

Achieving Reliable Parts-Per-Billion Calibration of Moisture Analyzers

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Abstract

One of the most difficult process gas contaminants to measure and control is water vapor. Industry directives like the *International Technology Roadmap for Semiconductors (ITRS)* define upper limits for its presence in bulk gases. These limits typically fall within the range of 0-100 parts-per-billion by volume (ppbv). Technologies capable of meeting the necessary uncertainty requirements have a high cost per point of measurement, limiting their application numbers. Aluminum oxide based hygrometers are much less expensive but were long considered too slow and unstable for this demanding application. Recent advances have dramatically improved their performance but regular calibration is still required for the most accurate results. Any claims will be evaluated against our ability to establish an accepted process for generation and control of moisture concentrations at verifiable levels. Complicating matters is the challenge of a universally accepted transfer standard covering this range. Other critical considerations are the demands of both product specifications and production goals. This paper outlines the engineering design and scientific analysis behind the construction of a moisture generation system capable of achieving the necessary performance. This involves both Type-A and Type-B evaluation of the standard uncertainties for the components making up the generator design.

1. Background

A line of new hygrometers was introduced to provide a less expensive approach to monitoring of trace moisture applications. The product uncertainty is ± 20 percent of reading or ± 5 ppbv whichever is greater. The intended range of operation is 0-100 ppbv. To validate this performance, a system to generate known moisture concentrations in this range is needed. The desired extended uncertainty of the system's final moisture content must be less than ± 6.5 percent of target or 2 ppbv whichever is greater.

For decades, moisture generation systems using the two-pressure, two-temperature method [1] have been in use at standards laboratories and calibration facilities worldwide. They use volume expansion of a saturated gas to reduce its absolute moisture content. This is a common method used to validate chilled mirror hygrometers, but it is generally limited to transfer standards with lower detection limits above 100 ppbv and cannot provide sufficient final flow capacity to meet production goals.

An alternate design relies on a permeation source to add moisture to the carrier gas at a controlled rate. Testing at NIST [2] has shown this method can achieve the level of uncertainty

required by our application. These systems can be the simplest to design but are unable to meet our final flow capacity requirements.

Another approach has first detailed in 1985 [3] and then improved in 1993 [4]. Since then, this basic design has been in continuous operation calibrating GE Sensing moisture probes. It uses multiple stages of gas-mixing control to dilute the wetter saturation gas against an ultra dry dilution gas to achieve the desired concentration range and flow capacity. The legacy systems were engineered to deliver a wide range of moisture content, spanning seven decades of water vapor pressure. The specifications of many control components will not allow sufficient fine control in our range of interest. The saturator pressure control is only 145 KPa (21 psia) to minimize volume expansion of the gas moving through the system. This is a disadvantage to us, as it requires higher volumes of dilution gas to sufficiently reduce the moisture concentration. Control element modification or replacement would cause an extended loss of current production capability and is not acceptable. Another disadvantage is the high maintenance cold-trap used to provide the final stage dilution gas at a frost point of -140°C . While it is a simple and effective metrological approach, this performance comes at a price. It is expensive to maintain and can take weeks for repair if it fails. Production demands will require near continuous operation of this cryogenic freezer.

Recently, a thermodynamic design known as the Low Frost Point Generator (LFPG) [5] has become operational at the National Institute for Standards and Technology (NIST). The system can achieve concentrations down to five ppbv with expanded relative uncertainties less than one percent. While this design offers superior performance over all others, its complexity makes it the most expensive to construct and not practical for our use.

No matter which generation method is used, a transfer standard must be chosen to provide the verifiable confidence needed in the generator performance. The standard could be a single instrument or derived from a transfer function involving a number of instruments. After reviewing the proposed meteorological timelines [6] for both paths, a single instrument would appear the easiest. Several available technologies could be applied. To make the final decision, the team visited and polled several plant sites with low parts-per-billion moisture limits. We found the instrument with the highest acceptance and most installed base to be the *Delta-F Model DF-750 Tunable Diode Laser Spectrometer (TDLAS)*. It was chosen to provide our final system output verification.

The new hygrometer has production and operational requirements that will affect our system design. It has a recommended sample flow range of 0.5-2 liters/minute. The transmitter is not sensitive to flow variance within this range. However, decreased flow will increase overall response times and reduce calibration throughput.

Based on this information, the engineering team determined the need for construction of a new flow-dilution system with design upgrades. It must be able to control moisture in a nitrogen carrier gas at user-selected levels, ranged from 1 to 100 ppbv.

An increased saturator pressure of 324 KPa (47 psia) will provide nearly three-to-one volume expansion. This will allow selection of more accurate and precise flow control elements. The

total volume flow capacity of the generated gas will be a maximum of 15 liters/minute, supplied to an electropolished distribution manifold (R_a of 5 micro-inches). This manifold will provide gas distribution for simultaneous connection of sixty hygrometers.

To provide the final stage dilution gas, a metallic oxide getter technology will replace the cryogenic cold-trap. Getter performance has been demonstrated using mass spectroscopy [7] and has wide industry acceptance for this application. The getter has a finite working life, specified for a minimum of two years. An annual replacement schedule will be implemented, minimizing the risk of lost production time on depletion. The cost of annual replacement is less than one-tenth the cost of a single freezer failure.

Operation of the system will be completely automated. A National Instruments PXI computer running LabView 7.0 software will automatically adjust dilution flow to achieve the desired concentration. It will collect historical data from system instruments and calibrated hygrometers then save it to a protected database.

2. Design Model

The following transfer function was derived to represent the design model and allow analysis of its predicted behavior from the measured values or assumptions entered for each variable.

$$e_3 = \left\{ \left(e_0 \times \left[\frac{P_1}{P_0} \right] \times \left[\frac{F_{W1}}{F_{W1} + F_{D1}} \right] + e_{D1} \right) \times \left[\frac{P_2}{P_1} \right] \times \left[\frac{F_{W2}}{F_{W2} + F_{D2}} \right] + e_{D2} \right\} \times \left[\frac{P_3}{P_2} \right] \times \left[\frac{F_{W3}}{F_{W3} + F_{D3}} \right] + e_{D3}$$

Definitions : (where $x = 1, 2$ or 3)

- e_0 Saturator outlet, water vapor pressure
- e_3 Final reduction stage outlet, water vapor pressure
- e_{Dx} Reduction stage x dilution gas, water vapor pressure
- P_0 Saturator total pressure
- P_x Reduction stage x , total pressure
- F_{Wx} Reduction stage x , dilution wet gas flow
- F_{Dx} Reduction stage x , dilution dry gas flow

Figure 1 is an illustration of a simplified instrumentation and control schematic for the moisture generator. The transfer function variables are also represented.

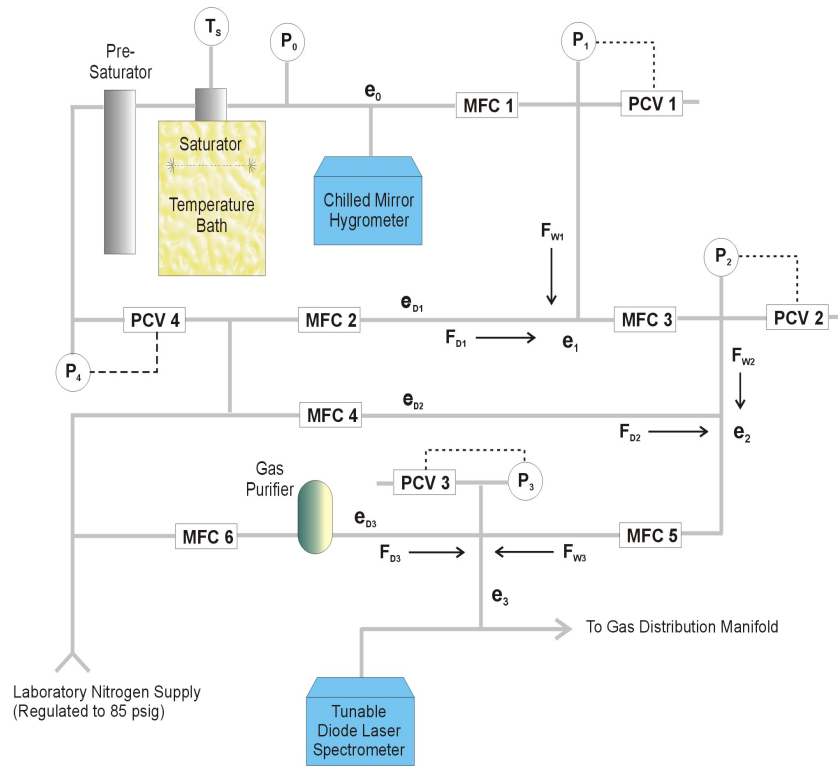


Figure 1 – Moisture Generator Schematic

Carrier gas saturation with water vapor is accomplished using two vessels of liquid water connected for series flow. The first vessel functions as the pre-saturator and left exposed at laboratory ambient temperature. The nitrogen carrier gas picks up water molecules as it bubbles up through the water. The second vessel is the saturator. Its liquid water is held at 10°C by immersion into a controlled temperature bath. The incoming gas from the pre-saturator releases some moisture to the cooler saturator, and then exits with a relative humidity near 90 percent.

The water content at the saturator outlet (e_0) is gauged using a NIST traceable chilled mirror hygrometer. For this report, a GE Optica/1311-XR was used. Derivation of its uncertainty has been detailed in earlier works [8]. The carrier gas is reduced to ambient pressure and the vapor pressure of water is calculated from the measured dew point using an iterative function [9]. The result is adjusted to saturator pressure, thus yielding the starting moisture content (e_0).

The flow and pressure control components provide three cascaded reduction stages. Each stage uses volume expansion and mixing dilution to reduce moisture content in the carrier gas, with the TDLAS monitoring the final stage outlet concentration.

Final stage outlet pressure is held to a constant 138 KPa (20 psia). The sample gas flows through the distribution manifold and is vented to ambient. Metal orifice plates installed in the outlet of

each leg of the manifold, allow the differential pressure to establish a controlled flow through each sample connection of 1.0 ± 0.25 liters/minute.

3. Uncertainty Analysis

The variance and error analysis were accomplished inside a spreadsheet model created using Microsoft Excel 2000. The error calculations were made with Crystal Ball 2000 utilizing Latin-Hypercube sampling. What follows is a description of the source data and assumptions made when analyzing for the confidence of the system design. All statements of uncertainty are as defined by NIST guideline [10] and all values will represent an extended uncertainty (U) with 95 percent confidence (K=2).

Manufacturers' published specifications were used to perform a Type-B evaluation of the generator's standard uncertainty [10]. This is usually the most conservative approach and has previously been presented as the worst-case scenario for system performance [11]. The table below displays the expanded uncertainties for each component.

Table 1 – Expanded Uncertainty from Manufacturer Specifications

Schematic	Function	±U	Unit
MFC 1	F _{W1}	5	sccm
MFC 2	F _{D1}	10	sccm
MFC 3	F _{W2}	5	sccm
MFC 4	F _{D2}	10	sccm
MFC 5	F _{W3}	5	sccm
MFV 6	F _{D3}	20	sccm
PCV 1	P ₁	10.3	KPa
PCV 2	P ₂	10.3	KPa
PCV 3	P ₃	4.14	KPa
PCV 4	P ₀	4.14	KPa
Chilled Mirror	e ₀	0.15	°C Td

The GE Sensing facility in Billerica, MA, is located approximately 76.2 meters above sea level. For our analysis, the ambient pressure used is a nominal 101 KPa (14.7 psia) and allowed to vary from 99.9 to 102.7 (14.5 to 14.9 psia) with a triangular probability distribution.

The facilities bulk nitrogen system, supplies the dilution dry gas source for reduction stages one and two. Its nominal dew point is -87°C at 689 KPa (100 psig). It may vary between -90°C and -85°C with a triangular probability distribution.

The metallic oxide getter used to produce the third stage dilution gas, is specified at less than one ppbv of outlet moisture. Here we applied a minimum of 0.1 and maximum of 1, with an equal probability distribution.

All instrumentation and control elements were evaluated for their contribution to the design model's predicted variance. This allowed the design engineers to identify the generator's most critical control components.

The uncertainty of the lowest generated point (1 ppbv) is mostly a function of the variation of background moisture in the zero gas supply. This is why the final stage dilution gas absolutely must be dried to sub-ppbv levels. The results of this analysis are shown in Figure 2.

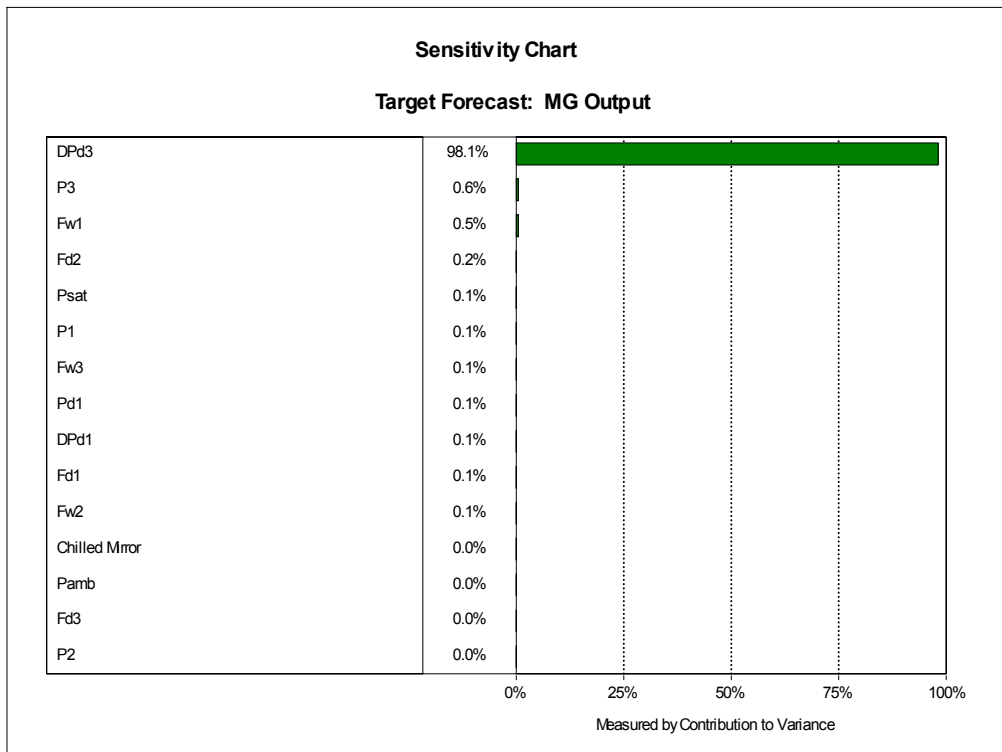


Figure 2 – Contribution to Variance at 1ppbv

At the high end of the generation range (100 ppbv), the analysis suggests the combined uncertainty will be reduced by improved control and monitoring of gas saturation and dilution flow. The results are shown in Figure 3.

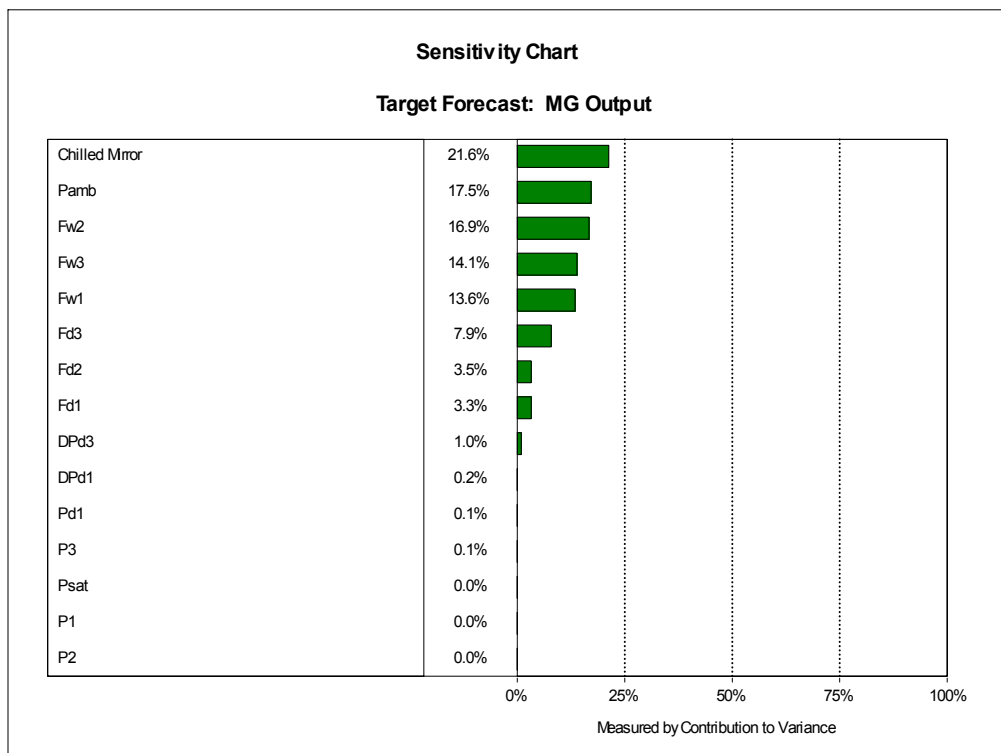


Figure 3 – Contribution to Variance at 100ppbv

4. Model Validation

In October of 2006, construction was completed on the new calibration system and it was put through a series of verification cycles. Multiple attempts at each generation point allow us to evaluate the repeatability and reproducibility of both the system and the TDLAS. The following table represents a comparison of the Type-B predicted error of the system versus a Type-A statistical analysis of TDLAS measurements.

Table 2 – Predicted vs. Measured Values

Desired Values		Predicted Values				TDLAS		
Generation	Target	Mean	σ	U	U_{REL}	Mean	σ	U
Point (0)	1	0.5	0.2	0.4	40%	1.2	0.16	0.3
Point (1)	5	4.6	0.3	0.6	12%	5.2	0.29	0.6
Point (2)	10	9.9	0.4	0.8	8.0%	10.0	0.34	0.7
Point (3)	15	15.2	0.5	1.0	6.7%	15.5	0.46	0.9
Point (4)	20	20.4	0.7	1.4	7.0%	20.1	0.34	0.7
Point (5)	25	25.7	0.8	1.6	6.4%	25.7	0.26	0.5
Point (6)	30	30.9	0.9	1.8	6.0%	30.5	0.94	1.9
Point (7)	40	40.8	1.1	2.2	5.5%	40.5	1.31	2.6
Point (8)	50	50.5	1.3	2.6	5.2%	49.7	1.30	2.6
Point (9)	70	69.1	1.8	3.6	5.1%	68.3	1.50	3.0
Point (10)	80	79.7	1.9	3.8	4.8%	79.2	2.13	4.3
Point (11)	90	89.3	2.1	4.2	4.7%	86.9	1.18	2.4
Point (12)	100	98.5	2.3	4.6	4.6%	96.3	1.48	3.0

Figures 4-5 display the results graphically. Error bars are attached to the predicted values.

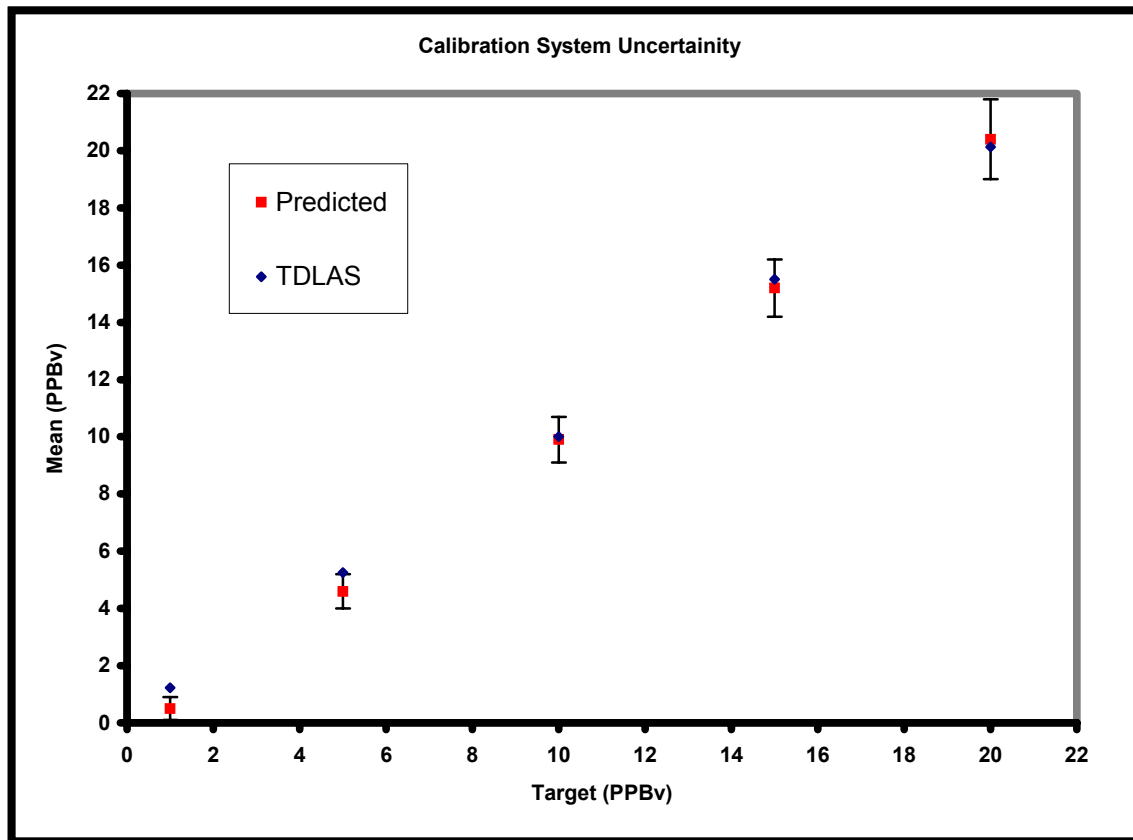


Figure 4 – Predicted vs. Measured Values (0-20ppbv range)

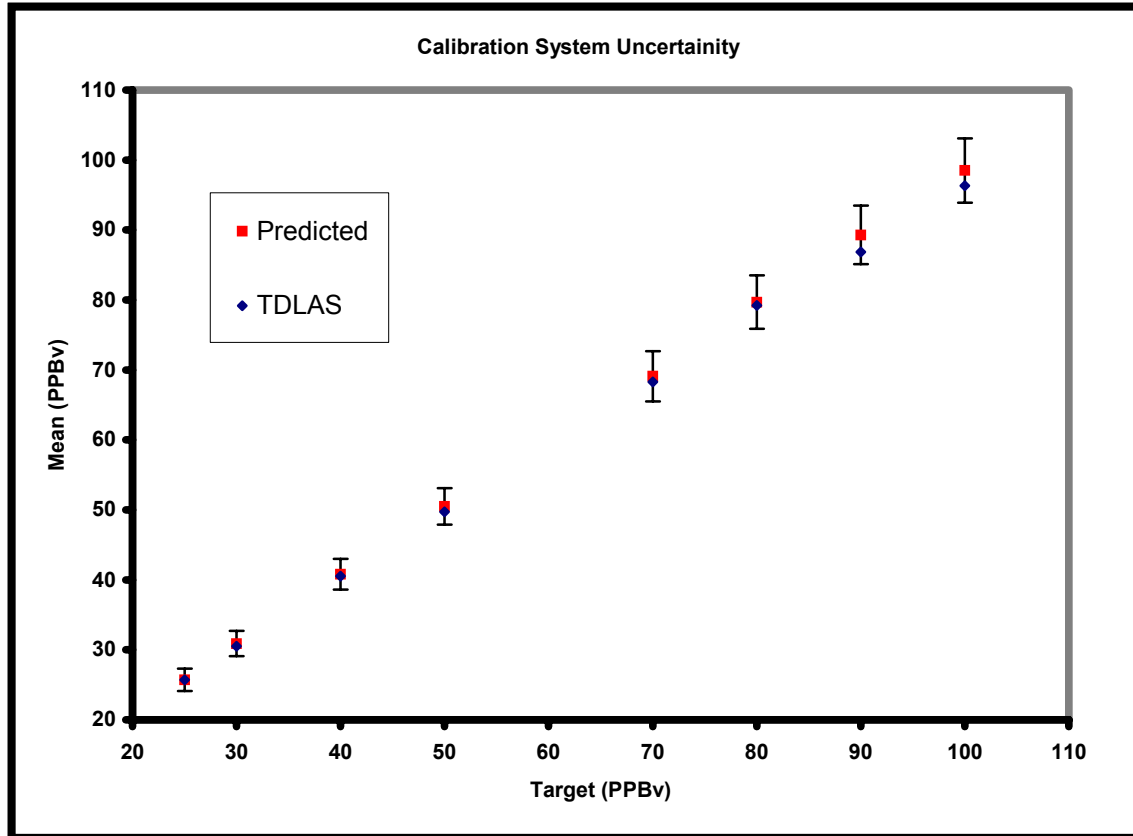


Figure 5 – Predicted vs. Measured Values (20-100ppbv range)

The TDLAS measured values are within the predicted generator uncertainty except for the lowest two points. Increasing the dwell time would reduce this error, but it is sufficiently low for calibration of the new hygrometer.

5. Zero-Check of TDLAS

A cryogenic cold-trap was used to perform a check and zero adjustment to the TDLAS. A nitrogen flow rate of 15 liters/minute was established through the trap's condensation coil and allowed to flush over-night. The freezer was powered on, then set to -140°C and allowed twenty-four hours to reach temperature equilibrium. The calculated moisture content at this temperature is 0.0003 ppbv. The analyzer was then "zeroed" following the steps outlined in its user manual. The freezer temperature was increased to -130°C then given twenty-four hours to reach equilibrium and monitored by a NIST traceable platinum RTD. The manufacturer's extended uncertainty of the RTD is ± 0.25 percent.

The predicted values for the cold-trap are crosschecked against TDLAS values. Type-A analysis was used for the cold-trap, as this data mostly reflects the quality of the freezer temperature control. For the TDLAS, a Type-B analysis was used because the manufacturer specification is nearly forty times greater than the actual measured result. The results are shown in Table 3.

Table 3– Cold-Trap vs. TDLAS

Cold Trap - Temperature						
T_{MEAN}	±U_{MFG}	σ_T	±U_T	e_T	C_{OUT}	U_{Cout}
Td °C	Td °C	Td °C	Td °C	KPa	ppbv	ppbv
-130	0.33	2.6	5.2	9.03E-10	0.009	0.007
TDLAS - Concentration						
C_{MEAN}	±U_{MFG}	σ_C	±U_C	e_C	Frost Point	U_{FP}
ppbv	ppbv	ppbv	ppbv	KPa	Td °C	Td °C
0.008	0.2	0.005	0.2	1.14E-09	-129	12.3

6. Conclusions

1. The moisture generator chosen and built by the design team does meet the requirements for calibration of the new hygrometers.
2. Continued improvement and application of state-of-the-art technologies for critical parameters will reduce overall generator uncertainty.
3. The ultimate goal is to achieve NIST traceability of the moisture generator output. This should be accomplished with the simplest meteorological time-line [6] and incorporating the TDLAS as the transfer standard. Its comparison against the NIST Low Frost Point Generator will further reduce our generator uncertainty.
4. Data collected during generator operation through 2007 will be used to expand the previous error analysis. A complete Type-A evaluation of all components will further reduce overall system uncertainty.

7. References

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