

MEASURING HYDROCARBON DEW POINT

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Introduction:

Hydrocarbon Dew Point (HDP) remains one of the key quality parameters of natural gas streams. Its determination is needed for operational and safety considerations, as well as to satisfy tariffs and regulations in US and overseas pipeline operations. The recent development of shale gas in US has added to the need for accurate and consistent measurement of HDP across a range of different mixtures of natural gas.

Theoretical methods for prediction of natural gas have been used in the past, but have been shown to have significant errors associated with them¹. In general, theoretical methods using GC component analysis and EOS models have too much error to be useful. Direct measurements, using a chilled-mirror, continue to remain the preferred method for measurement of HDP.

We introduced our line of hydrocarbon and water dewpoint measurement instruments about 5 years ago. These analyzers utilize CEIRS™ technology, which is a novel implementation of the chilled-mirror principle. It utilizes IR spectroscopy to not only detect the dewpoint but also whether it was a water dewpoint or hydrocarbon dewpoint.

We have collected the data from our analyzers corresponding to approximately 20 years' worth of data. In this paper, we discuss some of the findings from the analysis of this data.

Methodology:

All of our analyzers feature Data Box™ Technology. This technology records all operational parameters of the analyzers every 3 seconds and records them in a high density on board memory. This technology allows the polling of this data for future analysis or troubleshooting of the analyzer.

Selected customers shared their data with us. The total amount of data shared with us is approximately 20 years' worth of data.

CEIRS™ (Chilled-Evanescent Infrared Spectroscopy):

Our analyzers use CEIRS™ which is a patented technology. This method takes the core advantage of a manual chilled-mirror system, which is a direct first-principle observation of the condensation point. However, CEIRS™ completely removes operator subjectivity by using an advanced infrared technique using the evanescent wave of the electromagnetic beam at an interface, to detect the onset of condensation. It also uses a highly accurate temperature sensor to record the temperature at which condensation occurs (the dewpoint).

Evanescent Wave IR Spectroscopy:

When a light beam undergoes total internal reflection, the electromagnetic field is high on one side of the interface and close to zero on the other side. However, since there is no discontinuity in the field, the field actually decays from its full strength right at the interface to near zero, in a very small distance adjacent to the interface (See Figure 1). This small distance, referred to as penetration depth, is usually between few nanometers to a few microns, depending on the refractive indices of the two media and the angle of incidence. If there are no substances in the immediate vicinity of the interface to absorb the optical radiation, then 100% of the light is reflected back. However, if there are substances that absorb the radiation, then some of the light will be absorbed. Depending on the chemical structure of the substance, different wavelengths will be absorbed.

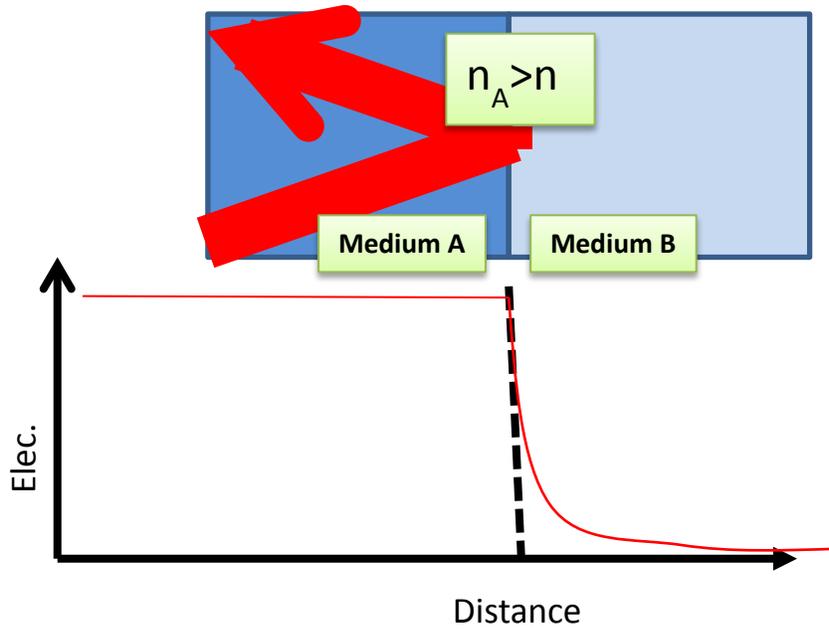


FIGURE 1 – Electric Field Decay

CEIRS™ technique takes advantage of this phenomenon. An optical crystal is placed in a gas stream in such a fashion that one side is exposed to the gas under analysis and the other side is not (Figure 2). Then multiple IR beams are sent through the back at incidence angles which cause the beams to undergo total internal reflection. This crystal is cooled, while the reflected beams are monitored for absorption at different wavelengths. At the onset of condensation (the dewpoint), one observes optical absorption at one or more wavelengths, depending on the chemical nature of the condensate. At this point, the temperature of the crystal is noted as the dewpoint.

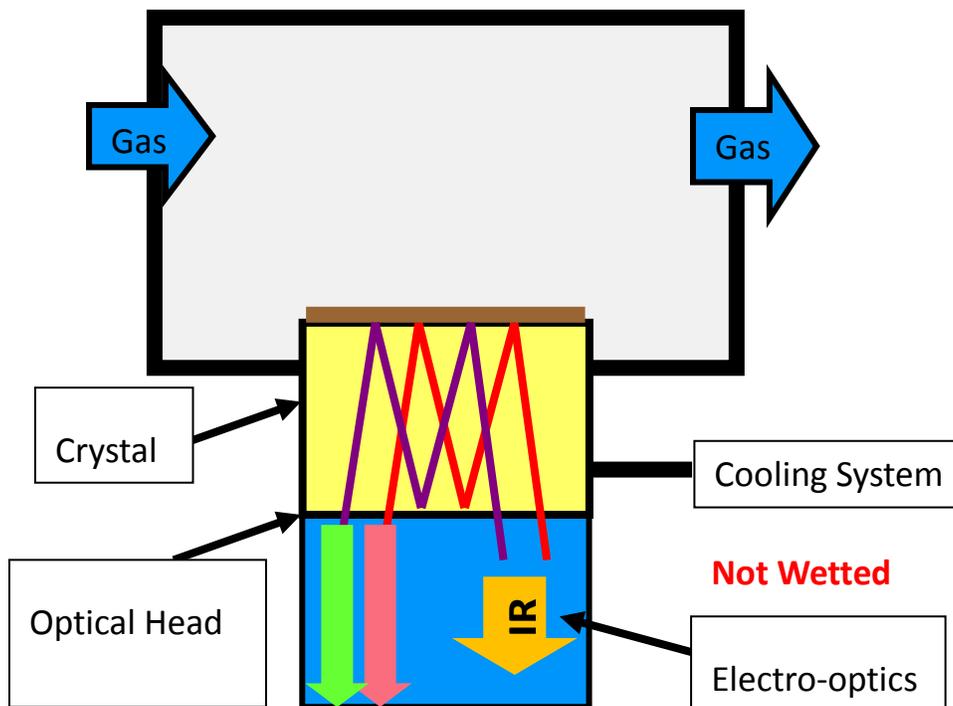


FIGURE 2 – CEIRS™ Technique

CEIRS™ not only accurately and unambiguously detects the onset of condensation, but it also can characterize the nature of the condensate. This is due to the fact that absorption is monitored at different wavelengths. Thus, one can distinguish between a hydrocarbon dewpoint and a water dewpoint. This is an added advantage of this technique.

HCD5000™ Hydrocarbon Dewpoint Analyzer:

CEIRS™ was embodied in the HCD line of hydrocarbon dewpoint analysis systems as well as in DewPort™ which is a line of portable dewpoint analyzers. Figure 3 is a picture of the HCD5000™ analyzer and Figure (4) is a picture of the DewPort™ portable hydrocarbon and water dewpoint analyzer. The gas sample is introduced to the system at line pressure. After the analysis, the pressure is reduced for safe venting. The measurement time of the system is from 2 to 8 minutes depending on how low the dewpoint of the gas is.



FIGURE 3 - HCD5000™ On-line Hydrocarbon Dewpoint Analyzer

Within the analysis cell, the cooling of the crystal is achieved by a multi-stage, thermoelectric cooler. There is a very high accuracy temperature sensor ($\pm 0.05^{\circ}\text{F}$) embedded within the optical crystal to continuously monitor the crystal temperature.



FIGURE 4 - DewPort™ Portable Dewpoint Analyzer

The crystal itself is a novel ceramic material, with very unique optical, chemical, and thermal properties. It is inert up to temperatures of 2000°F even in presence of acidic environments. Its surface will not adhere to any chemicals or contaminant and cannot be scratched by even metal shavings.

It is also important to note that the optical beam does not travel through the gas phase. Therefore the technique is immune to light-scattering particles that may be present in the gas phase.

Accuracy of CEIRS™:

The HCD5000™ unit was used to measure a gas mixture supplied to us by NIST. This mixture was prepared gravimetrically. Its dewpoint was measured at one pressure by the dual-densitometer method² and reported to us³. The phase diagram of this mixture was also calculated using the REFPROP program⁴ developed by Eric Lemmon at NIST. The REFPROP program is based on the 2008 expansion⁵ of the GERG model⁶. The phase diagram was then used to measure the dewpoint section of the phase diagram by HCD5000™. The phase diagram was also calculated using the SRK Equation-of-State by a commercially available software package. Figure (5) shows the results.

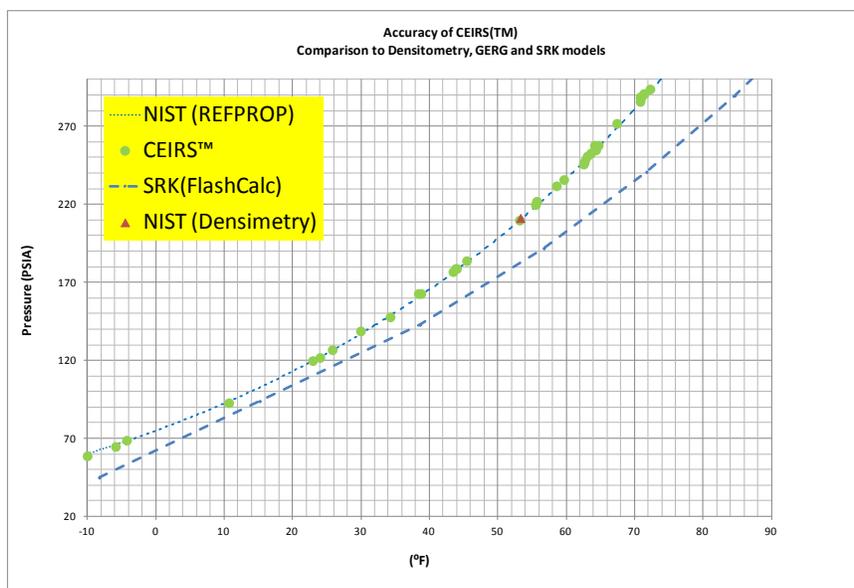


FIGURE 5 – Accuracy of CEIRS™

The results indicate close agreement between the densitometer results and the GERG model. They also indicate very close agreement between the CEIRS™ method and the GERG model and the densitometer results. The SRK model has significant deviation from the other three sets of data, particularly at higher pressures.

The above results indicate a very high accuracy for the CEIRS™ method for the determination of dewpoint in hydrocarbon mixtures.

Comparison of CEIRS™ and Manual Chilled-Mirror

Several users of HCD5000™ also compared the CERIS™ method with manual chilled-mirror readings for the pipeline gas. They also took GC readings at the same time. There was a very good agreement between the HCD5000™ and the manual chilled mirror unit. In almost all cases, the manual readings were 1-2 degrees lower than the readings with HCD5000™. This is probably due to the fact that by the time the human eye can detect the onset of the condensation, the CEIRS™ -based sensor has already detected it. Speed of cooling when using the manual system also affects the readings, with faster cooling resulting in a lower reading. Figure (6) shows the comparison of these two methods for pipeline gas.

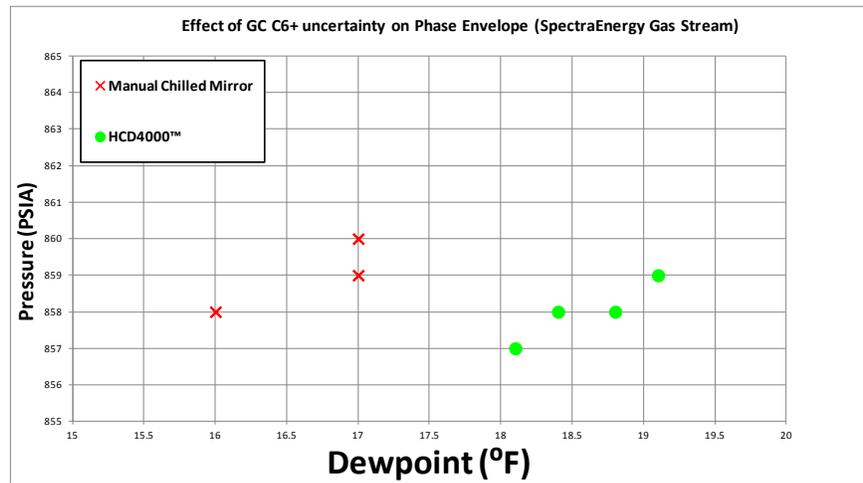


Figure 6 – Manual Chilled Mirror vs. HCD5000™

Discussion of the Data Collected:

All the data correspond to analysis of pipeline quality gas. Analysis of the data points to several trends:

- The actual dewpoints of the gas is almost always higher than the pipeline owner’s pre-conceived expectation of the dewpoint!
- The dewpoints of pipeline quality gas is different in the various regions of US and Canada.
- Where available, GC-EOS calculated dewpoints were compared with actual measured results. The GC-EOS based calculations are in significant error, sometimes by as much as 80F.
- “Process Upsets” are a fact of life. There are many instances where the HC dewpoint and/or water dewpoint deviate significantly from the historical trends.

A more detailed discussion of each finding is below.

A. *THE ACTUAL DEWPOINTS OF THE GAS IS ALMOST ALWAYS HIGHER THAN THE PIPELINE OWNER’S PRE-CONCEIVED EXPECTATIONS OF THE DEWPOINT!*

Most pipeline operators and gas processors have a pre-conceived notion of what their HC (or water) dewpoints are. Most of the pre-conceptions relate back to a spot sample that was taken at some point, analyzed using a GC (typically C6, but sometimes C9), and then the dewpoint was calculated using an EOS model. In some other cases, the pipeline customers (or gas users such as power plants) simply accept their vendor’s specification. In almost all cases, the actual dewpoint is higher than the pre-conception.

The exact reason for this discrepancy is not clear. It seems that in many cases, it is the result of a GC based analysis with an EOS calculation. Such analysis typically underestimates the actual dewpoint. The reason is several folds which will be discussed in the “C” section.

In cases where the dewpoint is specified by the vendor, there is a clear conflict of interest. The vendor obviously would like to report their dewpoint as low as possible to meet pre-specified tariffs. Given the difficult and ambiguity associated with “calculation” of the HC dewpoint, the vendor may choose preferential assumptions and techniques to report their HC dewpoint lower than reality.

B. *THE DEWPOINTS OF PIPELINE QUALITY GAS ARE DIFFERENT IN THE VARIOUS REGIONS OF US AND CANADA*

This observation was expected. In general, HC dewpoint tariffs are lower in northern areas with colder climates. However, the actual dewpoints were substantially lower. For examples, dewpoints in Canada were typically in the 0-12 °F, while dewpoints in southern US were averaging 20-50 °F. Moreover, the variations in the dewpoints were much lower in the

colder climates, typically with a standard deviation of ~7 °F, while variations in warmer climates were higher with a standard deviation of ~18 °F. (Note that these numbers relate to cases where none of the “process upsets” were taken into account.)

In general, pipelines that see colder climates have to pay more attention to the quality of their gas inputs. However, the dewpoints in the warmer climates should also monitor the inputs to their pipelines more diligently. In some cases, the dewpoints were so high that condensation could occur even in mild temperatures.

C. WHERE AVAILABLE, GC-EOS CALCULATED DEWPOINTS WERE COMPARED WITH ACTUAL MEASURED RESULTS. THE GC-EOS BASED CALCULATIONS ARE IN SIGNIFICANT ERROR, SOMETIMES AS MUCH AS 80F.

Surprisingly, many people are still using C6+GC analysis, combined with an equation of state (EOS) calculation to calculate the dewpoint. While GCs are quite adequate for calculation of BTU, they should not be used for calculation of dewpoints. Even GC manufacturers warn against the use of C6+ GCs for calculation of dewpoints.

There are many sources of errors when one uses a GC to calculate dewpoints. They include:

- a. EOS error. Given the same gas analysis, different models produce different results. Depending on the pressure and gas composition the EOS errors we have seen can be as high as 20 F.
- b. C6+ distribution error. Typically, the user chooses an assumption for the distribution of the C6-C7-C8. Some popular ones are 60/30/10 or 48/35/17. Presence of C8+ components is completely ignored. While these distribution assumptions may reflect reality in some limited sources of gas, they are not universally applicable. The error from the distribution assumption can be in excess of 50 F.
- c. Pressure regulation error. GCs work at close to atmospheric pressure. Most pipelines operate at >700psig. One has to sample the gas, and reduce the pressure in a manner that does not cause any changes to the constituents of gas. Although there are well-established protocols for doing this, many customers do not follow the needed procedure to ascertain the integrity of their sample.
- d. GC-embedded errors. GCs also have inherent measurement errors. An even small amount of errors in the determination of the heavy components translates to large errors in calculation of dewpoints.

Overall, when using a GC-EOS calculation, the errors are significant and they typically underestimate the dewpoint. The errors can be as high as 100 °F.

Unfortunately, the use of C6+-EOS calculations is a major contributor to the under-reporting of dewpoints in US. The situation in Canada and Europe is different and it is well accepted that dewpoints have to be measured rather than calculated.

D. “PROCESS UPSETS” ARE A FACT OF LIFE. THERE ARE MANY INSTANCES WHERE THE HC DEWPOINT AND/OR WATER DEWPOINT DEVIATE SIGNIFICANTLY FROM THE HISTORICAL TRENDS.

Gas processing is a well-known technology. However, there are many process upsets where the quality of the processed gas is compromised due to unforeseen circumstances. Saturation of water removal equipment can and will give rise to reduced water removal and thus increasing water dewpoints. Malfunctions in the liquid removal equipment will cause higher HC dewpoints. Several of our customers who are gas processors use dewpoint monitoring as an overall check on the integrity of their process.

Figure (7) shows one of these process upsets. The horizontal axis depicts time. As can be seen, the hydrocarbon dewpoints are in the -15 °C (4 °F) range. Then there is an upset condition where both water and hydrocarbon dewpoints rise rapidly and then fall again back to normal levels. The length of this upset is approximately 2 hours. There is another smaller “event” a bit later.

These process upsets are more common than expected. If there is no 24/7 monitoring of the gas, they can easily be missed. These process upsets will contribute to the liquid accumulation problems in the pipelines and cause increased need for pigging as well as other operation problems.

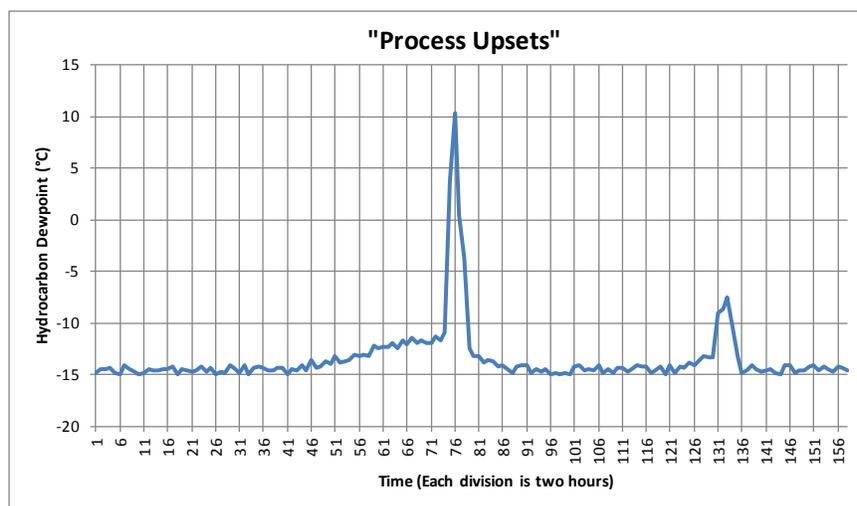


Figure 7 – Process Upset Example

Summary:

There are a lot of misconceptions about the need to monitor HC dewpoints in pipelines and power plants. In general, we have found that HC dewpoints are significantly higher than the expectation of the pipeline operators as well as the gas users elsewhere.

Our long term data indicates that dewpoints are also well above the pipeline tariffs, where there are tariffs in place. The only exceptions are locations where the inputs to the pipeline are strictly controlled using continuous monitoring equipment.

Acknowledgements:

This work would not have been possible without the collaboration of several individuals who generously contributed their time and expertise. Our customers at several locations provided valuable data and input to their operations.

Marc McLinden (NIST) provided the gravimetrically prepared gas mixture to be analyzed by HCD5000™. Eric Lemmon (NIST) provided the GERG-based phase-envelope calculations of the same mixture.

References:

¹ Darin George, Ph.D., Andy M. Barajas and Russell C. Burkey, Pipeline & Gas Journal, September 2005.

² Marc McLinden, M.O. McLinden and N.V. Frederick, "Development of a dual-sinker densimeter for high-accuracy P-V-T measurements," Proc. 11th Symp. on Energy Eng. Sci., Argonne, IL, 63-69 (1993).

³ Marc McLinden, Private Communication, March 2012

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⁵ O. Kunz and W. Wagner, The GERG-2008 Wide-Range Equation of State for Natural Gases and Other Mixtures: An Expansion of GERG-2004, J. Chem. Eng. Data, 2012, 57 (11), pp 3032–3091

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