

# Accurate Measurement of Hydrocarbon Dewpoint in Natural Gas Streams

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## ABSTRACT

Extraction of natural gas from shale formations has increased the focus on determining the quality of the gas extracted and processed. One of the key attributes of natural gas during its various stages of processing is its “Hydrocarbon Dewpoint”. This figure refers to the temperature at which the gas stream undergoes a phase transition to liquid at a given pressure. The knowledge of this figure is essential in the operation of natural gas pipelines, storage, as well as gas-powered turbines.

We have recently developed a new method for the accurate and unambiguous detection of this key parameter. CEIRS™ (Chilled-Evanescent Infra-Red Spectroscopy) uses a novel implementation of InfraRed spectroscopy to detect the Hydrocarbon Dewpoint while eliminating potential interferences in its measurement. In this paper, we present details of this method and compare the results with GC-based theoretical calculations. This method is also compared to manual chilled-mirror measurements. Long-term field data from measurement of this property is also presented.

## **INTRODUCTION**

Hydrocarbon Dewpoint of natural gas stream is the temperature at which first drops of liquid form at any given pressure. It is 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 them<sup>1</sup>. Direct measurements, using a chilled-mirror, continue to remain the preferred method for measurement of HDP. Although there have been several automated chilled-mirror systems available in the market, none have been shown to provide a consistent and reliable alternative to the manual chilled-mirror units. On the other hand, manual chilled-mirror systems, are subject to operator errors, cumbersome to use, and not suitable for on-line installations.

We have recently developed a unique method for direct measurement of HDP using a combination of a chilled optical crystal and Infrared spectroscopy. This method, Chilled-Evanescence Infrared Spectroscopy (CEIRS™) provides an unambiguous, consistent, and reliable method for direct measurement of Hydrocarbon Dewpoints.

In this paper, we present this method and discuss the technology behind it. We also present field data using this method, and compare it to manual chilled-mirror measurement as well as calculations based on Equation-of-State and GC data.

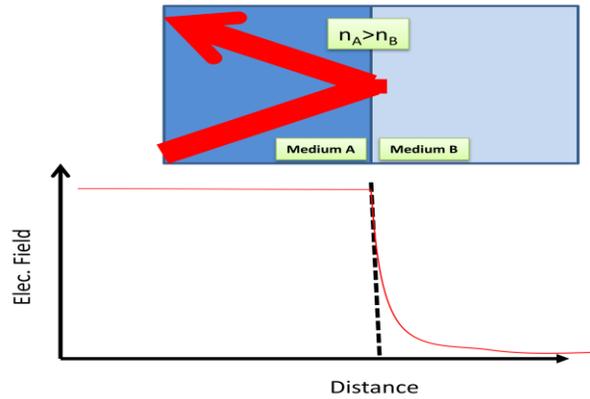
## **CEIRS™ (CHILLED-EVANESCENT INFRARED SPECTROSCOPY)**

The method we have developed, 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 out of the equation, 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 SPECTROSCOPY**

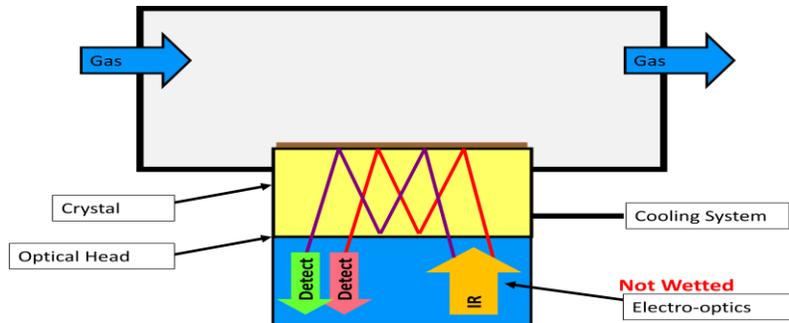
When a light beam undergoes total internal reflection, the electromagnetic field is high on one side of the interface and close to zero on the other side. However, since there is no discontinuity in the field, the field actually decays from its full strength right at the interface to near zero, in a

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)**

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**

CEIRST™ 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.

## **HCD4000™ HYDROCARBON DEWPOINT ANALYZER**

CEIRST™ was embodied in the HCD line of hydrocarbon dewpoint analysis systems. Figure 3 is a picture of the 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.

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 3**

The crystal itself is a novel ceramic material, with very unique optical, chemical, and thermal properties. It is inert up to temperatures of  $2000^{\circ}\text{F}$  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 HCD4000™ 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 method<sup>2</sup> and reported to us<sup>3</sup>. The phase diagram of this mixture was also calculated using the REFPROP program<sup>4</sup> developed by Eric Lemmon at NIST. The REFPROP program is based on the 2008 expansion<sup>5</sup> of the GERG model<sup>6</sup>. The phase diagram was then used to measure the dewpoint section of the phase diagram by HCD4000™. The phase diagram was also calculated using the SRK Equation-of-State by a commercially available software package. Figure 4 shows the results.

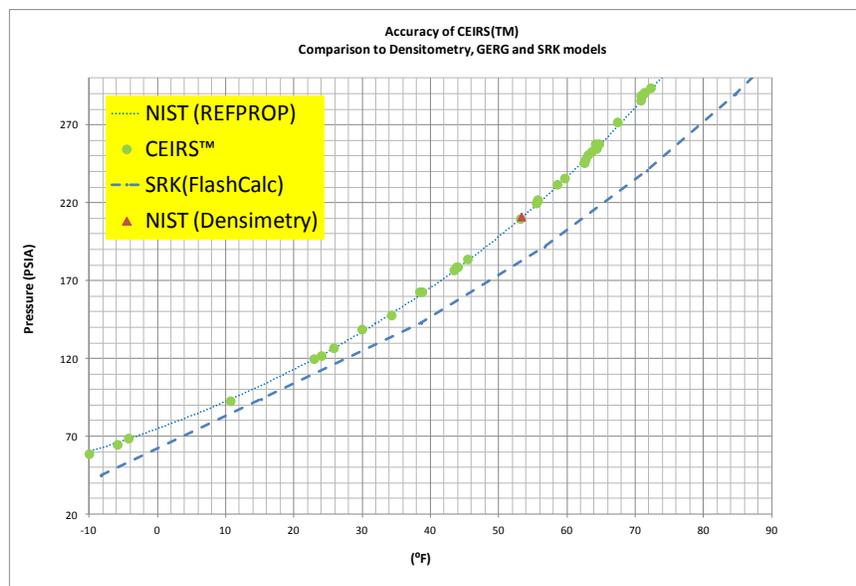


FIGURE 4

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

One of the users of HCD4000™ (James Posey of SpectraEnergy) also compared the CERIS™ method with manual chilled-mirror readings for the pipeline gas. He also took GC readings at the same time. There was a very good agreement between the HCD4000™ and the manual chilled mirror unit. In almost all cases, the manual readings were 1-2 degrees lower than the readings with HCD4000™. 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 5 shows the comparison of these two methods for pipeline gas.

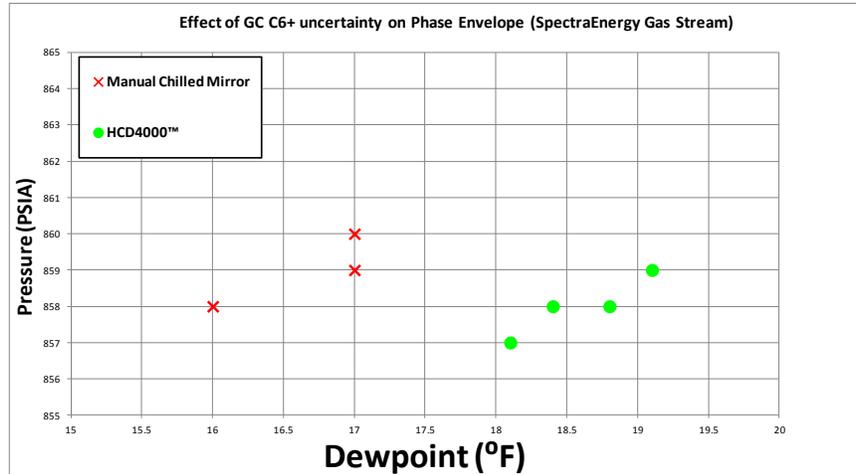


Figure 5

## COMPARING TO GC-BASED EOS CALCULATIONS

The same gas measured by the HCD4000™ and the manual chilled-mirror units, we are also analyzed by a field C<sub>6</sub><sup>+</sup> GC. Report summary is shown in figure (6).

Component Name	Mole Percent	Weight Percent	LiqVol Percent	Gallons/1000 SCF	BTU Gross	Relative Density
C6+ 47/35/17	33.3 PPM	0.0196	87.7 PPM	0.0015	0.18	0.0001
PROPANE	0.0317	0.0858	0.0514	0.0087	0.80	0.0005
i-BUTANE	39.2 PPM	0.0140	75.6 PPM	0.0013	0.13	0.0001
n-BUTANE	32.5 PPM	0.0116	60.2 PPM	0.0010	0.11	0.0001
NEOPENTANE	0.0000	0.0000	0.0000	0.0000	0.00	0.0000
i-PENTANE	12.0 PPM	53.1 PPM	25.9 PPM	0.0004	0.05	0.0000
n-PENTANE	9.07 PPM	40.1 PPM	19.4 PPM	0.0003	0.04	0.0000
NITROGEN	0.3285	0.5642	0.2127	0.0361	0.00	0.0032
METHANE	98.6299	97.0238	98.4273	0.0000	998.47	0.5463
CARBON DIOXIDE	0.5063	1.3664	0.5087	0.0864	0.00	0.0077
ETHANE	0.4910	0.9053	0.7730	0.1313	8.71	0.0051
TOTALS	100.0000	100.0000	100.0000	0.1446	1008.47	0.5631

'\*' indicates user-defined components

Compressibility Factor (1/Z) @ 14.73000 PSIA & 60.0 DEG.F= 1.00200

**Figure6**

Then the EzThermo<sup>7</sup> software package was used to run calculations based on a variety of different assumptions. In all calculation cases the SRK model was used.

In the first calculation, the GC analysis was used assuming no error in the GC analysis itself, and all C<sub>6</sub><sup>+</sup> was assumed to be hexane. In the next set of calculations, C<sub>6</sub><sup>+</sup> distribution of 48/35/17 (C<sub>6</sub>/C<sub>7</sub>/C<sub>8</sub>) was used. This minor assumption change results in a shift of 40<sup>0</sup>F in the cricondontherm (Figure 7). We then assumed an exponential distribution<sup>8</sup> of C<sub>6</sub>-C<sub>12</sub> components. This assumption change resulted in another 50<sup>0</sup>F shift in the cricondontherm. Finally we added 0.02% uncertainty in the molar percentage of C<sub>6</sub><sup>+</sup> components, and assumed an exponential distribution. The 0.02% uncertainty was quoted by one of the GC vendors as the uncertainty based on a routinely maintained and calibrated GC.

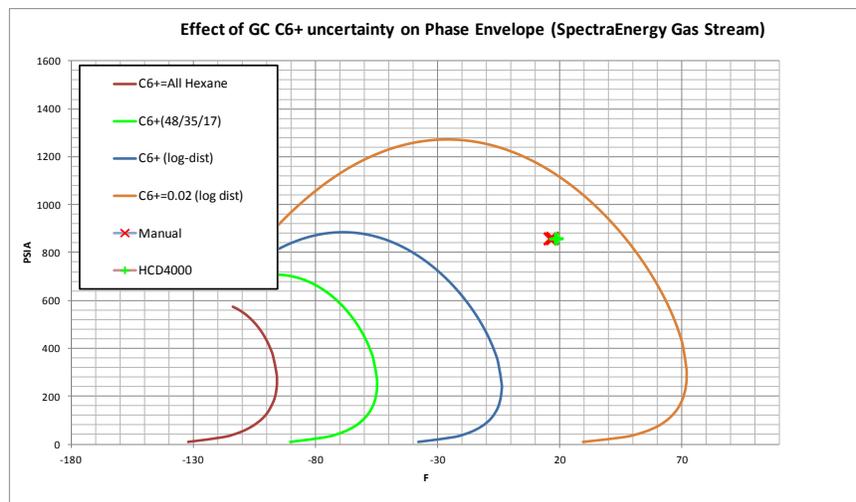


Figure 7

It has already been reported elsewhere<sup>1</sup> that the distribution assumptions for  $C_6^+$  components greatly effects the calculated phased diagrams. However, it is also apparent that the uncertainty in the GC analysis also has a major effect on the calculation of the dewpoints.

For the final calculation, we fit the  $C_6^+$  distribution so that the dewpoint at the given pressure would be what was observed with the manual chilled-mirror and the HCD4000™ system. This is shown in Figure 8 by the dashed black line.

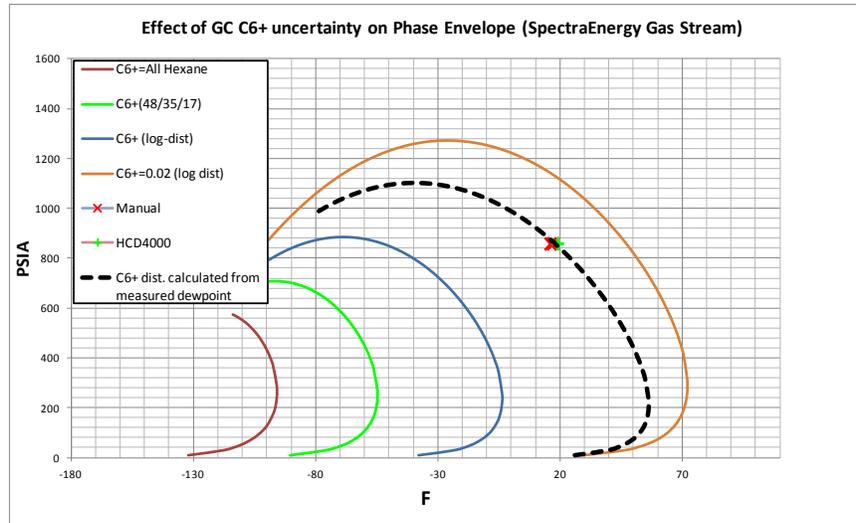


Figure (8)

Given that the HCD4000™ readings are very good indicator of the actual dewpoint, one can use it to refine the  $C_6^+$  distribution and in effect provide a very good approximation of the actual  $C_6^+$  distribution in the gas sample. Figure 9 compares the distribution of  $C_6^+$  components between the (45/38/17) distribution and the calculated exponential distribution.

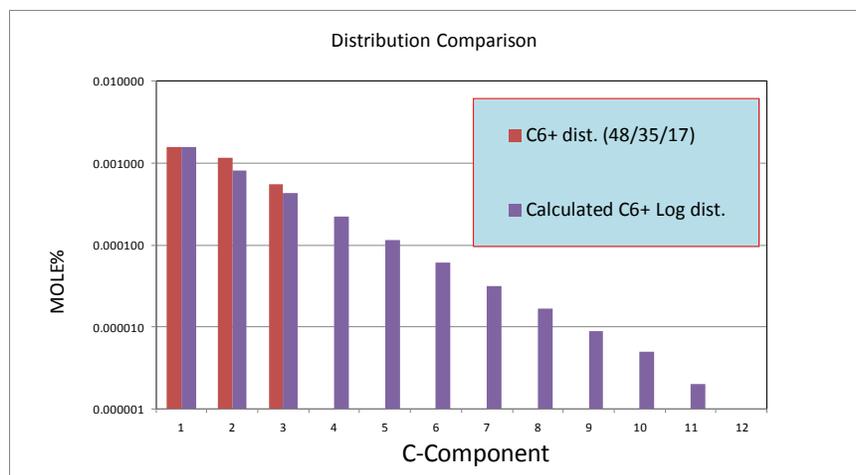


Figure 9

## SUMMARY

We have developed a new technique for accurate and unambiguous determination of Hydrocarbon dewpoints in natural gas mixtures. The new technology has excellent agreement with manual chilled-mirror units. It also has excellent agreement with a densitometer instrument at NIST for a gravimetrically prepared gas mixture.

We have also demonstrated GC  $C_6^+$  based EOS calculations have inherent assumptions and uncertainty that cause a significant impact on the calculated dewpoint. A direct measurement of the dewpoint is still the best way to accurately determine the hydrocarbon dewpoint of natural gas mixtures.

## ACKNOWLEDGEMENTS

This work would not have been possible without the collaboration of several individuals who generously contributed their time and expertise. Charlie Cook (Mustang Sampling) and Don Mayeaux provided early encouragement, invaluable input, and feedback on the overall design of the HCD4000™ Hydrocarbon Dewpoint system.

David Sells (DTE Energy) and James Posey (SpectraEnergy) were instrumental in collecting long-term data on the operation of HCD4000™ and comparing it to manual chilled-mirror systems and GC-based calculations. Thomas Marek (Williams) provided more long-term data on the operation of the system.

Marc McLinden (NIST) provided the gravimetrically prepared gas mixture to be analyzed by HCD4000™. Eric Lemmon (NIST) provided the GERG-based phase-envelope calculations of the same mixture.

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