designed as part of an extensive study by NPL Humidity Section for another project [2]. The design needs minor modifications to suit the type of bath proposed and to encompass further improvements not foreseen at the time of the original design. This design of the saturator could also enable the generator to be used in the two-pressure mode which may enable lower dew-points and a faster response.

7 PROGRESS TO DATE

The result of the analysis reported above has been to show that the most appropriate response to the requirement to reduce or eliminate the use of trichloroethylene in the NPL Humidity Section is, to construct a new bath and saturator system which would operate safely at low temperatures using a flammable fluid. Once this new facility is commissioned the operating range of the SHG would be limited to that which can be achieved using an ethylene glycol and water mixture in the baths. There would then be no further requirement for the use of trichloroethylene in the Section.

The minor modifications to the saturator design have been finished and its manufacture has been completed. Figure 2 shows a photograph of the new saturator. A bath whose design is based on the already proven baths in Temperature Section, but modified to be sealed, is nearing completion. The new bath, saturator and associated temperature control equipment will collectively be known as the NPL Low Frost-point Generator (LFG). The specification for the equipment necessary for completion of the LFG has been compiled and the most appropriate items identified.

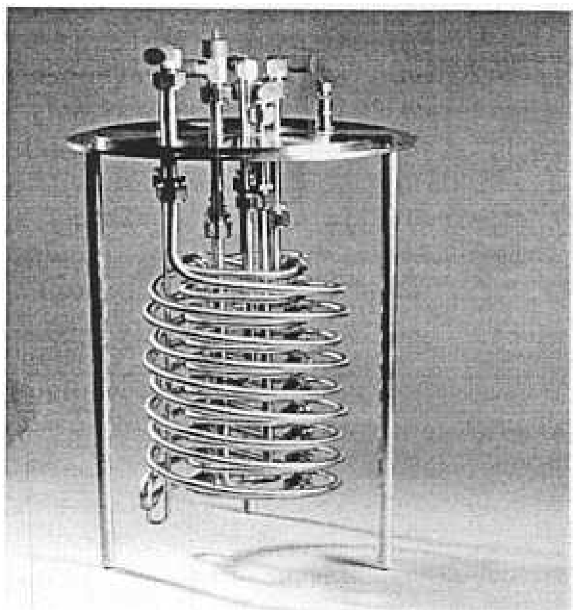

Figure 2: saturator coil

The validation of the LFG has been extensively planned and is due to start in April 1998 as part of the NMS Thermal programme 1998 to 2001.

8 CONCLUSION

Development of a specialised dew-point generator for operation between -75 °C and 0 °C offers the opportunity to eliminate the use of trichloroethylene completely. The temperature controlled bath of the new generator will be a fully sealed system, designed for safe use with flammable fluids. A pre-saturation system will be required for use with the new generator. This is being designed from the beginning as a flow-mixing system using ethylene glycol as a bath fluid, which will reduce the amount of flammable fluid required by approximately 50%.

The new LFG has been designed and is nearing completion and a programme of evaluation has been formulated. Once the LFG is commissioned and evaluated trichloroethylene will no longer be used in the Humidity Section. The use of the SHG will then be limited to that part of its range which can be achieved using ethylene glycol in both the pre-saturator and main saturator baths.

9 ACKNOWLEDGEMENTS

This work has been performed within the DTI's National Measurement System Programme for Mass, 1996 to 1999, project 4, Humidity Standards, sub-project 4.1. Presentation of this report is intended to satisfy the requirement of milestone 4.1.3 of that programme.

10 REFERENCES

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