A TRACEABLE CALIBRATION PROCEDURE FOR HYDROCARBON DEW POINT METERS

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ABSTRACT

Gasunie Engineering and Technology (formerly Gasunie Research) has carried out a number of tests for several gases with the new Condumax II Hydrocarbon Dew Point Analyser manufactured by Michell Instruments Ltd. The results were compared with liquid drop-out measurements carried out according to ISO 6570.

The measurements have shown that the Condumax II is able to determine dew points with a reproducibility of $\pm 0.1 ^\circ$C. The measured dew points correspond with approximately $10 – 40 \text{ mg/m}^3(n)$ liquid drop out at the same pressure and the measured dew point temperature.

From measurements over a period of more than one year at six different locations it can be concluded that European sales gases show large and rapid variations in dew point, which justifies the continuous monitoring of this important gas quality parameter.

In this paper, it will be shown that a direct relationship exists between hydrocarbon dew point and liquid drop-out content measured according to ISO 6570. This means that it is now for the first time possible to calibrate a hydrocarbon dew point analyser against the ISO 6570 standard. The measured dew points will therefore correspond to a fixed potential hydrocarbon liquid content at the same pressure, this way the measured hydrocarbon dew point is made traceable towards primary standards.

The results of this work can be considered as the first step in the process towards a harmonized measuring method for the hydrocarbon dew point and thus to improved interoperability at cross border points.
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1. INTRODUCTION

There are three commonly used measuring methods for determining the hydrocarbon dew point of natural gases: chilled mirror methods either manually or automatically operated, calculation methods using a detailed gas analysis in combination with an equation of state and finally gravimetric methods based on ISO 6570. Until now the manual cold mirror is the “de facto” standard to which both automatically operated chilled mirror analysers and calculation methods are adjusted. Due to the absence of reference instruments or materials, the aforementioned procedure doesn’t guarantee any traceability of the measured values.

In contracts either a hydrocarbon dew point is specified (e.g. hydrocarbon dew point < -2 °C from 1 to 70 bar abs.) or a potential hydrocarbon liquid content is (e.g. potential hydrocarbon liquid content < 5 mg/m³ from 1 to 70 bar abs. at a temperature ≥ -2 °C). Given the shape of the phase envelope, the measurement of hydrocarbon dew point and potential hydrocarbon liquid is usually carried out at a pressure between 25 and 30 bar where liquid drop-out occurs at the highest temperatures (see figure 1).

Because there is no proper calibration method for hydrocarbon dew point analysers, significant variations in the measured hydrocarbon dew point exists between the commercially available analysers [2]. Recently, some papers have been published, in which relations between measured and calculated dew points are discussed [3, 4, 5]. Although it appears to be possible to get good agreement between measured and calculated dew point at one location, it is doubtful whether this will be the case when the tests are extended to several types of process GC’s, each with their own measuring cycle, columns and calibration gases [6].

Gas Transport Services B.V., founded on 2 July 2004, is the independent operator of the national gas transmission system in the Netherlands. The network operator defines and controls the functional requirements for gas flow and gas quality measurements. Within this context Gas Transport Services regularly commissions Gasunie Engineering and Technology to carry out preliminary performance studies on new developments in measuring techniques. Last year a comparison was made between the Condumax II hydrocarbon dew point meter of Michell Instruments Ltd. and liquid drop-out measurements according to ISO 6570.

This recently introduced new hydrocarbon dew point analyser of Michell Instruments Ltd. appears to give very reproducible results due to a new temperature control algorithm and its ability to detect small traces of liquid on a mirror. In this paper it will be shown that adjustment and even calibration of this new hydrocarbon dew point analyser against the ISO6570 standard is possible, so that a measured dew point will corresponds unambiguously with a given liquid drop-out at this measured dew point temperature. In this way a much more objective measurement of the hydrocarbon dew point is possible. By doing on-site ISO6570 measurements it is even possible to correct for the gas dependent performance of the hydrocarbon dew point analyser, which exists to some extent for different natural gases as will be shown later on.

In 2005, EASEE-gas (European Association for the Streamlining of Energy Exchange) agreed upon harmonised values of the hydrocarbon dew point throughout Europe (Common Business Practice 2005-001/01) [7]. The required harmonised measuring method, which still has to be identified, can clearly benefit from the proposed traceable calibration procedure of the measured hydrocarbon dew point against the ISO 6570 standard.

In this paper a brief overview of the working principle and the limitations of today’s hydrocarbon dew point analysers, calculation methods and gravimetical methods will be given. A description and examples of the performance of the applied dew point analyser and the gravimetical method will be presented and subsequently results of comparison tests for different natural gases will be given. The results will be evaluated and conclusions will be drawn with respect to obtaining harmonised hydrocarbon dew point values.
2. MEASURING HYDROCARBON DEW POINTS

During storage, transportation and processing, natural gas may form small amounts of liquid at pressure decrease. This phenomenon is called retrograde condensation and sometimes may lead to problems in the operating facilities. The temperature and pressure at which the condensation occurs follows a curve that forms a so-called phase envelope, see in figure 1 the curve most to the right (the dew point curve with 0 mg/m³(n) liquid drop-out). Within the phase envelope - left from the dew point curve - condensate will be formed and the further left the more condensate will be formed. The maximum temperature and pressure at which condensate is formed is called the crycondentherm.

Gas transport companies want to prevent formation of condensate in their gas grid. Particularly at points were the pressure gets below 40 bar (as a result of pressure drop during transportation or at control stations and city gate stations at which the pressure takes place) there is a potential risk for liquid formation. Also end-users receiving high-pressure gas for their gas turbines are anxious for liquid drop-out during pressure reduction, because severe damage to hot gas path components can occur if hydrocarbon liquids enter a gas turbine.

Measuring techniques, which are able to detect the ability of the gas to form liquid at too high temperatures, are either based on the detection of an amount of liquid at specified temperature and pressure (gravimetric methods) or are based on the detection of the first droplets of liquid on a mirror at a certain temperature (hydrocarbon dew point meters).

2.1. Gravimetric method according to ISO 6570

The Potential Hydrocarbon Liquid Content (PHLC) of natural gas is defined as the measurement of the condensable liquid (in milligrams) at the pressure and temperature of the measurement per unit volume of gas at normal conditions, that is at a temperature of 0 °C and a pressure of 1.01325 bar(a). The procedure for measuring PHLC is standardized in the ISO standard number 6570. This international standard states that the quantity of condensate which can be formed at a certain pressure and temperature is determined by passing a representative sample of gas through the apparatus where it is first brought to the required pressure and then cooled to the required temperature. The liquids formed during cooling are separated from the gas flow and collected by means of a cyclone separator. In the manual method, as described in the ISO 6570 standard [1], this is actually done by comparing the mass of the condensate separator at the start and the end of the measuring period.

Gasunie Engineering & Technology developed an automatic method, which is derived from the measuring system used in the manual method. The principle of this automatic method is also described in ISO 6570. The main difference between the automatic and the manual ISO 6570 method is in the weighing of the collected liquid. In the automatic PHLC method a differential pressure transmitter determines indirectly the mass of the liquid in the measuring tube underneath the cyclone separator. A schematic overview of the Gasunie Automatic Condensate Meter (GACOM®) is shown in figure 1.

The measuring tube is automatically drained when it is totally filled-up with liquid. The liquid from the measuring tube is collected in a condensate drum. This method requires calibration of the differential pressure transmitter. By dosage of known amounts of a calibration liquid - usually n-decane - into the measuring tube at the temperature and pressure at which the PHLC measurement will be performed the differential pressure transmitter is calibrated. The pressure and temperature sensors are calibrated once a year and the gas flow is measured by a thermal mass flow meter, which is checked at regular intervals against a calibrated wet gas meter. In this way, reliable and accurate measurements can be performed. The uncertainty in PHLC-value depends on the pressure and temperature set points and the liquid drop-out behavior of the gas to be measured. Values above 5 mg/m³(n) are detected unambiguous. At low PHLC-values (<30 mg/m³(n)) the uncertainty is < 5 mg/m³(n).

Because all sensors applied in the GACOM are calibrated at a regular interval against standards it is ensured that the measurement conditions are traceable and that two distinct GACOM’s will give the same results.
The automatic condensate meter is operating with a gas flow of 1 m$^3$/h (n) at a fixed pressure most often between 27 and 30 bar (at the cricondentherm) and a temperature (e.g. −3 °C) at which the hydrocarbon liquid content (often 5 mg/m$^3$ (n)) is specified in contracts. A new value for the liquid dropout content is reported every 30 minutes. Based on extensive experiments carried out in the past, the reproducibility is under virtual all circumstances within ± 5 mg/m$^3$ (n). Later on the results of an experiment with stable gas composition will be shown, from these results it can be concluded that the random error (2σ) is ± 2 mg/m$^3$ (n).

2.2. Hydrocarbon dew point measurement methods

Theoretically, the hydrocarbon dew point is the temperature at which the first small droplets of liquid are formed at a fixed pressure. In practice, all dew point measurement methods are based on the observation of the formation of a film of hydrocarbon condensate on the surface of an illuminated cooled mirror. The observation can be done visually (manual mirror) or by an electronic sensor (automatic chilled mirror). The cooling can be achieved in two ways: expansion of natural gas, compressed air or carbon dioxide or by applying a Peltier cooling device. Either manual or automatic chilled mirrors can be applied to measure the hydrocarbon dew point of natural gas.

An alternative method for the determination of the hydrocarbon dew point is the calculation from a detailed gas composition. This method is based on several assumptions (highest hydrocarbon number required, grouping of hydrocarbon isomers, optimal equation of state) and often the outcome is adjusted against a manual or automatic chilled mirror.

It is not possible to calibrate commercially available hydrocarbon dew point analysers in a traceable way, because neither hydrocarbon dew point reference materials nor reference instruments are available. Since the working principles differ from instrument to instrument, analysers from different manufacturers may give different values for the hydrocarbon dew point for a given gas. In practice, the dew point of an automatic dew point monitor is often “tuned” to match the value measured by a manual chilled mirror, or “tuned” to the value calculated from the known gas composition using a thermodynamic model.

Moreover, from their working principle there are two major sources, which can be responsible for significant systematic errors in the measured hydrocarbon dew point, and which cannot be adjusted.
for because no proper calibration method exists. These two sources are: (1) the often significant amount of liquid needed to be formed on the mirror, before the instrument is able to detect the dew point temperature; (2) the cooling rate, which is often too fast to ensure that the temperature measured by a temperature sensor in the vicinity the mirror surface equals the temperature of the mirror surface itself and the temperature of the gas in the measuring cell.

2.3. **Systematic errors in automatic dew point analysers**

A dew point analyser does not determine the theoretical dew point temperature of a natural gas (the formation of the first infinite small droplet of liquid), but it measures the temperature at which a certain amount of liquid is condensed on the mirror so that a significant and reproducible change in light scattering is observed either by a skilled person or by a light detecting sensor. From calculations it can be shown that the amount of condensate, which is required to get a reproducible dew point observation often corresponds with 20 – 50 mg/m$^3$ (n) liquid drop-out. In fact the dew point meter can be considered as a condensate meter, and the measured dew point temperature is actually the equilibrium temperature at certain PHLC value, for example at 30 mg/m$^3$ (n) liquid drop-out.

Therefore, one has to realize beforehand that an automatic dew point monitor is certainly not determining the true thermodynamic dew point, but a temperature corresponding with a predetermined threshold value of the detector signal. This threshold value is determined by performing a “calibration” against a manual mirror or a dew point calculation, often in combination with the usage of a multi-component gas mixture.

As stated before, current dew point analysers measure the “dew point” temperature at a liquid drop-out ranging between 20 – 50 mg/m$^3$ (n). A reduction of these amounts results in measured values closer to the “true” hydrocarbon dew point. Ideally the dew point analyser should determine a dew point temperature corresponding with approximately 5 mg/m$^3$ (n) liquid drop out, being the value that can be determined accurately by ISO 6570 equipment. Based on this threshold value, the pipeline operator or end-user can be certain that no significant amounts of liquid will be formed upon pressure reduction. A further reduction of the threshold value below 5 mg/m$^3$ (n) seems to be not viable given the detection principle used in current hydrocarbon dew point analysers. Depending on the gas composition the difference in temperature corresponding with respectively 30 mg/m$^3$ (n) and <5 mg/m$^3$ (n) can be less then 1 °C, however the difference also can be more than 5 °C. Therefore, it is better to adjust the threshold level against traceable liquid drop-out measurements than by the methods used nowadays.

The cooling rate of the mirror of a dew point analyser appears to be another important parameter for a proper dew point measurement. Measurement of the dew point occurs in a small sized cell with the bottom surface made of polished metal. Only this bottom side is cooled, resulting in temperature gradients in both the measurement cell itself as well as in the gas inside the cell. Theoretically the applied cooling rate for the mirror surface should be that small that the gas temperature is always in equilibrium with the mirror temperature and that there is enough time for the condensate to drop out on the mirror surface. In practical applications, the cooling rate is often much higher. A high cooling rate results in a lag between the decrease in gas temperature and the condensate drop-out onto the mirror. Also, the temperature sensor, which is mounted in the vicinity of the mirror surface, will record a lower temperature then the actual surface temperature of the mirror. Both effects will result in readings at much lower temperatures than the real dew point temperature.
3. HYDROCARBON DEW POINT MEASUREMENTS

In the recent past, Gasunie Engineering & Technology carried out tests with different hydrocarbon dew point analysers and compared the outcome with liquid drop-out measurements. However, until now the agreement between hydrocarbon dew point and liquid drop-out was not satisfactory. In 2004, Michell Instrument Ltd. offered a possibility to test their newly developed Condumax II hydrocarbon dew point analyser. Some features of the Condumax II instrument are:

- Fully automatic on-line analyser with a cycle time of 10 minutes.
- Cooling by a Peltier element and application of an intelligent cooling ramp rate.
- Certified for installation in hazardous areas.

The measurement cycle of the Condumax II consists of two phases: the measurement phase followed by a recovery phase. At the start of the measurement phase a solenoid stops the gas flow through the sensor cell. Subsequently, the mirror is cooled down in a controlled way. The condensation of heavy hydrocarbons on the mirror surface does result in an increase of detector signal. An example of such a response curve can be seen in figure 2. The mirror temperature decreases until the detector signal matches with a factory set trip point value. The optimum value of this trip point is determined by the manufacturer but can be changed by the end-user. The mirror temperature, for example $T_1$, at the trip point value $TP_1$ can be presented as the hydrocarbon dew point measurement result. However, by setting the trip point value $TP_2$, the mirror temperature $T_2$ will be presented as the hydrocarbon dew point. The construction of the measurement cell is also shown in figure 2. The cooling rate is optimised after every measurement cycle. At the start of each cycle the mirror is cooled down fast (1 °C/s). Upon approaching the dew point temperature the cooling rate gradually decreases down to 0.02 °C/s. In this way the measurement cycle time can be kept relatively short without the disadvantages of a high cooling rate near the dew point temperature resulting in a significant too low measured hydrocarbon dew point value.

![Figure 2: The hydrocarbon dew point measurement cell of the CondumaxII and in the graph the relation between mirror temperature and detector signal.](image)

After the measurement phase the mirror is heated to 50 °C for at least 5 minutes and the gas flow through the sensor starts again. During this recovery phase all heavy hydrocarbons condensed on the mirror will re-evaporate. In this way contamination of the mirror surface with heavy hydrocarbons is prevented.
During the field tests the Condumax II is installed in a GACOM unit (a mobile container for automatic measurements of PHLC-values). The GACOM is always connected to a high pressure gas sampling probe, which samples the natural gas from the middle of the pipe line, thus avoiding interference by liquids adsorbed or running along the pipe wall. Gas at line pressure (50 – 70 bar) flows through a traced stainless steel tubing (< 10 meter) to the GACOM unit. In the GACOM unit itself, the tubing is traced as well. Before the gas enters the Condumax II, it passes a membrane filter and a traced pressure regulator (set at a fixed pressure between 27 and 30 bar). With a needle valve the gas flow through the Condumax II is adjusted to approximately 30 l/h (n).

4. RESULTS OBTAINED WITH L-GAS.

The first results obtained with L-gas are shown in figure 3. The GACOM was operated at 27.3 bar and a temperature of –3.3 °C. The Potential Hydrocarbon Liquid Content-value (that is the amount of condensate formed at these conditions) varied between 40 and 200 mg/m^3 (n). The variations in liquid drop-out is caused by changes in the gas composition, particularly small changes in the heavy hydrocarbon concentrations. The Condumax II was operated at exactly the same pressure and with the standard factory settings with respect to the trip point. The measured hydrocarbon dew point varied between –3 and 1 °C. The gray bands in the graph clearly show the good relationship between PHLC-value and hydrocarbon dew point. An increase in dew point corresponds with an increase in PHLC-value and vice versa.

The relationship between PHLC-value and hydrocarbon dew point is graphically shown in figure 4. From this figure it can be concluded that dew point and PHLC-value are directly related to each other and can both be used to monitor the ‘condensation behaviour’ of the natural gas.
Figure 4: Relationship between PHLC-value measured at –3.3 °C and 27 bar and hydrocarbon dew point measured at 27 bar for L-gas.

It is evident that small changes in dew point correspond to relatively large changes in PHLC-value. From figure 4 it can be concluded that for this particular gas a dew point variation of 1 °C corresponds with a variation in PHLC of approximately 30 mg/m$^3$ (n).

The amount of condensate, which is required to detect the hydrocarbon dew point, can be found quite easily. When the hydrocarbon dew point temperature equals the temperature of the cooling bath of the GACOM, the amount of liquid drop-out formed in the GACOM corresponds with the measured dew point. Looking at figure 3, this situation occurs already at the second day of the measurement. The first gray band shows hydrocarbon dew point values around –3.2 °C and the corresponding PHLC-values are around 40 – 45 mg/m$^3$ (n) at –3.3 °C. So, for this L-gas approximately a liquid drop-out of 40 mg/m$^3$ (n) is required to detect the hydrocarbon dew point using the factory setting for the trip point value. This observation agrees with the conclusion drawn in paragraph 2.3, that dew point analysers do not detect the dew point, but an equilibrium temperature at which already a significant amount of condensate is formed on the mirror surface.

To verify the amount of condensate formed on the mirror during stable gas conditions, the bath temperature of the GACOM was adjusted to the hydrocarbon dew point value measured by the Condumax II. The results are shown in figure 5. Again these results confirm that the measured hydrocarbon dew point value corresponds with approximately 40 mg/m$^3$ (n) at the same pressure and temperature.
From figure 5 it can be concluded that over a period of more than 12 hours the dew point remains at a value of $-0.7 \, ^\circ\text{C}$, only varying within $\pm 0.1 \, ^\circ\text{C}$ and the PHLC-value at a value of $40 \, \text{mg/m}^3 (n)$ with maximum variations of $\pm 2 \, \text{mg/m}^3 (n)$. These results confirm the stability and the small random errors in the measured values of both instruments.

It can be concluded that, by applying the factory settings of the dew point analyser, the obtained hydrocarbon dew point value and the equilibrium temperature at a PHLC-value of $5 \, \text{mg/m}^3 (n)$ according the ISO 6570 are not in close agreement and that the measured hydrocarbon dew point is surprisingly lower compared to this PHLC equilibrium temperature. However, the direct relationship between PHLC-value and dew point allows the change of the trip point setting of the hydrocarbon dew point analyser, so that the measured dew point will correspond with a significant lower PHLC-value of approximately $10 \, \text{mg/m}^3 (n)$.

The detector signal of the Condumax II does increase with decreasing mirror temperature due to the formation of more and more liquid on the mirror surface as can be seen in figure 2. So, a reduction of the trip point value will require less liquid formation on the mirror, before the dew point temperature is ‘detected’. This ‘detected’ dew point value will therefore be closer to the “true” hydrocarbon dew point of the gas.

Using the data of previously obtained cooling curves, it could be estimated that to ‘match’ the measured “dew point” with the equilibrium temperature at a value of $10 \, \text{mg/m}^3 (n)$ liquid drop-out, the value of the dew point measured by the Condumax II should be increased by approximately $2 \, ^\circ\text{C}$ for these L-gases. This temperature shift can be introduced in the Condumax II outcome by a decrease in trip point value from 275 down to 165 mV. To verify this adjustment in practice, the trip point value was decreased accordingly and again measurements were carried out with the same L-gas. The results for the measured dew points and PHLC-values measured at the same pressure and a cooling bath temperature of $-2 \, ^\circ\text{C}$ are shown in figure 6.
During the measurements the gas quality frequently changed and resulting in large variations in both hydrocarbon dew point and PHLC. The PHLC-value varied between 0 and 60 mg/m$^3$ (n) and the hydrocarbon dew point between –5 and 2 °C. The reduced trip point value of 165 mV still results in a good relationship between hydrocarbon dew point and PHLC-value. The amount of condensate, which is required to detect the hydrocarbon dew point, can be read from figure 6; the first and third gray band show that a hydrocarbon dew point of –2 °C corresponds with approximately 10 mg/m$^3$ (n) liquid drop-out, formed at an equal bath temperature of –2 °C. So, it can be concluded that a change in the trip point value of the detector signal, results indeed in an improved relationship between the measured hydrocarbon dew point and a low PHLC value (10 mg/m$^3$ (n)) for the potential hydrocarbon liquid content without deteriorating the outcome of the instrument.
5. CONCLUSIONS

The Condumax II hydrocarbon dew point meter is a simple and robust instrument and during laboratory tests and long term measurements at some field locations (from December 2003 until March 2005) no failures occurred and the instrument did not show any drift.

The Condumax II does not measure the thermodynamical dew point but the equilibrium temperature corresponding with a fixed liquid drop out. With standard factory settings, the measured dew point of the Condumax II instrument corresponds with a liquid drop-out of about $40 \text{ mg/m}^3\ (n)$ for L-gases and of $5 – 100 \text{ mg/m}^3\ (n)$ for H-gases.

The good relationship between PHLC-value and measured dew point can be used to develop a traceable on-site calibration procedure for hydrocarbon dew point meters, which is based on the ISO 6570 standard. The trip point value of the detector signal of the Condumax II can be optimized so that the measured dew point corresponds with $5 – 10 \text{ mg/m}^3\ (n)$ liquid drop out at the same pressure and temperature.

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7. REFERENCES

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9. PHOTOGRAPH