

DETERMINATION OF HYDROCARBON DEW POINT IN NATURAL GAS

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ABSTRACT

This paper considers the requirements for control of hydrocarbon dew point in natural gas and how measurement of this important gas quality parameter can be achieved. A summary of the commercially available on-line instrumentation is provided covering:

- Manual, visual technique with chilled mirror dewpointmeter
- Equation of state calculation from extended composition analysis by gas chromatograph
- Automatic, optical condensation dewpointmeter

The role of each measurement technology is described and assessed in terms of the effectiveness of the measurement method utilised together with other technical considerations as well as initial and operating cost implications.

Full consideration is given to the specific difficulties to be confronted resulting from the complex nature of the parameter concerned. Such peculiarities include the effects of pressure, fractional condensation, the minute proportion of heaviest molecular weight components within the gas composition that contributes to the formation of condensate at the hydrocarbon dew point, and the overall subjectivity of the measurement itself where no absolute reference or definition is possible.

A case is presented for the use of advanced optical techniques in an adaptation of the fundamental chilled mirror principle to provide automatic on-line measurement with a degree of objectivity and repeatability unobtainable with other measurement techniques.

INTRODUCTION

Hydrocarbon dew point in natural gas is an important quality parameter, stipulated in contractual specifications and enforced throughout the supply chain, from producers through transmission and distribution companies to final end users. Accurately monitoring hydrocarbon dew point temperature in natural gas is therefore vital if the integrity and quality of the gas are to be maintained, and contractual agreements complied with.

Hydrocarbon dew point is the temperature at which hydrocarbon condensates first begin to form when natural gas is cooled, at constant pressure, and thus ceases to be wholly gaseous. In many cases, however, avoiding the

formation of such liquids in natural gas is of critical importance. For example, in gas pipeline transmission the presence of liquid hydrocarbons in combination with traces of moisture leads to the formation of hydrates as virtual solid masses. Under pipeline operating conditions of high flow and pressure, these hydrates can cause impact damage to compressors and restrict or even block pipelines.

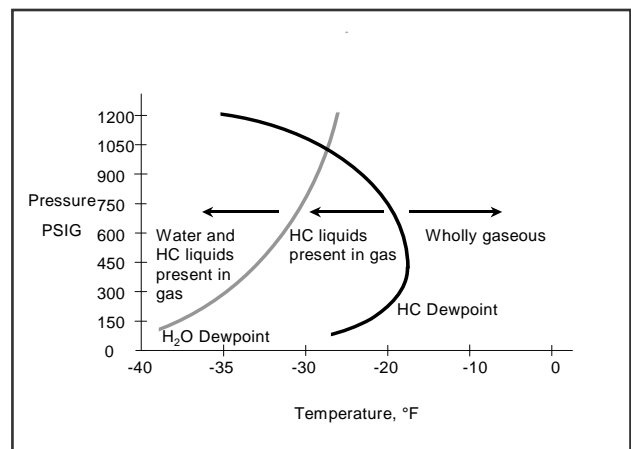


Figure 1. Typical retrograde phase envelope for natural gas

In addition, certain end users at electricity power stations have critical needs with respect to hydrocarbon dew point. The latest generation of natural gas fuelled turbines designed for low NOX emissions require at least 50°F of 'superheat' - the differential between dew point temperature and the delivery temperature of the gas on entry to the fuel gas/air pre-mixing system. If this is not achieved then the cooling effect of the expansion of large flows of fuel gas can cause liquid to be formed, resulting in possible flashback of the flame from the ignition nozzle into the mixing chamber. The cost repercussions of such a problem can be serious given the resultant sudden interruption to electricity generation, potential damage to the mixing system and increased maintenance cost/downtime to the power station.

For the natural gas producer, the control of hydrocarbon dew point can be a costly aspect of natural gas processing. The chiller plants, which are commonly used for low temperature separation of natural gas liquids, operate by expansion of the gas flow to develop a Joules Thomson effect. The lower the gas must be cooled, the lower the pressure by which the process gas has to fall, typically by 400 to 600 psi. This has a direct impact on production costs in terms of running the turbine

compressors to re-compress the gas to transmission pressures, typically 750 to 1500 psig. A further direct link to the economics of natural gas production is that the greater the proportion of natural gas liquids (condensates) separated out, the lower the heating value for the gas and thus the metered value of the gas sold.

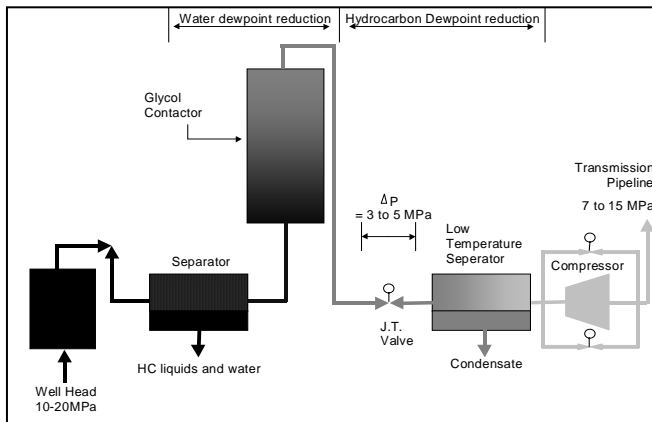


Figure 2: Natural gas processing method



Figure 3: Hydrocarbon dew point reduction plant

It is therefore in the interest of producers to monitor and control hydrocarbon dew point reduction plants within tight limits, to minimise processing costs while maximising the earnings potential for the gas produced. Such commercial pressures, however, often mean that plants run as close to the contractual limit for hydrocarbon dew point as possible.

This in turn raises the possibility of straying outside contractual specifications, leading to the requirement for continuous monitoring as part of tariff metering by operators downstream. This may include measurements being made by the pipeline transmission company initially receiving the gas and at all custody transfer points thereafter, through to final retail distribution or large industrial end user.

With increased global competition among natural gas producers, particularly as world markets deregulate and the network of interconnecting pipelines between countries continues to expand, the need to improve

production efficiency whilst administering vigilant quality controls has never been greater. As such, the methods of analysis for hydrocarbon dew point are a matter currently receiving the attention of companies operating throughout the natural gas industry.

THE METHODS FOR HYDROCARBON DEW POINT MEASUREMENT

Manual, visual technique with chilled mirror dewpointmeter

The use of manually operated chilled mirror dewpointmeters is the simplest and most widely applied method of hydrocarbon dew point measurement. These instruments have a metallic mirror surface mounted within a pressurised sample chamber, with a glass viewing port through which an eyepiece allows the operator to observe the mirror surface. The instruments are used for periodic spot check measurements.

This type of instrument utilise expanded carbon dioxide gas, supplied from a cylinder under operator control, to cool the underside of the mirror when performing each measurement. A flow valve manually adjusts the rate and degree of cooling, while the operator observes the mirror surface in order to detect the point at which condensate appears.

The aim is to detect the very first visible signs of condensate. This can, however, be extremely problematic given the virtually invisible film-like properties of natural gas liquids. At the same time, the decreasing temperature measurement reading, projected into the eyepiece, must be observed as the mirror temperature is cooled. The rate of mirror cooling is of critical importance and should be as slow as possible through the region in which the dew point is likely to be found, in order to achieve the best sensitivity and repeatability of measurement. The subjective nature of such a measurement technique means that anything less than the greatest of care and an experienced eye can result in great variability in results.

Even given these reservations, which question the objectivity of this measurement technique, this method is established as the de facto standard for this parameter by virtue of fundamental measurement principle and is in almost universal usage across the global gas industry. So, in the vast majority of cases, it is against this manual visual method that all forms of on-line automatic hydrocarbon dew point measurement are periodically compared and expected to agree irrespective of whether such automated techniques may have the capability to achieve a greater level of detection sensitivity and repeatability.

Strengths:

- The traditional and most widely used measurement technique

- The de facto standard for hydrocarbon dew point measurement
- Low capital investment - Instrument costs US\$5,000 to US\$10,000.

Weaknesses:

- Periodic spot checking only
- 'Subjective', operator dependant measurement of variable sensitive and repeatability
- Labour intensive, therefore high running costs

Equation of state calculation from extended GC analysis

Process gas chromatographs are widely used in the natural gas industry at custody transfer points for the calculation of metering parameters such as heating value and Wobbe index. Such process GC's commonly provide a composition analysis to C6+ hydrocarbons.

The use of an equation of state calculation to derive the hydrocarbon dew point of natural gas requires an extended analysis quantifying the trace quantities of individual heavy end components present. It is widely recognised that the variation in C10 and higher components, typically in the single figure ppm(mol) region or lower concentrations, has a significant effect in terms of hydrocarbon dew point.

To obtain the extended analysis required a more specialist form of GC might be used, with twin columns/ovens to enable separation and thus detection of the heavy end components. In such a GC, a higher temperature oven can be used to separate the heavier molecular weight components to help minimise the additional time taken for such an extended analysis. Even so, the extension of analysis typically reduces the frequency of measurement to between five to six times per hour, compared with up to twenty times per hour for a conventional Process GC performing a normal C1 to C6+ analysis.

			Mol%
C ₁	Methane	CH ₄	88
C ₂	Ethane	C ₂ H ₆	5
C ₃	Propane	C ₃ H ₈	2
C ₄	Butane	C ₄ H ₁₀	1
C ₅	Pentane	C ₅ H ₁₂	0.3
C ₆	Hexane	C ₆ H ₁₄	0.1
C ₇	Heptane	C ₇ H ₁₆	0.03
C ₈	Octane	C ₈ H ₁₈	0.01
C ₉	Nonane	C ₉ H ₂₀	0.001
C ₁₀	Decane	C ₁₀ H ₂₂	0.0002
C ₁₁	Undecane	C ₁₁ H ₂₄	0.0000
C ₁₂	Dodecane	C ₁₂ H ₂₆	0.0000
		CO ₂	1.5
		H ₂ O	0.005 (50ppm)
		H ₂ S	0.004
		N ₂	2.0
		O ₂	0.05

Table 1. Typical natural gas composition

As chromatography is an inferential form of measurement, a reference gas of certified composition is required for regular calibration. As such, to achieve accuracy in an extended analysis the reference gas used should be certified for the trace heavy end components, up to the highest molecular weight hydrocarbon of the extended analysis to be performed. Analysis of heavier components being of particular concern as they have such a significant influence on the hydrocarbon dew point. Quite simply, an analysis reporting single figure ppm(mol) of these components will have a calculated dew point 10°F or more higher than that obtained from an analysis in which no detectable traces are found. It is suggested that a limit of detection of 0.1 ppm(mol) is recommended for such an analysis to be suitable for the determination of hydrocarbon dew point¹. The skills required to maintain performance of this method of hydrocarbon dew point determination are therefore more suited to an analytical chemist's laboratory than to a natural gas process plant.

The significance of the extended composition analysis when calculating hydrocarbon is illustrated, albeit in an extreme case, by the example shown in table 2 of a laboratory analysis for actual pipeline natural gas taken in Canada. In this case, the calculated value for hydrocarbon dew point is underestimated by around 46°F based on C9+ compared to the C14 analysis, and more than 100°F if the analysis is shortened to C6+.

Strengths:

- Potential to combine a number of gas quality/fiscal metering parameters into one analyzer
- The components contributing to a high dew point level may be identified and so help to determine the reason/source
- Possibility to provide a theoretical phase envelope curve

Weaknesses:

- Accuracy of analysis, and thus hydrocarbon dew point calculation, is dependant on correct and regular use of specialist reference gases
- An indirect method of determining hydrocarbon dew point relying on the correct application and suitability of the equation of state being used
- Susceptible to measurement errors due to limit of analysis sensitivity and composition changes (presence of aromatics: benzene & toluene)
- Specialist staff required to operate/maintain performance
- High initial outlay (US\$150,000 plus for GC with C12 capability), installation costs (analyzer house) and running costs (personnel and reference gases)

Automatic, optical condensation dewpointmeter

A number of automatic, optical condensation dewpointmeters have been designed for on-line hydrocarbon dew point measurement over the past thirty years. All of these instruments function on the fundamental principle of direct measurement of the temperature at which hydrocarbon liquids start to form on a chilled surface exposed to the gas sample to be measured – by definition the hydrocarbon dew point.

The main difficulties in making such a direct fundamental measurement, however, are associated with two characteristics of hydrocarbon liquid formation in natural gas. Firstly, the colourless appearance and low surface tension of natural gas condensates means that the liquid film, which forms as the sample is cooled through the dew point temperature, is almost invisible to the human eye. Likewise, it is difficult to detect using the opto-electronic systems required by an automatic measurement system.

Secondly, natural gas has a spectrum of potentially condensable components that contribute to the liquid formed when the gas is cooled through the hydrocarbon dew point. This effect is complex in that some of the hydrocarbon compounds exhibit an affinity for one another while others repel, but effectively the heaviest end components condense first followed by the lighter compounds in descending order of molecular weight. The difficulty here is that, unlike the measurement of water dew point where the objective is to determine the temperature at which a single condensable component (water vapour) becomes saturated, hydrocarbon dew point is, by its very nature, indistinct, as condensation occurs gradually across a range of temperature.

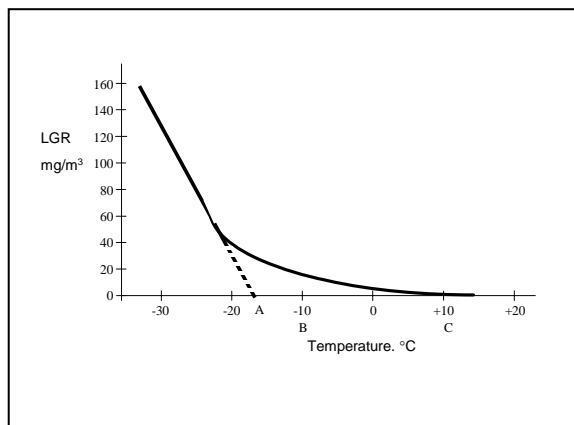


Figure 4. Typical liquid to gas ratio curve (at constant pressure, 400 PSIG)

The liquid to gas ratio (LGR) curve (Figure 4), which shows the region referred to commonly as the 'hydrocarbon tail', best illustrates this characteristic (points B to C). This shows that the theoretical (thermodynamic) dew point, if defined as the temperature

at which the first of the heaviest end components bond together from gaseous to liquid phase (point C). However, this would be some 36°F(20°C) or more higher than the temperature at which the first visible quantity of condensate could be detected using the manual cooled mirror technique and the temperature at which detectable formations of condensates may occur of significance to producers, transporters and end users of the gas. It is therefore accepted practice to take a regression of the linear portion of the LGR curve, to eliminate the otherwise exaggerated effects of the hydrocarbon tail, in order to determine an operational (applied) hydrocarbon dew point of significance in both process and gas quality terms² (point A).

Any form of automatic hydrocarbon dew-point analyzer must therefore allow the user to adjust the sensitivity of measurement in an informed manner. Ideally, this will be achieved by periodically providing a 'picture' for the condensate formation characteristic of the gas, from the first minute liquid formations into the linear region of the characteristic as shown on the LGR plot. In such a way, the true sensitivity of measurement can be periodically judged and verified by the user and, if desired by the user, could be set to achieve agreement with any analytical method stipulated in contractual agreement with their suppliers, fore example, a carefully performed manual visual chilled mirror measurement by an experienced operator.

Due to this fractional condensation effect, the repeatability and sensitivity of measurement will be adversely affected by the inter-relationship of sample flow rate and cooling rate during measurement cooling cycles. The amount of condensate formed on a cooled surface during a measurement cycle is not only dependant on the composition of the gas, but also the supply of components being condensed at that temperature, which in turn is influenced by both the cooling rate and sample flow rate. As such, to achieve good measurement performance, any such automatic technique should operate with a fixed sample volume trapped within the analysis cell prior to the start of each measurement cycle. This method de-couples the sample flow-rate/cooling rate interdependency and maintains the integrity of the sample throughout the measurement cycle.

The successful application of on-line, automatic measurement has been achieved by developing specialist measurement technologies that confront these issues. One of the most extensively applied methods over the last two decades is the "Dark Spot" optical technique utilised by Michell Instruments' CONDUMAX and latest CONDUMAX II Hydrocarbon Dew-Point Analyzers.

The Dark Spot automatic measurement technique

Operating with sensitivity of the order of 1mg/m³ of condensed liquid from gas, the "Dark Spot" optical principle is radically different to that of any other chilled

mirror instrument. The CONDUMAX II Hydrocarbon Dew-Point Analyzer comprises an EExd explosion proof certified Main Unit housing the measurement Sensor Cell, and all associated electronics. This Main Unit is located within the hazardous zone with a suitable sampling system either outdoors close to the pipeline or, if preferred, within an existing analyzer house. The self-contained Main Unit provides all automatic measurement functions, with touch screen interface and alphanumeric display, and providing analogue outputs and MODBUS communications for integration to SCADA/DCS.



Figure 5. CONDUMAX II Main Unit and Condumax II within Sampling System



Figure 6. CONDUMAX II Main Unit: Internal view

The Sensor Cell contains an optical surface, mounted on a Peltier heatpump with an embedded miniature precision thermocouple and optical detection components.

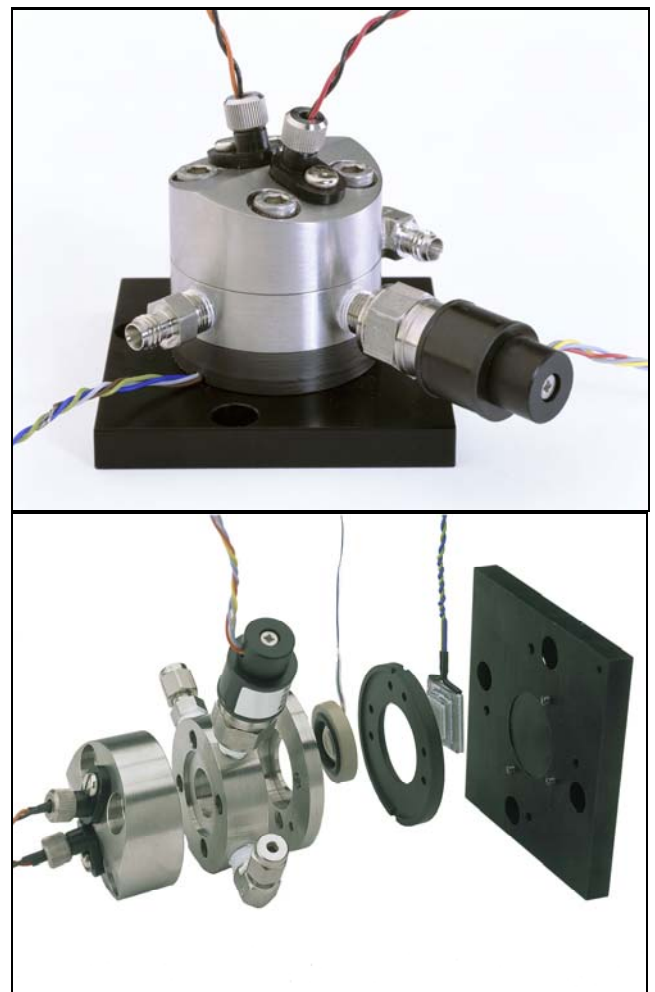


Figure 6. CONDUMAX Sensor Cell Assembly and exploded view

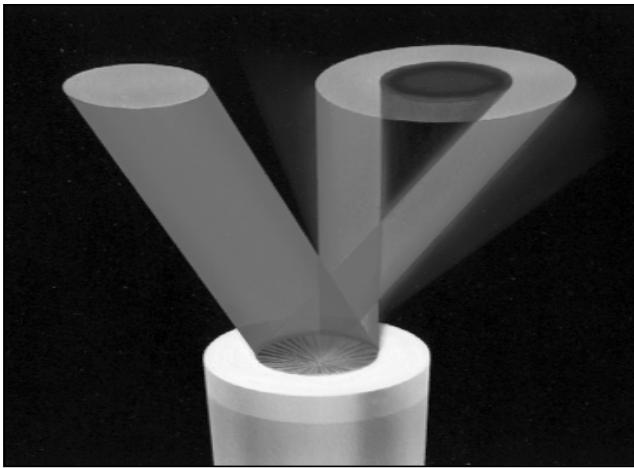


Figure 7. Dark Spot principle - Illustration

The optical surface is acid etched and semi-matt with a central conical shaped depression. As illustrated in figures 7 and 8, a well-collimated beam of visible spectrum red light is focused onto this central region, which, in dry conditions, reflects most of the beam from the surface to form an annulus ring of light. Optical detection is focused on light dispersed into the centre of the annulus ring - the “Dark Spot”.

During a cooling cycle, as hydrocarbon condensates form on the abraded surface, its optical properties are modified; the reflected light intensity of the annulus ring increases marginally whilst, more significantly, there is a dramatic reduction in the scattered light intensity within the “Dark Spot” region. Monitored by a photo-detector, the exact signal change depends on the amount of condensate formed on the surface, enabling the measurement sensitivity of CONDUMAX II to be set up to the user’s specific requirements.

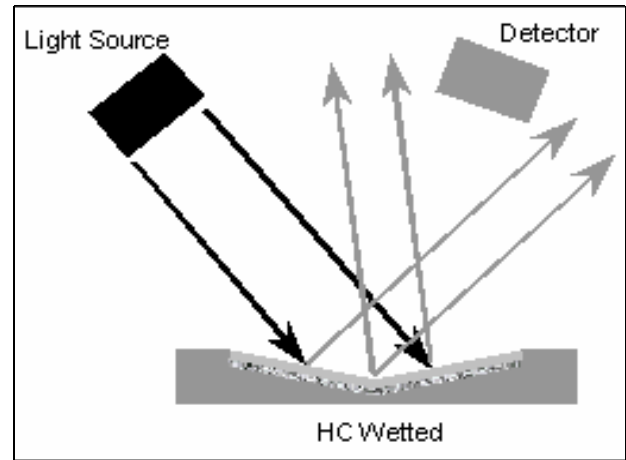


Figure 8. Dark Spot principle – Schematics – Dry and wetted optical surface

To enable the user to apply such judgement, the Main Unit software provides the facility to periodically run a ‘Sensitivity Calibration’ (figure 9) whereby a graph akin to the LRG plot is produced for the actual natural gas being analysed. In this case, the curve relates signal change in milliVolts from 0 to 1500mV, which increases dependant on the amount of condensate formed and is thus directly proportional to LGR for temperatures through the whole cooling range. As with the LGR plot, a regression of the linear portion of the Sensitivity Calibration curve can be taken to determine the dew point of the gas and thus verify the level of sensitivity set for the CONDUMAX II Analyzer, in terms of a ‘trip value’ for subsequent automatic measurement cycles. Such measurement cycles are highly repeatable for the set signal change measured by the optical system. A factory default trip value of 275mV has been proven to provide comparative measurements to those obtained by an experienced operator applying the manual, visual chilled mirror technique.

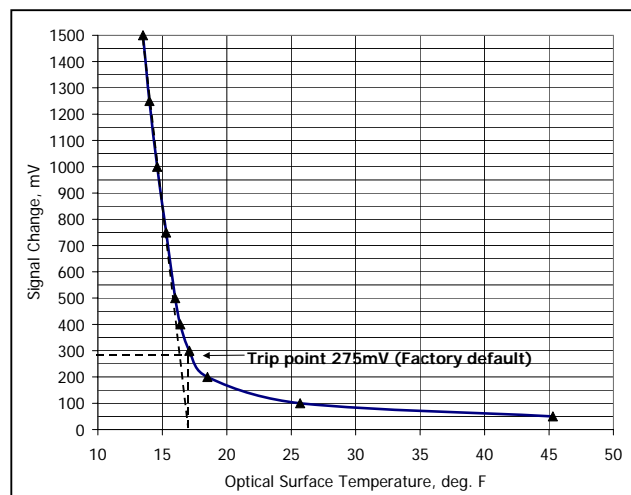
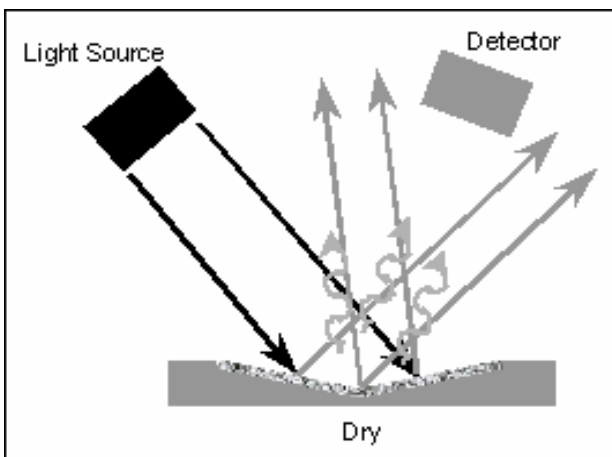


Figure 9. Typical ‘Sensitivity Calibration’

Furthermore, the high detection sensitivity of the Dark Spot technique counters problems associated with executing continuous, on-line measurements. It enables CONDUMAX to trap a fixed volume sample of gas for each analysis cycle, de-coupling flow rate and mirror cooling rate effects, and giving a liquid phase composition that is totally representative of the gas being measured.

This flexibility allows CONDUMAX II to be used for both condensate quantity and dew point temperature analysis. In the former, the optical surface is cooled to a fixed temperature pre-set by the user and the change in optical intensity is monitored. This data is interpreted as a liquid to gas ratio (mg/m^3 or lb/MMSCF) by periodic cross calibration against a recognised condensate analysis technique. In both operating modes the cycle time is normally 10 minutes, so 6 measurements are made each hour.

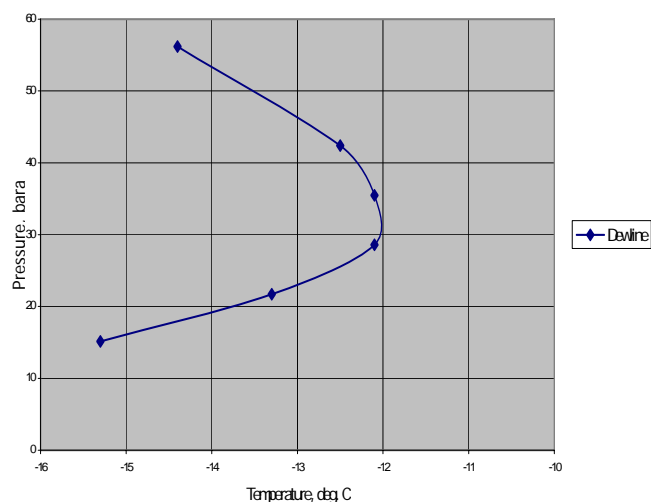


Figure 10. Example of phase envelope produced by CONDUMAX

In addition to such on-line monitoring, the CONDUMAX II can also be used to produce a phase envelope plot through a series of measurements performed at a number of pressure levels over the range of interest, which can be completed in one to two hours. An example for a typical European transmission pipeline gas is shown in figure 10.

Strengths:

- Direct fundamental 'objective' measurement of high sensitivity and repeatability
- Stand alone operation - In-built verification routines
- Sensitivity may be harmonized with measurement techniques/practices agreed between gas supplier and receiver at custody transfer
- No specialist operation/maintenance staff requirements

- Ability to produce phase envelopes through direct measurement rather than theoretical estimation

Weaknesses:

- Significant initial investment (US\$35,000 to 45,000) though low installation and running costs

CONCLUSION

As a process of global de-regulation of the natural gas industry continues, resulting in an increase in the commercial complexity of the gas supply chain, often involving transfer of custody between a number of independent companies and crossing national or even continental boundaries, gas quality specifications are being enforced more rigorously as each company must ensure that the gas they receive will meet the requirements of their customer onward through the supply chain to the end user. With the resultant rise in the number of parties needing to address gas quality issues, the effective, accurate measurement of hydrocarbon dew point grows in importance. As such, there is marked increase in the use of automatic, on-line instruments such as Michell Instruments' CONDUMAX II.

The combination of a fundamental measurement principle with the high sensitivity and objectivity afforded by the "Dark Spot" technique have led to CONDUMAX II being applied extensively throughout the whole supply chain. These applications range from performance monitoring and operational control of hydrocarbon dew point reduction plant, where producers look to achieve improved processing efficiency in order to remain competitive, through gas quality measurements at fiscal monitoring points, to reservoir engineering research work to improve extraction techniques. Furthermore, in the absence of any recognised international standard or even scientific definition for this parameter, the ability of the CONDUMAX II to inform the user of the condensate formation characteristic of the gas being measured, enables the actual sensitivity of measurement to be judged and, importantly, harmonised with measurement techniques/practices agreed between suppliers and receivers at custody transfer points.

REFERENCES

1. Cowper, C. J., "Natural gas hydrocarbon dew point; comparison of measurement and calculation methods", 2nd Gas Analysis Symposium & Exhibition 2002, Maastricht, Belgium, January 2002.
2. Bannell, J. L. K., Dixon A. G. and Davies T. P., "The Monitoring of Hydrocarbon Dewpoint", paper presented at the International Congress of Gas Quality, Groningen, The Netherlands, 1986.

Table 2. Example of equation of state (Peng Robinson) calculation of HC dew point value using extended C14, intermediate C9+ and standard C6+ analysis of the same natural gas composition

			Extended to C14	Intermediate to C9+	Standard C6+
helium	mol	He	4.9807	4.9807	4.9807
hydrogen		H2	0.9961	0.9961	0.9961
nitrogen		N2	183.2910	183.2910	183.2910
carbon dioxide		CO2	67.7380	67.7380	67.7380
Methane		C1	9298.0325	9298.0325	9298.0325
Ethane		C2	283.9018	283.9018	283.9018
Propane		C3	80.6879	80.6879	80.6879
I-butane		iC4	12.9499	12.9499	12.9499
n-butane		nC4	15.9383	15.9383	15.9383
I-pentane		iC5	3.9846	3.9846	3.9846
n-pentane		nC5	2.9884	2.9884	2.9884
cyclopentane		C5H10	0.2391	0.2391	0.2391
n-hexane		nC6	2.7892	2.7892	5.6879
cyclohexane		C6H12	0.1992	0.1992	
benzene		C6H6	0.1692	0.1692	
n-heptane		nC7	0.8965	0.8965	
toluene		C7H8	0.0598	0.0598	
n-octane		nC8	0.7471	0.7471	
p-xylene		C8H10	0.0100	0.0100	
n-nonane		nC9	0.3287	0.8169	
n-decane		nC10	0.2889		
n-undecane		nC11	0.1096		
n-dodecane		cC12	0.0598		
n-tridecane		nC13	0.0199		
n-tetradecane		nC14	0.0100		
			9961.4162	9961.4162	9961.4162
HC dew point, °F at 400 psig			79	33	-23